The Pennsylvania State University The Graduate School Department of Mechanical and Nuclear Engineering

FLOW REACTOR STUDIES OF NON-EQUILIBRIUM PLASMA ASSISTED COMBUSTION KINETICS

A Dissertation in Mechanical Engineering by

Nicholas Tsolas

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The dissertation of Nicholas Tsolas was reviewed and approved^{*} by the following:

Richard A. Yetter Professor of Mechanical Engineering Dissertation Advisor Chair of Committee

Robert J. Santoro George L. Guillet Emeritus Professor of Mechanical Engineering

Thomas A. Litzinger Professor of Mechanical Engineering

Randy L. Vander Wal Professor of Energy and Mineral Engineering and Materials Science and Engineering

Karen Thole Professor of Mechanical Engineering Department Head of Mechanical and Nuclear Engineering

*Signatures are on file in the Graduate School

Abstract

A new experimental facility was developed to study the reactive chemical kinetics associated with plasma-assisted combustion (PAC). Experiments were performed in a nearly isothermal plasma flow reactor (PFR), using reactant mixtures highly diluted in an inert gas (e.g., Ar, He, or N₂) to minimize temperature changes from chemical reactions. At the end of the isothermal reaction zone, the gas temperature was rapidly lowered to terminate any continuation in reaction. Product composition as a result of any observed reaction was then determined using ex situ techniques, including nondispersive infrared (NDIR), and by sample extraction and storage into a multi-position valve for subsequent analysis by gas chromatography (GC). Hydroxyl radical concentrations were measured in situ, using the laser induced fluorescence (LIF) technique. Reactivity maps for a given fuel system were achieved by fixing the flow rate or residence time of the reactant mixture through the PFR and varying the isothermal temperature. Fuels studied were hydrogen, ethylene and C₁ to C₇ alkane hydrocarbons, to examine pyrolysis and oxidation kinetics with and without the effects of a highvoltage nanosecond pulse duration plasma discharge, at atmospheric pressure from 420 K to 1250 K. In select instances, experimental studies were complimented with detailed chemical kinetic modeling analysis to determine the dominant and rate-controlling mechanisms, while elucidating the influence of the plasma chemistry on the thermal (neutral) chemistry.

In the hydrogen oxidation system, no thermal reaction was observed until 860 K, consistent with the second explosion limit at atmospheric pressure, at which point all the hydrogen was rapidly consumed within the residence time of the reactor. With the plasma discharge, oxidation occurred at all temperatures examined, exhibiting a steady increase in the rate of oxidation starting from 470 K, and eventually consuming all the initial hydrogen by 840 K. For ethylene, kinetic results with the discharge indicated that pyrolysis type reactions were nearly as important as oxidative reactions in consuming ethylene below 750 K. Above 750 K, the thermal reactions coupled to the plasma reactions to further enhance the high temperature fuel consuming chemistry. Modeling analysis of plasma-assisted pyrolysis revealed that ethylene dissociation by collisional quenching with electronically-excited argon atoms formed in the presence of the plasma, resulted in the direct formation of acetylene and larger hydrocarbons by way of the ethyl radical. Similarly, during plasma-assisted oxidation, excited argon was able to directly dissociate the initial oxidizer to further enhance fuel consumption, but also facilitate low temperature oxidative chemistry due to the effective production of oxygenated species controlled by $R+O_2$ chemistry. At the highest temperatures, the radical production by neutral thermal reactions became competitive and the effectiveness associated with the plasma coupled chemistry decreased. Under the effects of the plasma, alkane fuels exhibited extended limits of oxidation over the entire temperature range considered, compared to that of the thermal reactions alone. At atmospheric pressure, propane and butane exhibited cool flame chemistry between 420 K to 700 K, which normally occurs at higher pressures (P > 1 atm) for thermally constrained systems. This chemistry is characterized by the alkylperoxy radical formation, isomerization to the hydroperoxyalkyl radical, followed by dissociation to form aldehydes and ketones. Whereas, intermediate temperature chemistry between 700 K to 950 K, is characterized by β -scission of the initial alkyl radical to form alkenes and smaller alkanes. The culmination of these studies demonstrate new insight into the kinetics governing PAC and provides a new experimental database to facilitate the development and validation of PAC-specific kinetic mechanisms.

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Chapter 1 Introduction

1.1 Motivation

For the last 50 years, it has been estimated that nearly 86% of the world's primary energy consumption comes from the combustion of fossil fuel resources [1]. Despite increased efforts to promote and advance green-energy technologies at the commercial scale, they still constitute a small share (less than 4%) of the global energy production mainly due to cost, technological limitations, and reliability [1]. With anticipated technological advancements in exploration and extraction, the cost of providing energy from fossil fuels could remain competitive with carbon-free sources for decades to come. However, extracting energy from such fuels has several inherent concerns associated with them. Apart from being highly energy intensive to reform the crude resources into viable feedstock and their finite abundance, they also have the ability to generate harmful emissions. Combustion pollutants can include CO_x , NO_x , SO_x , particulates such as soot and aerosols, and unburned hydrocarbons (UHC), all of which can have serious implications on both the climate and the environment. Stringent environmental legislation, most notable the Clean Air Act of 1963 with subsequent amendments made in 1970, 1977 and 1990, mandate that future combustion emission levels be regulated [1], jeopardizing the feasibility of established combustion systems. The most promising approach to satisfying future emission levels is to improve the energy conversion efficiency, fuel flexibility, and the operability of lean-burn combustion of next generation engines. But to achieve these goals, challenging technical issues arise requiring the development of methods to enhance and control combustion processes beyond the limits of normal flammability, often at higher pressures, lower temperatures and leaner conditions. In recent years significant attention has been drawn towards plasma-assisted combustion (PAC), whereby plasma effects can induce the formation of "active" particles (such as free radicals, excited and charged molecules) and subsequently play an important role in the reactivity of a given mixture [2–4]. PAC as a combustion enhancement technique has proven the potential to improve the future design of several advanced combustion systems ranging from gas turbines [5–9], pulsed-detonation engines [10], internal combustion engines [11–16], hypersonic combustion engines [17–25] and even fuel conversion systems [26, 27]. Although many previous studies have demonstrated the effectiveness of plasmas to enhance combustion characteristics phenomenologically, the detailed enhancement mechanism remains largely unknown. Extensive efforts have been made to develop new experimental platforms, advanced diagnostic methods, kinetic models, and quantitative experimental databases to understand the underlying mechanism between plasma effects and combustion.

Modern combustion engines are optimized based on parameters specific to their intended applications and combustion stability strategies are implemented accordingly. The complete range of such operating conditions and parameters will not be considered here, but rather two important examples of possible applications of plasma-assisted combustion systems will be focused on - lean combustion in gas turbine engines (high pressure fuel-air mixtures, with moderate flow speeds in the combustion chamber, $P \sim 15$ -30 atms, $V \sim 60$ -100 m/s [4]) and hypersonic ramjet/scramjet propulsion engines (low dynamic pressures, P < 1 atm, with flow speeds at the subsonic, Ma < 1 to supersonic range, Ma > 2 [28]). The current state of research concerning plasma-assisted combustion relating to gas turbines and hypersonic propulsion systems will be covered in detail in Chapter 2.

1.1.1 Lean-Combustion in Gas Turbines

Gas turbines play an preeminent role in the stationary power generation market and are expected to remain a critical part due to the rapidly increasing world demand for energy [29]. This is especially the case in emerging markets where high population countries such as India and China are rapidly developing infrastructures for energy. The International Energy Agency has indicated that some 1750 billion kWh of additional energy will be needed in the next 20 years to keep pace with the demand [31]. Gas turbines offer the most attractive option due to their relatively low capital, operational and maintenance cost [30]. For aircraft propulsion, the gas turbine represents the principle source of thrust for both military and commercial applications. Meeting operability constraints are the main problem in deploying low emission solutions in turbine power generation and propulsion systems. The basic principle in operating gas turbines under lean conditions is illustrated in Fig. 1.1, where lean burning of fuel-air mixtures results in lower combustion temperatures and hence the NO_x formation regime (T > 1800 K) can be avoided [29]. With liquid fuels this process becomes more complicated



Figure 1.1: Motivation for operating under lean-burn conditions in combustion systems. Redrawn from [29].



Figure 1.2: Combustion operability issues for gas turbine combustors at a fixed inlet temperature and pressure. Redrawn from [34].

and higher emission levels are expected since non-thermal NO_x pathways become enhanced in the presence of higher-order hydrocarbons at a given temperature [32]. However, applying such lean combustion strategies can have several drawbacks.

Firstly, at low combustion temperatures incomplete combustion becomes a prominent occurrence causing increased UHC and CO emissions. Lower combustion temperatures also results in lower power outputs from power generating engines resulting in lower efficiencies, but can also effect jet engine performance parameters such as flight speed, altitude and thrust [33]. Flame stability in gas turbines is a major design consideration and its limit effectively defines the operating range of an engine. As the amount of air pushed through the combustor increases to maintain lean conditions. a stability limit is eventually reached where stable combustion is no longer sustainable and flame blow-off occurs (Fig. 1.2). These limits can change based on fuel, temperature and pressure and are highly coupled to the geometry of the flame-holding device [29]. Generally speaking, it was originally thought that gas turbines could technically operate on nearly any fuel source, but because they are now expected to operate on the edges of stability this is no longer the case. This leads to fine tuning fuel injection strategies and geometric modifications to accommodate specific fuels, both of which can be cost intensive solutions [29]. Along the limits of stability generally lie seemingly random isolation areas of high-frequency oscillations, where perturbations in heat release and pressure fields couple together in a resonant manner. If the perturbations become in phase with one another, the results can be destructive mechanical failure [29]. These oscillations are difficult if not impossible to predict and are a constant hurdle that faces the turbine OEM industry. In terms of land-based systems a major deterrent in the current pre-combustion carbon capturing techniques involved with IGCC (Integrated Gasification Combined Cycle), is the implementation of H_2 fuel. IGCC is a technology that uses a gasifier to turn coal or other carbon based fuels into syngas [35]. The syngas, which has a high yield of H_2 , is then used as a fuel in the gas turbines in the combined cycle. High H_2 content fuel can introduce significant combustion issues, where very high flame speeds can be attained and cause flashbacks [29,35]. This is an unwanted phenomena displaying poor combustion control where in the event of a sudden drop in premixer velocity or increase in reaction velocity, propagation of the flame enters a region in the combustor that it was not designed for [29].

1.1.2 Supersonic Combustion in Hypersonic Aircraft

Development of hypersonic vehicles and associated enabling technologies has been an ongoing effort since the late 1950's [36]. To put it into perspective a hypersonic vehicle traveling upwards



Figure 1.3: Comparison of propulsion efficiency between rockets and air-breathing engines. Redrawn from [39].



Figure 1.4: A schematic of a scramjet engine. Redrawn [39].

of Mach 6 speeds, at a cruising altitude of 29 km, can travel 13,000 km in less than 2 hours, nearly seven times faster than current conventional subsonic airliners [37]. Having the ability to travel such distances in relatively short flight times offers potential benefits to both the civilian and military sectors. Particular attention has been drawn for its possibility to be used as a reusable and costeffective means of transportation to low earth orbit. At higher flight speeds supersonic engines have proven to provide higher performance characteristics due to higher inlet efficiencies to offset pressure losses associated with combustion [38]. In terms of fuel efficiency, higher thrust at lower fuel flow rates is obtainable (i.e., high specific impulse, I_{sp} , Fig. 1.3) [39]. In essence a scramjet propulsion system is a hypersonic air-breathing engine in which combustion of fuel and air occurs in a supersonic flow relative to the engine. The concept of the engine can be described schematically in Fig. 1.4. The forebody and internal inlet take the incoming ambient air and compress it by shock waves into a high enthalpy supersonic air flow (this usually occurs at flight speeds of Ma >6). Upon exiting the inlet this supersonic flow continues on to the combustor where it mixes with injected fuel and burns. In the event that the incoming air flow has not obtained sufficient enthalpy for self-combustion (3 < Ma < 6), the supersonic flow is decelerated by use of a diffuser to obtain subsonic speeds and ensures that a complete combustion process will occur. This is known as a ramjet engine. Combustion of fuel with the incoming air generates a large local pressure rise causing separation of the boundary layer on the surfaces of the combustor duct. This separation, which can feed upstream from the point of fuel injection, acts to further compress the core flow by generating a series of shock waves known as a shock-train. A short length of duct, called the isolator, is usually added to the scramjet flowpath upstream of the combustor to contain this phenomenon and stop it from disrupting the operation of the inlet. The combustion products generate a high pressure gas flow that then passes through a sharply diverging section (i.e., internal nozzle and aftbody) causing rapid expansion and ultimately produces thrust.

Despite this relatively simplistic explanation, the actual realization of these subsystems working in tandem with one another is hindered by several design challenges. A combination of internal duct pressure, skin temperature, and dynamic pressure loading are some of the difficulties that need to be considered and their degree of severity is usually dictated by flight conditions. Based on these constraints successful flight based on ram air compression is limited to a narrow corridor of conditions (see Fig. 1.5). The lower limit is bound by the thermal and structural limitations that a vehicle can endure during the severe conditions of hypersonic flight. Heat generated by air-friction and high aerodynamic loads present material selection constraints. The upper limit is confined by low combustion stability where only a narrow range of fuel-to-air ratios will provide



Figure 1.5: Air-breathing hypersonic vehicle flight trajectory and operating limits. The bold red-line delimits the use of a rocket based engine at the end of the air-breathing segment to gain rapid ascent in altitude. Redrawn from [39].

adequate combustion at certain flight conditions. An effect that is exacerbated at higher flight altitudes due to lower dynamic air pressures available for ram compression [39]. The minimum Mach number that a scramjet can achieve is limited by the extent of compression the flow can attain, firstly to raise the temperature high enough to burn the fuel, but also to provide high enough pressure that the combustion reaction will finish before the air moves out the back of the engine. That is why hypersonic vehicles operate on multiple engine cycle modes in order to reach scramjet operating speeds. In the low speed regime, a vehicle may utilize a combination of TBCC or RBCC propulsion systems to accelerate from takeoff to Mach 3. As the flight Mach number increases a dual ramjet-scramjet mode engine is used (until $Ma \sim 6$), implying mixed characteristics of both subsonic and supersonic flow. Operation of any vehicle in this regime is critical for transition to scramjet mode, but presents some drawbacks. Decelerating the flow to subsonic speeds for combustion leads to significant stagnation pressure losses that can limit the engine's thrust and can induce engine unstart. Plus practical designs demand a vehicle with variable geometry nozzles to accommodate the transition between subsonic-to-supersonic burning. It is mainly for these reasons that operating a scramjet at lower Mach numbers is highly desirable. However, operating a scramjet at lower Mach numbers means that combustion will have to compete against low enthalpy and high-flow conditions, both of which have adverse effects on flame ignition and stability. The ignition delay time (τ_{ign}) in a low enthalpy flow is longer than that of a high enthalpy gas typically observed in a scramjet, while flow residence time ($\tau_{\rm res}$) in the supersonic combustor becomes shorter as flow speed increases. As a result, if τ_{ign} is greater than τ_{res} combustion will not occur. This is a particular important issue for hydrocarbon fuels due to their relatively long ignition delay times [29]. In the past, pyrophoric fuel additives such as silane (SiH₄) were used to self-ignite the air-fuel mixture. But this solution was not considered practical due to its explosive tendency and safety concerns associated with onboard fuel reservoirs [40, 41].

1.2 Introduction to Plasma Physics

1.2.1 Equilibrium versus Non-Equilibrium

From a physical perspective as temperature in matter increases, or becomes more energetic, matter will transform in sequence from, solid, liquid, gas and finally into a plasma. A plasma is essentially an ionized gas, a quasi-neutral particle system where equal amounts of positively charged ions and negatively charged electrons are dispersed in a medium of neutral (heavy) atoms and molecules. To generate such a plasma the act of ionization is required, whereby electrons are liberated from gas molecules and produce positive ions. The degree of ionization (ratio between the major charged particles density to the density of the neutral particles) varies from naturally occurring processes in nature to man-made plasmas at the laboratory scale. The plasmas discussed in this research refer to "weakly ionized plasmas", where ionization can be on the order of 10^{-7} to 10^{-4} , opposed to unity in "completely ionized plasmas" that are typically experienced in thermonuclear applications [42]. The state of the plasma is usually described in terms of a temperature, or the average energy its constituent particles may have, and as a multi-particle system it is capable of exhibiting different temperatures [43]. When a strong electrical field is applied to a gas medium, electrons accumulate kinetic energy during their mean free path causing them to collide with the heavy particles (Joule heating) surrounding them. Depending on the extent of energy transferred during these electron-heavy collisions (electron-impact) the physical properties and characteristics of the plasma can vary.

The mean electron temperature (T_e) in a plasma discharge can be approximated as [44]:

$$T_e = \frac{\sqrt{3\pi}}{4} \frac{eEl}{\sqrt{\delta}} = 0.8 \frac{eEl}{\sqrt{\delta}} \approx \frac{e}{\sigma_{en}\sqrt{\delta}} \frac{E}{N} \qquad \text{where} \qquad \delta = \frac{2m_e}{M_n} \tag{1.1}$$

where e is the elementary charge of an electron, l is the mean-free path, δ is a factor characterizing the average fraction of electron energy lost in a collision with a neutral particle, with m_e being the mass of an electron and M_n the mass of the neutral particle, and σ_{en} is the electron-neutral collisional crosssection. The reduced electrical field (E/N) is an important parameter in the context of plasmas as

Rotational	Vibrational	Electronic
~0.03	0.2-2	3-10
<1	4-110	120-1000
	Rotational ~0.03 <1	RotationalVibrational~0.030.2-2<1

 a 1 eV = 1.6×10^{-19} J = 11 600 K b Td: Townsend, 1 Td = 1×10^{-17} V \cdot cm^2

Table 1.1: Range of predominant plasma processes in air at room temperature. Note the specified ranges signify when the process becomes predominant

its value dictates the direction of energy deposition and hence governs the active particle production that may occur in a plasma discharge. In the simplest case the reduced electric field is a function of the electric field E, which is the measure of the applied voltage over the discharge geometry, and N is the number density of the gas [44, 45]. The relative temperature that electrons and heavy particles exhibit during Joule heating defines the local thermodynamic equilibrium (LTE). Based on this notion plasma discharges can be classified in one of two ways. At relatively low electron temperatures ($T_e \sim 1-20$ eV), electrons have insufficient amount of energy to elevate the kinetic energy of the heavy species (translational energy), mainly due to the large disparity in masses. This creates a plasma environment that is far from thermodynamic equilibrium where the electron temperatures can far exceed those of the ions (T_i) and heavy (T_o) species $(T_e \gg T_i \sim T_o)$. This is known as a "non-equilibrium" (non-thermal) plasma where the background gas temperatures are often at or near room-temperature [42]. However, the accumulated electron energy is still enough to effectively transfer energy onto the internal energy modes of the gas (rotational, vibrational, and electronic). Table 1.1 summarizes the range of electron energies needed for exciting internal energy modes.

Rotational excitation usually happens at low energy levels (T_r) , this means rotational-translational energy transfers can take place relatively fast since the two temperatures can equilibrate only after several collisions. Conversely, vibrational excitation occurs at higher energy levels (T_v) making vibrational-translational energy transfers slower and usually taking 10^3 to 10^8 collisions [46]. Thus, the energy modes in non-equilibrium plasmas are conventionally presented as ($T_e>T_v>T_r\sim T_i\sim T_i$ T_o). On the other hand if the electron temperatures are sufficiently high ($T_e \ge 100 \text{ eV}$) more energy is capable of being transferred to the translational energy of the heavy species. This effectively reduces the electron temperatures, and the temperature of the internal energy modes of the heavy species. This effect also proportionally increases the collisional frequency among the heavy species, which directly correlates to increasing the gas temperature. In the limit that the electrons and

heavy species temperatures approach each other, the plasma is said to be in thermal equilibrium $(T_e \sim T_i \sim T_o)$ and this is referred to as an "equilibrium" (thermal) plasma [42].

From the perspective of combustion enhancement, non-equilibrium plasmas offer the greatest potential. It is well agreed upon that the main mechanism in enhancing and subsequently accelerating the total rate of combustion under non-equilibrium conditions is the efficient ionization, dissociation and excitation of molecules due to electron-impact [47]. Although, equilibrium plasmas have the ability to be highly effective, the enormous thermal enhancement that they offer from electrical energy makes any chemical enhancement highly inefficient. This directly translates into poor utilization of any energy content the reactive gas mixture may have, and can potentially drive the chemical process to an endothermic direction. It is for this reason significant progress has been made to develop generators that can sustain strongly non-equilibrium plasmas. A number of results have shown that the most efficient non-equilibrium plasmas are generated using nanosecond duration, high-voltage pulses [48]. The basic idea is to create large volume ionization in a gas flow by the application of 5-50 kV pulses (~10 nsec in duration) at 1-100 kHz pulse repetition rates. There are two main advantages to this type of plasma discharge. Firstly, the very short pulse duration is much shorter than the time scale of Joule heating and ionization instability, reducing the potential of glow-to-arc transitions while improving plasma stability. Stable repetitively pulsed plasmas can generate diffuse, volume filling discharges at higher pressures with lower plasma gas temperatures. Secondly, the high reduced electric field during the high-voltage pulse can produce large amounts of chemically active radical species at relatively low power inputs.

1.2.2 Kinetics of Plasma Assisted Combustion

The fundamental aspects of non-equilibrium plasma-assisted combustion will be demonstrated by considering the simplest case of a H_2/O_2 containing mixture. The essential kinetics of this system can be characterized by the branched-chain mechanism [49]:

$$H_2 + M \to H + H + M \tag{1.2}$$

$$H_2 + O_2 \to HO_2 + H \tag{1.3}$$

$$H_2 + O_2 \to OH + OH \tag{1.4}$$

$$H + O_2 \to OH + H \tag{1.5}$$

- $O + H_2 \to OH + O \tag{1.6}$
- $OH + H_2 \rightarrow H_2O + H \tag{1.7}$



Figure 1.6: Explosive limits of stoichiometric H_2/O_2 mixture. Redrawn from [49].

$$O + H_2 O \to OH + OH \tag{1.8}$$

$$\mathbf{H} + \mathbf{H} + \mathbf{M} \to \mathbf{H}_2 + \mathbf{M} \tag{1.9}$$

$$H + O_2 + M \to HO_2 + M \tag{1.10}$$

Reactions (1.2)-(1.4) are the initiating steps to the mechanism providing the initial radicals for the chain system, where reaction (1.2) is more likely to prevail at higher temperatures in order to overcome its relatively large bond energy. These radicals then go on to feed the branching reactions, chemical reactions that further increase the free-radical concentration in the system (reactions 1.5, 1.6, and 1.8). But this entire process is limited by reaction (1.5), a highly endothermic reaction, which implies that the rate of termination reactions of this system is completely reliant on the H-atom radical concentration (reactions 1.9, 1.10). When a certain free-radical concentration is reached, the chemical system will undergo an exothermic reaction (1.10) in which the system will no longer be able to dissipate the heat and the reaction will become self-heating. At this point, the rates of chain-branching reactions and the rate of heat release increases exponentially causing a sudden change in the main chemical components leading to an explosion of the gaseous mixture (ignition). In other words the rate of chain-branching reactions become faster than the terminating reactions.

The limits of explosion under the effects of pressure and temperature for a stoichiometric mixture of hydrogen and oxygen are depicted in Fig. 1.6. The region of no explosion is characterized by a steady-state concentration of free-radicals and the reactions proceed with a constant or very low



Figure 1.7: Potential energy diagram for excited states of O_2 , H_2 and Ar. Note: $Ar[{}^3P_0]$, $[{}^3P_2]$ are long-lived metastable states and $Ar[{}^1P_1]$, $[{}^3P_1]$ are short-lived resonant states. Redrawn from [50–52].

rate. The transition from a slow to an explosive type of reaction occurs spontaneously under various circumstances and gives rise to the appearance of several explosive regions bound by limits. The first limit occurs when radicals diffuse to the walls of the system and recombine, effectively inhibiting the chain prolongation process. The second limit is bound by a balance between radical production and destruction. Then finally, at the third limit there is a balance between heat release by chemical reactions and heat dissipation by the system. An interesting note from these results is that below 400 °C no explosive event will occur regardless of pressure. What is important to realize here is that the extent of the explosive reaction is directly related to the concentration of free-radicals feeding the chain branching reactions and less so on the manner in which they are generated. It can then be intuitively implied that if the radical concentrations can be artificially altered, then the explosive characteristics of the system can also be altered.

It has already been mentioned that non-equilibrium plasmas provide an ideal environment for high temperature electrons to interact with neutral particles. The main advantage to this is the ability to artificially induce free-radical production, directly or indirectly, that are not possible in a thermal dependent system. Consider the flowing electron-impact reactions [3]:

$$H_2 + e \to H + H + e \tag{1.11}$$

$$O_2 + e \to O + O + e \tag{1.12}$$

At an reduced electric field of 100-300 Td, it is well known that electrons can obtain more than sufficient energy to directly dissociate the chemical species. These dissociative pathways occur by way of excitation to low level electronic states $H_2(b^3\Sigma_u^+)$, $H_2(a^3\Sigma_g^+)$ and $O_2(A^3\Sigma_u^+)$, $O_2(B^3\Sigma_u^-)$, respectively (Fig. 1.7). Dissociation can also occur indirectly, where excited states in a reactive mixture can be quenched with neutral particles, a process analogous to reaction (1.2). One such example is the collisional process with the electronically excited states of Ar, which then goes onto dissociate molecular oxygen [53, 54]:

$$Ar + e \to Ar^* [11.7 \text{ eV}] + e \tag{1.13}$$

$$Ar^* + O_2 \to Ar + O + O \tag{1.14}$$

Referring to Fig. 1.8 it can be demonstrated that these electron impact reactions are several orders of magnitude faster than thermal dissociation, reaction (1.2), producing an equivalent H-atom radical. This holds great significance because under the influence of the plasma the means to artificially inject radicals, enhance the radical pool and effectively manipulate the rate of chain branching is now possible with a higher degree of efficiency. Apart from enhanced radical production methods,



Figure 1.8: Comparison of reaction rates for plasma involved reactions (i.e., electron-impact dissociation and excited states - dashed lines [55–57]) and thermal reactions (solid lines) contributing to hydrogen oxidation. Modified and redrawn [2].



Figure 1.9: Extension of explosive limits for H_2/O_2 mixture with a plasma discharge. Curves correspond to the explosion limits when different amounts of current are applied to the primary circuit. Redrawn from [2].

plasmas can also produce excited intermediate species not typically observed in normal combustion systems. Such include [55–57]:

$$O_2(a^1\Delta_g) + H \to OH + O$$
 (1.15)

$$O(^{1}D) + H_{2} \rightarrow OH + H$$
(1.16)

Several studies have investigated reactions containing excited species states, more specifically excited oxygen states that are an integral part in understanding the kinetics of upper atmospheric chemistry. Figure 1.8 shows that reactions involving excited states can be significantly faster then their ground state counterpart. This can be directly attributed to the fact the excited states can significantly reduce the activation energy barrier required for the ground state reaction to occur [42]. Consideration of these processes together with the ability to increase the O-atom radical pool it has been proven experimentally that the explosion limits of the H_2/O_2 system can be shifted to lower temperatures and demonstrates the indicative enhancing effects plasmas can have on a combustion system (Fig. 1.9). Plasma discharges can also provide thermal and transport enhancements to the reactive flow. Localized heating from the plasma source can induce flow perturbations and provoke turbulization and mixing. The ionic wind effect (momentum transfer from the electric field to the gas due to charged particle interactions within the electric field) can lead to fluxes of active particles in the gradient flow [2].

1.3 Research Objectives

It is extremely important to understand the mechanism by which non-equilibrium plasmas have an effect on the combustion of gaseous mixtures from both a fundamental and a technological standpoint. The issue here is that the plasma chemistry involved in contributing to these enhancements has very different characteristics compared to the combustion kinetics. In Fig. 1.10 it can be shown that plasma chemistry happens on a very small time scale (~100 ns) at relatively low temperatures, whereas the combustion chemistry normally occurs at higher temperatures and at longer time scales (~ps to ~ms). The key process in plasma enhanced combustion involves the coupling of long-lived plasma species reacting with fuel and oxidizer at low temperatures. This essentially bridges the fast plasma chemistry with the high-temperature combustion processes. The role of different species in PAC has been widely discussed and despite increased interest in the problem, the kinetic mechanisms for plasma enhanced combustion are still not very well understood. In order to embark on such a task, well defined experiments capable of isolating such interacting pathways is necessary,



Figure 1.10: Comparison of characteristic time scales of different chemical processes. Redrawn from [2].

where minimizing the uncertainty in the combustion experiments is critical in order to elucidate any effects the plasma may have. Chapter 2 will highlight the progress in developing such experiments and the current state of the existing PAC kinetic mechanisms.

The goal of this work is to provide a fundamental understanding of the kinetic mechanism involved in plasma assisted combustion of various fuels at elevated pressures using a newly designed and fabricated flow reactor experimental facility. In this study a nanosecond pulsed discharge will be used to perturb a highly-diluted reactant mixture to elucidate product and intermediate species formation as a direct result of the plasma. As evident in the literature review in the next chapter, experimental techniques used in the past to provide mechanistic data have been limited to specific regimes, all at very low pressures (P < 0.6 atm) and for range of different temperatures (T = 300-1600 K). Also, experimental techniques have had difficulty decoupling the effects of the plasma and the thermal reactions due to excessive heat release by the enhanced reactions. Hence, the main objectives of this dissertation are as follows:

• Design and fabricate a new plasma flow reactor (PFR) experimental facility, to capture product and intermediate species as result of plasma perturbation effects on the pyrolysis and oxidation of various fuels. The experimental facility is capable of employing both *ex situ* and *in situ* diagnostic techniques. The focus of the experimental measurements and hence the mechanistic data presented within this dissertation will cover a dynamic range of temperatures from T = 420-1250 K all at P = 1 atm (see Chapter 3).

- Examine the oxidative characteristics of hydrogen under the effects of a non-equilibrium plasma. H₂/O₂ kinetics play an integral role in the growth of radical pools, and an understanding of this sub-mechanism will help elucidate the kinetic features associated with hydrocarbon oxidation. Studies will focus on the kinetic behavior of the OH-radical and the differences its participation has on the overall thermal and plasma-assisted oxidation schemes (see Chapter 4).
- Examine the oxidative characteristics of hydrocarbon fuels under the effects of a non-equilibrium plasma. Studies will begin by looking at the global oxidative trends in C₁-C₇ alkane fuels, while trying to elucidate the kinetic enhancement features the plasma effects offer over thermally constrained effects. The investigation is then extended to examine both the pyrolysis and oxidation of ethylene, a major intermediate in alkane oxidation (see Chapter 5).
- Using an existing PAC numerical kinetic model, a newly developed ethylene plasma-specific mechanism will be developed and evaluated against mechanistic data derived in this study. Preliminary analysis will be performed to bridge the gap between phenomenological observations to theoretical understandings and determine the main kinetic features that lead to enhanced oxidation (see Chapter 6).

Chapter 2

Literature Review

2.1 Demonstrating the Effectiveness of Plasma Assisted Combustion

There have been many impressive demonstrations of practical applications of plasma-assisted combustion over the last decade. The scope of this field is quite broad, where potential benefits have been realized in a variety of different combustion systems using numerous different plasma sources. The following review will mostly focus on the nanosecond pulsed plasma discharges, and their application to gas turbines and hypersonic propulsion systems.

2.1.1 Lean Combustion Stability

Towards the development of advanced gas turbines, plasma-assisted combustion has proven to be a promising new technique that can increase efficiency, reduce emissions, and improve combustion stability. Experimental and numerical studies performed by Serbin et al. [5] proposed that a modified gas turbine combustor using a pilot flame stabilized with a non-equilibrium plasma, can achieve better performance, wider turndown ratios, and lower carbon and nitrogen oxide emissions. The ecological characteristics of the study demonstrated a reduction in the maximum temperature of the combustion products by 190 K (from 2340 to 2150 K), effectively reducing the NO_x emissions from 16 ppm to 1 ppm without any CO emission increase. Similarly, the extension of the lean stability limit with improved combustion efficiency has been reported in the works by Pilla et al. [58, 59]. Using a nanosecond pulsed plasma discharge (10 kV pulse at 10 ns duration) and varying the pulse repetition rate from 1 to 30 kHz, significant reduction in the lean flammability limit was achieved in a turbulent ($Re_D = 30,000$) premixed propane-air flame (Fig. 2.1). By generating the plasma in the recirculation zone behind the bluff body of the flow, significant increase in heat release and



Figure 2.1: Critical equivalence ratio of the lean flammability limit in an propane-air flame as a function of air flow rate. Simple schematic of the experimental setup comparing the OH (A-X) emission with and without the plasma discharge ($\phi = 0.83$). Redrawn from [58,59].

efficiency were achieved. This improved flame stabilization under fuel-lean conditions would not have been possible without a plasma. These results also demonstrated that enhanced stability can be achieved with minimal plasma power input, or 0.3% of the maximum power output of the flame. Substantial flame stabilization enhancement was also claimed by Kim et al. [60] in a lifted methane-jet diffusion flame in coflow. Coflows surrounding a jet-flame are routinely used to stabilize both premixed and non-premixed flames. Using a ultra-short (10 ns) pulsed discharge, the authors experimentally were able to extend the coflow velocity limit by as much as 20 times the laminar flame speed. In a separate investigation, the same authors [61] also investigated improved stability of lean ($\phi < 0.6$) premixed methane-air flames. However, at the same time they observed an increase in the localized NO production, presumably due to the high reactivity of excited metastable states of nitrogen with atomic oxygen. Of notable mention are the efforts by Nikipelov et al. [62] where using a nanosecond distributed spark discharge they were able to ignite and stabilize ultra-lean ($0.06 < \phi < 0.3$) premixed methane-air flames.

Apart from flame stabilization, a known design challenge in maintaining combustion stability in lean gas turbines is overcoming the pressure pulsations that arise from interacting unsteady heat releases and acoustics in combustion chambers. Moeck et al. [6] coupled a nanosecond pulsed discharge to the nozzle exit of a swirl-stabilized lean premixed natural gas-air flame, and found that the plasma discharge can influence the pressure pulsations generated by the thermoacoustic dynamics in the combustor. With a plasma discharge outputting less than one percent of the total power of the flame, the maximum pressure pulsation amplitude was reduced by 50%. Several other authors have also experimentally proven reduced ignition delay and improved flameholding capabilities using non-equilibrium plasmas [3, 10, 17, 63, 64]. Specifically for fuel-lean mixtures, these capabilities have considerable benefit in improving lean-burn operability in gas turbine applications.

2.1.2 Supersonic Flows

A particularly relevant application of plasma-assisted combustion applies to the ignition and combustion control of high-speed reactive flows. Leonov et al. [65] analyzed the applicability of various (e.g., microwave, radio-frequency, nanosecond DC, etc.) plasma discharges to ignite such flows, along with their advantages and disadvantages to each system. In a later study, Leonov et al. [66] devised an appropriate experimental setup, where a modified combustion chamber was constructed capable of achieving gas velocities up to 500 m/s (Ma = 2) in air using a supersonic nozzle. From wall mounted fuel injectors, hydrogen or ethylene fuels were then injected into the airflow. With an electrical discharge (corresponding to a plasma power input range of 3-17 kW) producing oscillating plasma filaments, it was possible to both initiate and sustain a combustion process. A schematic of the experimental chamber and the electrode configuration is presented in Fig. 2.2. It was observed that the plasma initiated intensified mixing, but also a sequence of activated zones of reactive gas downstream from the immediate plasma-fuel interaction. In another experimental facility established by Do et al. [18, 67], a supersonic airflow was generated in an expansion tube producing reaction residence times on the order of 300-500 µs. In their first study they examined the stability of H_2 and C_2H_4 injected cavity flames. In conjunction with the cavity, a nanosecond pulsed plasma discharge (pulse peak 15 kV) was applied to the reactive flow, where both enhanced flame ignition and noticeable reduction in ignition delay were seen for a range of flow conditions. Additionally, a simple model calculation was carried out to qualitatively validate the experimental results. For H_2/O_2 mixtures it was determined that the sensitivity of flame ignition and flameholding to pulse repetition rates were highly depended on the initial temperature of the mixture. For a given fixed discharge power (~ 10 W), at higher repetition rates (up to 100 kHz) a greater amount of H- and O-radicals were produced in a 200 µs time span under low temperature conditions (T = 500-800 K), whereas at lower rates (50 kHz) it was found that ignition occurred faster in higher temperature mixtures (900 K). For their second study [68], the configuration of the experimental facility was modified to locate the discharge electrode in between two fuel nozzles. The dual fuel injection and electrode configuration was then mounted flush with the surface of the


Figure 2.2: Depiction of the experimental facility used to investigate plasma-assisted ignition and flameholding in high-speed flows for H_2 and C_2H_4 . Taken from [65].



Figure 2.3: OH PLIF images overlapped with typical Schlieren image at Ma = 2.4, (a) without the upstream jet, (b) with both jets active without plasma and (c) both jets in the presence of the plasma. Taken from [68].

flat wall adjacent to the freestream flow (Fig.2.3). Subsonic and supersonic hydrogen and ethylene fuel streams were then injected into a pure oxygen freestream at speeds corresponding to Ma =1.7-2.4. With this configuration, plasma enhanced supersonic combustion was interpreted as twostage process. The first stage consisted of channeling the plasma energy into a subsonic fuel-oxygen mixture that acted as a "pilot flame" with enhanced radical production. This flame would then facilitate the ignition of the main supersonic fuel stream where experimental evidence showed main jet flameholding was capable for flow times on the order of 300 µs. The authors also claimed that this easily integrated configuration into a flat wall would eliminate the need for wall features (e.g., cavities and backsteps) to generate flow circulation, hence minimizing any potential stagnation pressure losses. These practical experimental investigations have proven the use of plasma-assisted technologies in stabilizing ultra-fast combustion processes for hypersonic applications. Thus, the ultimate goal here is to be able to extend the engine stability region (Fig. 1.5) to low dynamic pressures and to higher Mach numbers.

2.2 Kinetic Studies of Plasma Assisted Combustion

2.2.1 Experimental Investigations

The field of plasma-assisted combustion can trace its historical roots as far back as 1904 by Kirby [69], who discovered that if an electrical discharge is applied to a low pressure combustible mixture it could ignite under conditions where it would not normally burn. In a series of experiments, Kirby [69] found that H₂O can be formed if electrical discharges are applied to low pressure (~ 2 Torr) H₂/O₂ mixtures. He postulated that atomic oxygen was being formed and directly collided with H₂ to form water [69]. Over the last 20 years considerable advancement has been made in developing new techniques to study the chemical interactions involved in PAC. Several unique experiments with varying diagnostic approaches have been devised and carried out by several research groups around the world.

The first significant contribution comes from the group at the Laboratory of Physics of Nonequilibrium Systems from the Moscow Institute of Physics and Technology, where in 1996 they developed a new type of plasma discharge known as the Fast Ionization Wave (FIW) [70]. The FIW was generated by applying nanosecond duration high-voltage pulses to a reactive mixture that could then propagate even faster to sustain a highly homogeneous plasma discharge. FIW generated plasmas had several advantages making them ideally suited for studying PAC. Firstly, they were able to generate relatively high E/N values to provide uniform ionization, efficient dissociation and the formation of electronically excited species at relatively high pressures. But more importantly, the rapid time scale in which the plasma was initiated was much shorter than any typical combustion process, allowing experiments to decouple the plasma and combustion chemistry effects [70]. These FIW discharges where then implemented into two types of experimental facilities capable of generating relatively different experimental conditions. The first was a quartz discharge tube that was filled with a reactive mixture and stored under extremely low pressures (P = 0.8-10 Torr) at ambient temperature. The high-voltage pulses were then administered by two electrodes placed at opposite ends of the tube. At one end of the tube, a window was placed to provide optical access to perform emission spectroscopy measurements. Starikovskaia et al. [71] used this facility to study the slow oxidation of hydrogen in stoichiometric mixtures of $H_2/O_2/N_2$. The excitation of the gas mixture by FIW and the dynamics of the H_2 concentration where monitored by measuring the absolute radiation intensity of its electronic state transition. A couple of years later, Anikin et al. [72, 73] used the same experiment to study the slow oxidation of stoichiometric mixtures of C_1 - C_6 alkanes in oxygen or air and then lean mixtures of n-butane and n-decane with oxygen. In both instances the radiation intensities of molecular bands for several species transitions were measured, including CH, OH, CO and CO_2^+ . Based on these optical measurements, the times for complete oxidation of hydrocarbons was determined. It was ultimately determined that at a given pressure and at the same energy deposition by the plasma, all hydrocarbons greater than ethane completely oxidized at the same time in oxygen. Methane however, was systematically always twice as long, and when air was used, oxidation times were two or three times lower than those similar mixtures in oxygen (Fig. 2.5).

At around the same time, the FIW was applied to a shock tube experiment to study the ignition characteristics of PAC. This experimental technique utilizes a plane shock wave to almost instantaneously compress a given fuel-oxidizer mixture to a desired temperature and pressure. The time interval between the shock wave arrival, which is determined by a pressure trace, and the onset of combustion, which is usually inferred from a spectral intensity measurement of an intermediate combustion species (e.g., OH, CH), is then measured. This time interval is known as the "induction time" or the "autoignition delay time". This technique was then further modified to include a plasma discharge at the beginning of the induction period. It was shown experimentally that a spatially uniform, low temperature nanosecond discharge could be generated to activate the mixture behind the reflected shock wave with minimal gas heating [74]. This precise control of the plasma initiation allows the kinetic effects of the discharged and the ignition processes to be extracted and



Figure 2.4: Experimental results for Anikin et al. [73], times for complete oxidation of hydrocarbons, determined from $CO(B^{1}\Sigma \rightarrow A^{1}\Pi)$ emission band, as a function of initial pressure of the stoichiometric mixture: (1) CH_{4}/O_{2} (2) CH_{4}/air (3) $C_{2}H_{6}/O_{2}$ (4) $C_{3}H_{8}/O_{2}$ (5) $C_{4}H_{10}/O_{2}$ (6) $C_{5}H_{12}/O_{2}$ (7) $C_{6}H_{14}/O_{2}$ (8) $C_{5}H_{12}/air$ (9) $C_{6}H_{14}/air$.



Figure 2.5: The delay time for autoignition and ignition with the discharge in 1 C_5H_{12} : 8 O_2 : 81 Ar mixture as a function of temperature taken by Kosarev et al. [54], using the FIW shock tube facility.

evaluated separately in time. The problem with shock tubes, however, are their departure from ideal behavior. For example, interference between boundary layer effects and reflective shock waves limit the possible experimental conditions to regimes with short chemical inductions times, often at relatively high temperatures. In all instances, the experiments were carried out using highly dilute mixtures using an atomic gas (Ar or He), such that the experimental results could be later interpreted using a quasi-one-dimensional model. Since its inception, this platform has been used to provide experimental data for the mechanistic behavior of plasma-assisted ignition (PAI) under a wide variety of temperatures (T = 700-2700 K), pressures (P = 0.6-228 atm) and mixtures. Such include H_2 oxidation by Bozhenkov et al. [75], C_1 - C_5 alkanes in oxygen by Kosarev et al. [53, 54, 76] (Fig. 2.5) and Aleksandrov et al. [77]. A review of all the major experiments and calculations based on this facility can be found in reference [70] by Starikovskaya et al. The main experimental conclusion drawn from all the investigations was that under a high-voltage plasma discharge not only was there a noticeable decrease in ignition gas temperature, there were orders-of-magnitude decrease in ignition delay times as well. The authors acknowledged that although the shock tube facility was fairly well designed, it was limited in its capabilities to provide an adequate picture of the plasma kinetics. The concluding consensus was that in order to fully understand the kinetic intricacies involved, experimental measurements of the dominant radicals and intermediates species were needed.

In more recent years, considerable efforts have been taken by the researchers at the Non-Equilibrium Thermodynamics Laboratory at the Ohio State University, to study the radical interactions involved in PAC. Mostly all their experiments in one form or another involved a discharge flow reactor. This facility basically involves flowing a premixed reactant mixture at a given flow rate through a test section, where a plasma discharge is administered by electrodes mounted on the walls of the reactor. At the exit of test section Fourier Transform Infrared (FTIR) absorption spectroscopy is used to identify and quantify the product species formed. The test section also has optical access ports to perform various *in situ* emission spectroscopy measurements in the discharge region. The first set of experiments were performed by Bao et al. [78], studying stoichiometric oxidation of CH_4/air and C_2H_4/air mixtures. At relatively low pressures (P = 70-100 Torr) and low discharge powers (~100 W), nearly 85% - 95% fuel consumption was achievable in preheated air (T = 100-300 °C) experiments. However, the experiments showed that adding fuel to the air flow considerably increased the flow temperature in the plasma, while adding fuel to a nitrogen flow did little to raise the temperature. This suggested that the plasma fuel oxidation reactions were responsible for enhanced flow ignition. The experiments were further extended by Lou et al. [79]



Figure 2.6: Time resolved mole fraction of oxygen atoms generated after a single high-voltage pulse in air and methane-air plasmas at P = 60 Torr and $\phi = 1.0$, compared to Adamovich et al. model [81].



Figure 2.7: Comparison of experimental and predicted temperature, OH concentration and OH (A-X) emission traces for H₂/air, at $T_o = 500$ K, P = 80 Torr and $\phi = 0.5$ [84].

and Mintusov et al. [80] for a wide range of equivalence ratios, flow velocities and pressures (P= 70 Torr). Their experiments demonstrated significant fuel conversion into CO, CO₂ and H₂O, while intermediates such as CH_2O and C_2H_2 were also observed. Again, the results suggested that significant fuel oxidation can occur with significant temperature rise in the flow at conditions when there is no ignition or detectable flame. Using a modified quartz reactor compared to the previous studies, Uddi et al. [81] made significant progress to measure radical generation in the plasma discharge. Two-atomic Laser Induced Fluorescence (TALIF) technique was implemented to measure the absolute O-atom concentrations formed in fuel-air and pure air mixtures. The experiments were able to reveal that peak atomic O-atom generation was related to the concentration of the air in the mixture, but the rate of O-atom consumption in fuel-air mixtures was much faster than in pure air (Fig. 2.6). Later experiments performed by Zuzeek et al. [82,83] in the same reactor, conducted rotational Coherent Anti-Stokes Raman Scattering (CARS) thermometry measurements in H_2/air and C_2H_4 /air mixtures. Time resolved temperature measurements indicated that the primary source of heat release was a result of fuel and O-atom interactions and entirely independent of equivalence ratio. Lastly, Yin et al. [84] and Choi et al. [85] studied the ignition delay of H_2/air mixtures by taking time-resolved temperature and absolute OH concentration measurements. They concluded that the OH concentration can increase nearly 20-50 times in the plasma discharge during an ignition process. As a result of this, it was reported that ignition delay can decrease by increasing the pulse repetition rate of the high-voltage pulses while the ignition temperature can decrease by 200 K. These studies provided further insight into the kinetics behind PAC, particularly in quantifying in situ generation of radical species. Despite efforts to quantify intermediate species, it can be said that the decoupling of thermal and plasma effects were not entirely achieved. Due to numerous mentions of excessive heat release, it is difficult to ascertain whether intermediate species formed were a direct result of the plasma or by-products of the accelerated thermal reaction.

Most of the investigations described thus far deal with experiments involving reactive mixtures under the action of a plasma discharge. However, researchers at the Advanced Combustion and Propulsion Laboratory at Princeton University decided to take a different approach and use flames to study the kinetic enhancing effects of plasmas. Such an experiment involved coupling a nanosecond plasma discharge to a counterflow diffusion flame system. Different from previous studies, counterflow systems offer several key experimental benefits namely, minimal buoyancy effects, simplified geometry, the ability to define a flow velocity gradient on the stagnation plane of the two impinging jets, and excellent optical access for laser diagnostic techniques. Recently Sun et al. [87, 88] performed experiments to study the effects of plasma produced species on flame extinction. In an argon



Figure 2.8: Relationship between OH^{*} emission intensity, local maximum temperature and fuel mole fraction (X_F) for oxygen mole fractions of $X_o = 0.34$ and $X_o = 0.62$. (solid square symbols represent increasing X_F and open square symbols representing decreasing X_F). Redrawn from [89].

diluted CH_4/O_2 diffusion flame, a plasma discharge was applied to the oxidizer side to induce the formation of O-atoms. Using TALIF to measure the absolute O-atom concentration, they were able to report that increasing the discharge frequency and hence increasing the O-atoms produced, the flames extinction strain rate could be extended significantly. Despite producing a significant amount of O-atoms, they found that the oxidizer flow temperature needed to be above 900 K (at low pressures ~ 60 Torr) for any enhancement to occur, otherwise most of the atomic O would be quenched or recombine before it reached the reaction zone. To avoid quenching, 2% methane fuel was added to the oxidizer flow, such that any active species generated in the plasma would react with the fuel instead of recombining. Product species concentrations as a result of low temperature plasma oxidation were measured by FTIR, Gas Chromatography (GC), and TALIF. The experiments showed that by increasing the discharge frequency, fuel consumption could increase, along with increases in the production of H_2 , CO, CO₂ and H_2O , accompanied by an increase in the flow temperature at the nozzle exit. Moreover, these experiments demonstrated an extension of the flames extinction limit at lower temperatures. It was postulated that when a flame approaches the thermal limit of extinction the residence time for complete oxidation is not long enough, but under the assistance of a plasma discharge oxidation could be drastically accelerated by prompting early chemical heat release [88]. Even though the experiments were successful in demonstrating the enhancing effects that active species can have on a flame, the authors claimed that the dominant effects of the plasma in the reaction zone were not entirely free of thermal enhancing effects due to the relatively short lifetime of the reactive species. In order to elucidate the direct coupling between the plasma and flame kinetics the experiments needed to be modified. Subsequently, Sun et al. [89] developed a counterflow flame system using porous stainless steel electrodes that were capable of generating a uniform *in situ* plasma discharge between the two burners. The purpose of this new experiment were to study the ignition and extinction characteristic of the flame using a plasma discharge applied to the reaction zone. To do this, OH^{*} emission intensity and the peak temperature in the reaction zone were measured. An abrupt change in OH^{*} emission would indicate an ignition or extinction event had occurred, whereas the temperature was measured using the Rayleigh Scattering method. Two sets of experiments were performed while keeping the pressure (72 Torr) and discharge frequency constant in both. In the first instance, the oxidizer loading was kept constant $(X_o = 0.34)$ and the fuel loading was varied (Fig. 2.8). Initially starting with no fuel, the amount of fuel was increased, where at some mixture ratio the flame would ignite. Once ignited the fuel loading was then decreased until the flame would extinguish. This hysteresis effect forms an S-curve defining the limits of ignition and extinction and is a fundamental phenomena observed in flames. In the second scenario, the oxidizer loading was increased $(X_o = 0.62)$ further and the experiments were repeated (Fig. 2.8). What was discovered is that at a relatively low fuel loading ($X_F = 0.09$), not only did the flame ignite but also that the limits of ignition and extinction merged, extending the stability range of the flame to lower temperatures. It was explained that this stretching of the flames limits was due to the fact that the plasma generated species were causing the flame stabilization mode to transition from an extinction mode to an ignition mode. In other words, the chemistry dictating the extinction limit did not exist in the presence of the plasma and the chemistry of flame stabilization was fully controlled by the ignition limit. In similar investigations, Ombrello et al. [90,91] studied the effect of long lifetime species, namely ozone (O₃) and O₂ $(a^1 \Delta_g)$ on the flame propagation. Using a lifted flame system where the height of the flame was correlated to the flame speed, excited species were transported to the flame. At atmospheric pressure, injecting 1260 ppm of ozone produced an 8%enhancement in flame speed of a $C_3H_8/O_2/N_2$ lifted flame. Similarly, it was found that O_2 ($a^1\Delta_g$), which has a mean radiative lifetime of 2700 s, could change the lift off height in a C_2H_4 flame. The experimental technique in producing and quantifying $O_2(a^1\Delta_g)$ is quite intricate and can be found fully explained in reference [91]. What is interesting to note from these experiments, is that in all instances, the enhancement of the radical pool is the predominate reason to any observed enhancement in flame characteristics. In contrast, in the already mentioned works of Kim et al. [61], they concluded that the reforming of methane into H_2 and CO played an integral role in enhancing the flame's stability. To further verify this claim, flame stability experiments were performed in H_2/air flames without any significant reduction in the blowout limit compared to a CH_4/air flame. This led them to conclude that enhancement was not due to radical generation by the plasma, but rather due to CH_4 reforming.

2.2.2 Development of Kinetic Mechanism

In an effort to describe the kinetic processes involved in PAC, several numerical modeling studies have been performed in conjunction with the experimental investigations described above. For the most part, the numerical procedure is the same throughout, where plasma kinetic mechanisms are implemented with combustion kinetic mechanisms and linked together by known interactions between active species and neutral species found in the afterglow. In order to determine the density of the active particles, an idea of the electron energy distribution function (EEDF) is needed first. This is achieved by solving the two-term Boltzmann equation for electrons at a given reduced electric field. For relatively low reduced electric fields (< 600 Td), representative of non-equilibrium plasmas, the two-term approximation has been validated and verified for its applicability in modeling PAC [70]. Also, because of the relatively low degree of ionization experienced in these plasmas, electron-electron, electron-ion and ion-ion chemistry is usually neglected and found not to be an essential contributor to the enhancement mechanism [71]. From here known electron-impact crosssections are implemented to compute the rate coefficients of ionization and excitation processes for desired species. Considering that the discharge time (on the order of nanoseconds) is significantly smaller than the typical combustion time (on the order of milliseconds), it can be viewed that the density of active particles acts as an initial step to computing the density of species involved in the combustion scheme. The results obtained from these models are then compared to the experimental measurements to test ones understanding of the underlying chemistry. Generally, the comparison of results have been less than satisfactory, demonstrating there is still a lack of fundamental understanding in PAC kinetic mechanisms.

Starikovskaia et al. [71] was the first to develop a kinetic model to compare the FIW experiments. The H₂/air mechanism is the most comprehensive including some 750 chemical and 8700 vibrational exchange process, with 254 participating species. Under the conditions of their experiments (1-8 Torr at ambient temperature, E/N = 100-500 Td), non-equilibrium vibrational kinetics played a principle role in hydrogen oxidation, where the strongest influence in forming water was exerted by:

$$H_2(v) + O \to OH(w) + H \tag{2.1}$$

The activation energy of reaction (2.1) decreases significantly when molecular hydrogen becomes vibrationally excited, subsequently leading to an increase in the reaction rate and an enhanced source of OH and H-atom radicals. Despite earnest efforts, the modeling comparison with the experiments did not agree well, and it was recommended by the authors that further detailed studies be performed, specifically reaction pathways regarding radical and intermediate species formations. Nonetheless, Starikovskaia's model was used as a precursor for later modeling efforts involving the FIW shock tube experiments at high initial temperatures, usually at or close to the self-ignition threshold. Bozhenkov et al. [75] reduced the number of electron-impact reactions leading to the excitation of H_2 and O_2 molecules to study hydrogen oxidation and implemented electron-impact reactions involving CH_4 dissociation to study methane oxidation. To simulate the high temperature combustion kinetics in the afterglow, GRI-Mech 3.0 mechanism [92] was used. In both instances, the concentrations of atoms and radicals created in the discharge were taken as initial conditions for the high temperature calculations. From these calculations, the ignition delay time between the thermal and discharge scenarios could be compared based on a sharp rise in OH concentrations. The same model was once again modified by Kosarev et al. [76] to examine C_1 - C_5 oxidation. Only this time they opted to use a combination of mechanisms to model the combustion chemistry. Methane combustion was provided by the RAMEC mechanism [93], which is an extension of the GRI 1.2 mechanism complemented with reactions involving methyl- and ethylperoxides. The second was Curran et al. mechanism [94], which is usually adapted to describe the ignition of more complicated hydrocarbons at relatively lower temperatures 550-1700 K. Since no reliable cross-sectional data exists for C_3H_8 , C_4H_{10} , and C_5H_{12} , the authors assumed that the cross-sections were similar to C_2H_6 . In all instances it should be mentioned that the effects of the non-equilibrium plasma discharge in the model were reduced to the accumulation of active particles that influence the ignition process, meaning that only excited species leading to dissociation were considered. Such include excitation of metastable Herzberg states for oxygen:

$$O_2 + e \to O_2 \left(A^3 \Sigma_u^+ \right) \to O + O + e \tag{2.2}$$

The authors mentioned that because there is little known about the quenching rates of excited species with neutral species they were excluded. This is still an issue nowadays and is a major challenge that inhibits the advancement of PAC specific mechanisms. However, increased efforts have been made to investigate the role that specific excited species play in the overall reaction mechanism. Most notable mentions, are the works of Ombrello et al. [90,91] and Popov et al. [95,96], regarding the efficiency of singlet delta oxygen (SDO) $O_2 (a^1 \Delta_g)$. Specifically, numerical studies performed by Popov et al. [96] examined the dynamics of SDO quenching in H₂/O₂ mixtures for temperatures ranging from 300-1050 K. It was determined that despite being an important contributor to the rapid production of active particles (reaction 2.3), SDO is 80% more likely to deactivate though collisional quenching with molecular hydrogen (reaction 2.4). The rate of this process increases significantly with the temperature of the mixture. For the most part this process has been widely disregarded by many researchers and is an important process that can reduce the effectiveness of SDO on the reduction of induction times. A similar effect was claimed with HO₂, having significant implications at higher pressures.

$$O_2 \left(a^1 \Delta_g \right) + H \to OH + O \tag{2.3}$$

$$O_2 \left(a^1 \Delta_g \right) + H \to O_2 + H \tag{2.4}$$

Based on these findings, it was recommended that gas discharged systems that produce efficient production of atomic particles (e.g., H- and O-atoms) should be preferred. With these initial kinetic studies and their relatively good agreement with experimental results (Fig. 2.5), it is nowadays acknowledged that the primary mechanism in PAC within the self-ignition threshold at high initial temperatures is the rapid decomposition of fuel and chain reactions induced by electron-impact reactions leading to molecular dissociation and chemically activated radicals.

A similar PAC kinetic model was developed by Adamovich et al. [17] to analyze the experiments performed by the Ohio State University group. The model consists of combining an air-plasma mechanism developed by Kossyi et al. [97] and a hydrocarbon oxidation mechanism, either GRI-Mech 3.0 or USC Mech II developed by Wang et al. [98]. The model has also been extended to include CH_4 , C_2H_4 and C_2H_2 electron-impact dissociation reactions and collisional quenching reactions with excited states of N_2 . Using both combustion mechanisms the experimental data obtained by Uddi et al. [81] and Mintusov et al. [80] in low temperature CH_4/air and C_2H_4/air plasmas were analyzed. Overall the kinetic model predictions agreed well with the TALIF O-atom (Fig. 2.6) and the major fuel oxidation product (e.g., CO and H_2O) measurements. However, some of the other product species concentrations (e.g., CO₂ and CH₂O) predicted by the two mechanisms differed significantly, in some instances by one order of magnitude. It was claimed that in all cases the same set of plasma reactions and rates were used and that the difference in the predictions lied in the differences in reactions and rates used by GRI-Mech 3.0 and USC Mech II. This is an understandable argument considering most combustion mechanisms are validated at high temperatures, and can possess large uncertainties at low temperature conditions. Not only that, but certain mechanisms are tailored to specific fuels, for instance GRI-Mech 3.0 has been developed for CH_4 oxidation in the range of 1000-2500 K, whereas USC Mech II is only suited for C_1 - C_4 hydrocarbons for temperatures greater than 950 K. This limitation in available data for low temperature combustion kinetics is another major challenge that makes validating and understanding the kinetic mechanisms of PAC difficult. Moreover, since the conventional combustion chemistry is relatively slow at low temperatures, it is expected that the not-well understood kinetics of long-lived excited species may participate more actively in the kinetic processes of the afterglow. For example, when using the conventional combustion mechanisms, model predictions of the Yin et al. [84] OH decay time were found to be more than two orders of magnitude faster than measured. By implementing a new chain process proposed by Starikovskiy et al. [99] involving vibrational-to-vibrational exchange (reactions 2.5 and 2.6) the model was able to correctly capture the slow decay of OH as found in the experiments.

$$N_2(v) + HO_2 \rightarrow N_2(v) + HO_2(v)$$

$$(2.5)$$

$$\mathrm{HO}_2(v) \to \mathrm{O}_2 + \mathrm{H} \tag{2.6}$$

2.3 Summary

It has been shown experimentally that plasma-assisted combustion techniques have the potential to extend the lean-burn operability range of gas turbines, but also provide a means to ignite and sustain combustion in high-speed flows for hypersonic aircraft applications. Despite the observable enhancement that plasmas offer, the fundamental kinetic mechanisms contributing to their enhancement are still not well known. Over the last two decades, several research groups have made considerable efforts to elucidate these mechanisms. Several experimental approaches integrated with nanosecond pulsed plasma discharges have been attempted with the aim of trying to decouple the plasma and thermal kinetic effects. Previous investigations, have included the shock tube technique, where homogeneous ignition of a combustible mixture is studied at elevated temperatures behind a reflected shock wave, flow reactor experiments at relatively low pressures and temperatures, and in counterflow diffusion flames at low pressures. In all instances, the experimental measurements involve monitoring the concentrations of excited species, radicals and atoms using in situ emission and absorption spectroscopy methods. However, each of these experiments had their inherent limitations, either lacking the ability to measure intermediate species formations, or operating at finite conditions usually at very low pressures and/or very high temperatures. As a result of these studies, mechanisms involving H_2 and various hydrocarbon fuel containing mixtures have been formulated and analyzed by kinetic modeling calculations. For the most part, oxidation close to the self-ignition threshold (high initial temperatures) can be explained by the efficient molecular dissociation instigated by the plasma through electron-impact reactions leading to the production of active radical species to facilitate the enhancement of the conventional high temperature combustion kinetics. However, at lower temperatures well below the self-ignition threshold, the kinetics become unclear mainly due to the lack of detail in understanding potential reaction pathways. Such details include electron-impact reactions of different fuels and fuel fragments, interactions between excited species and neutral particles, intermediate species formed as a direct result of the plasma, and the inapplicability of high temperature combustion mechanisms to describe low temperature combustion kinetics. Mechanistic data at elevated pressures and experimental concentration measurements of intermediate species at this low temperature regime are critical for proper numerical validation, and up until now has been very limited.

Chapter 3

Experimental Techniques

3.1 Introduction

As mentioned in the previous section, experimental facilities designed to elucidate the chemical kinetics associated with PAC have been complicated by either excess heat release or the inability to accurately quantify intermediate species as a result of enhanced reactions. Moreover, most of the experiments thus far have been limited to a narrow regime of operating conditions, achieving reactions times appropriate to the experiments being performed (e.g., shock tubes, flow reactors and diffusion flames). In the present work, a new flow reactor experimental facility is described with a spatially movable nanosecond plasma discharge to extend the mechanistic data relevant to PAC kinetic studies. Flow reactors are a simple chemical reactor configuration used for the study of fundamental kinetics and have been an integral tool in combustion research since their inception. In essence, a flow reactor is a continuous flow device, that brings a reactant mixture to a desired temperature and pressure and then allows it to convect down a tube. Such devices are much better suited to experimentally follow the evolution of intermediate and product species involved in a chemical reaction. The reactive mixtures implemented in these studies will be highly diluted with an inert gas in an attempt to reduce the exothermicity (temperature rise) of enhanced oxidation reactions and subsequently cause the reaction to stretch spatially over a large physical distance (reaction zone). This extended reaction zone provides an experimental opportunity to locally apply the plasma discharge to different extents of the reaction, such that the effects of the plasma processes on the chemical kinetics may be isolated. With knowledge of the gas velocity in the reactor, the sampling distance is correlated with experimental time and thus transforms the one-dimensional, quasi-steady spatial problem, to a zero-dimensional temporal problem. It is due to this simplicity that flow reactors are a preferred device to experimentally derive detailed measurements regarding chemical reactions. However, in any real experiment, there are a number of physical processes that may lead to non-idealities, these issues regarding the experiment will be discussed in detail in the following sections.

3.2 Plasma Flow Reactor Facility

In order to facilitate the reaction kinetic studies with plasma discharges, a variable temperature and pressure, plasma flow reactor (PFR) experiment was designed similar to that of Rasmussen et al. [100]. A unique feature of the PFR is its two-component modular design: the inner plasma-discharge reactor assembly and the outer enclosure assembly. Cut-away views of the plasma-discharge assembly are shown in Fig. 3.1. The gas phase reaction takes place in a fused-quartz reactor, 1524 mm in length, consisting of circular (I.D. 7 mm x O.D. 9.5 mm) and rectangular (I.D. 7 mm x I.D. 9 mm x 1.3 mm-thickness) tube sections. The system prevents the reactant gases from having any contact with surfaces other than the quartz wall throughout the reaction zone. Two rectangular copper electrodes (12.7 mm x 50.8 mm x 1.6 mm-thickness) are mounted on the top and bottom surfaces of the rectangular quartz tubing by a glass-mica ceramic housing. The electrodes are rounded on all edges to prevent high electric field concentrations which can lead to plasma arcing. Between the contact surfaces of the electrodes and quartz tubing, ceramic sheaths (1 mm-thick) are inserted to minimize corona discharges that can form outside the reactor tube due to any air gaps, but also to facilitate a uniform volume-filling plasma discharge within the reactor. This configuration effectively generates a plasma typically categorized as a dielectric barrier discharge (DBD), and has been an established method of generating highly non-equilibrium plasmas at elevated pressures. For atmospheric pressure and below, the entire reactor is placed inside a circular (I.D. 52 mm x O.D. 58 mm x 1219 mm-length) quartz tube which acts as a protective enclosure to isolate the plasma cell from the surroundings (Fig. 3.2). This allows nitrogen to be purged over the outside surface of the reactor to obtain an oxygen free environment, such that electrode erosion can be minimized at high temperatures. The ends are sealed by Teflon end caps which are bolted together and held in place by Silicone O-rings. The inner reactor tube passes through the center of the Teflon flanges and is held in place by another set of Silicone O-rings. High-voltage tinned copper wires (14 AWG) encased in a dense-alumina extruded ceramic (I.D. 1.64 mm x O.D. 3.18 mm) are brazed onto the surfaces of the electrode and run parallel to the reactor. The wires are then connected to two copper-ceramic electrode feedthroughs (CeramTec, 21324-01-A with a 0.125 in. NPT fitting) attached to a single end cap downstream of the reactor, thus providing a closed loop circuit to sustain a high-voltage





(c) Actual image of assembly.

Figure 3.1: Detailed views of plasma discharge assembly around quartz reactor. Note: Drawings not to scale.







Figure 3.3: Detailed view of the PFR experimental facility and auxiliary equipment, showing *ex situ* measurement devices. Note: Drawings not to scale.

pulse inside the reactor cell.

The PFR is then incorporated in a larger experimental facility with appropriate auxiliary equipment (Fig. 3.3). To achieve the desired temperature of the reactant mixture the PFR is placed into a tube furnace (Lindberg/Blue, Model HTF5500, 7315.2 mm long heated section) where three individually controlled electric heating elements can raise the flow reactor temperature up to 1250 K. The electrode feedthroughs on the reactor provide a terminal connection to connect a high-voltage nanosecond duration pulser (provided by the Ohio State University), capable of producing a plasma discharge in the reactor cell at 1-40 kHz repetition rates with peak voltages as high as 20 kV. Input voltage to the pulser is provided by a 2 kW DC power supply (Magna-Power Electronics, XR1000-2.0, maximum voltage output 1000 VDC). The pulser output voltage and current are measured using a high-voltage probe (Tektronix, P6015A) and a current probe (Pearson Electronics Inc., 2877), connected to a four-channel digital oscilloscope (Tektronix, TDS-714L) with a $\pm 1.0\%$ vertical accuracy. A GPIB-USB (National Instruments, GPIB-USB-HS) connector connects the oscilloscope to a computer to record live data of the oscilloscope waveforms using LabVIEW. Diagnostic signals such as internal current through the insulated gated bipolar transistor (IGBT) switches and pulser current waveform are also monitored to ensure proper functioning of the pulser.

Three reactant gases are premixed before entering the reactor, with the capability of adding a second carrier gas stream. To ensure sufficient mixing and gas phase homogeneity, the fuel and oxidizer are fed into the carrier gas stream (either Ar, N₂ or He) by two impinging jet streams. The flow rates are regulated by analog mass flow controllers (MKS, M100B), accurate to within $\pm 1.5\%$ of full-scale (FS) and connected to a four-channel digital power supply/readout unit (MKS, 247D). The maximum flow rates for fuel, oxidizer, and carrier gases are 10 sccm (or 1 SLPM), 20 sccm and 5 SLPM, respectively. All gases used during the experiment had purities greater than 99.5 % (supplied by GTS-Welco), where in some instances reactant fuels were provided as calibration standards diluted in Ar (~2000 ppm C_xH_y balanced in Argon, GTS-Welco, $\pm 2\%$ accuracy). The gas mixture is then fed and exhausted from the quartz reactor through 6.4 mm Teflon tubing, attached by Cajon vacuum connectors that define the inlet and outlet of the reactor.

3.2.1 Ex Situ Sample Analysis

Intermediate and product species analysis is performed downstream of the reactor using both online and offline analytical instruments. Online analysis consists of a non-dispersive infrared (NDIR) analyzer (Horiba, Model VS-3011), which is continuously fed in series with the exhaust stream of the



Figure 3.4: Examples of raw signal data obtained from GC analysis for (a) 100 ppm calibration standard of $C_1 - C_6$ n-paraffins and (b) plasma assisted experimental sample from PFR at T = 620 K, P = 1 atm. Both chromatograms obtained for the same GC conditions.

reactor to measure carbon monoxide (CO) and carbon dioxide (CO₂) species concentration. Before each set of experiments the analyzer is zeroed with pure diluent and spanned against a certified mixture with an accuracy of $\pm 2\%$ in nitrogen (GTS-Welco), for an overall uncertainty of $\pm 4\%$ in the analyzer measurements. A three-way valve in parallel to the NDIR sample line can be manipulated to transfer gaseous samples to 15 stainless-steel sample storage loops (VICI Valco Inc., 10 mL volume) attached to a multi-position valve (MPV). The inlet pressure of the MPV is regulated by a vacuum pump connected at the outlet. This ensures that the reactor pressure is maintained due to any mitigating pressure effects the presence of the MPV may have while inline with the reactor.

The collected gas samples are then analyzed by an offline gas chromatograph (Agilent Technolo-

gies, 7890A) equipped with a methanation catalyst and a flame ionization detector (FID). Using helium as the carrier gas, the GC is capable of eluting hydrocarbons $C_1 - C_{12}$, both paraffins and olefins, and oxygenated compounds by passing the analytes through a gas-to-solid column with a polystyrene-divinylbenzene stationary phase (Agilent Technologies, J&W HP-PLOT Q, 30 m length, 0.535 mm diameter, and $40 \,\mu$ m film-thickness). A prescribed GC column temperature program from 223-523 K is utilized to achieve favorable chromatographic separation of sampled species. Species identification is made by comparing the retention time of sampled species against known calibration standard mixtures (Scott Specialty Gases) for the same chromatographic conditions. Experimental samples are subsequently analyzed using the GC-FID in the same manner as the calibration samples (see Fig. 3.4). The complete analysis for a single storage valve takes more than 15 hours. For species that are liquid at ambient conditions, pure liquid samples (e.g., acetaldehyde, Sigma-Aldrich) are pre-vaporized into gas sampling bulbs and diluted with argon to produce a gas phase mixture. The effective carbon number (ECN) method is used to quantify the mole fraction of these samples. The method is based on the fact that samples composed of the same chemical functional groups will have the same FID signal response per carbon atom as a reference component, namely methane [101,102]. The fidelity of this method is verified in its ability to predict the total carbon content of a single experiment, but also a known calibration standard with little discrepancy (i.e., methane calibration is predicted using the ECN number with a 2.9% discrepancy). The overall relative uncertainty of the GC-FID quantification measurements are $\pm 5\%$ for hydrocarbons $\leq C_7$ and $\pm 2\%$ for CO and CO₂. Quantification of CO and CO_2 was cross-verified with measurements made by the NDIR analyzer, which was in generally good agreement, with less than $\pm 1\%$ deviation. The analytical equipment described above enable the calculation of the elemental balance of carbon with a high degree of accuracy. The steady total carbon concentration at the outlet sampling location for a typical experiment was conserved within $\pm 10\%$ of the specified input, providing verification of the current experimental measurements.

Ex situ measurements are extended to measure H_2 and O_2 concentrations using an online micro gas chromatogram (Agilent Technologies, Micro 3000). Samples are extracted from the exhaust stream at the exit of the reactor. The micro GC is equipped with a thermal conductivity detector (TCD) and a gas-to-solid column (Agilent Technologies, Mol Sieve 5A Plot, 10 m-length, 0.32 mm-diameter, and 30-mm film-thickness) using Ar as the carrier gas. The column conditions are maintained at 383 K and 206 kPa for favorable chromatographic separation of sampled species. Calibration for the GC-TCD was performed by premixing H_2/Ar and O_2/Ar samples on a massflow basis to obtain a linear calibration curve. Overall uncertainty in quantification measurements are $\pm 4\%$. Inline with the exhaust stream, but before sample extraction, the reactor sample is passed through a chemical trap filled with desiccant (anhydrous calcium sulfate) to remove any potential H₂O formation to ensure minimal degradation of the GC column.

The reported errors associated with each type of species measured can be considered conservative overestimates. If errors associated with experimental reproducibility (which has less than $\pm 5\%$ deviation between experiments) and the lower detectability of the GC (~ 1 ppm) are considered, it is expected that the calibration standards (the reported values above) have the greatest influence on the overall error, and should be taken as the error in a given measurement.

3.2.2 In situ Laser-Based Diagnostics

A schematic of the PFR facility expanded to perform in situ OH laser induced fluorescence (LIF) studies is shown in Fig. 3.5. A pulsed Nd:YAG laser (Continuum Lasers, PR 8010) equipped with a second-harmonic generator crystal outputting at 532 nm, is used to pump a tunable dye laser (Continuum Lasers, ND6000) and generate a fundamental output near 566 nm (Rhodamine 590 as the dye). From here, a frequency doubling unit (Continuum Lasers, UVT-3) is used to generate and separate a UV beam at around 283 nm from the fundamental. The laser pulse has repetition frequency of 10 Hz and pulse duration of about 8 ns (FWHM) as measured with a photodiode. At the exit of the laser, a zero-order waveplate and a thin-film polarizer are used to attenuate the beam energy and maintain LIF operation within the linear-regime (below $\sim 10 \mu$ J). The beam energy is monitored and recorded in real-time for every pulse with an energy meter (Ophir-Spiricon LLC, PE10-C) placed behind a 50:50 beam splitter. Laser energy measurements have a calibrated accuracy to within $\pm 4\%$. A selection of UV specific mirrors and lenses (see Fig. 3.5) are used to align and focus a vertically polarized laser beam through the centerline axis of the reactor. At the inlet and outlet of the reactor, modified gas port connectors with UV grade windows set at Brewster's angle, provide optical access through the reactor while the gas mixture is fed and exhausted. The tube furnace is mounted on a rig to tilt it forward and is propped open to provide an unobstructed view of the reactor. Independent temperature measurements made with a thermocouple show that during the course of an experiment the experimentally derived temperature profiles do not deviate appreciably from the steady-state profiles (see Fig. 3.7).

For relative OH concentration measurements, excitation of the $(A^2\Sigma^+ \leftarrow X^2\Pi)$ OH (1,0) band¹

¹Throughout this dissertation fluorescence bands describing a transition between vibrational levels (e.g. (1,0) band is from v' = 1 to v'' = 0) where a single prime denotes the upper state (v') of the transition and a double prime (v'')denotes the lower state.



Figure 3.5: Detailed view of the PFR experimental facility expanded to perform in situ OH laser-induced fluorescence (LIF). Note: Drawings not to scale.



Figure 3.6: Schematic of laser pulse firing and ICCD camera gate timing with respect to the nanosecond plasma discharge for LIF experiments. Variable timing of the laser pulse allows for LIF measurements at different extents in the plasma afterglow. LIF fluorescence signal is captured within the camera gate time.

is made through the $Q_1(4)$ transition at 282.522 nm. Signal imaging is captured by an intensified charged-coupled device (ICCD) camera (Princeton Instruments, PI-MAX2:1003 Gen III, 1024 x 1024 CCD array) with a UV lens (Nikon Nikkor, 105 mm, f/4.5). The OH fluorescence is isolated by bandpass filters attached to the lens to allow strong transmittance of the (1,1) band at ~312-322 nm and the (0,0) band at ~306-316 nm. This particular excitation scheme is usually employed to discriminate against any inherent scattered laser light that may affect the fluorescence signal, but it also improves the lower detectability limit of OH, below 5×10^4 molecules/cm³. The camera is mounted on a custom-built translational stage positioned coaxially to the reactor to track the fluorescence signal along the length of the isothermal reaction zone. The field of view of the collected LIF signal encloses the entire plasma discharge region with a spatial resolution of approximately 5 cm in length. To discriminate between the OH LIF signal intensity and the background plasma emission intensity, final LIF images were created as follows: $S_{\text{LIF}} = I_{\text{on}} - (I_{\text{off}}) * E_{\text{on}}/E_{\text{off}}$. The on-resonance image (I_{on}) contained the LIF signal on top of the plasma emission background, while the off-resonance image (I_{off}) had only the plasma emission. This method also accounts for any variation in laser energy between the two measurements ($E_{\rm on}$ and $E_{\rm off}$). Typical images are integrated over 1000 laser shots. Using delay/pulse generators (Stanford Research System, DG535 four-channel) and a narrow temporal camera gate (400 ns), the laser, ICCD and plasma discharge can be synchronized such that LIF signal can be captured at various extents within the afterglow generated by a high-voltage discharge pulse (see Fig. 3.6). Relative OH measurements are calibrated using the Rayleigh scattering technique at the wavelength identical to the (1,0) excitation scheme. Details about obtaining absolute OH densities will be covered in Chapter 4.

3.3 PFR Characterization

3.3.1 Temperature Profiles and Residence Time

For correct interpretation of the experimental results it is important to have a good understanding of the temperature profile during the course of the reaction. In the current study, the PFR experiments are performed with the flow rates of each reactant and carrier gas held constant. All the experimental data presented here have been conducted at 1 atm pressure, with the total flow rate of the reactant mixture held at 1 SLPM (calibrated at 298 K and 1 atm), or unless otherwise specified. This gives rise to an isothermal reaction zone with steep temperature gradients towards the inlet and outlet of the reactor. Examples of the measured temperature profiles are shown in Fig. 3.7, using a Type-K thermocouple probe $(\pm 2.2 \text{ K})$ with a 304-SS sheath of 1.6-mm-diameter (Omega, KMTSS-062G-72). From the measured temperature profiles an empirical correlation to determine the isothermal temperature inside the reactor based on the tube furnace temperature can be established. The length of the plasma region accounts for approximately 11% of the isothermal region, such that the excessive length of the reactor provides the capability of moving the plasma cell axially along the length of the isothermal zone. By locally applying the plasma at different locations along the reaction zone, the reactive process can be perturbed at different extents of reaction such that the effects of the plasma discharge on the chemical kinetics may be isolated. For all the results presented here the plasma cell is located at the beginning of the isothermal region (see Fig. 3.7). The measurements confirm that an isothermal reaction zone of 45 cm is achievable, based on a ± 10 K variation. By placing the thermocouple downstream of the plasma discharge such to reduce the possibility of any electromagnetic interference in the measurement, independent experiments carried out at a 10 kV discharge voltage and a pulsed repetition rate of 1 kHz have shown that the energy deposited into the diluent flow raises the temperature by less than 3 K. A similar effect was observed with 3000 ppm oxygen in the flow (see Fig. 3.8). Hence, it can be assumed that the effects of the plasma on the observed chemistry will be dominated by the plasma reactions introduced by the discharge, while the indirect effects of quenching and recombination reactions that increase the gas temperature to alter the chemistry will not be important. In situ thermometry measurements



Figure 3.7: Measured temperature profiles along the reactor length for 1 SLPM of Ar. The dashed lines delimit the isothermal reactions zone, $L_{iso} = 45$ cm and the hatched region shows the position of the plasma discharge. Isothermal region is based on ± 10 K variation.



Figure 3.8: Plasma effect on flow temperature: (top) 1 SLPM of Ar (V = 10 kV, v = 1 kHz) (bottom) 1 SLPM of Ar with $X(O_2) = 3000$ ppm, initially heated to T = 814 K (v = 1 kHz).

will be described in Chapter 4, further validating negligible heat generation due to plasma effects. The energy coupling characteristics of a nanosecond pulsed dielectric barrier discharge (DBD) in a plane-to-plane geometry have been rigorously modeled and studied by Adamovich et al. In brief, the amount of coupled energy (dependent on the magnitude of the voltage pulse and the frequency rate) exerted on a reactive mixture is proportional to number density. For experiments maintaining a constant pressure and increasing temperature, coupled energy effectively decreases, but the coupled energy per molecule remains nearly constant for the entire temperature regime considered. Here, this metric takes precedence and ultimately dictates the manner in which the experiments are performed (i.e., constant flow rate). Details about the numerical determination and validation of coupled energy at the experimental conditions relevant to these studies, will be presented in Chapter 6.

The experimental data will be presented as the mole fraction of a given species as a function of the reactor temperature (T = 420-1250 K), pressure (P = 1 atm), and flow rate (Q = 1 SLPM). Based on these conditions, a reference residence time τ is obtained [100]:

$$\tau_{ref} = \frac{V}{Q} = \frac{\pi}{4} D^2 L_{iso} \left(Q \frac{T}{298 \text{ K}} \frac{1 \text{ atm}}{P} \right)^{-1} \approx \frac{311.4 \text{ s} \cdot \text{K}}{T \text{ (K)}} \text{ at } P = 1 \text{ atm}$$
(3.1)

where V is the volume of the isothermal reaction zone and Q is the volumetric flow rate (m^3s^{-1}) of the gas. The quartz reactor has been idealized to a tube reactor with a constant inner diameter D (m) and L_{iso} (m) is the length of the isothermal region. The reference residence times for the mentioned conditions range from 0.74 s to 0.25 s. From this a comparable residence time for the plasma discharge section can also be inferred by considering the discharge region is approximately 11% of the reaction zone, correlating to 0.08 s to 0.03 s.

3.3.2 Flow Field

Flow reactors are well suited for studying isolated elementary reactions, where experimental measurements can be used to deduce specific reaction rates [103–105]. In order to do so, an understanding of the characteristic flow pattern through the reaction zone is needed for the purposes of numerical modeling. Flow patterns can exist in one of two forms. The first is a simple plug flow pattern, where fluid elements experience no mixing with fluid elements ahead or behind, with the exception that radial mixing of matter is possible. Hence, in order to satisfy the ideal plug flow criterion, fluid elements must pass orderly through the reactor while exhibiting the same residence

time. Furthermore, under steady-state plug flow conditions, the characteristic velocity profile of the reactive mixture remains flat as it passes through the reactor [106]. In most cases, these flow patterns are desired since they are easily integrated into one-dimensional models. The second flow pattern is that of laminar flow. Here, parallel layers or streamlines describe fluid motion with no velocity component occurring across the layers. The only exchange of matter across these layers occurs solely by molecular diffusion. This flow pattern arises when viscous forces gain relative importance over the inertial forces as expressed by the Reynolds number (Eq. 3.2). As a result, radial velocity gradients develop leading to characteristic parabolic velocity profiles with the maximum fluid velocity at the center [107]:

$$Re = \frac{\text{inertial forces}}{\text{viscous forces}} = \frac{\rho u^2 D^2}{\mu u D} = \frac{\rho u D}{\mu}$$
(3.2)

where ρ is the fluid density, D is the diameter of the flow cross-section (i.e., reactor diameter), u is the linear flow velocity, and μ is the dynamic fluid viscosity. Under such conditions where reactive mixtures experience fully-developed laminar flows, computationally more intensive two-dimensional numerical models need to be considered to account for the spatial variation. Compared to simple plug flow assumptions, laminar flows are avoided if possible. The Reynolds number delimits the transition between laminar and turbulent flows (hence plug flow) at Re > 2100 [107].

3.3.2.1 Calculating Transport Coefficients

The following section will present a brief outline of the methodology behind the calculation of key transport coefficients necessary for the determination of the flow characteristics to be made in the subsequent section [107, 108]. This includes viscosity, μ , and the binary diffusion coefficients, \mathcal{D}_{AB} , for low density gas mixtures as a function of pressure and temperature. Using the Chapman-Enskog Theory for multicomponent gases, the required transport coefficients will be derived based on the potential energy interactions between a pair of molecules in the gas phase. The force of interaction between two molecules separated by their distance, r, is given by the empirical Lennard-Jones potential energy function:

$$\varphi(r) = 4\epsilon_{AB} \left[\left(\frac{\sigma_{AB}}{r} \right)^{12} - \left(\frac{\sigma_{AB}}{r} \right)^6 \right]$$
(3.3)

Where σ_{AB} is the collisional diameter between molecules A and B, and ϵ_{AB} is the maximum energy of attraction typically given as ϵ/κ , with κ the Boltzmann constant. These so called Lennard-Jones parameters are rarely available for gas mixtures, but satisfactory estimates using the properties of pure substances can be obtained using the following empirical combination rules:

$$\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B} \tag{3.4}$$

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \tag{3.5}$$

Bird et al. [107] recommends that the viscosity of pure monatomic and polyatomic gases of molecular weight, M_w , be determined from:

$$\mu = 8.4411 \times 10^{-5} \frac{\sqrt{M_w T}}{\sigma^2 \Omega_\mu} \tag{3.6}$$

such that Ω_{μ} is the value of the collisional integral for use with the Lennard-Jones potential as a function of the dimensionless temperature κ^T/ϵ . For multicomponent mixtures the semi-empirical mixing formula is used. Bird et al. [107] had proven Eq. (3.7) to be accurate to within an average deviation of 1.9% based on comparisons between experimental and calculated values for a wide range of gas mixtures.

$$\mu_{mix} = \sum_{i=1}^{n} \frac{y_i \mu_i}{\sum_{j=1}^{n} y_j \Phi_{ij}}$$
(3.7)

where
$$\Phi_{ij} = \frac{1}{\sqrt{8}} \left(1 + \frac{M_{w,i}}{M_{w,j}} \right)^{-1/2} \left[1 + \left(\frac{\mu_i}{\mu_j} \right)^{1/2} \left(\frac{M_{w,j}}{M_{w,i}} \right)^{1/4} \right]^2$$
 (3.8)

Here, n is the number of species in the mixture, y_i and y_j are the molar fractions of components iand j with molecular weights $M_{w,i}$ and $M_{w,j}$, respectively. The pure component viscosity of μ_i and μ_j can be computed from Eq. (3.6). The coefficient Φ_{ij} is a dimensionless quantity that assumes a value of unity when i = j.

Ideal gas behavior is a reasonable assumption for low density compounds under the conditions relevant to the present experimental work. Hence, the binary diffusion coefficient \mathcal{D}_{AB} is given by:

$$\mathcal{D}_{AB} = 1.8583 \times 10^{-3} \frac{\sqrt{T^3 \left(\frac{1}{M_{w,A}} + \frac{1}{M_{w,B}}\right)}}{P \sigma_{AB}^2 \Omega_{\mathcal{D}_{AB}}}$$
(3.9)

Again, $\Omega_{\mathcal{D}_{AB}}$, is a function of the dimensionless temperature $\kappa T/\epsilon$ similar to Ω_{μ} . It should be noted that \mathcal{D}_{AB} is independent of mixture composition. Moreover, values of diffusion obtained from direct calculation of Eq. (3.9) are known to be accurate to within an average deviation of 6% from experimental values. The collision integrals have been curve-fitted by Neufeld et al. (taken from [107]) as follows:

$$\Omega_{\mu}\left(\frac{\kappa T}{\epsilon}\right) = \frac{1.16145}{\left(\kappa T/\epsilon\right)^{0.14874}} + \frac{0.52487}{\exp\left(0.77320\kappa T/\epsilon\right)} + \frac{2.16178}{\exp\left(2.43787\kappa T/\epsilon\right)}$$
(3.10)

$$\Omega_{\mathcal{D}_{AB}}\left(\frac{\kappa T}{\epsilon}\right) = \frac{1.06036}{\left(\kappa T/\epsilon\right)^{0.15610}} + \frac{0.19300}{\exp\left(0.47635^{\kappa T/\epsilon}\right)} + \frac{1.03587}{\exp\left(1.52996^{\kappa T/\epsilon}\right)} + \frac{1.76474}{\exp\left(3.89411^{\kappa T/\epsilon}\right)} \quad (3.11)$$

3.3.2.2 Axial Dispersion and Plug Flow Assumption

Insight into the flow conditions experienced inside the PFR will be demonstrated by an example considering a representative gas mixture of C_2H_4 , O_2 , and Ar. The analysis begins by calculating the Reynolds number, given in Eq. 3.2. For this purpose a volumetric flow rate of 1 SLPM at a pressure of 1 atm and temperatures between 420 K and 1250 K are considered through the isothermal reaction zone. The viscosities are calculated from Eqs. (3.7) and (3.8), while the mass density is approximated from the ideal gas law, where \overline{M}_w is the molecular weight of the weighted average of the multicomponent mixture:

$$\bar{\rho} = \frac{P\bar{M}_w}{RT} \tag{3.12}$$

Linear velocity is obtained by converting volumetric flow rate based on the reactor cross-sectional area. Based on the above conditions, calculated Reynolds numbers span from 65 < Re < 214. This clearly indicates that the flow operates in the laminar flow regime.

Under laminar conditions, parabolic velocity profiles give rise to a distribution of residence times for reactive species in the radial direction. Those traveling closer to the wall experience longer periods of reaction than those traveling along the center-line [104]. The problem that one then encounters is that reaction time cannot be related to axial distance along the reactor. In such a case the concentration profiles in the axial and radial directions need to be resolved making the derivation of the rate parameters more complicated, but can also lead to inaccuracies [103]. However, under certain conditions one can assume that the radial concentration profile is approximately flat, such that the concentration of the reactive species is independent of the radial distance and the reaction time is equal to axial distance divided by the average axial velocity. To satisfy such a condition requires: (a) diffusive-transport to be relatively slow compared to convective-transport in the axial direction, while (b) in the radial direction diffusion is relatively fast compared to axial convective transport [103]. Conditions under which uniform concentration profiles and negligible axial mixing



Figure 3.9: Spreading of a pulse tracer according to the concept of dispersion in a tubular reactor. Redrawn from [106].

can be expected is confirmed by the application of the dispersion model for streamline flow in pipes that satisfy the criterion $D \ll L$ [106].

The measure of radial gradients in laminar flows is characterized by axial dispersion, where the spreading of fluid elements is a result of different local flow velocities and molecular diffusion [106]. The extent of the dispersion process can be measured by the dimensionless vessel dispersion number:

$$\frac{D_{disp}}{uL_{iso}} = \frac{\text{movement by axial dispersion}}{\text{movement by bulk flow}}$$
(3.13)

where L_{iso} is taken as the characteristic length, to distinguish mixing in the direction of the flow. The axial dispersion in a given system is best characterized by an experiment where a pulse of a tracer is introduced at the inlet of a reactor at t = 0. Figure 3.9 shows how dispersion can cause the pulse to broaden as it moves down the reactor and becomes less concentrated. This gives rise to a residence time distribution (RTD), where a dispersion model can then be formulated based on the imposed-pulse experiment such that an analytical solution (Eq. 3.14) to the RTD can be obtained for an axially-dispersed flow reactor [106]:

$$\frac{C}{C_i} = E\left(\theta\right) = \frac{1}{\sqrt{4\pi \left(\frac{D_{disp}}{uL}\right)\theta}} \exp\left[\frac{-\left(1-\theta\right)^2}{4\theta \left(\frac{D_{disp}}{uL}\right)}\right] \quad \text{where} \quad \theta = \frac{\tau}{\tau_{\text{mean}}} \tag{3.14}$$

Here, θ represents a dimensionless mean residence time and E a dimensionless concentration. Referring to Fig. 3.10, when the value of D_{disp} is low, the tracer curve is narrow, symmetrical, Gaussian, and the flow field can be expected to experience small deviations from plug flow. For large values of D_{disp} the flow field experiences rapid spreading and hence mixed flow, thus causing the tracer



Figure 3.10: Tracer response curves related to the dispersion model. Redrawn from [106].

curve to start trailing off and deviations from plug flow are no longer minor. Application of the dispersion model onto actual flow reactor systems is delimited by the empirical critical limit of $D_{disp}/uL_{iso} < 0.01$, where small deviations from plug flow are acceptable [106].

The numerical value of the dispersion coefficient can be derived from Eq. (3.14) readily when experimental data are available. Otherwise, it can be deduced from Eq. (3.15) which has strong functional dependence on molecular diffusion as indicated by Levenspiel [106]:

$$D_{disp} = \mathcal{D}_{AB} + \frac{u^2 D^2}{192 \mathcal{D}_{AB}} \tag{3.15}$$

At low flow rates, dispersion is promoted by molecular diffusion, while at higher flow rates it has the opposite effect and instead dispersion is facilitated by axial convection and radial diffusion. Values of vessel dispersion number are now calculated from the same representative gas mixture considered in the previous calculation for the Reynolds number. For the volumetric flow rate of 1 SLPM, the vessel dispersion number yields values of $0.0059 < D_{disp}/uL_{iso} < 0.0123$. For temperatures greater than 520 K the dispersion number is well below the critical number, however, below this temperature the critical limit is surpassed slightly. A range of RTD's have been computed from Eq. (3.14) for various representative values of the vessel dispersion number along with those of the considered experimental conditions. The results are shown in Fig. 3.11, which confirms a narrow and symmetrical RTD for the experimental applications and a reliable plug flow approximation. This analysis is carried out for all reactive mixtures considered in the present study (see Table 3.1), where the dispersion numbers

Reactive Mixture			T :	T = 420 K		T = 1250 K	
X_{inert}	$X_{\rm fuel}$	$X_{ m oxi}$	Re	D_{disp}/uL_{iso}	Re	D_{disp}/uL_{iso}	T_{crit}
Ar	C_2H_4	O_2	65	0.0123	214	0.0059	520 K
Ar	$\mathrm{C}_{2}\mathrm{H}_{4}$	-	65	0.0138	214	0.0065	$520~\mathrm{K}$
N_2	$\mathrm{C}_{2}\mathrm{H}_{4}$	O_2	45	0.0119	149	0.0057	$475~{ m K}$
He	$\mathrm{C}_{2}\mathrm{H}_{4}$	O_2	6	0.0046	21	0.0027	
Ar	H_2	O_2	65	0.0042	214	0.0024	
Ar	CH_4	O_2	65	0.0098	214	0.0048	
Ar	$\mathrm{C}_{2}\mathrm{H}_{6}$	O_2	65	0.0127	214	0.0061	$570~{ m K}$
Ar	$\mathrm{C_{3}H_{8}}$	O_2	65	0.0146	214	0.0069	$620~{\rm K}$
Ar	C_4H_{10}	O_2	65	0.0160	214	0.0075	$620~{\rm K}$
Ar	$\mathrm{C_7H_{16}}$	O_2	65	0.0189	214	0.0088	$670~{ m K}$

Table 3.1: Range of vessel dispersion numbers for representative reactive mixtures at the experimental conditions (T = 420-1250 K, P = 1 atm, at 1 SLPM) carried out in this work.



Figure 3.11: Computed residence time distributions from Eq. 3.14 at varying $\frac{D_{disp}}{uL_{iso}}$. The solid black curves denote the range obtained at conditions relevant to the experimental conditions. The solid red curve is the limiting trace curve where deviations from plug flow are considered.

indicate that the upper limit of all experiments meet the dispersion criterion. In select cases the lower limits deviates at the indicated critical temperature, T_{crit} .

3.3.3 Plasma Uniformity

It has been already indicated that non-equilibrium plasmas often accommodate a large number of energy transfer processes and chemical reactions involving radicals and excited species. It is quite challenging to consider all these processes when trying to interpret experimental results or develop numerical models. In addition, any potential inhomogeneities that may exist in the plasma discharge, such as filamentation (electrical arcing), can introduce further complications by requiring complex geometric and numerical computational strategies in order to simulate their effects. In order to simplify any models to be developed, it is necessary to create diffuse, volume filling plasmas (glow discharges) that approach homogeneous conditions during the experiments. Plasma spatial nonuniformities can arise due to a variety of different reasons. Possible causes of instability development in a glow discharge are thoroughly discussed in reference [44]. One such possible source of induced filamentation is when the discharge is unable to dissipate a local increase in Joule-heating as a result of a localized increase in the electron number density (n_e) . As a result of this, a local rise


Figure 3.12: Schematic of ICCD camera gate timing with respect to the nanosecond plasma discharge for qualitative plasma imaging.

in gas temperature occurs, causing the total number density to decrease and effectively increases the reduced electric field. This proportional increase in reduced electric field enhances the electronimpact ionization process and further increases the local n_e , leading to the creation of a positivefeedback loop (ionization-heating instability) [44]. Such instabilities are on the order of millisecond time scales and a means to effectively reduce their occurrence is to reduce the characteristic time of energy coupling by the discharge pulse (i.e., the duration of applied voltage). This is one of the prime motivational factors in using nanosecond pulsed discharges.

The discharge configuration described in the previous section is referred to as a dielectric barrier discharge (DBD) and is considered another solution to reduce filamentation formation. The ceramic sheaths placed in between the electrodes act as a dielectric medium, displacing the electrical charge induced by the local electric field (dielectric polarization). When an applied voltage to a gas medium exceeds its breakdown threshold, an electron avalanche occurs (i.e., ionization) resulting in a "forest" of micro-streamers forming conductive channels between the electrodes. From here a charge accumulation occurs on the surfaces of the dielectrics imposed by the experienced polarization, which inherently reduces the local electric field and in turn rapidly reduces the net voltage applied across the discharge gap. This self-limit of energy loading into the plasma helps stabilize the plasma discharge. This often leads to a glow discharge, characterized by a large area density of randomly distributed micro-streamers that processes the entire gas volume, and results in a diffuse and homogeneous plasma discharge [109].

The uniformity of the plasma discharge in the PFR was examined for different experimental conditions. To do so, an intensified charge-coupled device (ICCD) camera (Princeton Instruments,



Figure 3.13: Normalized spectrum of Ar plasma generated in the PFR at 1 SLPM, T = 620 K and P = 1 atm. Plasma conditions: V = 10 kV, v = 1 kHz.

PI-MAX) with a macro lens (Tamron, SP 90 mm, f/2.8) was used to take images perpendicular to plasma field of view (Fig. 3.2). The camera was externally triggered with the pulser by the function generator, so as to synchronize the intensifier to collect emission at the start of the discharge pulse. A sufficiently wide camera gate (10 µs) was used in all instances to envelop the discharge pulse, as well as a significant portion of the afterglow. The camera gating scheme is illustrated in Fig. 3.12. For all cases the discharge is operated at a pulse repetition rate of 1 kHz, while the gas mixture is set to 1 SLPM of Argon at 1 atm pressure. It should be mentioned that the images are taken well after the initial breakdown has been achieved, thus providing a representative analysis of the steady-state quality of the plasma. Using a spectrometer (Ocean Optics, HR2000) capable of detecting emission between 200-1100 nm (optical resolution of 1.33 nm) and attached to an optical fiber, it was determined that emission provided by the Argon plasma is predominately from the Ar I lines (see Fig. 3.13). This transition is from the $3p^5 4p$ (second highest electronic state) to $3p^5 4s$ (lowest electronic excited state) states, which contains both metastable $Ar[^{3}P_{0}]$ and $Ar[^{3}P_{2}]$ states (see Fig. 1.7).

Figure 3.14 shows a series of single-shot and time-averaged single-shot (50 images) ICCD images of the plasma discharge as a function of temperature for a constant discharge voltage of 15 kV. For images at elevated temperatures the tube furnace was opened slightly to expose the plasma assembly. However, images were limited to temperatures below 814 K, any higher, emission intensity from the irradiating coils of the tube furnace became comparable or exceeded that of the plasma and image analysis becomes non-representative. All the intensity distributions have been plotted on the same scale to make them directly comparable. As can be seen, at room temperature multiple confined filamentary structures appear in the plasma. By increasing temperature, the plasma uniformity significantly improves as the number density of the gas decreases and Joule heating can dissipate more effectively. Even though time-averaged images seemed to have improved the plasma uniformity, this can be misleading since the random high-number of filaments can fuse together and "wash" out the non-uniformity. Despite this, the non-uniformity of the plasma appears in the formation of "hot-spots", indicating localized heating, which by 620 K have been completely eliminated. From this it can be claimed that the onset of reasonable plasma uniformity occurs at 620 K and knowing that number density decreases with increasing temperature it is expected the plasma uniformity should only improve for temperatures greater than 814 K.

Figure 3.15 presents a similar analysis in relation to applied voltages. Cells that have been replaced with "no plasma" indicate that at those specific gas conditions with the corresponding applied voltage was insufficient to cause breakdown and generate a plasma discharge. From these images a similar conclusion can be derived, as gas temperature increases, plasma uniformity improves independent of applied voltage. However, the emission intensity increases with applied voltage since energy coupling into the plasma increases and higher degrees of ionization are achieved. Regardless, by 620 K in all instances the plasma has eliminated concentrated regions of hot spots and reasonable uniform plasma discharges have been produced. Based on the qualitative analysis, it is obvious that volume filling plasmas in the current PFR are possible for the considered experimental conditions. However, experimental results below 620 K may need to be interpreted with caution as it seems likely that the plasma structure may exhibit some level of irregularity due to the formation of filamentation. Above this regime, it is reasonable to assume the plasma is diffuse and uniform.



Figure 3.14: ICCD images of plasma uniformity as a function of gas temperature for 1 SLPM Argon flow at P = 1 atm. Camera gate: 10 µs, Plasma conditions: V = 15 kV, v = 1 kHz.



Figure 3.15: Multi-shot ICCD images of plasma uniformity as a function of gas temperature and discharge voltage for 1 SLPM Argon flow at P = 1 atm. Camera gate: 10 µs. Plasma conditions: v = 1 kHz.

Chapter 4

Plasma Assisted Oxidation of Hydrogen

4.1 Introduction

The initiation of any hierarchical mechanism development begins with the examination of the H_2/O_2 chemistry. Insight into this sub-mechanism is critical as it plays an integral role in the growth of radical pools, which ultimately dictates the oxidative characteristics of hydrocarbon fuels [110]. The thermal H_2/O_2 mechanism has been extensively developed and studied over the years and for the most part is well suited to describe a system's behavior dominated by chain-branching reactions. Such mechanisms include those of Mueller et al. [111] and Konnov [112]. Since their inception both mechanisms have been thoroughly revised with updated kinetic and thermodynamic data to classify them as "comprehensive" mechanisms (a term used to distinguish a mechanism that has good predicative capabilities across several experimental systems and conditions, e.g., flow reactors, shock tubes and flames [113–115]). Scenarios describing the slow oxidation of hydrogen that involves HO_2 and H_2O_2 at T < 850 K are still subject to some discrepancies.

Experimental investigations into PAC of hydrogen (with O_2 or air) have primarily been focused on ignition delay studies. These include diluted shock tube studies (T = 850-1300 K, P = 0.3-0.6atm [75]) and flow reactor studies with initial preheating of non-dilute reactants (T = 473-500 K, P =0.1-0.2 atm [83–85,116]). The latter works were intended to be an extension of the shock tube studies, where low temperature plasma-assisted ignition data could be captured at temperatures significantly lower than thermal ignition. In both instances, experimental data comprises of *in situ* techniques to capture the ignition event through OH emission spectroscopy, time-resolved OH concentration using LIF and time-resolved temperature measurements using CARS (Coherent Anti-Stokes Raman Spectroscopy - in N₂ containing mixtures) or OH LIF thermometry. Several years after the works of [75] were completed, Popov [117] developed a PAC specific H_2 -air kinetic mechanism to describe the experimental results. The same mechanism was also used to model the experiments of [84,85,116]. Unequivocally, the culmination of all these studies demonstrated (which was explicitly predicted by Popov before [84,116]) that the enhanced deposition of radicals close to the ignition threshold would result in significant self-heating due to recombination reactions. At this point, the significance of the non-equilibrium characteristics of the discharge diminishes and the high temperature chainbranching reactions would cause the ignition threshold to shift. This type of behavior at such low pressure conditions can kinetically be described by the well understood second-explosion limit. At higher pressures and lower temperatures, the dynamics of the system before the explosion limit (slowoxidation) have not been thoroughly explored and could provide particular insight into the kinetic mechanism driving the ignition process under the effects of non-equilibrium plasma discharges.

4.2 OH Laser-Induced Fluorescence

Over the last three decades laser-induced fluorescence (LIF) spectroscopy has become an integral diagnostic tool in studying the intermediate (e.g., OH, CH, O, H) and pollutant (e.g., NO, CO) concentrations in combustion phenomena [118]. Its ability to detect species concentrations on the ppm and sub-ppm levels, has provided combustion researchers the ability to probe into the chemistry that dictates the combustion process and has eventually led to a better understanding of how to improve combustion systems. With increased interest developing in the field of plasma-assisted combustion, LIF has naturally been adapted to examine such systems, where it has been widely employed to detect atomic species (e.g., C, H, O, N) [119], ions (e.g., N₂⁺) [120] and metastable species (e.g., N₂ $A^3\Sigma_u^+$) [121].

The simple classical explanation of LIF can be thought of as a two step process. First, laser radiation excites a molecule (or atom) from a lower electronic state (often the ground state) to higher state by absorption of a photon. After a finite time the excited molecule de-excites by spontaneous emission (fluorescence) back down to the ground state. The level of fluorescence signal measured is then directly related to the number density of the lower state. The concept of LIF has spawned into several variants involving different laser excitation schemes including, linear LIF, predissociative LIF, saturated LIF, and multi-photon LIF (i.e., when an excitation transition from the lower state involves more than one-photon, such as two-photon absorption LIF (TALIF) to detect atomic species). Figure 4.1 shows the LIF scheme used to perform OH LIF relevant to the experimental work carried out in



Figure 4.1: Illustrative depiction of the excitation dynamics in OH $A^2\Sigma^+$ $(v' = 1) \leftarrow X^2\Pi(v'' = 0)$ LIF.

this dissertation. OH molecules initially exist in the ground vibrational state (v'' = 0) of the ground electronic state $(X^2\Pi)$. Laser radiation in the form of photons are absorbed near 283 nm (upward red arrow), bringing molecules from rotational level *i* to rotational level *j* in the first vibrational state (v' = 1) of the electronically excited state $(A^3\Sigma^+)$. According to the Frank-Condon principle, electronic transitions changing from one vibrational level to another will have a greater probability of absorption (transition strength) when the vibrational wave functions of the two levels have greater overlap [122]. Considering that the internuclear distances of both electronic states in OH are similar, the transition strength from v'' = 0 will decrease rapidly with increasing v' [118]. The primary disadvantage of exciting the $(v' = 1 \leftarrow v'' = 0)$ band is that the transition strength is considerably weaker than the corresponding $(v' = 0 \leftarrow v'' = 0)$ band [124]. Upon excitation, fluorescence proceeds (downward blue arrow), where OH molecules de-excite from rotational level *k* in $A^3\Sigma^+$ (v' = 1) back down to rotational level *m* in $X^2\Pi$ (v'' = 1), while simultaneously emitting photons at a wavelength of 315 nm. Typical radiative lifetimes of the rotational levels in the v' = 0 and v' = 1 states are on the order of ~750-1000 ns [123]. However, in reality several quantum states have the ability to become populated for a given laser excitation scheme. From a different perspective, laser excitation can be considered a perturbing process. Here, a single state is selectively populated and disrupts the OH molecule out of its thermal equilibrium state (i.e., the Boltzmann distribution is altered) [118]. The act of fluorescence is one of many ways in which the OH molecule counteracts this process in a way to revert back to thermal equilibrium. Other such methods are collisional-induced processes that are categorized based on the type of internal energy being changed [118]:

- Collisional Quenching: Electronically excited OH molecules represents the largest leap in internal energy change. In the event that they collide with other atoms or molecules present in the probing environment, excited OH can potentially de-excite, with a key feature being that no photon is emitted in the process. Quenching effects result in reduced lifetimes of the excited states, which directly correlates to a reduction in fluorescence intensity of the OH molecule. The dependence of the collisional environment means that the effects of quenching become reliant on temperature, pressure and environment species composition.
- Vibrational Energy Transfer (VET): Vibrational energy levels are typically separated by one-to two-orders of magnitude smaller than the corresponding electronic level separations. A VET collisional process acts to redistribute the population distribution in the v' levels. In the scenario where the v' = 1 ← v'' = 0 excitation scheme is employed, VET brings excited molecules in v' = 1 back down to v' = 0 before emitting fluorescence. Thus fluorescence signal from the v' = 0 level will be Stokes shifted by ~26 nm with respect to the laser excitation wavelength. Laser background scattering can often be an issue in experimental LIF scenarios, especially if the probing medium is enclosed in a reactor. By collecting fluorescence from v' = 1 and the v' = 0 bands, stray laser light can be easily attenuated by optical spectral filtering.
- Rotational Energy Transfer (RET): Rotational energy levels are about two-orders of magnitude smaller than the vibrational energy level separation. Similar to VET, RET is a collisional process that redistributes the population of rotational levels in a given vibrational level. In instances where the rate of RET redistributes the population of the rotational level considerably faster then the analogous quenching and VET processes, the rotational levels can be assumed to be in thermal equilibrium. Thus, instead of considering a set of several tens of rovibrational levels independently, a single rotational manifold can be assumed with a fixed rotational distribution.

Accurate description and evaluation of each of these processes are important considerations when deriving an absolute OH number density from experimentally derived relative LIF signals. The rates of collisional-induced processes are found in the literature and the motivation for their inclusion will be presented in detail in the following sections.

4.2.1 Hydroxyl (OH) Radical

In order to derive quantitative measurements from LIF experiments, the spectroscopic characteristics of the target species must be known. Fortunately, the OH molecule has been rigorously characterized, in large part due to its importance in hydrocarbon combustion systems. The electronic transitions between the ground state OH molecule to its many excited states are well known and documented, with transition strengths readily available in the literature or tabulated in accessible databases (e.g., LIFBASE [124]). The OH molecule in general can posses complicated spectroscopic features, and will be briefly summarized below. For a thorough review of the OH coupling interactions see the works of Herzberg [125], and Brown et al. [126].

In the ground state $(X^2\Pi)$ coupling between the nuclear rotation and the electron motion is relatively weak. For low values of J (where J represents the rotational level) the OH molecule behaves in a manner described by Hund's case (a). Here, the orbital angular momentum of the electrons, L, is coupled to the internuclear axis by electrostatic forces. The angular moment of the electron spin, S, couples to L by spin-orbiting interactions. The projection of both L and S onto the internuclear axis (defined as Λ and Σ respectively) form a well defined vector Ω (see Fig. 4.2a). When Ω is vector added to the nuclear rotational angular moment, R, the resultant is the total angular moment, J, excluding the nuclear spin (i.e., $J=R+\Omega$). The spin-orbit interaction between the two spin components results in two rotational energy ladders, termed F_1 and F_2 , which start from total angular moment quantum numbers J = 3/2 and J = 1/2. Apart from the spin-orbital splitting in each rotational level, each fine level is further split into two levels denoted by F_e and F_f with a weak energy difference between the two (i.e., in total there are four fine states F_{1e} , F_{1f} , F_{2e} , F_{2f}) for the ground rotational states [127].

As J increases the spin-orbit interaction becomes increasingly weak and the energy difference between F_1 and F_2 becomes smaller. Basically, the rotational velocity of the molecule will become comparable to the precession (precession is a change in the orientation of the rotational axis of a rotating body) velocity of the spin about the internuclear axis. The spin vector, S, becomes uncoupled from the internuclear axis and the vector Ω is no longer defined. L processes about the



(a) $J = R + \Omega$ (b) J = N + S

Figure 4.2: Orientation of the angular momentum vectors for Hund's case (a) and (b). Redrawn and modified from [118].

internuclear axis and the projection vector Λ remains intact. However, Λ becomes coupled to the nuclear rotational angular moment, \mathbf{R} , to form \mathbf{N} (i.e., $\mathbf{N}=\mathbf{R}+\Lambda$), from which \mathbf{N} and \mathbf{S} couple to form \mathbf{J} (i.e., $\mathbf{J}=\mathbf{N}+\mathbf{S}$). This coupling description is known as Hund's case (b) (see Fig. 4.2b). When coupling case (b) dominates the rotational level, the J nomenclature changes to N (i.e., to describe the ground state OH, $J = N \pm 1/2$). Since the excited state will have one spin component, only one energy ladder exists. Transitions between the rotational levels in the ground state with those in the first excited state will create different transition branches. Examples of such transitions can be seen in Fig. 4.3 using Hund's case (b) notation, where the number in the parenthesis describes the N number of the lower level and the subscript indicates between which energy ladders the transition occurs.

Lastly, the OH molecule has three repulsive electronic states that cross the electronic $A^{3}\Sigma^{+}$ (only the repulsive ${}^{4}\Sigma^{-}$ is shown in Fig. 4.1) [128]. Due to a spin-orbital interaction in the crossing region, molecules will cross over and dissociate in a process known as predissociation. All rotational levels in v' = 2 are predissociative [123], with the predissociation rates increasing exponentially for increasing vibrational state and causing a proportional decrease in the radiative lifetimes [129]. Regarding the v' = 2 state, radiative lifetimes are on the order of ~150 ns [123], with the v' = 3 state having lifetimes of ~100 ps [129]. Although high lying rotational levels in the v' = 0 and v' = 1 are susceptible to predissociation, low lying rotational levels of $A^{3}\Sigma^{+}$ ($v' \leq 1$) are essentially non-existent [123].



Figure 4.3: Example of some transitions for OH $A^2\Sigma^+$ $(v'=1) \leftarrow X^2\Pi(v''=0)$. The lower rotational levels have two energy ladders F_1 and F_2 , with two lines denoting further fine splitting due to F_e and F_f levels. The excited state has a single energy ladder, denoted by a shaded region. Transition branches are denoted with a letter where O-branch: $\Delta N = -2$, P-branch: $\Delta N = -1$, Q-branch: $\Delta N = 0$, R-branch: $\Delta N = +1$, S-branch: $\Delta N = +2$, respectively. Note: Drawing not to scale. Redrawn and modified from [118, 128]

4.3 Details of OH Diagnostics

4.3.1 LIF Model

Considerable success has been achieved in obtaining absolute OH measurements in plasma environments in the past, with the following derivation taking particular influence from the studies of Yin et al. [130, 131]. With an understanding of the relevant collisional processes that dictate the excitation dynamics of OH LIF, a quantitative concentration measurement can ultimately be deduced from the experimentally captured relative LIF signals. Usually a simple two-level model is enough to characterize OH LIF under low pressure conditions, since the collisional frequency of processes leading to the population redistribution of the excited-state is smaller than the time scale of laser excitation. At atmospheric pressure however, the collisional frequency of such processes increases significantly, thus requiring the use of a more complex model to account for their influence [132]. Such processes include, rotational energy transfer (RET), vibrational energy transfer (VET) and collisional (electronic) quenching (see Fig. 4.1).

In this study, a three-level model is employed assuming:

- 1. Negligible upward VET to higher vibrational levels $(v' > 1, v' = 1 \leftarrow 0)$, which only acts to populate the excited state v' = 0 from v' = 1 [133]. The probability of upward transfer is significantly smaller than the downward process and hence is neglected [174].
- 2. At all times the rotational distribution in all vibrational levels is in equilibrium with the gas temperature (the rotational manifold is fully thermalized) [132, 133]. This second assumption alleviates the need to consider all rovibronic states independently, instead a given vibrational level can be considered as one cumulative state with a fixed rotational distribution. The RET rates of OH ($A^2\Sigma^+$, v' = 1, N' = 5, F_1) with Ar as the collider medium have been reported by Kienle et al. [134] and under the present conditions it can be inferred to be on the order of $2 \times 10^9 \text{ s}^{-1}$. It should be mentioned that this rate is an underestimate, since in the current study the $F_1(4)$ state is pumped and RET rates increase with decreasing rotational number. Moreover, any admixtures of O₂ and H₂O will further facilitate the increase of RET since they have considerably higher rate coefficients than Ar [134, 135]. The typical pumping rate of the experiment is $W \leq 1.9 \times 10^8 \text{ s}^{-1}$. Hence, for the experiments presented in this study the RET rate in the excited v' = 1 state is more than 10 times faster than the time scale of laser excitation and fluorescence. It can then be assumed that complete rotational relaxation towards gas temperatures is achieved and will not change appreciably between laser pulses. This is expected to hold greater relevance at higher temperatures, where Ar is known to be an



Figure 4.4: Mathematical description of the three-level model of OH $A^2\Sigma^+$ $(v'=1) \leftarrow X^2\Pi (v''=0)$ LIF excitation dynamics with infinitely fast RET assumed in all levels.

inefficient quencher and very efficient for RET [136]. Both the excited v' = 0 and ground-states can also be assumed thermalized, since RET rate coefficients for the v' = 1 are generally the same for v' = 0 state [134], while RET rates for the ground-state tend to always be higher then the excited-state [137].

3. The above assumption imposes that if the laser energy is kept as low as possible (e.g., linear regime - fluorescence scales linearly with energy), negligible perturbation in the ground-state can be considered and it can be assumed constant for the entire laser pulse.

The physical description of the LIF process can be translated into a mathematical description as shown in Fig. 4.4, with the following system of rate equations describing each level's population:

$$\frac{dN_1'}{dt} = N''W - N_1'(A_1 + Q_1 + Q_{10})$$
(4.1)

$$\frac{dN_0'}{dt} = N_1' Q_{10} - N_0' \left(A_0 + Q_0 \right) \tag{4.2}$$

$$\frac{dN''}{dt} = N_0' \left(A_0 + Q_0 \right) + N_1' \left(A_1 + Q_1 \right) - N'' W \tag{4.3}$$

where N'_1 , N'_0 , and N'' are the number densities (cm⁻³) in each state after laser excitation; A_0 and A_1 are spontaneous emission rates (s⁻¹); Q_0 and Q_1 are electronic quenching rates (s⁻¹); Q_{10} is the VET rate (s⁻¹); and W is the rate of laser excitation (s⁻¹). To simplify the derivation mathematically the ground-state is taken as a single vibrational level, even though spontaneous emission from the excited-states can fall into separate vibrational levels in the ground-state. For

1

steady-state approximation with negligible perturbation of the ground-state, Eqs. (4.1) and (4.2) can be integrated assuming the initial conditions $N'_0(t=0) = N'_0(t=\infty)$ and $N'_1(t=0) = N'_1(t=\infty)$, resulting in:

$$0 = \int_{N'_0(t=0)}^{N'_0(t=\infty)} dN'_0 = Q_{10} \int_0^\infty N'_1 dt - (A_0 + Q_0) \int_0^\infty N'_0 dt$$
(4.4)

$$0 = \int_{N_1'(t=0)}^{N_1'(t=\infty)} dN_1' = \int_0^\infty W N'' dt - (A_1 + Q_1 + Q_{10}) \int_0^\infty N_1' dt$$
(4.5)

Rearranging Eqs. (4.4) and (4.5), time integral expressions for the populations of N'_1 and N'_0 , with respect to the unperturbed laser coupled state, N'', are derived:

$$\int_{0}^{\infty} N_{0}' dt = \frac{Q_{10}}{(A_{1} + Q_{1} + Q_{10})(A_{0} + Q_{0})} \int_{0}^{\infty} W N'' dt$$
(4.6)

$$\int_{0}^{\infty} N_{1}' dt = \frac{1}{(A_{1} + Q_{1} + Q_{10})} \int_{0}^{\infty} W N'' dt$$
(4.7)

These expressions will be used to derive the absolute OH number density as function of the fluorescence signal in the upcoming sections.

4.3.1.1 Boltzmann Population Distribution and Boltzmann Factor

Already mentioned, the LIF process is instigated by the absorption of laser radiation, thus to generate a strong LIF signal it is highly desirable to excite from a rovibronic level that has a significant population. Moreover, for accurate determination of OH concentration, the excited rotational level should be relatively insensitive to temperature. For these reasons, it is important to consider the distribution of OH molecules over the different quantum states. Based on statistical mechanics, the population distribution of an ensemble of molecules in thermal equilibrium is given by the general Boltzmann equation [118], which describes the fraction of the total species population that populate each energy level:

$$f_B = \frac{N_i}{N} = \frac{g_i \exp\left(\frac{-E_i}{k_B T}\right)}{\sum g_i \exp\left(\frac{-E_i}{k_B T}\right)}$$
(4.8)

where f_B is the Boltzmann factor; N_i is the number density of the particles in the *i*th state with energy E_i ; N the total number density; k_B Boltzmann's constant; T temperature and g_i the degeneracy factor of state *i*. The denominator in Eq. (4.8) is often referred to as the partition function. The Boltzmann relation is only valid in thermally equilibrated systems, meaning that all internal energy modes of the molecule are the same (i.e., translational, rotational, vibrational and electronic modes are equilibrated or similarly have the same temperature) [118]. The fractional population distribution of the vibrational states of OH can be examined by considering a degeneracy factor of $g_v = 1$:

$$f_B = \frac{N_v}{N} = \frac{\exp\left(\frac{-E_v}{k_B T}\right)}{\sum\limits_v \exp\left(\frac{-E_v}{k_B T}\right)}$$
(4.9)

This expression reveals that at 300 K the entire OH population is found to be in the lowest vibrational level in the ground state, with the v'' = 0 population being several orders of magnitude greater than the corresponding v'' = 1 level. Even at 2000 K the Boltzmann factor indicates that more that 92% of the OH vibrational population still remains in the lowest vibrational level. The same principle can be applied to examine the rotational population distribution, with each rotational level J, having a degeneracy of $g_J = 2J + 1$ [118]. To reiterate, the ground-state rotational levels of the OH molecules are split into two energy ladders, F_1 and F_2 , and fine split even further for a total of four fine states (i.e., F_{1e} , F_{1f} , F_{2e} , F_{2f}). When considering the distribution in the ground state the differences in the rotational energy term values, E_J , should be accounted for. For example in the OH $X^2\Pi(v'' = 0)$ level:

$$f_B = \frac{N_{J_i''}}{N} = \frac{(2J''+1)\exp\left(\frac{-E_{F_i}}{k_BT}\right)}{\sum\limits_{F_{1e}} g_J \exp\left(\frac{-E_{F_{1e}}}{k_BT}\right) + \sum\limits_{F_{1f}} g_J \exp\left(\frac{-E_{F_{1f}}}{k_BT}\right)} + \sum\limits_{F_{2f}} g_J \exp\left(\frac{-E_{F_{2f}}}{k_BT}\right)} + \sum\limits_{F_{2f}} g_J \exp\left(\frac{-E_{F_{2f}}}{k_BT}\right)$$
(4.10)

In this work energy term values tabulated in Ref. [127] are taken for both the excited- and groundstate calculations.

Figure 4.5 demonstrates the change in the fractional populations of the OH rotational levels in the F_1 energy ladder with temperature. At low temperatures where the slope of the Boltzmann factor is steep, the specified rotational level is highly temperature dependent. As temperature increases the slopes flatten out for all the rotational levels considered, and their respective population distributions become less dependent on temperature. For the experiments presented here, where the



Figure 4.5: Fractional populations (Boltzmann fraction - f_B) in the J'' = 3/2, 5/2 and 9/2 rotational levels of the F_1 ladder in the OH $X^2 \Pi(v'' = 0)$ state as a function of temperature.

 $Q_1(4)$ transition is chosen (i.e., rotational level J'' = 9/2 is excited) the measurements are performed in a relatively populated level over a broad range of temperatures, but more importantly the population of the designated rotational level does not change appreciably over the desired experimental conditions of T = 500-1000 K.

4.3.1.2 Radiative Decay

The total radiative decay rate, A, for a given transition is dependent on the conditions in the probing medium. In actuality, the fluorescence transition is not limited to the two rotational levels involved in the absorption process, but rather it is composed of several rovibronic transitions.

$$A_{v',J'} = \sum_{v'',J''} A_{v'',J''}^{v',J'}$$
(4.11)

In the event that RET acts quickly to redistribute the rotational population to adjacent J' levels, fluorescence will originate from an even larger manifold of rotational levels. Furthermore, if RET has thermalized the excited vibrational state, A can be evaluated as a weighted average with its Boltzmann factor (considering only the relative rotational energies of the excited state and excluding the vibrational and electronic energies):

$$A_{v'} = \sum_{J'} f_B(v', J') \cdot \sum_{v'', J''} A_{v'', J''}^{v', J'}$$
(4.12)



Figure 4.6: Radiative decay rates computed for the OH $A^2\Sigma^+ \leftarrow X^2\Pi$ (v'=1, v''=1) and (v'=0, v''=0) bands. (a) $A_{v',J'}$ as function of upper rotational level (only F_1 considered) based on Eq. (4.11); (b) $A_{v'}$ as a function of temperature based on Eq. (4.12).

such that the $A_{v'',J''}^{v',J''}$ transitions are taken from LIFBASE [124]. In Fig. 4.6, the dependence of A with respect to J' and the population distribution of v' is illustrated. Firstly, the transition probability from v' = 0 to v'' > 0 is 2-3 orders of magnitude less than the corresponding (v' = 0, v'' = 0) band [124], thus in this work when referring to A_0 , only the (v' = 0, v'' = 0) emission is considered. Similarly, for A_1 , only the (v' = 1, v'' = 1) emission is considered. As demonstrated in Fig. 4.6(a), radiative decay rates decrease with increasing J', approximately 30% from J' = 0.5 to J' = 17.5. This is attributed to the centrifugal distortion effect on the transition dipole moment [138,139]. Using Eq. (4.12), with f_B calculated from rotational term values from [127], the relationship between $A_{v'}$ and temperature is obtained. Despite such a large temperature range, A_0 and A_1 decrease by less than 10%, largely in part due to the thermal distribution weighing heavily towards low J' levels even at high temperatures. Notice that both A_0 and A_1 converge to their rotationless condition of 1.451 × 10⁶ s⁻¹ and 8.595 × 10⁵ s⁻¹, respectively [138,139].

4.3.1.3 Quenching Rates

Quenching, Q, is an important factor to consider during the LIF process, and it can ultimately hinder the amount of allowable fluorescence signal available in an experiment. In the case of linear LIF, the rate of Q is often greater than the rate of A (~10⁸ in atmospheric flames), which means it dominates the fluorescence decay rate. It is highly dependent on the probing medium conditions and is generally represented by the following formulation [140]:

$$Q = \sum_{i} n_i k_i = \sum_{i} n_i \sigma_{Q_i} \left[\frac{8k_B T}{\pi \mu_i} \right]^{1/2}$$

$$\tag{4.13}$$

where n_i is the total number density; k_i quenching rate coefficient, σ_{Q_i} is the thermally average quenching cross-section; and μ_i is the reduced mass of the colliding pair. Investigation into the quenching of OH $A^3\Sigma^+$ has been an elaborate and extensive initiative over the years, largely in part due to the importance and advances made in combustion and atmospheric chemistry research. The characteristics of OH $A^3\Sigma^+(v'=0)$ collisional quenching can be summarized in the following manner [141–147]:

- For most quenching colliders, the state-specific, thermally averaged quenching cross-section $\sigma_{Q_0}^{J'}$ decreases with increasing J'-level and approaches a constant value at high J'-levels [143, 146, 147].
- For most quenching colliders, the dependence of quenching cross-section $\sigma_{Q_0}^{J'}$ diminishes with increasing T [144, 147].
- The quenching cross-section $\sigma_{Q_0}^{J'}$ decreases with increasing T and approaches a constant value at sufficiently high T (e.g., ~2000 K, flame temperatures) [141, 144, 147].

Based on these finding several phenomenological models have been postulated to explain and predict the quenching cross-sections with various collisional partners. The first is the "complex formation" model [140, 141, 143]. The indication of rather large quenching cross-sections (usually 30-100 Å²) derived from experimental results, indicates that attractive forces are contributing to the quenching process. Furthermore, the influence of J'-levels on quenching suggests that these attractive forces depend on the molecule orientation (i.e., anisotropic effect), which leads into the idea that upon collision a so-called "complex formation" is formed. Due to the inherent dipole moment of the OH molecule, under certain orientations attractive force interactions with the collider dominate and effectively enhance quenching. For rotationless OH, attractive interaction is easily achieved and the complex is formed. With increasing J'-level, the effectiveness of the attraction effect is undermined and the cross-section for complex formation decreases and hence so does the quenching cross-section. At sufficiently high J'-levels, the attractive interaction effect averages out and no further increase in quenching cross-section is achieved. A similar analogy can be inferred based on temperature. At low T, thus low collisional energy, the attractive force effect has more time to form the complex. As T increases and the collisional velocities increase, the time for effective interaction of the attractive force effect decreases causing a decrease in quenching cross-section. At very high T, it is possible that repulsive forces may begin to contribute to the quenching process, counteracting the loss of attractive forces and rendering a constant quenching cross-section. However, implementing these concepts into predictive models only showed limited agreement with the T-dependence, and generally missed the quenching magnitude and species dependence of the quenching cross-section [141].

The second model is described by the "harpoon" mechanism, which found considerable success in describing the quenching of NO $A^3\Sigma^+$ [148]. This mechanism involves the transfer of an electron donated by a collisional partner (M) and converting OH $A^3\Sigma^+$ into OH⁻ $X^1\Sigma^+$. As a result of the electron transfer, strong Coulomb forces bring OH⁻ $X^1\Sigma^+$ and M⁺ into close proximity and revert OH⁻ $X^1\Sigma^+$ to the ground state. Unlike the complex formation model, the harpoon model predicts that collisional partners who are unlikely to contribute an electron (i.e., high ionization potentials), such as He and Ar, and would not quench OH $A^3\Sigma^+$. This is in agreement with experimental measurements, where both He and Ar have quenching cross-sections < 0.06 Å² [148]. However, the biggest discrepancy in the harpoon model is that it postulated virtually no *T*-dependence and was found only to be applicable in the high *T* limit.

It was then argued that the quenching process was a cumulative effect of both the complex formation hypothesis and the harpoon mechanism [136]. By comparing existing experimental results for a range of temperatures, empirical expressions were derived for the rotationally averaged and thermally averaged cross-sections, σ_{Q_0} . The first is a two-parameter expression [149]:

$$\sigma_Q = \sigma_{Q_\infty} \exp\left(\frac{\epsilon}{k_B T}\right) \tag{4.14}$$

where $\sigma_{Q_{\infty}}$ (Å²) is the harpoon cross-section at infinite temperature and ϵ/k_B (K) is the well depth parameter. This expression found reasonably good agreement with several important quenching partners relevant to combustion systems (e.g., CO₂, CH₄, N₂) for a range of T = 300-2300 K. In some instances, $\sigma_{Q_{\infty}}$ was adjusted for some species to better predict the experimental results at low temperatures [149]. To extend the model to even lower temperatures, T < 300 K, the empirical three-parameter expression was derived [150–152]:

$$\sigma_Q = A \left[1 + B \exp\left(-C\frac{T}{296}\right) \right] \tag{4.15}$$



Figure 4.7: Quenching cross-sections of OH $A^3\Sigma^+(v'=0)$, denoted as σ_{Q_0} . Symbols represent experimental data extracted from the literature: Copeland et al. [142,143], Smith et al. [159], Heard et al. [152], Fairchild et al. [141], Wysong et al. [145], Paul et al. [136,158], Bailey et al. [150,151], Hogan et al. [160], Dilecce et al. [120]. Lines represent the calculations based on the two- and three-parameter empirical formulations given by Eq.s (4.14) and (4.15).

giving good predictive agreement for T = 200-2300 K for many similar collisional partners [152]. In Fig. 4.7 experimentally derived quenching cross-sections for OH $A^3\Sigma^+(v'=0)$ for various collisional partners relevant to the current experiments are compared to the empirical formulations of Eqs. (4.14) and (4.15). Overall the formulae agree with each other over a wide temperature range, with Eq. (4.15) showing better agreement at lower temperatures. Notice that there is substantial lack of data with respect to Ar as a collisional partner and is the main proponent for not developing a similar empirical formulation. However, what limited data presented does corroborate the trend presented in the above discussion that Ar is an inefficient quencher for temperatures considered.

Similar efforts were extended to investigate the quenching (σ_{Q_1}) and VET $(\sigma_{Q_{10}})$ behavior for OH $A^3\Sigma^+(v'=1)$, with similar observations claimed [153–158]. Firstly, $\sigma_{Q_{10}}^{J'}$ decreased with increasing

Collider	T (K)	σ_{Q_0}	Ref.	σ_{Q_1}	Ref.	$\sigma_{Q_{10}}$	Ref.
H_2	196	11.6 ± 0.7	[147]				
	300	7.2 ± 1.0	[161]	6.5 ± 0.9	[161]	8.0 ± 0.9	[161]
	1330	6.0	[141]				
	1760	4.5	[162]	4.5	[162]	7.65	[162]
O_2	196	22.4 ± 1.3	[147]				
	300	12.7 ± 1.6	[155]	24.5 ± 2.0	[155]	2.8 ± 0.3	[155]
	1760	13.40	[162]	15.1	[162]	1.68	[162]
	2300	7.4 ± 1.1	[158]	8.0 ± 1.9	[158]	0.83 ± 0.29	[158]
$\rm H_2O$	211	119.0 ± 12.0	[150]				
	300	74.0 ± 8.0	[154]	84.0	[148]	14.0 ± 0.2	[154]
	1200			29.0	[148]		
	1760	25.5	[162]	28.6	[162]	0.3	[162]
Ar	300	0.059 ± 0.006	[163]	0.047 ± 0.008	[163]	0.180 ± 0.004	[163]
	300	0.051	[120]	0.041	[120]	0.369	[120]
	1900	0.050	[158]	0.080	[158]	0.220	[158]
	2300	0.050	[158]	0.070	[158]	0.180	[158]

Table 4.1: Comparison of quenching cross-sections σ_{Q_0} , σ_{Q_1} , $\sigma_{Q_{10}}$ for OH A³ Σ^+ .

J'-level and rotationally averaged $\sigma_{Q_{10}}$ was observed to decrease with increasing T [154, 155, 158]. This trend is quite similar to the σ_{Q_0} behavior, and it has been led to believe that VET quenching is governed by anisotropic attractive forces as well [154]. As for σ_{Q_1} , they tend to be slightly greater than σ_{Q_0} as predicted by the harpooned model [156, 158]. By comparing the quenching cross-sections of σ_{Q_0} , σ_{Q_1} and $\sigma_{Q_{10}}$ the collider partners can be classified into three groups [131]. (1) species such as O₂ and H₂O have large quenching cross-sections with $\sigma_{Q_0} \approx \sigma_{Q_1}$, with relatively small $\sigma_{Q_{10}}$. (2) species such as H₂ have nearly equal quenching cross-sections $\sigma_{Q_0} \approx \sigma_{Q_1} \approx \sigma_{Q_{10}}$ and lastly (3) species such as N₂, He and Ar have comparable quenching cross-sections for $\sigma_{Q_0} \approx \sigma_{Q_1}$ and larger $\sigma_{Q_{10}}$. A comparison of experimentally derived cross-sections are presented in Table 4.1.

4.3.2 Deriving Absolute OH Concentration

The fluorescence signal power, P_F , of the OH density of laser-induced OH $(A^2\Sigma^+)$ is proportional to $\sim N'A'$ of the excited state, where it can be expressed in terms of the number of photons absorbed in volts (or counts):

$$P_F = \dot{S}_F \left[\frac{\# \text{ of photons}}{\text{seconds}} \right] hc\nu_o \tag{4.16}$$

$$S_F \left[\# \text{ of photons (counts)} \right] = \int_0^\infty \dot{S}_F dt$$
 (4.17)

such that the fluorescence signal S_F at a given laser frequency ν_L (cm⁻¹) can be expressed as [118]:

$$S_F(\nu_L) = \frac{\beta\Omega}{4\pi} V_F \int_0^\infty \epsilon A' N' dt$$
(4.18)

here V_F is the probe volume (cm⁻³); ϵ represents the transition-dependent signal collection efficiency and β is the overall effectiveness of the detector system. Considering $N'A' = N'_1A_1 + N'_0A_0$, and implementing Eqs. (4.6) and (4.7), S_F becomes:

$$S_F(\nu_L) = \frac{\beta\Omega}{4\pi} V_F \int_0^\infty \left[\epsilon_1 N_1' A_1 + \epsilon_0 N_0' A_0\right] dt$$

$$= \frac{\beta\Omega}{4\pi} V_F \left[\epsilon_1 A_1 \int_0^\infty N_1' dt + \epsilon_0 A_0 \int_0^\infty N_0' dt\right]$$

$$= \frac{\beta\Omega}{4\pi} V_F \left[\epsilon_1 A_1 C_1 \int_0^\infty W N_0'' dt + \epsilon_0 A_0 C_2 \int W N_0'' dt\right]$$

$$= \frac{\beta\Omega}{4\pi} \cdot V_F \cdot N_0'' \cdot \Phi \cdot \int_0^\infty W dt$$
(4.19)

with the quantum yield (fluorescence efficiency) being appropriately defined as $(C_1 \text{ and } C_2 \text{ are the} \text{ integral coefficients from Eqs. 4.6 and 4.7}):$

$$\Phi = \frac{\epsilon_1 A_1 \left(A_0 + Q_0 \right) + \epsilon_0 A_0 Q_{10}}{\left(A_0 + Q_0 \right) \left(A_1 + Q_1 + Q_{10} \right)} \tag{4.20}$$

Both the radiative and quenching rates are taken from representative values from Sections 4.3.1.2 and 4.3.1.3. It is often the case that the laser excitation (absorption) rate be expressed in a more convenient form. This begins by recognizing that the absorption rate is linearly dependent on the Einstein coefficient b = B/c (cm³J⁻¹cm⁻¹) and the spectral irradiance I_{ν} (Wcm⁻²s⁻¹). However, I_{ν} can be expressed as a product of normalized spectral irradiance, I_{ν}° , laser lineshape, $g_L(\nu)$, and absorption lineshape, $g_a(\nu)$ [118,168].

$$\int_{0}^{\infty} W dt = \int_{0}^{\infty} \int_{\nu} \frac{B}{c} I_{\nu}(\nu, t) d\nu dt$$

$$= \int_{0}^{\infty} \frac{B}{c} I_{\nu}^{\circ}(t) \Delta \nu_{L} \int_{\nu} g_{L}(\nu) g_{a}(\nu) d\nu dt$$

$$= \frac{B}{c} \Delta \nu_{L} g(\nu_{L}) \int_{0}^{\infty} I_{\nu}^{\circ}(t) dt$$
(4.21)

This derivation reveals the dimensional form of the overlap integral, $g(\nu_L)$ (1/cm⁻¹), which mathematically represents the convolution of the laser lineshape and the absorption lineshape for a give ν_L , with $\Delta \nu_L$ (cm⁻¹) representing the FWHM of the laser profile. Lastly, the irradiance can be represented as a function of spectrally averaged laser pulse energy, E_L (J), and laser cross-sectional area, A_L (cm⁻²):

$$\int_{0}^{\infty} W dt = \frac{B}{c} \Delta \nu_{L} g(\nu_{L}) \int_{0}^{\infty} I_{\nu}^{\circ}(t) dt \qquad (4.22)$$
$$= \frac{B}{c} \Delta \nu_{L} g(\nu_{L}) \frac{E_{L}}{\Delta \nu_{L} A_{L}}$$
$$= \frac{B}{c} g(\nu_{L}) \frac{E_{L}}{A_{L}}$$

Substituting Eq. (4.22) back into Eq. (4.19) and taking l to be the probe volume length, with the consideration that the total ground-state OH density, N_{OH} , can be related to the laser couple state by the Boltzmann factor (Eq. 4.10), S_F resembles:

$$S_F(\nu_L) = f_B N_{OH} \cdot \frac{B}{c} \cdot g(\nu_L) \cdot E_L \cdot \Phi \cdot \frac{l\Omega\beta}{4\pi}$$
(4.23)

4.3.2.1 Line Broadening and Overlap Integral

To gain an understanding of the forthcoming section, a brief overview of the theoretical concepts of transition lineshapes (or profiles) will be described. The radiative transition of a molecule or atom is not discrete at a given wavelength (i.e., not monochromatic), rather it exhibits a spread or finite "linewidth" brought on by broadening effects [118, 164]. The broadening of spectral lines is an important concept to grasp in order to properly interpret the spectral signal of a measurement and hence its accuracy. Broadening mechanisms can be classified as either homogeneous (e.g., collision/pressure broadening - the collision of molecules interrupts the interaction of radiation with the molecules) or inhomogeneous (e.g., Doppler broadening - thermally induced relative motion of molecules with respect to the radiation source) depending on whether their cumulative effects act on all the molecules equally or on a subset of molecules. At certain conditions the transition lineshape is dominated by either one of these mechanisms, such as at low temperatures and high pressures where collision broadening dominates, or at high temperatures and low pressures where Doppler broadening dominates. However, at conditions where the two processes are comparable in effect, the transition lineshape can become the convolution of the two.

The normalized lineshapes describing Doppler and collision broadening effects with respect to frequency, ν (cm⁻¹), can be expressed mathematically as a Gaussian (Eq. 4.24) and Lorentzian (Eq. 4.25) function [164]:

$$g_D\left(\nu,\Delta D\right) = \frac{4\sqrt{\ln 2}}{\sqrt{\pi}\Delta D} \exp\left[-4\ln 2\frac{\nu^2}{\Delta D^2}\right]$$
(4.24)

$$g_{C}(\nu, \Delta C) = \frac{\Delta C}{2\pi} \frac{1}{\nu^{2} + (\Delta C/2)^{2}}$$
(4.25)

Its general practice in spectroscopy to describe lineshapes in terms of linewidths (as FWHM), where the Doppler linewidth ΔD (cm⁻¹) is given by [164]:

$$\Delta D = \nu_o \sqrt{\frac{8kT\ln 2}{mc^2}} \tag{4.26}$$

here ν_o (cm⁻¹) is the center of the transition and m is the mass of the atom or molecule of interest (e.g., OH). The collision linewidth ΔC (cm⁻¹), is highly dependent on the collision environment and in turn becomes a function of temperature, pressure and gas composition. In the following studies, this expression is taken from [165, 166]:

$$\Delta C = \sum_{i} 2\gamma_o \left(\frac{T_{ref}}{T}\right)^{n_i} P_i \tag{4.27}$$

where $2\gamma_o$ are experimentally derived linewidths for a given species *i*, for a partial pressure P_i (atm), measured at a reference temperature T_{ref} . For representative species at the experimental conditions relevant to the present work, calculations for ΔC were made by interpolating data from [165, 166].

Convolution mathematically describes the amount of overlap between two functions when one is shifted relative to the other. Physically, convoluting the Doppler and the collision lineshapes derives the absorption lineshape, resulting in a new lineshape that is known as a Voigt profile. For the



Figure 4.8: Examples of numerically calculated Voigt profiles demonstrating the influence of the Doppler and collision broadening effects. Chemical composition of air used for $Q_1(3)$ transition for OH $A^2\Sigma^+ \leftarrow X^2\Pi$ (v' = 0, v'' = 0) band at P = 1 atm.

purposes of this study broadening effects from Doppler and collisions are only considered and are expected to have the greatest effect on the absorption lineshape. The Voigt profile can be thought of as multiplying every frequency of the first lineshape by the second lineshape, and then integrating over all possible frequencies. Substituting Eqs. (4.24)-(4.25) into Eq. (4.28) results:

$$g_a\left(\nu,\nu_o,\Delta D,\Delta C\right) = \int_{-\infty}^{+\infty} g_D\left(\nu'-\nu_o,\Delta D\right) g_C\left(\nu-\nu',\Delta D\right) d\nu'$$
(4.28)

$$=\frac{2\sqrt{\ln 2}}{\sqrt{2\pi}\Delta D}\frac{a}{\pi}\int_{-\infty}^{+\infty}\frac{e^{-t^{2}}}{(u-t)^{2}+a^{2}}dt$$
(4.29)

$$=\frac{2\sqrt{\ln 2}}{\sqrt{2\pi}\Delta D}H\left(a,u\right) \tag{4.30}$$

where a (Voigt parameter) and u are defined as:

$$a = \frac{\sqrt{\ln 2\Delta C}}{\Delta D}$$
$$u = \frac{2\sqrt{\ln 2\nu}}{\Delta D}$$

and H(a, u) is the Voigt function:

$$H(a,u) = \frac{a}{\pi} \int_{-\infty}^{+\infty} \frac{e^{-t^2}}{(u-t)^2 + a^2} dt$$
(4.31)



Figure 4.9: LIF excitation scans across the $Q_1(4)$ transition for OH $A^2\Sigma^+ \leftarrow X^2\Pi$ (v' = 1, v'' = 0) band measured in a mixture of $X(H_2) = 2000$ ppm, $X(O_2) = 3000$ ppm, X(Ar) = 0.995 at P = 1atm. At T = 668 K spectrum collected in plasma-assisted oxidation case (10kV at 1 kHz), while at T = 921 K collected in thermal oxidation case (no plasma).

The Voigt function has no closed form solution, thus making it numerically intensive to solve and difficult to apply fitting techniques to experimental results. Hence, analytical approximations have been adopted to evaluate the Voigt function, such as using the real part of the Faddeva function. Here, the Voigt function has been numerically computed using a single proper integral method developed by M. R. Zaghloul [167]. Figure 4.8 illustrates an example of the influence the Doppler and collision broadening lineshapes can have on the absorption profile (Voigt profile). When a > 1 the Voigt profile resembles the Lorentzian lineshape, as temperature increases the Doppler effects start to dominate (0 < a < 1) and the Voigt profile resembles the Gaussian lineshape.

Similarly, the overlap integral $g(\nu_L)(1/\text{cm}^{-1})$ is the convolution of the laser lineshape, g_L , and the absorption lineshape, g_a , defined as [168]:

$$g(\nu_L) = \int_{-\infty}^{+\infty} g_L(\nu_L - \nu) g_a(\nu) \, d\nu$$
(4.32)

Both lineshape functions are normalized to unity in this expression, with the end lineshape having a Voigt profile. Determining the overlap integral begins by estimating the laser linewidth by measuring the fluorescence signal when scanning the laser wavelength across the $Q_1(4)$ transition (Fig 4.9). The measured line profile is a convolution of the laser lineshape and the absorption lineshape. These



Figure 4.10: Illustrated examples of calculated broadening profiles and overlap integrals demonstrating minimal change in overlap integral for representative experimental range of T = 400-1000 K at P = 1 atm. Chemical composition of $X(H_2O) = 2000$ ppm, $X(O_2) = 2000$ ppm, X(Ar) = 0.996 used.

measurements were performed within the linear regime at the lowest mean pulse energy, such to reduce the effects of power broadening. Since the actual laser lineshape is unknown, a semi-analytical solution of the overlap integral is used assuming a Gaussian laser lineshape (Eq. 4.33 - details of derivation in [131]), from which numerical least-squares Voigt fitting ("lsqcurvefit", built-in function in Matlab) can be applied to the excitation spectrum. Deconvoluting the laser lineshape from the Voigt fit reveals that the laser linewidth is $\Delta \nu_L = 0.6 \text{ cm}^{-1}$ FWHM.

$$g\left(\nu_L\right) = \frac{2\sqrt{\ln 2}}{\sqrt{\pi}\sqrt{\Delta D^2 + \Delta\nu_L^2}} H\left(\frac{\sqrt{\ln 2}\Delta C}{\sqrt{\Delta D^2 + \Delta\nu_L^2}}, \frac{2\sqrt{\ln 2}\Delta\nu_L}{\sqrt{\Delta D^2 + \Delta\nu_L^2}}\right)$$
(4.33)

The excitation spectra shown in Fig. 4.9, shows little variation with temperature, indicating that the overlap integral has little dependence on both temperature and gas composition under the current experimental conditions. This is entirely attributed to the relatively wide laser linewidth, and its influence on broadening the excitation spectrum. Figure 4.10 illustrates that over a temperature range of T = 400-1000 K, the combined Doppler and collision linewidths (less than 0.2 cm^{-1}) remain less than the laser linewidth at all conditions relevant to the experimental studies, with the overlap integral experiencing less than 3% change in the same range. Due to this, a constant overlap integral is employed to reduce all the OH LIF data in the present study.

4.3.2.2 LIF Calibration: Rayleigh Scattering Measurements

All that remains in Eq. (4.23), is the determination of the calibration factor of the optical collection system $(l\Omega\beta)$. Here, l is the path length of the laser seen by the collection optics (cm); Ω is the solid angle of the detector (sr); and β is the conversion coefficient that represents the efficiency of the collection optics and the detector system. Rayleigh scattering as an *in situ* calibration technique has it origins from Luque and Crosley [169] who used it to obtain absolute CH measurements. Since then its been demonstrated as an applicable technique for OH LIF in plasma systems [130,132,133]. The calibrations are done using the same optical setup and beam alignment as the LIF measurements, to ensure that the Rayleigh scattering beam occupies the same path as the fluorescence beam path. Pure N₂ (99.9% purity, Praxair) was used as the calibration gas. The measured signal intensity of a laser pulse scattering from a homogeneous gas molecule is given by:

$$S_{\text{Rayleigh}} = \frac{\epsilon_{\text{R}}}{hc\nu_L} \left(\frac{\partial\sigma}{\partial\Omega}\right) l\Omega\beta \cdot (NE_L)$$

$$= D_{Rayleigh} \cdot (NE_L)$$
(4.34)

where ϵ_R is collection efficiency of the Rayleigh scattering signal; $hc\nu_L$ is the photon energy at the laser wavelength (J); $N = P/k_BT$ is the number density of the calibration gas (cm⁻³); E_L is the measured laser pulse energy (J); and $(\partial \sigma / \partial \Omega)$ is the differential Rayleigh scattering cross-section (cm²/sr) that depends on the scattering medium (i.e., calibration gas). For a vertically polarized incident laser beam, while collecting both horizontal and vertical polarization components of the scattered light, the differential cross-section is:

$$\frac{\partial \sigma}{\partial \Omega} = \frac{9\pi^2 \nu^4}{N_o^2} \left[\frac{n_o^2 - 1}{n_o^2 + 2} \right]^2 \frac{3}{3 - 4\rho_p} \left(1 + \rho_p \right)$$
(4.35)

Here n_o is the index of refraction, and N_o is the number density evaluated at a reference condition. The depolarization ratio of polarized light, ρ_p , is taken from dispersion formulations found in [170]. Details regarding the theory and applications of laser Rayleigh scattering along with the derivation of Eqs. (4.34) and (4.35) can be found in [171–173]. For a $\nu_L = 282.522$ nm the differential crosssection was determined to be 8.76×10^{-27} cm²/sr. Rayleigh measurements were made by varying either the pressure of the calibration gas or the laser pulse energy through the plasma reactor and collecting the corresponding signal. Plotting S_{Rayleigh} vs. (NE_L) reveals a linear relationship, to which the slope $D_{Rayleigh}$ can be used to calculate the unknown calibration factor. Calibration measurements are independently performed after each set of LIF measurements for a given day to account for any inherent drifts in the optical setup. Combining Eqs. (4.23) and (4.34) the final expression for the absolute N_{OH} concentration of the ground-state OH is given as:

$$N_{OH} = \frac{4\pi S_{\text{LIF}}\epsilon_{\text{R}} \left(\frac{\partial\sigma}{\partial\Omega}\right)}{f_B b E_L \Phi g\left(\nu\right) h c \nu_L D_{Rayleigh}}$$
(4.36)

4.3.3 OH Thermometry

Absolute OH LIF measurements can be extended to measure temperature, by inferring the ground-state rotational temperature of OH and assuming that it is in equilibrium with the translational temperature of the gas. In past studies involving plasma-assisted systems [84, 85, 132],



Figure 4.11: Single pixel (S_F) example of inferring temperature based on Boltzmann plot. The best fit temperature is 626 ± 37 K with $R^2 = 0.9945$.

fluorescence based thermometry has proven to be a reliable technique when considering linear LIF. This method is based on the premise that the collected fluorescence intensity across several different transitions scales linearly with the population density of the rotational level of the ground-state. Thus, LIF signals can be fitted to a Boltzmann expression, Eq. (4.37), by manipulating Eq. (4.23).

$$\ln\left[\frac{S_{\rm F}}{b\left(2J''+1\right)}\right] = -\frac{E_{J''}}{k_BT} + const \tag{4.37}$$

An example of temperature inference based on a Boltzmann plot is shown in Fig. 4.11, with measurements corresponding to excitation transitions $Q_1(2)$ up to $Q_1(7)$. The slope of the fitted line through the experimental points is equal to $1/k_bT$, providing temperature. For best accuracy, temperature inference based on OH thermometry can only be determined when good S/N (signal-to-noise ratio) is achieved. Signal obtained across the field of view of the camera extended beyond the regions of the discharge section. At certain transitions, S/N at these extremities was determined to be poor $(S/N \sim 1)$. For this reason, the temperature profiles were cropped to include measurement portions that presented reasonably good Boltzmann fits with $\pm 10\%$. The uncertainty in the inferred temperature is about $\pm 15\%$.

4.3.4 Error Analysis

For evaluating the quenching rates with Ar the values from the Dilecce et al. [120] source were used. Several plasma OH LIF studies [132,133,174–177] using Ar have claimed to have used the same values with minimal discrepancy in quantified measurements, for applicable temperatures ranging from T = 300-1000 K. It was assumed that the mixture composition for a given experimental condition is taken from (refer to Fig. 4.13b at T = 668 K), where the reaction has gone to full completion forming H₂O and balanced by Ar and the remaining O₂. This is considered a conservative estimate, since H₂O is known to be the most efficient quencher of excited OH. However, due to the large proportion of Ar present in the mixtures, collisional rates with Ar become dominant and the overall rates essentially become independent of any uncertainty in inferring mixture composition. Based on a standard propagation analysis [178]:

$$\varepsilon = \left[\sum_{i=1}^{n} \left(\varepsilon_{x_i} \frac{\partial R}{\partial x_i}\right)^2\right]^{1/2} \tag{4.38}$$

where ε_{x_i} is the uncertainty associated with a given measurement or variable; and R is the variable with the inherent error (e.g., N_{OH}). Considering inherent errors associated with measured temperature, laser energy, cross-section of various collisional processes, Rayleigh scattering calibration and overlap integral, the uncertainty in the measured OH concentration is on the order of $\pm 30\%$.

4.4 Plasma Flow Reactor (PFR) Kinetic Model

The experimental results to be presented in the next sections were part of a collaborative effort to develop and validate a plasma-specific kinetic mechanism for H_2 oxidation [183]. This involved experimentally validating numerical results using a newly developed volume-averaged, zero-dimensional chemical kinetics model specifically tailored to replicate the characteristics of the PFR experiment. The model has the ability to perform rigorous formal sensitivity analysis to study the reaction kinetics specific to PAC. Briefly, the model consists of a modified SENKIN module [179] from the CHEMKIN III suite, coupled with the ZDPlasKin [180] package that provides access to a Boltzmann equation solver, BOLSIG+ [181]. The governing equations are a system of time-dependent differential equations (ODEs) describing mass (species), energy and electric-charge [182] conservation equations. BOLSIG+ supplies SENKIN with the plasma parameters at every time step, which enables the model to consider the temporal effects of the chemistry with respect to the plasma pulses. Results derived and presented from this model are based on isothermal simulations (energy conservation equation is neglected). When similar adiabatic simulations are considered, a maximum 35 K rise in temperature for the reactive mixture is experienced across all conditions studied for H_2 oxidation. Further details regarding the model can be found in Togai et al. [183].

A unique feature of the SENKIN module is its ability to perform sensitivity analysis, where normalized sensitivity coefficients, $\tilde{S}_{i,j}$, are given as:

$$\tilde{S}_{i,j} = \frac{k_j}{X_i} \frac{\partial X_i}{\partial k_j} = \frac{\partial \ln X_i}{\partial \ln k_j}$$

mathematically, these coefficients represent the fractional change in the mole fraction, X_i , of species i, caused by a fractional change in the rate coefficient, k_j , of reaction j. These coefficients can provide physical insight to the dynamics of the chemical system when coefficients are compared to one another. It is often informative to examine the sensitivity coefficients of reaction products specifically, since their formation represents the progress of the overall reaction. When coefficients are compared in this manner, reactions with the highest sensitivities are considered the rate-limiting steps of the overall reaction [184, 185].

The chemical reaction mechanism employed within this model consists of 39 species and 418 reactions specifically developed to study H₂ oxidation. It is based on the HP-Mech-Plasma mechanism [186], which is an expansion of the H₂/O₂ mechanism originally developed by Burke et al. [187]. Furthermore, it has been extended in this study to include additional reactions pertaining to electronically excited species of Ar (excited states are individually considered and lumped according to 4s metastable, 4s resonant and 4p), O₂ $(a^1\Delta_g \text{ and } b^1\Sigma_g)$, O $(^1D \text{ and } {}^1S)$, and ionic reactions. Vibrationally excited species are neglected in the current iteration of the mechanism.

4.5 Results

4.5.1 Gas Temperature and Plasma Uniformity

A qualitative analysis of plasma uniformity similar to Yin et al. [130] was carried out in the current plane-to-plane plasma discharge experiment. Figure 4.12 shows single-shot broadband images of the plasma at various pulse repetition rates at the same experimental conditions (T = 668 K, P = 1atm) intended for plasma OH LIF measurements. These images were taken after the discharge had been running for some elapsed time and are representative of the discharge's steady-state operation. The camera gate is set to 300 nsec, which was synchronized to open just before the high-voltage pulse and envelopes the entire duration of the applied high-voltage event (~ 250 nsec). Previous measurements (see Section 3.3.3) indicate emission from the plasma is predominately from the Ar $4p \rightarrow 4s$ transitions (Ar I lines), located between 690 to 850 nm, and are consistent with the works of [188, 189]. Images show that the plasma remains diffuse and occupies the entire volume between the electrodes before it rapidly decays within a 300 ns (not shown in Fig. 4.12). From this it can be inferred that the excited species leading to light emission generated in the plasma are present only when the high-voltage pulse event occurs and quench rapidly in the afterglow. Plotted below each image (all on the same arbitrary scale) are emission intensity profiles along the centerline of the discharge to demonstrate the quality of axial uniformity. At all plasma conditions, the bulk of the profiles are smooth and relatively constant, reaffirming that under the present experimental conditions the plasma is void of any significant filamentary structures. This is particularly important to validate since the formation of filament structures can lead to localized hot-spots and induce unwanted thermal effects [130]. However, slight inflections in the profiles are observed at the left (inlet) and right (outlet) edges of the plasma, similarly observed by Yin et al. [84], suggesting that some filamentation may exist at the boundaries of the electrodes. Increasing the pulse repetition rate increases the global emission intensity of the profiles as would be expected, since coupled energy deposited into the reactive mixture increases with the number of pulses and hence increases the propensity of excited species being generated.

To verify minimal plasma induced thermal effects centerline temperature measurements were also performed using the OH thermometry technique (Fig. 4.12). These measurements were taken a few nanoseconds after the high-voltage pulse, where maximum temperature influence from the discharge is expected. Average axial temperature profiles indicate that the plasma has a relatively constant temperature profile through the bulk of discharge section of the reactor, with negligible global temperature rise deviating by a maximum of ± 44 K axially along the length. Increasing the deposited energy by increasing the pulse repetition rate has some effect on increasing the global temperature, where temperature increases from 624 K, 638 K and 647 K for 1, 3 and 5 kHz, respectively. These measurements have a maximum deviation of $\pm 7\%$. The boundaries of the discharge regions have localized temperature rise of ~70 K due to localized filamentation as mentioned previously. Based on these results it can be claimed that any enhancement provided by the plasma is entirely due to chemical effects and any deficiencies in the physical attributes (i.e., temperature and uniformity) of the plasma may be considered negligible in influencing the results.



Figure 4.12: ICCD single-shot broadband images of plasma, axial centerline emission intensity (bottom curves) and centerline temperature distribution (top curves) at pulse repetition rates of (a) 5 kHz (b) 3 kHz (c) 1 kHz. Initial conditions: $X(H_2) = 2000$ ppm, $X(O_2) = 3000$ ppm, X(Ar) = 0.995, T = 668 K, P = 1 atm. Plasma conditions: V = 10 kV. The uncertainty in the inferred temperature is $\pm 15\%$.

4.5.2 Hydrogen Oxidation

Figure 4.13 shows a comparison of H_2 oxidation between the thermal and plasma-assisted system between T = 420-1010 K. In the thermal system, hydrogen oxidation was not observed at temperatures lower than 860 K, for given flow residence times within the reactor. Above 860 K, an abrupt reaction occurs, where oxidation proceeds to completion consuming all the fuel present. The results experimentally demonstrate the explosive behavior of the H_2/O_2 system when the reactive mixture crosses the second explosion limit at 1 atm [111]. With the application of the plasma discharge, the oxidation characteristics of the system extend to temperatures lower than 860 K, with the onset of hydrogen consumption beginning at temperatures as low as 470 K. In this region, the plasma effects are entirely driving the oxidation process at a steady rate of reaction whose effectiveness increases with temperature. Comparing the two sets of experiments the plasma alone does not have the ability to drive the oxidation to completion with the same effectiveness as the thermal reaction at a given temperature below 860 K. However, by 840 K the plasma has managed to consume all the fuel, nearly 40 K before the onset of any thermal effects. For T > 840 K both the plasma and thermal effects are driving the oxidation process to full completion. Model predictions with the experimental data are in relatively good agreement, with the model predicting 50% fuel consumption shifted towards higher temperatures by approximately 50 K.

4.5.3 OH Radical Production

For a constant temperature above the explosive regime (T = 921 K, Fig. 4.14a), the thermal kinetics induce an OH profile experiencing both exponential growth and decay. This profile is consistent with flow reactor experimental results of Linteris et al. [190], which is indicative of chainbranched chemistry. On the same plot, the temperature profile shows the magnitude of temperature rise associated with exothermic reactions that are typical within this chemical regime. Even under dilute conditions approximately 60 K rise in temperature is experienced, which further facilitates the chain-branched reactions. At a constant temperature well below the thermal explosive regime (T = 668 K, Fig. 4.14b), the extent of the OH profile is entirely confined to the boundaries of the discharge. Upon entering the discharge, OH attains rapid growth, linearly increases and decays rapidly upon exiting. This behavior suggests that the plasma is inducing a linear chain-propagating effect in OH formation, effectively a slower reaction than that experienced in the high-temperature thermal system.

When the reactive mixture is perturbed by a greater frequency of pulses at the same constant



Figure 4.13: H₂ and O₂ consumption measurements of (a) thermal oxidation and (b) plasma-assisted oxidation as a function of isothermal reactor temperature. Initial conditions: $X(H_2) = 2000$ ppm, $X(O_2) = 3000$ ppm, X(Ar) = 0.995, P = 1 atm, $\tau = 311.4$ s·K/T. Plasma Conditions: v = 1 kHz, V = 10 kV. Symbols are experimental data; solid lines are model predictions.


Figure 4.14: Axial OH profiles at (a) T = 921 K for thermal oxidation and (b) T = 668 K for plasma-assisted oxidation for 10 µs delay after the high-voltage pulse, the uncertainty in the inferred temperature is $\pm 15\%$. Initial conditions: $X(H_2) = 2000$ ppm, $X(O_2) = 3000$ ppm, X(Ar) = 0.995, P = 1 atm. Plasma Conditions: v = 1 kHz, V = 10 kV. Symbols are experimental data; solid lines are model predictions.



Figure 4.15: (a) Comparison of axial OH concentration profiles for different pulse repetition rates of 1, 3, 5 kHz at T = 668 K at 150 µs delay after the high-voltage pulse. (b) For a given axial location in the discharge region (x = 45 mm), the local OH concentration as a function of pulse delay after the high-voltage pulse. Initial conditions: $X(H_2) = 2000$ ppm, $X(O_2) = 3000$ ppm, X(Ar) = 0.995, P = 1 atm. Plasma Conditions: v = 1 kHz, V = 10 kV. Symbols are experimental data; Solid lines are model predictions.

temperature, the effect on the plasma induced OH profiles are shown in Fig. 4.15a. Here the linearly propagating feature of OH formation persists, while the absolute magnitude of OH increases proportionally. Interestingly, even though OH has increased nearly 5-times the plasma-assisted system is still unable to revert to a fast, branched-chain system. In Fig. 4.15b the temporal effects within the plasma are examined for a given axial position within the discharge. Maximum OH is achieved rapidly near the end of the high-voltage pulse, and are predominately consumed in the afterglow of the discharge, albeit at a relatively slower rate than its formation. The absence of chain-branching processes in low temperature plasmas and its temporal behavior within the plasma are experimentally comparable and consistent to the observations made by Choi et al. [85] in a single-pulse discharge for a hydrogen-air plasma (T = 300-400 K, P = 54 - 94 torr). The kinetic model is observed to capture both the trend and the absolute magnitude of the OH profiles, for both different temperatures (Fig. 4.14b) and different pulse repetition rates (Fig. 4.15).

4.6 Discussion

Initiation of thermal oxidation at the present experimental conditions is likely related to reaction (4.39). At relatively higher temperatures (T > 1000 K), the H₂ dissociation reaction prevails, reaction (4.40), for its relatively lower bond energy compared to that required for O₂ dissociation [49].

$$\mathrm{H}_2 + \mathrm{O}_2 \to \mathrm{HO}_2 + \mathrm{H} \tag{4.39}$$

$$H_2 + M \to H + H + M \tag{4.40}$$

Regardless, the thermal experiments indicate that the system still requires sufficient temperature (T > 860 K) to induce an explosive reaction (see Fig. 4.13a). In the presence of the plasma, this high temperature dependence is no longer a constraint, but more importantly, it can be assumed that both H₂ and O₂ dissociation act as initiation steps. The low temperature oxidation of H₂ can be attributed to unique plasma chemical processes that enhance molecular dissociation. These include direct electron-impact and collisional quenching with excited species. This concept is demonstrated in Fig. 4.16, where the effects of a single high-voltage nanosecond pulse are simulated in an environment replicating the experimental conditions at T = 668 K. The process begins when a high-voltage pulse induces an electrical field that causes the reactive mixture to ionize and breakdown (a term used to indicate that a plasma discharge has been achieved). At which point high-energy electrons accumulated in the discharge impart their kinetic energy onto neutral Ar molecules (see reaction



Figure 4.16: Modeling simulation of time evolution of plasma E/N and species concentration after a single high-voltage pulse V = 10 kV. Initial conditions: $X(H_2) = 2000$ ppm, $X(O_2) = 3000$ ppm, X(Ar) = 0.995, P = 1 atm, T = 668 K. Taken from [183].

4.41) and cause them to excite electronically (the lowest excited configuration of Ar is the $[3p^54s]$ state forming metastable ${}^{3}P_{2}$ or ${}^{3}P_{0}$ states [183], denoted as Ar^{*} herein). Subsequent reactions of Ar^{*} with H₂ and O₂ predominately result in dissociation, and are the leading source of H-atom and O-atom radicals in the plasma induced system.

$$Ar + e \to Ar^* + e \tag{4.41}$$

$$Ar^* + H_2 \to Ar + H + H \tag{4.42}$$

$$Ar^* + O_2 \to Ar + O + O \tag{4.43}$$

Characteristic of such plasma instigated systems are the varying times scales of the underlying kinetic regimes. Demonstrated in Fig. 4.16, the plasma breakdown, generation of Ar^{*}, and its collisional quenching process all happen on a timescale t < 1000 ns, whereas the instigated thermal (neutral) chemistry leading to oxidation occurs on timescales $t \sim 0.1$ ms and longer. Based on these assertions, the forth-coming discussion will assume that H-atoms and O-atom reservoirs are in abundance within the plasma and the underlying thermal chemistry marks the behavioral differences between the two systems.



Figure 4.17: Modeling simulation of time evolution of species concentration (a) major species and (b) radical species in the PFR experiment for plasma perturbations at v = 1 kHz and V = 10 kV. Initial conditions: $X(H_2) = 2000$ ppm, $X(O_2) = 3000$ ppm, X(Ar) = 0.995, P = 1 atm, T = 668 K. Hatched region denotes the region of the plasma discharge section in isothermal region of the PFR. Taken from [183].

The fast, chain-branched chemistry characteristic of the thermal system can be described as an imbalance of radical fluxes. Entirely dependent on the influx of H-atoms, reactive radicals (e.g., H, O, OH) are regenerated and provided as surplus by the following reactions [111]:

$$\mathbf{H} + \mathbf{O}_2 \to \mathbf{O} + \mathbf{O}\mathbf{H} \tag{4.44}$$

$$O + H_2 \to H + OH \tag{4.45}$$

$$OH + H_2 \to H_2O + H \tag{4.46}$$

The first two chain-branching reactions kinetically dominate the system and accelerate the global rate of reaction at sufficiently high temperatures [111], with reaction (4.46) contributing the most to the system's exothermicity (~68 kJ/mol). Early on in the reaction, reactions (4.44) and (4.45) are the main source of OH production, out-competing reaction (4.46) leading to excess OH formation. As the extent of reaction progresses, fuel and oxidizer consumption continues. At this point, the production rates of reactions (4.44) and (4.45) proportionally decrease, causing the system to consume OH faster than it can produce it (see Fig. 4.14a).

In Fig. 4.17 the single-pulse simulation has been extended to consider multiple pulses, a more representative simulation of the experimental conditions. When a plasma discharge perturbing the

reactive mixture is applied at 1 kHz repetition rate, the consumption of fuel and oxidizer proceeds linearly within the confines of the plasma region (indicated by the first 85 ms of the simulation gray hatched region), with no reaction continuing upon exiting the discharge. The simulations also demonstrate that the evolution of radical species are directly coupled to the plasma perturbations, continually being formed and consumed for every single discharge pulse (see Fig. 4.17b - the periodic behavior of the species profiles). Despite the artificially induced influx of initiating radicals by the plasma, it is evident from the experiments that the plasma-assisted system does little to promote or sustain the chain-branched system even within the self-ignition threshold limit. This can mainly be attributed to the low temperature and high pressure behavior of $H+O_2$, which favors the production of the hydroperoxyl radical, HO₂, a stable and essentially less reactive species [111]. Moreover, at low temperatures reaction (4.44) is very slow due to its endothermicity [183]. This slow behavior is essentially the reason why the system loses its exponential growth characteristics that would otherwise facilitate reaction (4.45) at high temperatures. From a kinetics perspective HO₂ formation as an intermediate works to inhibit the oxidation process. It acts as an H-atom sink diminishing the production capabilities of more active O-atoms and OH radicals (see reaction 4.44) and consequently decreases the overall reactivity of the system. This is demonstrated by the balance of radical fluxes leading to the straight-chain propagation of OH given by reactions [111]:

$$H + O_2(+M) \rightarrow HO_2(+M) \tag{4.47}$$

$$\mathrm{HO}_2 + \mathrm{H} \to \mathrm{OH} + \mathrm{OH}$$
 (4.48)

with reaction (4.46) remaining as the primary consumption route for OH (see Fig 4.18). Although it can be shown that H-atoms along with OH have become self-sustaining in this system of reactions, the branching factor of these radicals compared to the thermal system has diminished considerably (i.e., every H-atom or OH injected into the system produces an equivalent H-atom or OH out). The same cannot be said for O-atoms, which results in a net loss of the radicals through the system.

$$O + HO_2 \to O_2 + OH \tag{4.49}$$

$$O + H_2 \to H + OH \tag{4.50}$$

$$O + OH \to O_2 + H \tag{4.51}$$

These reactions are mainly sustained due to the continual pumping of O-atoms generated by the plasma and are an excellent example of how the effects of the plasma may be used to facilitate the



Figure 4.18: Rate of production of OH radical within the plasma region for plasma perturbation at v = 1 kHz and V = 10 kV. Initial conditions: $X(H_2) = 2000$ ppm, $X(O_2) = 3000$ ppm, X(Ar) = 0.995, P = 1 atm, T = 668 K. Taken from [183]

neutral chemistry. Reaction (4.51) is due to super equilibrium of reaction (4.44) at 668 K, and in turn, contributes to the O-atom consumption route. It should be recognized that the effectiveness of O-atoms as chain-carriers cumulatively decreases the reactivity of the system and works to inhibit the oxidation process, mainly by promoting and exacerbating terminating reaction routes, reactions (4.49) and (4.51). Despite reaction (4.50) being a branching step at 668 K, the reaction rate of (4.49) dominates over reaction (4.50) due to the abundance of HO₂ driving reaction (4.49). This competition effectively makes the reaction system (4.49)-(4.51) net radical terminating. Although the plasma alleviated the temperature constraint in initiating the reactions, the importance of temperature on the secondary kinetics limits the chain length, and prevents the overall reaction in going to completion.

Increasing the pulse repetition rate of the plasma effectively increases the rate at which H-atoms and O-atoms are injected into the system. To clarify Fig. 4.15a, the profiles show the development of OH through the discharge region of the flow reactor at a given instant in time with respect to the highvoltage pulse. Considering a particle element traveling at a fixed residence time, the same element will experience more perturbations with increases in repetition rate. Thus the observed enhancement of OH can be correlated to the enhancement of production routes by the acceleration of reactions (4.47) and (4.48) due to the proportional increase in H-atoms. Due to the given enhancement of OH for a given axial position, this also implies that an increase in the rate of consumption is expected leading to a proportional acceleration in reaction (4.46). What these results imply is that there is a shift in the rate-limiting phase in the reaction chain. With low repetition rates, the rate limiting reaction steps are the consumption of H-atoms (reaction 4.48). As the repetition rate increases, this "bottle-neck" shifts downstream in the reaction chain and the consumption of OH (reaction 4.46) becomes the rate-limiting process [183]. Figure 4.15b, demonstrates that for a given set of conditions (T and P = constant) the neutral chemistry can be manipulated to experience varying degrees of effectiveness by changing the plasma's perturbation timescale. In other words, if it can be inferred that H₂ consumption rate is proportional to OH density, then increasing the ability to generate OH, the rate of H₂ consumption can be increased as well. This holds particular significance because the intrinsically disadvantageous slow chemistry inherent to the plasma-assisted system can be made to act in a more favorable manner and potentially contribute to the enhancement of the oxidation process.

An interesting feature in the experimental results of Fig. 4.15a is that a gradual rise in the tail of the OH profiles is observed as pulse repetition rate increases. In tandem with the above enhancement, for a given pulse rate, the rate of consumption from reaction (4.46) declines as the amount of available H₂ remaining proportionally decreases as the oxidation process proceeds. More strictly speaking, the decline in $k_{R4.48}$ [HO₂][H] and $k_{R4.49}$ [HO₂][O] are both less than $k_{R4.46}$ [H₂][OH]. Subsequently, the production fluxes from reactions (4.48) and (4.49) dominate over the consumption fluxes resulting in a net build up of OH. As a secondary minor effect, the proportional accumulation of H₂O suggests that new production channels leading to the formation of OH become more relevant, such as [183]:

$$Ar^* + H_2O \to Ar + OH + H \tag{4.52}$$

$$O(^{1}D) + H_{2}O \rightarrow OH + OH$$

$$(4.53)$$

The enhancement of the oxidation with temperature is evident and expected since E/N scales proportionally to temperature, which increases the rate of plasma-specific reactions and subsequently H₂ and O₂ dissociation. The same can be claimed for all the neutral chemistry, which accelerates the global rate of the oxidation scheme. Figure 4.19, shows the temperature dependence of the normalized sensitivity coefficient for H₂O with respect to the reactor exit (corresponding to the



Figure 4.19: Normalized sensitivity coefficients of H_2O formation with respect to the exit of the PFR experiment. Taken from [183].

species concentrations shown in Fig. 4.13b). At temperatures below T < 550 K, although reaction (4.49) is chain-terminating in behavior it out competes reaction (4.48) in producing OH. Due to equilibrium the main thermal branching reaction (4.44) is driven backwards and participates in consuming OH. As temperature begins to increase, reaction (4.48) increasingly dominates the OH production over (4.49). At ~720 K reaction (4.44) reverts back to its branching characteristic and contributes to the overall production of OH and the overall oxidation process. At T > 860 K (above the second explosion limit), almost all the sensitivity coefficient go to zero since the chain-branching nature of the system consumes all the fuel well before the exit of the reactor.

4.7 Conclusions

The plasma-assisted oxidation characteristics of hydrogen were studied experimentally under highly dilute conditions using a novel plasma flow reactor. *Ex situ* experiments were performed to measure H_2 and O_2 consumption, while *in situ* LIF was used to measure the absolute concentration OH formation. Qualitative image analysis and OH thermometry were also performed to characterize the physical attributes of the plasma discharge at low temperature conditions for varying pulse repetition rates of 1, 3, and 5 kHz. Results indicate that under the present experimental conditions the plasma remains diffuse and uniform, with a relatively constant centerline temperature axially across the discharge. This further concludes that the plasma is void of any severe filamentary structures that may induce unwanted thermal effects and potentially affect the interpretation of the chemical kinetic features of the system. Oxidation of H₂ under the effects of the plasma extend to lower temperatures (T < 860 K) at a slow steady rate compared to that of thermal system where oxidation does not proceed until T > 860 K with an abrupt fast reaction. Insight into the dynamics of the OH formation reveal that at low-temperatures the plasma induces a linear chainpropagation effect with HO₂ as an active intermediate with complete absence of any chain-branching kinetics. Temporal studies within the plasma show that peak OH formation occurs near the end of the high-voltage pulse and that consumption kinetics dominate the afterglow event. Furthermore, the experiments demonstrated that the plasma system is capable of accelerating the inherent slow kinetics to enhance oxidation by increasing the frequency of pulse perturbations.

Chapter 5

Plasma Assisted Combustion of Hydrocarbons

5.1 C_1 - C_7 n-Alkanes

For practical purposes, studying alkane PAC is important due to their high concentrations in practical fuels for use in reciprocating engines and gas turbines [54], but it is also an important step in extending the overall mechanistic framework. Mechanistic data provided by past investigations into the kinetics of PAC for alkane oxidation [53, 54, 72, 73, 76, 77, 191–193] have been constrained by the operating limits of a given experiment. For example, a series of papers have been published combining both experimental and numerical results using the shock tube technique (T = 880-1970K and P = 0.2 - 2.2 atm) [53, 54, 76, 77] and more recently using a rapid-compression machine (T = 665-960 K and P = 7.5 -15 atm) [191, 192]. Combined the two studies demonstrated reduced ignition delays with the discharge for a range of hydrocarbon fuels from CH_4 up to C_5H_{12} , all highly diluted in Ar or N_2 . Through numerical simulations, it was concluded that enhancement of the radical pools was the main mechanism in driving the high temperature chain-branching processes (e.g., $H+O_2 \rightarrow OH+O$) to initiate ignition. The role of such processes is dependent on fuel and system conditions, and because the experiments typically observed substantial heat generation and large temperature gradients, other processes that couple the heat release to the chemistry could have been important. The authors acknowledged that full elucidation of the kinetics were difficult due to the lack of data on the dominant intermediate species formed, limited by the *in situ* measurement techniques employed.

5.1.1 Overview of Thermal Alkane Oxidation Kinetics

The oxidative characteristics of alkane fuels, especially at low temperatures, are highly dependent on the mechanism of free radical generation and destruction. The rate at which these radicals (e.g., OH, H, HO₂ and R - being an alkyl radical) are produced or destroyed is typically associated with the chemical "chain-reactions" of the system [49,194]. These reactions ultimately dictate the rate of global oxidation and are largely dependent on the chemical structure of the fuel molecule. Generally speaking, oxidation can proceed in one of two ways; either in a controlled manner (slow reaction) or through a rapid increase in rate that leads to an explosion (autoignition). The main macroscopic processes that describe the evolution of radical chains are: (i) initiation: initial formation of radicals from the parent fuel molecule; (ii) propagation: the maintenance of the same number of radicals; (iii) branching: the increase in the number of radicals; (iv) degenerate branching: includes the formation of radicals from quasi-stable intermediate species to increase the number of radicals; and (v) termination: the decrease in the number of radicals formed [194].

The general mechanism of alkane combustion has been widely discussed in the literature, and is considered readily understood for a wide range of conditions. An example of such is the mechanism by Metcalfe et al. [195]. Unlike simple hydrocarbon fuels, propane and larger alkanes show a range of activity depending on temperature and pressure. The classical definition of oxidation chemistry regimes can be defined in terms of the main chain-branching processes that prevail at three distinct temperature regions [196]. The "high" temperature limit (T > 1000 K) is defined by the branching of reaction (5.1), where alkyl radicals decompose rapidly and H-atom chemistry becomes important. The lower temperature chemistry is centered around reversible reaction (5.2) (RO₂ being an alklyperoxy radical). At "intermediate" temperatures (700 < T < 1000 K), alkyl radicals are favored thermodynamically, which eventually leads to HO₂ formation and/or β -scission to form smaller olefinic hydrocarbons. Finally, at "low" temperatures (T < 700 K), equilibrium favors the products, and the fate of RO₂ becomes the most important feature of the chemical reaction pathways. It should be reiterated that the temperature regions described here are approximate, and the actual extent of the regions are highly influenced by the pressure as well as the chemical structure of the fuel in the system.

$$H + O_2 \to OH + O \tag{5.1}$$

$$R + O_2 \rightleftharpoons RO_2 \tag{5.2}$$

There are two important features that distinguish the high temperature and low temperature oxidative reaction processes. The first is the manner in which the initial carbon chain of the fuel molecule is broken apart. High temperature reaction pathways result in the rapid decomposition of the fuel molecule (i.e., $C_4 \rightarrow 2C_2$), whereas low temperature oxidation reactions tend to gradually decompose the fuel (i.e., $C_4 \rightarrow C_3 \rightarrow C_2 \rightarrow C_1$) [194]. The second is the influence of the radicals being produced, where radicals involved in the high temperature region tend to be far more reactive (e.g., OH, O) than radicals produced at lower temperatures (e.g., R, HO₂) [194].

The initiation of high temperature oxidation begins by breaking the C-C bond of the initial alkane fuel molecule, or from O_2 attack to cause H-atom abstraction (5.3) [49]. Due to its high endothermicity, this initiation reaction has little importance in maintaining the supply of R-radicals once other radicals (X) are formed in the system [49]. The most important initiation steps come from the radical attack on the fuel (i.e., RH+X \rightarrow R+XH), with the fastest and most effective reaction being with OH (5.4), since it is highly exothermic due to the formation of water as a product [49].

$$\mathrm{RH} + \mathrm{O}_2 \to \mathrm{R} + \mathrm{HO}_2 \tag{5.3}$$

$$RH + OH \rightarrow R + H_2O$$
 (5.4)

From here, the radicals produced are rapidly decomposed into stable intermediate and product species (e.g., CO, CO₂, CH₂O) or small saturated hydrocarbons [194]. The fate of HO₂ actually results in another chain-branching mechanism in the high temperature region, where it can react again with the initial fuel molecule to form hydrogen peroxide (H₂O₂) (5.5) and then decomposes to form two further OH radicals (5.6) [194].

$$\mathrm{HO}_2 + \mathrm{RH} \to \mathrm{H}_2\mathrm{O}_2 + \mathrm{R} \tag{5.5}$$

$$H_2O_2(+M) \to OH + OH(+M)$$
(5.6)

A general kinetic scheme for low and intermediate temperature oxidation is depicted in Fig. 5.1. Unlike high temperature conditions where the high activation energy required to decompose the formed alkyl radicals is possible, at lower temperatures this is not the case. Rather alkyl radicals go on to react with O_2 to form either the RO_2 complex (5.7) or an olefin and HO_2 (5.8).

$$R + O_2 \to RO_2 \tag{5.7}$$

$$\mathbf{R} + \mathbf{O}_2 \to \mathbf{H}\mathbf{O}_2 + \mathbf{C}_n\mathbf{H}_{2n} \tag{5.8}$$



Figure 5.1: Kinetic scheme for low temperature alkane oxidation. Redrawn and modified from [197].

The latter is favored at intermediate temperatures. Since HO_2 is relatively unreactive at these intermediate temperatures and its removal reaction mostly produces H_2O_2 , (which is fairly stable up to $T \sim 1100$ K) this route effectively becomes chain-terminating [194]. At even lower temperatures and moderate pressures the highly temperature dependent RO_2 becomes favored. From here, RO_2 reactions display a range of different possibilities, with kinetic behavior changing based on temperature and pressure [194, 196, 197]. Several theoretical RO₂ kinetics schemes have been postulated over the decades, with the specifics still being a debatable topic. The reaction of RO_2 begins by undergoing internal H-atom isomerization to form a hydroperoxyalkyl radical (QOOH), which in turn, can follow four distinct reactive pathways, with each having a different effect on the macroscopic behavior of the system. It should be mentioned that the weakly bound QOOH intermediate has never been directly observed experimentally, and due to it elusiveness, its thermochemical reactive features have been entirely based on quantum chemical calculations [197]. However, with that being said, notable acknowledgment needs to be given to the recent works achieved by Savee et al. [198]. At the lowest temperatures, QOOH can react with another O_2 to form a hydroperoxy-alkylperoxy (OOQOOH) radical. This radical can react by internal H-atom abstraction forming an OH-radical and a ketohydroperoxy radical ($OQ_{-H}OOH$), followed by further decomposition via several different paths to produce at least two radicals. Such an example is the formation of OH and a diketone radical (OQ_{-H}O). This route results in a highly reactive degenerate chain-branching pathway that takes one alkyl radical and forms three reactive radicals. As temperatures increases three alternative chain-propagating reactive pathways for QOOH emerge: (i) is the production of an OH-radical from a cyclic ether (O-atom heterocycle) by a concerted ring structure, (ii) β -scission to form an OHradical and a ketone and (iii) decomposition to form an olefin and HO₂. The resulting decrease in reaction rate with increase in temperature based on the above scheme is a unique feature of alkane oxidation, known as the negative temperature coefficient (NTC) regime. This region gives rise to the cool-flame phenomena, a subdued ignition process that leads to partial oxidation and moderate heat release and is a crucial subset of chemistry that dictates the autoignition characteristics of a hydrocarbon system. It is obvious that the number of reactions can exponential increase and the complexity of the kinetic mechanism can increase with an increase in fuel size. The most current review of the work into low temperature combustion chemistry can be found in Zádor et al. [197].

5.1.2 Results and Discussion

5.1.2.1 Plasma Assisted Oxidation Trends in Alkane Fuels

A comparison of the normalized fuel consumption profiles for different fuels with respect to temperature is shown in Fig. 5.2. Part (a) of the figure presents the results of the thermal reaction (without plasma), and part (b) with application of plasma discharge. Experimentally, in all the reactive mixtures studied, a constant C/O loading is maintained to ensure the amount of heat release is kept constant across the fuel systems. The normalized major product species profiles of combined carbon monoxide and carbon dioxide $[CO+CO_2]$, and ethylene $[C_2H_4]$ are shown in Figs. 5.3 and 5.4. In all instances for both the thermal and the plasma-assisted experiments, these were consistently the dominant products formed over the temperature regime considered. Some qualitative observations from these results are:

- 1. Without the plasma, the onset of fuel consumption occurs at T > 900 K. The order in which ignition occurs is consistent with available shock tube and flow reactor data [199,200] for similar conditions. The anomalously early ignition of ethane (C₂H₄) is also consistent, attributed to its high branching factor compared to the other fuels [200] (see Fig. 5.2a).
- 2. For each system the effect of the plasma enhances the low temperature decomposition of the



Figure 5.2: Comparison of fuel consumption trends (a) without and (b) with the plasma. Initial conditions: $X(C_xH_y) = 1600 \text{ ppm}/x$, $X(O_2) = 3000 \text{ ppm}$, X(Ar) = 1 - 1600 ppm/x - 3000 ppm, P = 1 atm, $\tau = 311.4 \text{ s} \cdot \text{K}/T$. Plasma conditions: V = 10 kV, v = 1 kHz. CH₄ (Black), C₂H₆ (Blue), C₃H₈ (Purple), C₄H₁₀ (Orange), C₇H1₁₆ (Grey).

fuel. Also the temperature at which complete consumption of fuel occurs has been lowered (the temperature for the onset of high temperature ignition). For a particular fuel, at least two distinct consumption rates can be observed in the profiles. For C_2 fuels and less, the rate of consumption is slow and then transitions to a faster rate at temperatures greater than 900 K. For C_3 and larger fuels, the opposite occurs, initially a fast then slow reaction is observed, where the transition in reaction rate is observed between 600-700 K (see Fig. 5.2b).

- 3. For T < 960 K the plasma has a relatively constant effect on the formation of $[CO+CO_2]$. Between 670-870 K a NTC regime appears indicating a change in chain-branching for fuels greater than C₂. While the C₂H₆ fuel profile does not necessarily indicate a NTC region, its $[CO+CO_2]$ profile does show a NTC type behavior. Above 960 K, both plasma and thermal reactions contribute to forming and consuming $[CO+CO_2]$ (see Fig. 5.3).
- Below 960 K, a nearly constant amount of CO₂ formation is observed, accounting for ~3% of the initial fuel input. At temperatures higher than those required for complete fuel consumption,

thermal branching dominates over the plasma and drives the oxidation of CO to CO₂. Here, the plasma offers no added benefit in driving the reaction to complete oxidation. Interestingly, this is not the case for the methane (CH₄) system. The plasma facilitates the high temperature chemistry in oxidizing the system at conditions where the pure thermal effect could not (T >1100 K, see Fig. 5.3).

5. With the exception of CH_4 , all the fuels appear to form similar amounts of C_2H_4 , from 420 K until the temperature where C_2H_4 consumption exceeds its formation. C_2H_4 as a major product species of alkane oxidation is expected and is consistent with the known understanding of alkane oxidation schemes [50] (see Fig. 5.4).

The reader should keep in mind that individual experimental data points effectively display the extent of reaction for a particular species at a given temperature. Thus, the transition in gradient profiles for fuel consumption can be interpreted as a change from a slow, steady reaction, to a fast, chain-branched reaction.

It is obvious that the plasma facilitates the consumption of fuel at lower temperatures, suggesting that O-atom attack and the production of OH and H are likely being enhanced. Before any appreciable thermal effect (T < 900 K), the plasma induces a constant effect at a given temperature since the $[CO+CO_2]$ and $[C_2H_4]$ concentrations are nearly identical regardless of the fuel. Low temperature CO formation is particularly advantageous as it provides early heat-release to aid the oxidation process. As the size of the fuel increases it should be expected that the number of steps (or the number of intermediates formed) in the kinetic routes leading to oxidation should increase proportionally. However, with nearly proportional amounts of $[CO+CO_2]$ and $[C_2H_4]$ being formed, and varying degrees of RH consumption, suggests that secondary kinetic effects are leading to the enhancement of fuel consumption of fuels of increasing size. The slow reaction experienced by CH_4 and C_2H_6 is wholly attributed by plasma reactions considering thermal effects were not observed until 900 K. By 850 K for C₂H₆, and 1120 K for CH₄, the plasma has enhanced the H-radical pool to such an extent that high temperature branching reactions have accelerated the rate of fuel consumption by way of OH. This demonstrates the plasma's ability to instigate the high temperature chemistry at lower temperatures or within the "self- ignition" threshold and is consistent with analysis of Kosarev et al. [54] considering the same fuels. From the discussion in Section 5.1.1, the increase in the R-radical concentration is expected to have a greater effect on the low temperature fuel consumption rates of the higher order hydrocarbons. This is evident since more than 50% fuel



Figure 5.3: Normalized [CO+CO₂] reactivity plots for plasma-assisted experiments (a) 400 < T < 1250 K (b) 400 < T < 950 K. Initial conditions: $X(C_xH_y) = 1600$ ppm/x, $X(O_2) = 3000$ ppm, X(Ar) = 1 - 1600 ppm/x - 3000 ppm, P = 1 atm, $\tau = 311.4$ s·K/T. Plasma conditions: V = 10 kV, v = 1 kHz. CH₄ (Black), C₂H₆ (Blue), C₃H₈ (Purple), C₄H₁₀ (Orange), C₇H1₁₆ (Grey).



Figure 5.4: Normalized $[C_2H_4]$ reactivity plots for plasma-assisted experiments. Initial conditions: $X(C_xH_y) = 1600 \text{ ppm}/x$, $X(O_2) = 3000 \text{ ppm}$, X(Ar) = 1 - 1600 ppm/x - 3000 ppm, P = 1 atm, $\tau = 311.4 \text{ s}\cdot\text{K}/T$. Plasma conditions: V = 10 kV, v = 1 kHz. CH₄ (Black), C₂H₆ (Blue), C₃H₈ (Purple), C₄H₁₀ (Orange), C₇H1₁₆ (Grey).

conversion is achieved by 700 K, whereas 50% conversion was not achieved until 800 K for C_2H_6 and 1120 K for CH_4 . Moreover, the enhancement of fuel consumption for increase in fuel size is also consistent with the works of Wu et al. [86], which relates this behavior to the increase in reaction rate of (5.4) for larger hydrocarbons. By 700 K the rates of the fuel consumption begin to slow down, which is also supported by the fact an NTC region appears in the CO profile in the same temperature region. This inhibition can most likely be attributed to the formation of HO₂, and its presence can also explain the minimal conversion of CO into CO₂. The lack of CO₂ formation could also be explained by considering the preferential role of OH-attack on RH over CO. The fact that the temperature at which the turnover for the NTC occurs at lower temperatures for increasing fuel size is consistent with equilibrium calculations when considering different R-radicals. This is known as the "ceiling temperature" where $[R] = [RO_2]$ [196].

5.1.2.2 Phenomenological PAC Kinetic Analysis in Propane and Butane

The thermal and plasma-assisted (at 1 atm) fuel consumption profiles are compared to the works of Koert et al. [201] for propane oxidation using a high-pressure flow reactor at 10 atm (Fig. 5.5). Fuel consumption below 800 K under the effects of the thermal reaction does not occur until elevated pressures due to difficulties in forming the alkyl radical, and when initiated a NTC regime emerges between 740-770 K. Considering that the rate of fuel consumption actually slows down in the same vicinity (vertical dashed lines) for the plasma results, it can also be inferred that the kinetics responsible for the NTC behavior are being reproduced in the context of the plasma, albeit at considerably lower pressures. In a thermal system the initial consumption of fuel is most likely through unimolecular dissociation (5.9) [195] or H-atom abstraction (5.10) [195], requiring sufficient kinetic energy (i.e., higher pressures) to overcome the high-barrier to initiate these reactions [49].

$$C_3H_8 + M \to CH_3 + C_2H_5 + M$$
 (5.9)

$$C_3H_8 + O_2 \to C_3H_7 + HO_2$$
 (5.10)

However, in the presence of the plasma, the system is no longer constrained by such energy intensive processes, but rather electron-impact reactions enhance molecular dissociation. Two such examples are direct electron-impact (5.11) and collisional quenching with excited states (5.12) (where Ar^{*} is a metastable electronically excited state of Ar formed via an electronic collision) [54].



Figure 5.5: Comparison of thermal (1, 10 atms) and plasma (1 atm) normalized propane fuel consumption as a function of temperature.



Figure 5.6: Intermediate species as a result of NTC thermal oxidation of C_3H_8 at P = 10 atm. Data taken from Koert et al. [201].

$$C_3H_8 + e \to C_3H_7 + H + e$$
 (5.11)

$$Ar^* + C_3H_8 \to Ar + C_3H_7 + H \tag{5.12}$$

The same processes can also be considered for O_2 , with the added benefit that electronically excited states can also be readily formed (e.g., $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g)$ [2,4]). Reactions involving such excited states can be significantly faster than their ground state counterparts at lower than normal combustion temperatures [2]. Note, below the self-ignition temperature, O-atom formation is essentially non-existent through thermal reaction routes. From here on, it is expected that the radical reservoirs of both propyl ($i-C_3H_7$ and $n-C_3H_7$) radicals and O-atoms (e.g., $Ar^*+O_2 \rightarrow Ar+O+O$) have enhanced considerably in the plasma-assisted experiments and that the focus of the remaining discussion leans towards uncovering secondary kinetic chain-branching processes that enhance oxidation.



Figure 5.7: Reactivity plots of propane plasma-assisted oxidation experiments. Initial conditions: $X(C_3H_8) = 533$ ppm, $X(O_2) = 3000$ ppm, X(Ar) = 0.9964, P = 1 atm, $\tau = 311.4$ s·K/T. Plasma conditions: V = 10 kV, v = 1 kHz.

Figure 5.7 shows the reactivity plot of the measured product species of plasma-assisted propane oxidation. Firstly, chain-branching through the O-atom attack route is most likely enhanced, providing a highly reactive OH radical (5.13) [202]. The second route is through the propyl radical, where O_2 addition can form a propylperoxy radical (C_3H_7OO) (5.14) [195].

$$C_3H_8 + O \to C_3H_7 + OH \tag{5.13}$$

$$C_3H_7 + O_2 \rightarrow C_3H_7OO \tag{5.14}$$

The current understanding of this reaction is that it proceeds through a barrierless pathway where its equilibrium constant is highly temperature dependent and favors C_3H_7OO at lower temperatures (T < 700 K) [203]. At increasingly higher pressures, the effectiveness of this reaction increases as the collisional stabilization of C_3H_7OO increases [204]. The intricacies of this type of reaction are quite complex and have been theoretically studied in general for alkyl radicals [203], with few experimental and theoretical studies examining the propyl+ O_2 system specifically [205–207]. From here, the propylperoxy radical undergoes an intermolecular isomerization process, where the terminal O-atom approaches an extractable H-atom to form a cyclic transition state. The isomerizations in the alkyl radical can be categorized according to the position of the atoms between which the H-atom is transferred and the type of C-H bond being broken. The atoms in the ring shaped transition state are numbered beginning from the terminal O-atom and proceed down the the carbon backbone. A 1.4 transfer hence refers to a five-membered (O-O-C-C-H) transition state (see Fig. 5.8). A letter is then added to designate the type of C-H bond being broken, either primary, secondary or tertiary [197]. The rate of isomerization can be influenced by several factors, including the relative size and structure of the original fuel molecule, the location of the O_2 group, the number of atoms in the transition state ring, but also the type of C-H bond broken [208]. Knowing this, the number of possible isomerizations of propylperoxy results in three distinct hydroperoxypropyl (C_3H_6OOH) isomers. The fate of C_3H_6OOH can follow several different pathways all of which can have an effect on the chain-propagation rate of the system (see Figs. 5.8 and 5.9). The first possibility is to decompose into HO₂ and a conjugate alkene (C_3H_6) by way of β -scission, effectively a terminating step. The second is a chain-propagating step where scission of the O-O bond in either the 1-hydroperoxy-1-propyl forms propanal (CH₃CH₂CHO) and OH, or the 2-hydroperoxy-2propyl forms acetone (CH_3COCH_3) and OH. One of the discrepancies that exist within the present scheme is whether propanal and acetone form through a cyclic transition state. Several studies have suggested that this is not that case, due to the strong temperature dependence that 1,3 H-atom



Figure 5.8: Chemical structure depiction of C_3H_7 radical through RO_2 isomerization sequence.



migration reactions exhibit [203]. This difference is attributed to the formation of a highly unstable a-QOOH molecule that spontaneously dissociates to form an aldehyde or ketone. However, others have defended the cause by demonstrating that the energetic barrier to direct dissociation is much greater than those involving a route through a concerted ring structure [207]. The emergence of propanal, acetone, propene and ethylene below 700 K in the experimental results are consistent with this scheme and the experimental results of Koert et al. [201] (see Fig. 5.6), suggesting that low temperature chain-propagation is taking part in the presence of the plasma. Furthermore, it is also possible for a second O_2 to add to C_3H_6OOH , creating hydroperoxy-propylperoxy radical (OOC₃H₆OOH), which can then isomerize further via an internal H-atom abstraction and decompose into a stable ketohydroperoxide (OC_3H_5OOH) and OH [197, 205–207]. The ketohydroperoxide acts as a degenerate branching agent, which can decompose into at least two radical species (5.15). The experimental results do show considerable acetaldehyde (CH_3CHO) formation below 700 K and the formation of HCO could explain the low temperature route for CO formation. In addition, because of O-atom formation from the plasma, radical-radical reactions could also contribute to acetaldehyde formation, (5.16) [195], whereas the CH_3 would explain the formation of C_4 products by way of recombination reactions, and CH₄ by H-atom abstraction. As to the relative contribution of either reaction is unknown at this point.

$$OC_3H_5OOH \rightarrow CH_3CHO + HCO + OH$$
 (5.15)

$$C_3H_7 + O \rightarrow CH_3CHO + CH_3 \tag{5.16}$$

The above discussion emphasizes the current understanding of RO_2 kinetics, which favors the isomerization route (forming QOOH). However, it should be noted that earlier studies have suggested that for small alkyl radicals (such as C_3H_7) an alternative route exists where the RO_2 reacts with the initial fuel molecule (RH) to form an alkylhydroperoxide ROOH (5.17) and subsequently decomposes to form a reactive OH-radical (5.18) [209]. This scheme has been known to replicate NTC behavior in thermal propane oxidation experiments.

$$C_3H_7OO + C_3H_8 \rightarrow C_3H_7OOH + C_3H_7$$

$$(5.17)$$

$$C_3H_7OOH + M \rightarrow C_3H_7O + OH + M$$
(5.18)

As temperature increases (T > 700 K), C₃H₇OO decomposition becomes favored and the route to forming oxygenated species decreases (signifying the decrease in chain-propagation/branching). Here, the alkene+HO₂ and thermal decomposition of products becomes competitive, which would explain the increase of $[C_3H_6]$, $[C_2H_4]$ and $[CH_4]$. Decomposition of propyl radicals follow the β scission rule, where the bond one position removed from the radical site will break. When there is a choice between a primary C-C bond versus a primary C-H bond, the weaker C-C bond will be favored, thus explaining the dominance of C_2H_4 over C_3H_6 as an intermediate in the experimental results [49]. By 800 K, the chain-branching induced by the plasma through O-atom attack is likely dominating the system and enhancement of fuel consumption resumes. As the temperature continues to increase (T > 1000 K) the thermal effects of the reaction dominate, and it is expected that the high temperature chain-branching reactions accelerate the rate of fuel consumption once again.

The application of the RO_2 kinetic scheme is quite consistent amongst the alkane fuels. In Fig. 5.10, the plasma-assisted butane oxidation results are presented for 1 atm. The thermal oxidation of butane within the NTC regime for elevated pressures has been studied both experimentally and numerically in the past [210–214]. Comparison of product and intermediate species formation with these investigations to the present work shows constancy, namely with the formation of acetaldehyde, propanal, and butanone (CH₃CH₂COCH₃). With an understanding of the scheme, one can interpret the pathways that potentially derive these oxygenated species and promote low temperature chainbranching. Unique to the effects of low temperature plasmas, radical-radical recombination reactions become apparent again, where hydrocarbon growth is observed resulting in the formation of pentene (C₅H₁₀) and hexene (C₆H₁₂).

5.1.3 Conclusions

For all fuels, while under the effects of the plasma, the rate of fuel consumption increased across the temperature domain considered compared to the thermal reactions. In addition, depending on the fuel, transitions in the rates of fuel consumption are observed at different temperatures. For all fuels, high temperature chain-branching is initiated at lower temperatures. For fuels C_3 and greater, fuels experience multiple transitions in overall reaction rates, particularly at lower temperatures (T <800 K). Using propane and butane as examples, low temperature chain-branching is postulated based on a phenomenological interpretation of the formation of product species indicating the presence of NTC behavioral chemistry at lower pressures. In PAC applicable systems, these results suggest that different strategies can be implemented to enhance combustion based on specific fuels, and different temperatures and pressures. This has particular relevance in compression-ignition and pulse-detonation engines that would benefit from low temperature chemistry enhancement to initiate



Figure 5.10: Reactivity plots of butane plasma-assisted oxidation experiments. Initial conditions: $X(C_4H_{10}) = 400$ ppm, $X(O_2) = 3000$ ppm, X(Ar) = 0.9966, P = 1 atm, $\tau = 311.4$ s·K/T. Plasma conditions: V = 10 kV, v = 1 kHz.

early ignition. Furthermore, the following experimental data provides a database for any future modeling studies.

5.2 Ethylene

Ethylene is an important intermediate constituent in the combustion of hydrocarbon fuels, as well as a high-speed propulsive fuel candidate. An understanding of its ignition and oxidation process will have a large influence on the constructive framework for the mechanism of hydrocarbons under PAC. The thermal kinetics of ethylene pyrolysis and oxidation have been studied and modeled extensively over the years. Its reaction mechanism for the most part is well established and is based on the notable works of Westbrook et al. [215, 216], Dagaut et al. [217], Marinov et. al [218], Carrier et al. [219] and recently Lopez et al. [220]. Most of the thermal kinetic studies of ethylene oxidation at atmospheric pressure and above have been performed in the intermediate and high temperature regime, achieving reaction times appropriate to the experiment being performed (e.g., shock tubes and flow reactors). The most recent flow reactor experiments performed at high-temperatures include those of Carrier et al. [219] for pressures at 5-10 bar between 850-950 K and Lopez et al. [220] for 60 bar to obtain kinetic data at 600-900 K. Mechanistic data at even lower temperatures and atmospheric pressure or higher, are significantly lacking. Such data are important to the development of PAC chemistry models of interest to the present work. The results of intermediates and product species as a function of temperature are analyzed and compared with other plasma-assisted flow reactor data, which were conducted at 300-600 K and 70 torr with non-dilute ethylene-air mixtures [78–80]. The results form a unique data set for detailed modeling initiatives to be presented in the next chapter.

5.2.1 Results

5.2.1.1 Plasma-Assisted Pyrolysis of Ethylene

Figure 5.11, shows a comparison of experimental results between thermal and plasma-assisted pyrolysis. The reactive mixture consisted of 800 ppm of C_2H_4 diluted in Ar. Thermal pyrolysis has minimal effect throughout the temperature regime, a result verified by the claims made by Hidaka et al. [221], where the onset of thermal decomposition occurs at temperatures greater than 1100 K. For temperatures greater than 1150 K, the only detectable product of C_2H_4 dissociation was acetylene (C_2H_2). Westbrook et al. [215] made a similar observation in their pyrolysis experiments using a



Figure 5.11: Comparison of (a) C₂H₄ and (b) C₂H₂ concentration profiles for thermal (hollow marks) and plasma-assisted (solid marks) pyrolysis as function of isothermal reactor temperature. Initial conditions: $X(C_2H_4) = 800$ ppm, X(Ar) = 0.9992, P = 1 atm, $\tau = 311.4$ s·K/T. Plasma conditions: V = 10 kV, v = 1 kHz.

turbulent flow reactor. With the application of a plasma discharge, the onset of fuel decomposition is observed at temperatures as low as 420 K compared to 1150 K in the thermal reaction. The direct effect of the plasma seems to have a constant effect on the decomposition of C_2H_4 , where nearly 300 ppm is consistently consumed (38% fuel removal) in the temperature regime of 520-1050 K. At temperatures greater than 1050 K, the consumption of C_2H_4 progresses further, suggesting that both the plasma and the thermal reaction are contributing to the decomposition enhancement. In the presence of the plasma, the reaction is initiated at a lower temperature, shifting the onset to about 100 K lower than previously observed in the thermal reaction. At the highest temperature studied (1250 K) and for the given flow rate, maximum extent of reactivity reaches nearly 64% consumption with the plasma versus 18% without. Acetylene was once again observed to be the dominant product of C_2H_4 decomposition. Its formation is fairly constant between 520-820 K and begins to gradually increase with increasing temperature (T > 820 K).

Figure 5.12 shows the reactivity plot of the all the measured product species of plasma-assisted pyrolysis of C_2H_4 . It is evident from the number of minor species formed that the decomposition of fuel under the effects of the plasma can be considered more efficient, since none are seen in the thermal reaction for the same temperature regime considered. For temperatures less than 900 K several higher-order hydrocarbon species appear, including propane (C_3H_8) and n-butane (C_4H_{10}). An interesting fact considering that apart from decomposition, a small portion of C_2H_4 consumption actually goes towards hydrocarbon growth. As temperature increases the thermal decomposition on such intermediates becomes evident as both C_3 - and C_4 -hydrocarbon species begin to disappear for



Figure 5.12: Reactivity plots of ethylene plasma-assisted pyrolysis experiments. Initial conditions: $X(C_2H_4) = 800$ ppm, X(Ar) = 0.9992, P = 1 atm, $\tau = 311.4$ s·K/T. Plasma conditions: V = 10 kV, v = 1 kHz.



Figure 5.13: Comparison of (a) C_2H_4 , (b) CO and (c) CO_2 concentration profiles for thermal (hollow marks) and plasma-assisted (solid marks) oxidation as function of isothermal reactor temperature. Initial conditions: $X(C_2H_4) = 800$ ppm, $X(O_2) = 3000$ ppm, X(Ar) = 0.9962, P = 1 atm, $\tau = 311.4$ s·K/T. Plasma conditions: V = 10 kV, v = 1 kHz.

temperatures greater than 820 K. Above this temperature, plasma reactions become less selective forming mostly ethane (C_2H_6) and methane (CH_4). By 1100 K, the effectiveness of the plasma diminishes considerably as all minor species begin to disappear. At this point, both the plasma and thermal reactions work in parallel to drive and accelerate the decomposition of C_2H_4 and enhance the formation of C_2H_2 .

5.2.1.2 Plasma-Assisted Oxidation of Ethylene

In these sets of experiments, the thermal and plasma-assisted reactions are compared when 3000 ppm of O_2 was added to the C_2H_4/Ar reactive mixture (Fig. 5.13). In both types of experiments, C_2H_4 , CO and CO₂ were predominately the major species formed. For the thermal reaction the only other observable species were those of CH_4 (~60 ppm) and C_2H_6 (~20 ppm) for the limited temperature range of 950-1050 K. The formation of these species as intermediates is consistent with the observations of Lopez et al. [220].

Under the effects of the plasma, decomposition of C_2H_4 exceeds that of the thermal reaction for temperatures between 420-950 K. In the presence of O_2 , fuel consumption progresses further another 100 ppm from the plasma-assisted pyrolysis reaction achieving 45% fuel removal by 760 K. Moreover, nearly 63% of the fuel is consumed before any noticeable consumption is observed in the pure thermal reaction at 950 K. By 1020 K, all of the fuel is consumed. Further enhancement of the plasma oxidation reaction compared to the plasma pyrolysis suggests that there are additional processes that contribute to the C_2H_4 consumption. At low temperatures (T < 650 K), the CO



Figure 5.14: Reactivity plots of ethylene plasma-assisted oxidation experiments. Initial conditions: $X(C_2H_4) = 800 \text{ ppm}, X(O_2) = 3000 \text{ ppm}, X(Ar) = 0.9962, P = 1 \text{ atm}, \tau = 311.4 \text{ s}\cdot\text{K}/T$. Plasma conditions: V = 10 kV, v = 1 kHz.



Figure 5.15: Comparison of CO (red circles) and CO₂ (green circles) concentration profiles for varying plasma discharge voltages at (a) 8 kV, (b) 10 kV and (c) 15 kV as a function of isothermal reactor temperature. Initial conditions: $X(C_2H_4) = 800$ ppm, $X(O_2) = 3000$ ppm, X(Ar) = 0.9962, P = 1 atm, $\tau = 311.4$ s·K/T. Plasma conditions: v = 1 kHz.

enhancement is linearly dependent on temperature indicating a short radical chain with moderate formation of CO₂. At intermediate temperatures (650 K < T < 850 K) a constant amount of CO and CO₂ formation is formed possibly indicating a constant rate of branching and termination. Suddenly at 850-1050 K there is a non-linear effect in the observed CO formation, suggesting that the branching factor contributing to its formation is dramatically increasing. As temperature increases (T > 1050 K), the CO and CO₂ profiles for both the thermal and plasma reactions appear similar, although the onset of this conversion occurs at approximately 50 K lower with the plasma.

The range of minor species formed during the plasma oxidation reaction can be seen in the reactivity plot presented in Fig. 5.14. Firstly, the formation of intermediate species of the thermal reaction, CH_4 and C_2H_6 , have increased substantially and their occurrence has been extended over a greater temperature range (450 K < T < 1050 K). Several minor species are formed not seen in the thermal reaction, namely propene (C_3H_6), C_3H_8 , C_2H_2 and acetaldehyde (CH_3CHO). At temperatures greater than 1050 K, the thermal reaction begins to dominate and all minor species begin to disappear.

5.2.1.3 Variation of Discharge Voltage

The effectiveness of the plasma discharge can be characterized by the amount of energy it deposits into the reactive mixture. Experimentally this is similar to changing the applied discharge voltage. In Fig. 5.15, the effect of the plasma discharge voltage on the CO and CO₂ formation is examined for the plasma-assisted oxidation reaction. The C_2H_4 (800 ppm) and O_2 (3000 ppm) ratios remained the



Figure 5.16: Concentration profiles for $C_2H_4/O_2/Ar$ mixtures with initial O_2 concentrations ranging from $X(O_2) = 0$ to $X(O_2) = 0.5$. Initial conditions: $X(C_2H_4) = 800$ ppm, X(Ar) = 0.9992 to X(Ar) = 0.4992, T = 814 K, P = 1 atm. Plasma conditions: V = 15 kV, v = 1 kHz.

same, while the voltage was adjusted between 8-15 kV. The pulse repetition rates were held constant at 1 kHz for all the experiments. Referring to the 8 kV experiments (see Fig. 5.15a), the onset of a stable plasma discharge does not occur until 620 K. For the low temperature regime (420 K < T < 620 K) the rate of propagation increases with increasing voltage. This suggests a linear relationship exists between discharge voltage and radical formation. In the intermediate regime (620 K < T< 820 K) for the 8 kV and 10 kV experiments, there is a constant rate of formation indicating the rate of branching and termination have reached steady-state. This rate once again increases with increasing voltage. In the 15 kV experiments, the intermediate regime gives indication of a slight NTC regime, where the reaction rate of the branching step increases suddenly. For the higher temperature regime (T > 820), the branching factor leading to CO formation increases dramatically for increasing discharge voltage. At approximately 950-1000 K, CO formation peaks, where the peak CO formation increases from 1223 ppm, to 1287 ppm and 1302 ppm for increasing voltages of 8, 10 and 15 kV, respectively. For the temperature regime after the ignition point the thermal reaction dominates regardless of the plasma voltage and CO is converted into CO₂.

5.2.1.4 Variation of Initial O₂ Concentration

In these sets of experiments, the initial O_2 concentration was varied over several orders of magnitude while the other variables were held constant for a constant temperature of T = 814 K. Oxygen has a strong electron affinity and by increasing the proportion of O_2 in the mixture, the likelihood of inelastic energy losses and attachment processes increases as well [222]. For this reason, these experiments were conducted using a higher electric field (15 kV at pulse repetition rate of 1 kHz)



Figure 5.17: Concentration profiles for $C_2H_4/O_2/Ar$ mixtures with initial N_2 (solid marks) concentrations ranging from $X(N_2) = 0$ to $X(N_2) = 0.9962$ and He (hollow marks) concentrations ranging from X(He) = 0 to X(He) = 0.9962. Initial conditions: $X(C_2H_4) = 800$ ppm, $X(O_2) = 3000$ ppm, X(Ar) = 0 to X(Ar) = 0.9962, T = 814 K, P = 1 atm. Plasma conditions: V = 15 kV, v = 1 kHz.

in order to ensure a sustained plasma in the bulk. The first data point correlates to the plasmapyrolysis experiment where the reactive mixture is C_2H_4/Ar only (see Fig. 5.16). At 15 kV nearly 500 ppm of fuel is consumed, demonstrating the enhancing effect increasing discharge voltage has on pyrolysis (at 814 K for 10 kV only 300 ppm of C_2H_4 is consumed). Increasing the amount of O_2 by 12.5% (125,000 ppm) a substantial increase in fuel consumption is observed, achieving more than 90% fuel removal. In relation to this, both the formation of CO and CO₂ increase as well. However, it is observed that nearly 75% of the fuel is converted into CO and the remainder into CO₂. When the amount of O_2 was increased even further to 50% (500,000 ppm) the results indicate that the formation of CO and CO₂ has stagnated, suggesting that the reactions leading to their formation have reached their maximum extent of reactivity, due simply to the fact that all the fuel has been rapidly consumed. The relative modest increase in CO₂ despite increasing the formation of CO considerably suggests that the rate of CO oxidation is moderately affected by O₂ concentration and still does not have a significant impact under these conditions.

5.2.1.5 Variation of Bath Gas Concentration with N_2 and He

Figure 5.17, shows a comparison of experimental results when the Ar diluent gas was substituted with either He or N₂. Again, both the C_2H_4 (800 ppm) and O_2 (3000 ppm) loading were kept constant, while the temperature was maintained at T = 814 K for plasma conditions at 15 kV and 1 kHz repetition rate. Focusing on the Ar/N_2 mixture first, as the amount of N_2 increases fuel consumption decreases from 70% to 40%. If the reactive mixture is replaced with He instead of N₂, the fuel removal improves somewhat from the perspective of the N_2 and achieves 54% fuel removal. Comparing the effectiveness of the three different bath gases in terms of fuel consumption, Ar ranks the most effective, with He next and than N_2 as being the least. The maximum CO and CO_2 conversions are proportional to the degrees of fuel consumption where 49% and 4% is achieved in the Ar system, 33% and 3% in the He system, and 26% and 2% in the N₂ system. The effectiveness of fuel decomposition by the plasma regardless of bath gas composition is demonstrated in the results, as several intermediates species including higher-order hydrocarbons were formed that were not observed in the thermal reaction. In both the Ar/He and Ar/N_2 mixture systems no differing intermediates appeared. Based on the relative magnitude of species formed, Ar is more effective in producing these minor species followed by He and than N_2 . In the Ar/He system, the formation of C_2H_2 remains relatively constant, as its formation seems to have no dependence on whether the bath gas was Ar or He.

5.2.2 Discussion

The plasma discharge is effectively the electrical breakdown of the Ar carrier gas leading to ionization and forming Ar^+ ions. This process subsequently leads to the excessive formation of electrons needed for electronic excitation and dissociation of neutral species by electron-impact. Apart from ionization, a significant portion of the plasma discharge energy can potentially go into exciting various electronic states, mainly forming metastable Ar^* (i.e., $Ar+e \rightarrow Ar^*+e$) [53, 54, 75].

In the presence of C_2H_4 , collisional quenching with Ar* (i.e., Ar*+ $C_2H_4 \rightarrow Ar+C_2H_2+H_2$) becomes a dominate route for fuel decomposition. Unlike a thermal system where an analogous collisional process leading to fuel decomposition is limited to high temperatures (T > 1100 K) [215, 221, 223, 224], in the presence of a plasma, fuel will decompose regardless of temperature as long as such excited species exist. Mintusov et al. [80] observed a similar feature in their experiments, claiming that C_2H_2 was derived from direct electron-impact of C_2H_4 and by collisions with electronically excited states of N₂. Such collisional quenching processes can offer an explanation to the lower temperature enhancement of fuel consumption seen in both the plasma-assisted pyrolysis and oxidation experiments (refer to Figs. 5.11 and 5.13).

In an oxidation system, collisional quenching reactions can be extended to consider O_2 and Ar^* , which leads to direct dissociation and an increase in the O-atom radical pool (e.g., $Ar^*+O_2 \rightarrow Ar+O+O$) [53]. Electronically excited states of O_2 by electron-impact can also provide several channels to produce radicals by way of chemical chains (e.g., $O_2(b^1\Sigma_g) + H_2 \rightarrow OH + OH$ [72]). What is significant about these reactions is that they provide new low temperature reactions channels, of which there is no parallel in ordinary combustion. Of particular relevance are the $H+O_2 \rightarrow O+OH$ pathways, which define the boundary between the low and high temperature chemistry. Reactions involving such radicals are typically observed at higher temperatures in thermal systems, but can now be added as potential pathways that accelerate the combustion chemistry at lower temperatures in a plasma system. With this in mind, it should be assumed that apart from direct plasma effects, enhancement of the radical pools are in some form or another contributing to the consumption of fuel between 420-1050 K. This was demonstrated by Uddi et al. [81], who at near room temperatures concluded that increases in the O-atom radical pool led to the acceleration of the chain-branching reactions, which in turn were followed by exothermic oxidation reactions that enhanced the overall combustion process. The overlap of the thermal and plasma reactions above 750 K suggests that the chain-branching factor of the thermal reaction has increased significantly, and the generation of radical groups by neutral reactions controls the growth of radicals and hence reduces the significance of the plasma reactions.

The range of minor species formed during the plasma-assisted experiments is an indicative process of non-equilibrium plasmas known as plasma polymerization [42]. Radical recombination reactions due to the efficient decomposition of the fuel leads to the formation of such species. The results indicate that the effectiveness of addition and recombination reactions involving hydrocarbon radicals proceed as a function of temperature and become less effective at higher temperatures. C_2H_2 was a minor species not observed in the thermal oxidation reaction and its appearance in both the plasma-assisted oxidation and pyrolysis reaction suggests that its formation is directly coupled to a plasma-specific reaction at temperatures less than 1000 K. CH_3CHO is a particularly unique intermediate to be formed in the oxidation of C_2H_4 . In the past, its formation has been postulated several times in various mechanisms, but experimental evidence to its existence as an intermediate has never been validated [215, 219, 225]. Interestingly enough, at intermediate temperatures (~700 K) it appears as a conceivable intermediate when considering $R+O_2$ chemistry in alkane oxidation schemes (R being an alkyl radical i.e., C_2H_5) [197, 226]. Furthermore, in environments that have
an abundance of O-atoms (e.g., non-equilibrium plasma) R+O chemistry can have significance as well [226–228].

The experimental results presented in Fig. 5.16 are effectively showing that by increasing the amount of O_2 in the reactive mixture the plasma discharge is capable of enhancing O_2 dissociation and increasing the O-atom radical pool by either collisional quenching or electron-impact dissociation processes. Already mentioned, a subsequent effect leads to the enhancement of chain-branching rates and offers an explanation to the corresponding increase in fuel consumption. It should be reiterated that despite increasing the amount of O_2 , a proportional decrease in Ar was also made to maintain a constant flow rate of the mixture. This implies that O_2 dissociation becomes more reliant on direct excitation due to electron-impact rather than collisional quenching as the abundance of O_2 increases. From the results, as O_2 concentration increases (above 12.5%) the degree of O_2 dissociation seems to be maintained, and the rate of chain-branching leading to CO formation increases steadily. This increase can be attributed to the fact that dissociating O_2 by electron-impact is far more efficient than collisional quenching. This should be expected since the energy required to produce one excited Ar^* (~11.6 eV) state is about 2 times more than the energy required to dissociate O_2 (~5.7 eV) [42]. Despite doubling the O_2 concentration (from 25% to 50% mole fraction), there is no reciprocal effect in the product species formation and this could suggest that the O-atom density has reached its peak. At a 15 kV discharge voltage setting, energy deposition into O_2 dissociation saturates and regardless of O₂ concentration, the plasma is unable to generate further O-atoms.

In plasma discharges, the energy gained by electrons from an external electric field are lost in collisions with neutral particles and the degree of this loss measures how well the plasma is able to generate radicals [44]. It is well known that electronically excited states of N₂ (e.g., N₂ $(a^1\Sigma_u)$, N₂ $(A^3\Sigma_u)$, N₂ $(B^3\Sigma_u)$, N₂ $(C^3\Sigma_u)$) can effectively be quenched by O₂ to produce O-atoms [80,81]. However, the addition of N₂ leads to a noticeable decrease in combustion enhancement (refer to Fig. 5.17) and this decrease can be correlated to the decrease in the mean electron-energy for a given plasma discharge voltage. Unlike in an excited Ar system where no vibrational modes exist, in the presence of N₂ however, apart from electron energies being lost to exciting electronic states they can also be lost to exciting vibrational states. These vibrationally excited states are not as effective in contributing to generating active particles [53]. This leads to inefficiencies in generating active particles as the propensity of electrons to lose energy through elastic collision increases, but also reduces the probability of colliding with O₂ directly [53], which has already been described as an efficient process in generating O-atoms. The same could be said about the presence of the fuel. Uddi et al. [81] reported that the O-atom number density within the plasma would decrease as a

result of collisions between fuel and excited N_2 states effectively reducing O_2 dissociation reactions. Helium is well known to be an efficient ionizing medium since it has a higher secondary ionization coefficient, despite having a higher ionization potential (~24.5 eV) compared to Ar (~15.8 eV) [42], which means that positive ions generated in the plasma can contribute to increasing the electron density by colliding with neutral particles [53]. It is also the same reason why it requires a lower breakdown voltage at a given pressure. He as the ionization medium has been used in several PAC studies most notably the work of Uddi et al. [202]. Because of this efficiency in generating electrons, it can be expected that the mean electron energies contributing to active particle generation would be greater than N_2 . However, experimentally (refer to Fig. 5.17) at given plasma condition the He system still proves to be less effective in enhancing fuel conversion and this can be attributed to the subtle inefficiencies that the He system has in respect to the Ar system. Firstly, He is substantially smaller than an Ar atom, the electron densities are expected to be lower as diffusion of charged particles out of the plasma become an issue [229], which in turn contributes to a loss in active particle generation. In addition, excited states of He have higher excitation potentials than excited states of Ar [202, 229] making them more energy consuming. To add to this inefficiency, there has been no reported evidence that excited states of He contribute to active particle generation that can lead to combustion enhancement. The only analogous reaction involving O_2 dissociation involves He ions (e.g., $He^++O_2 \rightarrow Ar+O+O^+$) [202] and based on the experimental results, it seems that quenching of Ar^{*} is more effective in generating O-atoms.

5.2.3 Conclusions

In all instances the plasma-assisted pyrolysis and oxidation of C_2H_4 demonstrated considerable enhancement versus the thermal reactions for temperatures ranging from 420-1250 K at 1 atm. The onset of PAC fuel consumption was observed at 420 K where as the thermal oxidation and pyrolysis reactions did not initiate until 960 K and 1150 K, respectively. For the entire temperature regime considered, greater fuel consumption was observed under the effects of the plasma discharge. Enhancement in fuel decomposition was attributed to the effective collisional quenching with Ar^{*} forming hydrocarbon radicals that recombine to form several intermediate hydrocarbon species not seen in the thermal reaction. In the presence of O₂, quenching with Ar^{*} and electron-impact collisions led to O₂ dissociation and directly increased the O-atom radical pool. Influx of such radicals at low temperatures enhanced the basic combustion chemistry for temperatures between 420-1050 K, which resulted in significant enhancement in CO formation. At temperatures greater than 1050 K, radical production by neutral thermal reactions becomes more favorable and the effectiveness of the plasma decreased. Enhancement of the plasma-assisted oxidation reaction can be achieved by increasing the O_2 concentration in the mixture, whereby O-atom radical production increases. It was shown that dissociation of O_2 is more efficient by electron-impact than by quenching with Ar^{*}. The efficiency in active particles production decreases with different ionization mediums, where Ar outperforms He and N₂, due to various collisional losses and inefficiencies. The phenomenological interpretation of the experimental results provide the basis for conducting kinetic modeling studies of the plasma-assisted reactions.

Chapter 6

Kinetic Modeling of Plasma-Assisted Pyrolysis and Oxidation of Ethylene

6.1 Introduction

The kinetic model implemented in this study has it origins from the Ohio State University group [230], initially developed to facilitate the understanding of their experimental studies [78, 82–85]. It has been under active development ever since its inception and has proven to be a robust tool for providing insight into the non-thermal kinetics of plasma-assisted combustion. Prior to this work, this model had been extensively utilized to compare experimental results of enhanced ignition [78–80], O-atom concentration measurements (TALIF) [81,231], rotational temperature (CARS) [82,83] and OH concentrations (LIF) [84] in nanosecond pulsed discharges in air and fuel-air mixtures (i.e., H₂, CH_4 , C_2H_4), all at fairly low pressures (P < 350 torr) and for a range of different temperatures. To do this, air plasma processes were considered based on the reaction mechanism of Kossyi et al. [232], including chemical reactions of ground state species and excited electronic species, electron-ion recombination, ion-ion neutralization processes, ion-molecule reactions, and electron attachment and detachment. The full list of air plasma chemistry processes and the kinetic rates used can be found in [230]. To model methane-air and ethylene-air plasmas, the air plasma kinetic model was combined with either GRI Mech 3.0 [92] or USC Mech-II [98] hydrocarbon oxidation mechanisms and supplemented with methane and ethylene electron dissociation reactions along with quenching reactions involving excited states of nitrogen [230]. As mentioned earlier several challenges arise when trying to construct such plasma-specific mechanisms. Firstly, the system cannot be described by a single temperature due to the involvement of electron-impact processes. Secondly, plasma chemistry models are typically validated at room temperature whereas the relevance of most combustion

mechanisms and their validation are at elevated temperatures (i.e., at or near autoignition or flame temperatures). As a result, comparison of developed plasma-specific mechanisms and experimental results showed relatively good agreement with major radical densities, but poor quantitative prediction of major intermediate and product species.

6.2 Kinetic Model Overview

An overview of the mathematical details of the model will be presented here along with the amended modifications. In brief, the model consists of a set of ordinary differential equations describing the number density of different species (i.e., neutral, excited and charged), the energy equation to predict the mixture temperature, as well as quasi- 1D flow equations. The species concentration equations are coupled together with the steady, two-term expansion of the Boltzmann equation to determine the electron energy distribution function (EEDF) of the plasma electrons [233]. Using experimental cross-sections as inputs, the Boltzmann equation solver solves the EEDF iteratively to yield rate constants for electron-impact excitation, dissociation and ionization processes as a function of E/N. These equations are then solved using a stiff ODE solver (LSODE) to compute the evolution of species concentration as the extent of reaction progresses down the flow reactor due to plasma and thermal chemical kinetic effects.

6.2.1 Governing Equations

6.2.1.1 Quasi-One-Dimensional Flow Equations

In the present model the spatial specification of the flow field within the pulsed discharge and afterglow are based on a Lagrangian descriptor. Here, flow parameters for a given fluid particle are calculated as a function of elapsed time from a specified initial axial coordinate, $x_{0p} = x_p$ (t = 0),

$$\Theta_p = \Theta\left(x_{0p}, t\right) \tag{6.1}$$

where Θ_p is the fluid particle parameter, such as axial coordinate x_p , velocity u_p , temperature T_p , pressure P_p or number density N_p . Eq. (6.1) can also be translated into a time-dependent coordinate description $x_p(t)$,

$$\Theta_p = \Theta\left(x_{0p}, \, x_p\left(t\right)\right) \tag{6.2}$$

where for example, particle velocity u_p , becomes.

$$\frac{dx_p}{dt} = u_p \tag{6.3}$$

All calculations for a fluid particle performed in the model are initially at the entrance of the computational domain or at $x_p = 0$. The model describes the fluid particle in terms of the one-dimensional flow equations [230], which include the motion equation,

$$\frac{du_p}{dt} = \frac{1}{u_p} \cdot \left\{ \frac{(\gamma - 1) \cdot M^2}{1 - M^2} \cdot \left[\frac{dQ}{dt} - \sum_{i=1}^k \left(\frac{h_i}{N_p} \cdot \frac{dn_i}{dt} \right) \right] \right\}$$
(6.4)

the energy equation,

$$\frac{dT_p}{dt} = \frac{\left(1 - \gamma M^2\right)}{c_{pm}} \cdot \left[\frac{dQ}{dt} - \sum_{i=1}^k \left(\frac{h_i}{N_p} \cdot \frac{dn_i}{dt}\right)\right]$$
(6.5)

and the number density equation.

$$\frac{dN_p}{dt} = \sum_{i=1}^k \frac{dn_i}{dt} \tag{6.6}$$

The specific heat of the gas mixture at a constant pressure is given by c_{pm} , the number densities of individual chemical and excited species are given by n_i (molecules/m³), and their respective enthalpies are given by h_i . The specific heat of the gas mixture on a per unit mass basis is evaluated as

$$c_{pm} = \frac{C_{pm}}{MW_m} = \frac{1}{N_p} \cdot \sum_{i=1}^k \left(C_{pi} \cdot n_i \right)$$
(6.7)

where C_{pi} is the mole-specific heat of the *i*th species (J/kmol·K) and the molecular weight of the mixture is

$$MW_m = \frac{1}{N_p} \cdot \sum_{i=1}^k (MW_i \cdot n_i)$$
(6.8)

where MW_i is the molecular weight of *i*th species (kg/kmol). Lastly, the pressure of the mixture is calculated from the equation of state for an ideal gas

$$P = N_p k_b T_p = \frac{N_p R_u T_p}{N_A} \tag{6.9}$$

where k_b is the Boltzmann constant, R_u is the universal gas constant and N_A is the Avogadro number.

In Eqs. (6.4) and (6.5), the rate of energy deposition into the flow by the plasma discharge is

represented by the power loading term dQ/dt (W/kg) and is a function of the current density j, and the electric field E in the discharge,

$$\frac{dQ}{dt} = \frac{j \cdot E}{\rho_p} \tag{6.10}$$

where ρ_p is the density of the fluid particle.

$$\rho_p = \frac{N_p M W_m}{N_A} \tag{6.11}$$

The discharge current density is evaluated from Ohm's Law

$$j = e \cdot n_e \cdot W_{dr} \tag{6.12}$$

where n_e is the electron density and W_{dr} is the electron drift velocity. The electric field can be estimated from experimentally measured discharge voltage U, with w being the distance between the electrode configuration.

$$E \approx \frac{U}{w} \tag{6.13}$$

However, it should be explicitly mentioned that using Eq. (6.13) does not account for the significant voltage drop that may exist in the near-electrode region (sheaths). Thus, in the present calculations the voltage is determined based on an analytical model for the given experimental conditions (see Section 6.2.2). From here, the total electric discharge power Q_T (W) to the flow can be described as

$$\frac{d\Psi}{dt} = \dot{m}\frac{dQ}{dt} = \dot{m}\frac{j\cdot E}{\rho_p} = j\cdot E\cdot A\cdot u_p \tag{6.14}$$

where A is the cross-sectional area of the flow channel and m is the mass flow rate through the flow reactor given by,

$$\dot{m} = \rho_p \cdot u_p \cdot A = const \tag{6.15}$$

and is determined from experimentally derived values and conditions. The power loading metric from here on in, will be represented as discharge energy per unit molecule (eV/molecule) and is calculated as such

$$Q_{dis} = \frac{Q \cdot MW_m}{e \cdot N_A} = \frac{1}{e} \cdot \frac{\Psi}{\dot{m}} \cdot \frac{MW_m}{N_A}$$
(6.16)

with e being the elementary charge ($e = 1.602 \times 10^{-19}$ C). Furthermore, the energy provided by a single voltage pulse can be determined based on a time-dependent evaluation of current density as

found in Eq. (6.12),

$$Q_{pulse} = \int j(t) \cdot E(t) dt \cdot wA = \int I(t) \cdot U(t) dt$$
(6.17)

with the voltage pulse approximated as a Gaussian shape function,

$$U(t) = U_o \exp\left[-\left(\frac{t-t_1}{t_2}\right)^2\right]$$
(6.18)

where t_1 is the time at which the voltage pulse reaches maximum voltage, and t_2 is the pulse width. The time delay between voltage pulses is determined by the pulse repetition rate, $v = 1/t_3$.

Once all the time-dependent fluid particle parameters have been calculated, the steady-state flow description is determined by averaging the results over a group of particles with an initial set of coordinates at

$$0 \le x_{0p} \le u_{0p} \cdot t_3$$

Hence, the steady-state distribution of the flow parameters can be expressed as

$$\bar{\Theta}\left(\bar{x}\right) = \frac{1}{u_{0p} \cdot t_3} \int_0^{u_{0p} \cdot t_3} \Theta\left[x_{0p}, t\right] dx_{0p}$$
(6.19)

where

$$\bar{x} = \frac{1}{u_{0p} \cdot t_3} \int_0^{u_{0p} \cdot t_3} x_p \left[x_{0p}, t \right] dx_{0p}$$
(6.20)

This methodology ultimately converts the time-dependent fluid particle parameters in a repetitively pulsed discharge into a steady-state description of the flow parameters.

6.2.1.2 Chemical Reactions and Species Concentration Equations

Chemical reactions are considered in the current model as set of reversible reactions that include k chemical species. An elementary reaction is represented in the following general form

$$\sum_{i=1}^{k} \nu_i' A_i \leftrightarrow \sum_{i=1}^{k} \nu_i'' B_i \tag{6.21}$$

where ν'_i and ν''_i are stoichiometric coefficients, and A_i (reactant) and B_i (product) are chemical species symbols for the *i*th chemical species. The rate of progress variable of a chemical reaction for the jth reaction is given by the difference of the forward and reverse rates as

$$q_j = k_{f_j} \cdot \prod_{i=1}^k n_i^{\nu'_i} - k_{r_j} \cdot \prod_{i=1}^k n_i^{\nu''_i}$$
(6.22)

where n_i is the concentration of *i*th species, and k_{f_j} and k_{r_j} are the forward and reverse rate constants of the *j*th reaction. Then the production rate (total rate of species concentration change) of the *i*th species can be expressed as the summation of all rate of progress variables involving the *i*th species, with *m* being the total number of reactions containing the *i*th species.

$$\dot{\omega}_{i} = \frac{dn_{i}}{dt} = \sum_{j=1}^{m} \left(\nu_{i}'' - \nu_{i}'\right) \cdot q_{j}$$
(6.23)

The rate constant for the jth reaction is prescribed in the Arrhenius temperature-dependent form

$$k_j = A_j T^{\beta_j} \exp\left[\frac{-E_{a_j}}{R_u T}\right]$$
(6.24)

where A_j is the pre-exponential factor, β_j the temperature exponent, and E_j the activation energy. The forward and reverse rate constant of a particular reaction are related to one another through the equilibrium constant,

$$K_{eq_j} = \frac{k_{f_j}}{k_{r_j}} = \exp\left[\frac{\sum_{i=1}^k \nu_i'' G_i - \sum_{i=1}^k \nu_i' G_i}{R_u T}\right]$$
(6.25)

here G_i is the Gibbs free energy of the *i*th species in a given reaction. As a result of this relationship the reverse rates are calculated using Eq. (6.25) based on the known forward rates using Eq. (6.24). For some reactions the simple temperature dependence of the rate constant is not enough to accurately describe the kinetic behavior of the reaction, this is particularly true when referring to hydrocarbon radical recombination reactions that are highly pressure dependent. The rate constants of pressure-dependent unimolecular/recombination fall-off reactions are evaluated using the Lindemann approach, where the constants for the high-pressure k_{∞} (described by a two-body reaction, i.e., A+B \leftrightarrow AB) and low-pressure k_0 (described by a three-body reaction, i.e., A+B+M \leftrightarrow AB+M)



Figure 6.1: Rate constant as a function of pressure at T = 814 K for the recombination reaction $C_2H_4+H(+M) \leftrightarrow C_2H_5(+M)$. The Lindemann form k is illustrated along with both the low-pressure $k_0(\text{cm}^6/\text{s})$ and high-pressure $k_{\infty}(\text{cm}^3/\text{s})$ limiting forms.

limits are given in the Arrhenius form.

$$k_{\infty} = A_{\infty} T^{\beta_{\infty}} \exp\left[-E_{\infty}/R_u T\right] \tag{6.26}$$

$$k_0 = A_0 T^{\beta_0} \exp\left[-E_0/R_u T\right] \tag{6.27}$$

The rate constant at any intermediate pressure between the pressure limits is taken as,

$$k = k_{\infty} \left(\frac{P_r}{1 + P_r}\right) \tag{6.28}$$

where the reduced pressure is given by

$$P_r = \frac{k_0 \,[\mathrm{M}]}{k_\infty} \tag{6.29}$$

and [M] is the number density of the mixture (or concentration). At high pressures the rate constant approaches the high-pressure limit $(k \to k_{\infty})$ and becomes independent of number density. Conversely, as pressure is decreased $(P_r \ll 1)$, the rate constant asymptotically approaches the lower limit and becomes proportional to number density $(k \to P_r k_{\infty} = k_0[M])$ (see Fig. 6.1).

The thermochemical data for species such as specific heats, enthalpies, entropies and Gibbs free

energy are calculated using the polynomial fits taken from the CHEMKIN thermochemical database.

$$C_{pi} = C_{vi} + R \tag{6.30}$$

$$H_{i}(T) = \int_{0}^{T} C_{pi}(T) dT$$
(6.31)

$$S_{i}(T) = \int_{0}^{T} \frac{C_{pi}(T)}{T} dT$$
(6.32)

$$G_i(T) = H_i(T) - T \cdot S_i(T)$$

$$(6.33)$$

Once the time-dependent species concentration of the fluid particle is calculated from Eq. (6.6), the steady-state description of the species concentration can be evaluated as discussed in the previous section, where \bar{x} is given in Eq. (6.20).

$$\bar{n}_{i}\left(\bar{x}\right) = \frac{1}{u_{0p} \cdot t_{3}} \int_{0}^{u_{0p} \cdot t_{3}} n_{i}\left[x_{0p}, t\right] dx_{0p}$$
(6.34)

6.2.1.3 Electron-Impact Reactions and the Boltzmann Equation

The rate constant of electron-impact reactions producing excited species A^{*}

$$A + e \to A^* + e \tag{6.35}$$

are calculated using experimentally derived cross-sections $\sigma = \sigma(\varepsilon)$ for a given process as a function of the electron energy ε , where cross-sections are integrated over the electron energy distribution function (EEDF) $f(\varepsilon)$. In the current model the steady-state two-term expansion of the Boltzmann equation for plasma electrons is used to determine the solution to the EEDF [233]. The steady-state Boltzmann equation can be described in terms of three components:

$$0 = \phi_Q + \phi_{elastic} + \phi_{inelastic} \tag{6.36}$$

1. ϕ_Q is the component relating to plasma electron heating (Joule heating) induced by the applied electric field, which is a function of the reduced electric field E/N, the electron energy and

 $\sigma_T(\varepsilon)$ is the effective transport cross-section as function the electron energy,

$$\phi_Q = \frac{N_p}{3} \cdot \left(\frac{E}{N}\right)^2 \cdot \frac{\partial}{\partial \varepsilon} \left[\frac{\varepsilon}{\sigma_T(\varepsilon)} \frac{\partial f}{\partial \varepsilon}\right]$$
(6.37)

$$\sigma_T(\varepsilon) = \frac{1}{N_p} \sum_{i=1}^{\kappa} \sigma_{T_i}(\varepsilon) \cdot n_i$$
(6.38)

where $\sigma_{T_i}(\varepsilon)$ are transport cross-sections for individual species in the mixture, and $f(\varepsilon)$ is the exponential component of the EEDF, normalized as

$$\int \sqrt{\varepsilon} \cdot f(\varepsilon) \cdot d\varepsilon = 1 \tag{6.39}$$

2. $\phi_{elastic}$ is the elastic collisional term, describing the electron energy loss due to elastic collisions (momentum transfer) of electrons with heavy particles, where m_e is the mass of an electron, and M_i are the individual masses of the heavy particles.

$$\phi_{elastic} = \sum_{i=1}^{k} \frac{2m_e}{M_i} \frac{\partial}{\partial \varepsilon} \left[\varepsilon^2 \cdot \sigma_T(\varepsilon) \cdot N_p \left(f(\varepsilon) + \frac{k_b T}{e} \frac{\partial f}{\partial \varepsilon} \right) \right]$$
(6.40)

3. $\phi_{inelastic}$ is the inelastic collisional term, describing the electron energy loss of electrons due to rotational, vibrational, electronic excitation, and ionization with heavy species.

$$\phi_{inelastic} = \phi_{rot} + \phi_{vib} + \phi_{elec} + \phi_{ion} \tag{6.41}$$

In the current iteration of the model rotational and vibrational excitation processes are neglected since they are not expected to have a major influence on the chemical processes at the relatively high reduced electric field values typical of the experimental conditions presented herein (E/N > 80 Td). The process of ionization due to electron-impact is treated in an identical fashion as electronic excitation, meaning that the second electron produced by the ionization process (i.e., $A+e \rightarrow A^++e+e$) is assumed not to effect the distribution of the EEDF solution. As a result of these postulates, the inelastic term becomes

$$\phi_{inelastic} = \phi_{elec-ion} \tag{6.42}$$

During an electronic excitation process via electron-impact, an electron with energy ε (point 2, see Fig. 6.2) causes the heavy molecule (or atom) to excite from its ground state to its



Figure 6.2: Schematic of electron-impact electronic excitation process. Redrawn and modified from [230].

electronic excited state with energy ε' . Subsequently, the colliding electron's energy decreases by ε' (transition from point 2 to point 1) and reduces the number of electrons with initial energy ε . In tandem however, another electron with initial energy $\varepsilon + \varepsilon'$ (point 3) can collide with the molecule during the same excitation process and impart the same amount of energy ε' resulting in an electron with final energy ε (transition from point 3 to point 2). Hence, the general expression for electronic excitation will be expressed as

$$\phi_{elec-ion} = N_p \sum_{k=1}^{g} \left[\sigma_k \left(\varepsilon + \varepsilon' \right) \cdot f \left(\varepsilon + \varepsilon' \right) \cdot \left(\varepsilon + \varepsilon' \right) - \sigma_k \left(\varepsilon \right) \cdot f \left(\varepsilon \right) \cdot \varepsilon \right]$$
(6.43)

where $\sigma_k(\varepsilon)$ are the cross-sections for electron-impact electronic excitation processes.

With the established terms that constitute the Boltzmann equation, the EEDF turns into a second order differential equation. Using experimentally derived cross-sections of electron-impact processes as inputs, the model solves the Boltzmann equation iteratively to derive a solution for the EEDF. From here, rate coefficients for specific electron-impact processes are calculated as

$$k_{e-impact} = \left(\frac{2 \cdot e}{m_e}\right)^{1/2} \int \sigma\left(\varepsilon\right) \cdot \varepsilon \cdot f\left(\varepsilon\right) d\varepsilon$$
(6.44)

Figure 6.3 shows an example of the computed rate constants as a function of E/N for electron excitation of Ar based on experimental cross-sections using the Boltzmann solver. The electron drift velocity W_{dr} , which is the particle velocity of an electron attained by an induced electric field used to compute the current density in Eq. (6.11), and also the electron temperature T_e are then computed by



Figure 6.3: (a) Experimental cross-sections of electron-impact excitation of $\operatorname{Ar}[{}^{3}P_{0}]$ [11.55 eV] metastable state taken from [236]. (b) Corresponding rate constant as a function of E/N for electron-impact excitation reaction of $\operatorname{Ar}+e \to \operatorname{Ar}[{}^{3}P_{0}]+e$ calculated from the Boltzmann equation solver. Plasma conditions: T = 668 K, P = 1 atm, $X(\operatorname{Ar}) = 1$.



Figure 6.4: Computed bulk electron parameters from the Boltzmann equation solver as a function of E/N (a) electron drift velocity W_{dr} and (b) electron temperature T_e . Plasma conditions: T = 668 K, P = 1 atm, X(Ar) = 1.

$$W_{dr} = -\frac{eE}{3N_p} \cdot \left(\frac{2}{m_e}\right)^{1/2} \cdot \int \frac{\varepsilon}{\sigma\left(\varepsilon\right)} \frac{df}{d\varepsilon} d\varepsilon$$
(6.45)

$$T_e = -\frac{1}{k_b} \cdot \frac{\int \frac{\varepsilon}{\sigma(\varepsilon)} \cdot f(\varepsilon) \, d\varepsilon}{\int \frac{\varepsilon}{\sigma(\varepsilon)} \cdot \frac{df}{d\varepsilon} d\varepsilon}$$
(6.46)

Examples of calculated drift velocity and electron temperature are given in Fig. 6.4.

6.2.2 Modeling Modifications and Methodology

In order to use the existing code to analyze the plasma-assisted pyrolysis and oxidation of ethylene under dilute conditions using the PFR, several modifications to the model needed to be implemented. The reduced electric field is an important input parameter to the kinetic model as it dictates the solution to the EEDF and subsequently controls the extent of the plasma chemistry. As mentioned before, E/N is dependent on both the electric field induced by the discharge pulses (see Eq. 6.13) and the number density of the reactive mixture. Moreover, accurate experimental determination of the E/N becomes complicated when considering the dielectric layers and the breakdown characteristics of the gas medium (i.e., breakdown voltage, temperature and pressure). In the past, a quasi-1D, driftdiffusion, local ionization analytic model of a nanosecond pulse discharge in plane-to-plane geometry with dielectric covered electrodes developed by Adamovich et al. [234] was used to analyze the timedependent behavior of E/N in dry-air plasmas. In short, the same model will be implemented here to derive appropriately scaled E/N values that are representative of the experimental conditions (P= 1 atm, T = 420-1250 K) and gas mixture (X(Ar) > 0.99). Furthermore, the model also provides a means to verify the amount of energy deposited into the reactive mixture known as "coupled energy" (see Eq. 6.16).

The process begins by considering experimentally determined voltage waveforms of the pulse discharge and approximating them to a Gaussian fit in the model using an appropriate time constant at FWHM (see Fig. 6.5a). Based on this input, the model is able to predict the time-dependent electric field variation and the degree of ionization experienced in the plasma. The breakdown voltage U_{br} , occurs when the electric field reaches its maximum. After breakdown, the field in the plasma rapidly drops, due to strong shielding by the sheath layer (a region in the plasma that has a concentrated amount of ions) and charge accumulation of the dielectric surfaces (i.e., ceramic sheaths and quartz channel walls), both of which can contribute to the termination of the ionization process and limit the energy coupling into the plasma [235]. Neglecting this effect can considerably overestimate the E/N in the plasma, since the combined voltage drop across the sheaths



Figure 6.5: Single-pulse time-dependent calculations of (a) electric field and ionization fraction, and (b) E/N and coupled energy based on the model of Adamovich et al. [234]. Modeling conditions: T = 620 K, P = 1 atm, X(Ar) = 1, $U_{applied} = 10$ kV.

and dielectric layers can be quite significant [81]. For the discharge geometry and experimental conditions relevant to this study, the breakdown voltage was found to scale as follows

$$U_{br} = U_{applied} \left[\left(\frac{620 \text{ K}}{T} \right) \cdot \left(\frac{P}{760 \text{ torr}} \right) \right]^{1/2}$$
(6.47)

The temporal behavior of electric field also translates into a temporal behavior of E/N, where the peak value occurs at U_{br} . Eq. (6.47) is then incorporated into the model and an effective E/N value is computed based on Eq. (6.13), along with the number density of the mixture (see Fig. 6.6). These representative values are ultimately fed into the Boltzmann solver to derive a solution to the EEDF.

The energy coupled to the plasma during the applied voltage pulse is dependent on the electron density from the ionization process (see Eqs. 6.12 and 6.14). In fact, analysis of the model reveals that the degree of coupled energy is primarily controlled by the accumulation of charge on the dielectric surfaces and sheath development. Basically, the surface charge layers on the inside of the dielectrics and the outside of the electrodes act like capacitors (denoted as "coupled+stored" in Fig. 6.5b), storing some of the deposited pulse energy and resulting in a fractional loss of coupled energy to the reactive mixture. In the present study, the severity of this effect is unknown, and hence the input parameter current (which computes the current density and in turn the electron number density, Eq. 6.12) is taken as an unknown parameter, which is determined by matching the fuel consumption results of the pyrolysis experiments for all considered temperatures. This methodology



Figure 6.6: (a) U_{br} as a function of temperature based on Eq. (6.47) and (b) predicted E/N values a function of temperature using U_{br} . Modeling conditions: $U_{applied} = 10$ kV, P = 1 atm.



Figure 6.7: (a) Global current calibration curve to model coupled energy in the PFR experiments and (b) computed Q_{dis} and Q_{total} from the kinetic model as a function of temperature. Modeling conditions: $U_{applied} = 10$ kV, v = 1 kHz, P = 1 atm. Pyrolysis calibration $X(C_2H_4) = 800$ ppm, X(Ar) = 0.9992 (circle data points) and oxidation calibration $X(C_2H_4) = 800$ ppm, $X(O_2) = 3000$ ppm, X(Ar) = 0.9992 (square data points).



Figure 6.8: Select comparison of experimental (solid data points) and numerical model (solid lines) temperature profiles. Hatched region denotes the plasma discharge section at the beginning of the isothermal temperature region.

ultimately generates a global current calibration-fit, specific for the PFR experiments (see Fig. 6.7a), which is then applied to model the oxidation experiments. The validity of this procedure lies in two assertions. First, the derived coupled energy values from the model corroborate the physical trends and conclusions made by Adamovich et al. [234] in earlier studies. For a reactive mixture experiencing multiple pulses, coupled energy by a single pulse is cumulative and total coupled energy (summed by the number of pulses) by the plasma discharge scales linearly with number density. However, the total specific energy coupled by the plasma remains approximately constant and nearly independent of number density. Secondly, if the current calibration is performed using the oxidation experiments, for experimental data T < 910 K (for T > 910 K all the fuel has been consumed), the current curve fit deviates from the pyrolysis calibration consistently by less than 30% (see Fig. 6.7a). But more importantly, it translates into less than a 10% change in the model predictions of all major and minor species. In Fig. 6.7b, bulk coupled energy in the plasma discharge as a function of temperature (number density) is shown, where Q_{dis} decreases with increasing temperature, but on a per molecule basis remains relatively constant with a global average of 5.36 ± 1.6 meV/molecule. From here on, the latter metric of coupled energy will be referenced to quantify the amount of enhancement the reactive mixture attained during the experiments. Also shown in Fig.6.7b, is Q_{total} , which is the bulk energy deposited into the reactive mixture due to thermal heating. It can be demonstrated that the highly dilute nature of the reactive mixtures employed, decouples the plasma chemical enhancement effects since less than 15% of the total energy deposited into the reactive mixture comes from the plasma, while the remaining energy comes from thermal effects induced by temperature.

In order to appropriately capture the effects on the chemical kinetics experienced within the



Figure 6.9: Numerical model prediction of species evolution through the PFR for plasma-assisted oxidation of ethylene. Modeling conditions: $T_{iso} = 862$ K, P = 1 atm, Q = 1 SLPM, $X(C_2H_4) = 800$ ppm, $X(O_2) = 3000$ ppm, X(Ar) = 0.9962, $Q_{dis} = 5.36$ meV/molecule. Hatched region denotes plasma discharge section at the beginning of the isothermal zone.



Figure 6.10: Numerical model prediction of species evolution through the PFR for plasma-assisted oxidation of ethylene. Modeling conditions: $T_{iso} = 620$ K, P = 1 atm, Q = 1 SLPM, $X(C_2H_4) = 800$ ppm, $X(O_2) = 3000$ ppm, X(Ar) = 0.9962, $Q_{dis} = 5.36$ meV/molecule. Hatched region denotes plasma discharge section at the beginning of the isothermal zone.

PFR during the experiments, prescribed temperature profiles are implemented in the model such to replicate similar heating and cooling ramps as observed in the experimental temperature profiles (Fig. 6.8). Again, the temperature profiles are delimited by an isothermal reaction zone (T_{iso}) , where the reactive mixture comes in at a constant inlet temperature and exits at approximately the same temperature. Also, due to the change in temperature along the length of the reactor, the model is able to accurately consider the change in species residence time due to changing flow velocity. Once the temperature profiles have been implemented, the numerical simulation is performed for a specified reaction zone temperature, which presents the output as position-dependent concentration profile along the length of the reactor. Figure 6.9 shows such a profile prediction for a single experiment at T = 862 K with an applied plasma discharge of $U_{applied} = 10$ kV at a pulse repetition rate of v = 1 kHz. The reactive mixture enters the reactor at the inlet (reactor length = 0 m) where it undergoes no reaction while being preheated in the heating ramp section. Once preheated to the desired reaction temperature most of reaction is confined to the plasma region (hatched region), with some further reaction occurring in the remainder of the isothermal reaction zone. What is interesting to note from this result, is that the enhancement provided by the plasma perturbation has caused the reaction to react thermally, compared to no reaction in the pure thermal reaction. Once the reaction is completed by the end of the reaction zone, the product species are immediately quenched due to the cooling ramp where upon they exit the reactor at the outlet (reactor length =1.2 m). Comparison of experimental and numerical predictions correspond to species concentration at the exit of the reactor.

6.2.3 Kinetic Processes and Rates

The last modification, and truly, the main objective of the work carried out in this chapter was to develop a new plasma-specific kinetic mechanism to predict and describe the plasma-assisted ethylene pyrolysis and oxidation experimental results. The full list of reactions and their rate coefficient parameters can be found in Appendix B, along with the references detailing their source of origin. Based on the conclusions derived from previous modeling studies (see Chapter 4 and [237]), under the present experimental conditions, electron-ion recombination reactions have almost no effect on the electron and ion distribution due to the very short voltage pulse duration (~ 50 nsec). Basically, ionic chemistry (i.e., ion-ion neutralization, ion-molecule, and electron attachment/detachment reactions) occurs on time scales longer than the pulse duration. Thus, in the current iteration of the mechanism ionic chemistry is neglected. The global set of reactions considered, can be categorized into three

groups:

6.2.3.1 Electron Impact Reactions

These reactions involve the collision of a high energy electron and a ground-state heavy (neutral) particle, leading to electronic excitation of the target species, as well as ionization and dissociation. Reactions leading to vibrational excitation are neglected. The mechanism accounts for electron interaction of all major constituent particles in the reactive mixture, including Ar, O₂ and hydrocarbon fuels C₂H₄, C₂H₂, and CH₄. For molecular O₂ the two low-lying excited states are considered O₂ $(a^1\Delta_g, b^1\Sigma_g^+)$, as well as the first two excited states leading to dissociation O₂ $(A^3\Sigma_u^+, B^3\Sigma_u^+)$ forming O(³P) and O(¹D). For Ar, a single effective state (denoted as Ar^{*}) is considered to represent the first two electronic states, namely metastable Ar(³P₀, ³P₂). The only ionization reaction included in the mechanism is that of Ar, since a large portion of the reactive mixture is diluent, it is expected that the actual formation of the plasma is due to Ar⁺ ions. Lastly, all electronic collisions with hydrocarbons lead solely to dissociation and the formation of hydrocarbon radicals.

6.2.3.2 Quenching Reactions of Electronically Excited States

The greatest inherent source of error in the proposed mechanism lies in the use of these reactions. Firstly, most of the available literature reaction rates have been derived at or near room-temperature conditions, and as a result, none of the quenching reactions with an excited species implemented in the mechanism have any validated temperature dependence. Moreover, the dearth of available rates regarding quenching reactions with hydrocarbons is the greatest limiting factor in truly exploring the influence of plasma generated species on the basic combustion phenomena (with the exception of a select number of reactions found involving C₁-species). From the provided reactions involving excited O_2 , their influence mainly effects the H_2/O_2 sub-chemistry. Regardless, the studies of concern here deal with oxygen content on the order of thousands of ppm (~3000 ppm), their influence on the overall enhancement mechanism is not expected to be grossly important. In Fig. 6.11 the justification for neglecting vibrational states of O_2 is justified in the fact that for the range of E/Nvalues applicable to the experimental conditions (~80-120 Td), electron energy loss to vibrational modes of O_2 is negligible. However, in the same figure, it can be shown that most of the energy loss goes to electronically exciting or ionizing Ar. It can then be claimed with some certainty, the collisional quenching with Ar^{*} will be the dominate consumption route for fuel and oxidizer. Both



Figure 6.11: Electron energy loss fraction balance in plasma-assisted ethylene oxidation as a function of E/N. Results derived from the Boltzmann equation solver. Hatched region denotes the range of E/N values that are experimentally relevant. Modeling Conditions; P = 1 atm, $X(C_2H_4) = 800$ ppm, $X(O_2) = 3000$ ppm, X(Ar) = 0.9962.

the total quenching rate and branching ratios of major constituent particles (i.e., O_2 , CH_4) can be found in the literature, however for C_2H_4 and higher order hydrocarbons only the total rate could be found. As a result of this, only quenching of C_2H_4 is considered and the branching ratio is derived uniquely in studying the pyrolysis experiments.

6.2.3.3 Neutral Species Reactions

The plasma chemical reactions are then coupled to a recently developed (2013) combustion mechanism, AramcoMech 1.3. This mechanism is considered a comprehensive mechanism due to its robust ability to predict results across several different experimental platforms and a wide range of conditions. Due to its hierarchical development approach, the mechanism has a large inclusion of several sub-mechanisms to describe the kinetics of hydrocarbons ranging from C_1 - C_4 and oxygenated species. The main motivation in choosing this mechanism is for its comprehensive and updated RO_2 chemistry, indicative of low-temperature combustion relevant to PAC.



Figure 6.12: Flow chart of OSU plasma-assisted kinetics numerical code. Redrawn and modified from [230].

6.2.4 Description of Numerical Code

The kinetic model based on the formulations described in Section 6.2.1, consists of three main modules: (i) the main driver code, which reads and processes the input data, sets up the flow and chemical kinetic equations and prints out the results, (ii) an ordinary differential equation solver LSODE, and (iii) the Boltzmann equation solver. A schematic of the code is shown in Fig. 6.12. The main driver begins by reading three input files. The first is "input.inp", which contains the initial conditions of the calculation (i.e., mass flow rate, initial composition of reactive mixture, temperature, etc.) and relevant plasma discharge parameters (i.e., applied voltage, current, repetition rate and discharge geometry). Second is a kinetic mechanism file "PSU-TSOLAS MECH.rea", which has a list of all plasma and chemical reactions with their associated rate coefficient parameters written in the Arrhenius form. Electron-impact reactions are set to a value of zero in the mechanism file. During the reading of the mechanism file, the main driver calls on the RATECO subroutine, which identifies and "tags" electron-impact reactions to be calculated by the Boltzmann solver. Lastly, a thermochemical file is read "PSU-TSOLAS THEMO.trm", which contains the polynomial curve fit coefficients to calculate the species thermodynamic properties given by Eqs. (6.30)-(6.33). The code calculates these properties as a function of temperature for each species and saves them in an external file "JANAF SPECIES TABLE.tbr" in the JANAF table format.

From here the calculation begins, where the subroutine DIFFUN calculates the forward and reverse reaction rates as function of temperature and moves on to calculate the right-hand side of the chemical kinetic equations and the flow equations. On the first call of DIFFUN, the Boltzmann equation solver is called through the BOLINT subroutine. Here, a list of electron-impact processes and their collisional cross-sections are read from "AR_O2_CxHy.ar" and "AR_O2_CxHy.crs" input files. The Boltzmann solver integrates the Boltzmann equation to derive a solution to the EEDF for an array of E/N values. Finally, the solver calculates the rate coefficient for the desired electronimpact reactions by integrating the provided cross-sections over the array of EEDF solutions. The rate for the relevant E/N at the simulation's particular conditions is then linearly interpolated from the tabulated results. These rates are then stored and returned to DIFFUN, which processes the given data based on the "tags" provide by the RATECO subroutine.

LSODE integrates the system of equations until it converges on to a solution and reaches the next output point, where it then returns to the main code. At the output point the results of the calculation are printed to an output file "output.dat", at which point the main code either calls LSODE again, which calls DIFFUN, to calculate the next time-step ($x < x_{end}$) or exists and ends



Figure 6.13: Comparison of ethylene thermal pyrolysis experiments. Initial conditions: $X(C_2H_4) = 800$ ppm, X(Ar) = 0.9992, P = 1 atm, $\tau = 311.4$ s·K/T. Hollow symbols are experimental data; solid symbols are model predictions.

the calculation $(x = x_{end})$.

6.3 Results

6.3.1 Thermal Reaction

The reader is suggested to refer to the original reference to obtain an understanding of the development methodology, and the validation of specific rates used to describe the kinetics associated with the combustion characteristics of ethylene from the employed thermal mechanism. Also, it needs to be mentioned that the flow reactor experimental data used to validate the mechanism are the same as those mentioned in Chapter 5, restated here for convenience, Lopez et al. (P = 60 bar, T = 600-900 K) [220] and Carrier et al. (P = 5-10 bar, T = 850-950 K) [219]. It should be made apparent that both of these experiments were performed at relatively higher pressures than the experiments presented here. As such, the main purpose of this section is to test the applicability of the mechanism at new experimental conditions (P = 1 atm, T = 420-1250 K), while presenting a brief overview of the key reaction pathways that control the thermal chemistry of ethylene. In doing so, this should provide a datum to understand the enhancing effects that non-equilibrium plasmas offer in the sections to come.

Figure 6.13, presents a comparison between the experimental and modeling results of the thermal pyrolysis reaction. The model displays approximately 8% deviation from the experiments at the

maximum point of reactivity, with acetylene being the only product of ethylene consumption at temperatures greater than 1100 K. Kinetically, this behavior can be described by the following chain-propagating reactions, where all the H-atom yield comes from the thermal decomposition of the vinyl radical (C_2H_3).

$$C_2H_4 + H \to C_2H_3 + H_2$$
 (6.48)

$$C_2H_3(+M) \to C_2H_2 + H(+M)$$
 (6.49)

In Fig. 6.14. the comparison of the experimental and modeling results of thermal oxidation reaction are presented. For major product species, namely C_2H_4 consumption, CO and CO₂ the model has relatively good agreement with the experimental data for T > 860 K, while the model predicts an earlier hot-ignition by approximately 50 K. The biggest discrepancy lies in the model's prediction of the minor species for T = 900-1050 K. For methane and ethane the model overpredicts both species by a factor of 2 at the maximum extent of their formation, while it predicted acetylene in appreciable amounts, which was a species not observed in the experiments.

The primary pathways leading from C_2H_4 consumption at T = 960 K fall under three major routes, with the OH-abstraction reaction dominating and mainly competing against the H-addition reaction, with the O-atom reaction being of secondary importance.

$$C_2H_4 + OH \rightarrow C_2H_3 + H_2O \tag{6.50}$$

$$C_2H_4 + H(+M) \to C_2H_5(+M)$$
 (6.51)

$$C_2H_4 + O \to CH_3 + HCO \tag{6.52}$$

Reaction (6.51) formed significant amounts of the ethyl radical (C_2H_5) early on in the reaction, with more than 90% reacting quickly with oxygen to reform ethylene. This cycle consumed most of the H-atoms in the system, producing large amounts of HO₂. The other proportion of the ethyl radicals react with H-atoms to form methyl radicals, leading to products, mainly methane and ethane.

$$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2 \tag{6.53}$$

$$C_2H_5 + H \to CH_3 + CH_3 \tag{6.54}$$

The extent of CO formation is dictated by reactions (6.50) and (6.52) through the HCO interme-

diate, with the formaldehyde (CH₂O) channels resulting in about 38% of the total HCO produced in the system and close to 60% from reactions (6.52) and (6.55) combined.

$$C_2H_3 + O_2 \rightarrow CH_2O + HCO \tag{6.55}$$

$$CH_2O + H \rightarrow HCO + H_2$$
 (6.56)

$$CH_2O + OH \rightarrow HCO + H_2O$$
 (6.57)

The second route through the vinyl radical leads to acetylene formation (see reaction 6.49) that in turn reacts with O-atoms to form the HCCO intermediate (reaction 6.58). This route effectively leads to CO and CO₂ formation and accounts for approximately 5% of the CO formation in the system.

$$C_2H_2 + O \to HCCO + H \tag{6.58}$$

$$\mathrm{HCCO} + \mathrm{O}_2 \to \mathrm{CO} + \mathrm{CO}_2 + \mathrm{H} \tag{6.59}$$

It is expected that this route is what leads to the model's mishandling of acetylene prediction. Firstly, under the present experimental conditions both HCO formation and consumption pathways are comparatively faster than the C_2H_2 -HCCO consumption pathways. Secondly, in the experimental data of [219, 220], C_2H_2 was not a reported intermediate, since it was conclusively demonstrated that reaction (6.55) dominates the destructive pathways of C_2H_3 under high-pressure conditions over C_2H_2 formation. However, at these relatively lower pressures (i.e., 1 atm) reactions (6.49) and (6.55) become competitive with one another, and more than 60% of the vinyl destruction results in the formation of C_2H_2 . The inhibition in the system then lies in the system's inability to oxidize C_2H_2 since the C_2H_4+O kinetics account for more than 80% of the O-atom depletion routes. The lack of C_2H_2 predictive capability in the present comparison is not unique, since this mechanism was also unable to appropriately predict C_2H_2 in ethylene oxidation studies by Dagaut et al. [217] using a jet-stirred reactor (P = 1-10 bar, T = 880-1253 K). In the thorough literature review presented in [238], the authors acknowledged that despite the relative importance of the $C_2H_3+O_2$ reaction, the dynamics of its behavior under a range of different conditions have not been thoroughly explored and it is expected that considerable uncertainty still remains in its rate constant.



Figure 6.14: Comparison of ethylene thermal oxidation experiments. Initial conditions: $X(C_2H_4) = 800$ ppm, $X(O_2) = 3000$ ppm, X(Ar) = 0.9962, P = 1 atm, $\tau = 311.4$ s·K/T. Hollow symbols are experimental data; solid symbols are model predictions.

6.3.2 Plasma-Assisted Pyrolysis Reaction

Figures 6.15-6.16 present the comparison of experimental and modeling results of the plasmaassisted pyrolysis reaction of ethylene. To recap the modeling methodology, this system is modeled by adjusting the current parameter in the model to match the total experimental fuel consumption at a given temperature. As result of this, the model predicts the C_2H_4 profile with little discrepancy. From here the model will then be used to investigate the kinetics associated with the formation of secondary species. The model's prediction of the total carbon conservation indicates that the experiments have accounted for all the secondary species due to the plasma-assisted pyrolysis reactions. The comparison of results also displays that the main kinetic trends in each species in appropriately captured with respect to temperature. For acetylene, ethane and propane the model demonstrates good agreement with the experimental measurements for all temperatures considered. As for the remaining species, subtle differences exist. For C_4 - species (i.e., butane and butene) at T < 800 K the model overpredicts the experiments by a maximum deviation of 35%, while for minor C_3 -species (i.e., propene- C_3H_6 , propyne- C_3H_4) they are consistently underpredicted for a maximum deviation of roughly 60% at their maximum extents of formation. Lastly, methane is overpredicted for T >900 K by a maximum deviation of 40% at its maximum extent of formation.

6.3.3 Plasma-Assisted Oxidation Reaction

Figures 6.17-6.19 present the comparison of experimental and modeling results of the plasmaassisted oxidation reaction of ethylene. In these results the current parameter calibration obtained in the plasma-assisted pyrolysis modeling studies have been used to predict the plasma-assisted oxidation system. The greatest influence as a result of this procedure results in an overestimation of the fuel consumption profile for T = 750-1000 K compared to the experimental results. Moreover, the model also displays the appearance of a NTC regime, where reactivity of ethylene decreases as temperature increases from 520 K to 750 K, a kinetic trend not seen in the experimental results. Similar to the thermal reaction, the model predicts the hot-ignition temperature approximately 50 K earlier than the experimental results. The prediction of major and minor species are in relatively good agreement, with CO, CO₂, C₂H₆, C₃H₈ and C₃H₆ observing correct kinetic trends and minimal absolute discrepancies with respect to temperature. For methane, the model overpredicts its prediction by a maximum deviation of 40% between T = 850-1000 K. Similarly, acetylene is underpredicted for T < 900 K, consistently by a factor of 2, whereas acetaldehyde is completely mis-



Figure 6.15: Comparison of ethylene plasma-assisted pyrolysis experiments. Initial conditions: $X(C_2H_4) = 800$ ppm, X(Ar) = 0.9992, P = 1 atm, $\tau = 311.4$ s·K/T, $Q_{dis} = 5.36$ meV/molecule. Hollow symbols are experimental data; solid symbols are model predictions.



Figure 6.16: Comparison of ethylene plasma-assisted pyrolysis experiments. Initial conditions: $X(C_2H_4) = 800$ ppm, X(Ar) = 0.9992, P = 1 atm, $\tau = 311.4$ s·K/T, $Q_{dis} = 5.36$ meV/molecule. Hollow symbols are experimental data; solid symbols are model predictions.



Figure 6.17: Comparison of ethylene plasma-assisted oxidation experiments. Initial conditions: $X(C_2H_4) = 800 \text{ ppm}, X(O_2) = 3000 \text{ ppm}, X(Ar) = 0.9962, P = 1 \text{ atm}, \tau = 311.4 \text{ s} \cdot \text{K}/T, Q_{dis} = 5.36 \text{ meV/molecule}$. Hollow symbols are experimental data; solid symbols are model predictions.



Figure 6.18: Comparison of ethylene plasma-assisted oxidation experiments. Initial conditions: $X(C_2H_4) = 800 \text{ ppm}, X(O_2) = 3000 \text{ ppm}, X(Ar) = 0.9962, P = 1 \text{ atm}, \tau = 311.4 \text{ s}\cdot\text{K}/T, Q_{dis} = 5.36 \text{ meV/molecule}$. Hollow symbols are experimental data; solid symbols are model predictions.



Figure 6.19: Comparison of ethylene plasma-assisted oxidation experiments. Initial conditions: $X(C_2H_4) = 800 \text{ ppm}, X(O_2) = 3000 \text{ ppm}, X(Ar) = 0.9962, P = 1 \text{ atm}, \tau = 311.4 \text{ s}\cdot\text{K}/T, Q_{dis} = 5.36 \text{ meV/molecule}$. Hollow symbols are experimental data; solid symbols are model predictions.

interpreted in terms of the model prediction compared to the experimental results for T < 700 K. Based on the total carbon conservation, the model also predicts several product species at T < 800K in appreciable amounts not seen in experiments, including formaldehyde, formic acid (HOCHO), performic acid (HO₂CHO), several alcohols, and hydroperoxides. The formation of these species can be attributed to the model's prediction of enhanced consumption at temperatures in the NTC regime.

The emergence of these species brings to light some of the limitations that the current experiment and modeling studies may have. From an experimental perspective, the current GC column and detector setup is optimized for hydrocarbon species detection, and detailed detection for oxygenated species may be lacking. This is a known issue from attempts with pure formaldehyde and methanol sample tests, where GC signal peaks became convoluted and explicit discrimination was not achievable. To resolve this issue would require further optimization of the current GC system, including new run procedures to amplify and isolate certain species, but also incorporating different GC columns optimized to elute specific species other than hydrocarbons. Secondly, highly diluted samples can sometimes exhibit poor chromatogram signal area resolution with poor lower limit species detectability. Depending on the GC column's chemical attributes to elute a compound, signal areas can be masked by baseline level noise if a certain concentration of a given species is not sufficient for detection. Basically, the chromatogram signal area per unit of concentration is highly coupled to the chemical structure and properties of the eluting compound. Explicit less dilute experiments would need to be performed to verify the existence of any of the aforementioned species in the experiments in order to increase their concentrations. Lastly, some of the mentioned species predicted by the model present practical experimental difficulties in using the current GC system for detection. Absolute pure samples of desired species are often difficult to come by since they are not available or are often stabilized with a reagent, which then makes absolute detection difficult. As such, more direct and explicit experimental methods would need to be employed to tailor the detection of a specific species (i.e., CH₂O LIF). Such in situ methods would resolve any concerns as to whether the species of interest is being formed and consumed within the confines of the reaction zone (or isolated to the plasma discharge section) of the flow reactor, or actually surviving as a product to be measured in the exhaust. From the modeling perspective the greatest inherent source of error lies in the inability to appropriately define an experimentally equivalent quantification of coupled energy. The basis of the employed methodology is that coupled energy is based on a reactive mixture consisting of only argon, and it is evident from the results, that ppm levels of fuel and oxidizer do have varying effects on the coupled energy of the system. The original
model from which this metric was derived from, would need to be validated against experimental results specific to C_2H_4/Ar and $C_2H_4/O_2/Ar$ mixtures to define definitively its effect on coupled energy.

6.4 Discussion

The formation of the plasma discharge is effectively the electrical breakdown of the carrier gas leading to ionization of argon atoms (ionization potential 15.8 eV) to form Ar^+ ions. This process subsequently leads to the excessive formation of electrons needed for electronic excitation and dissociation of neutral species in the reactive mixture by electron-impact reactions. Apart from ionization, a significant portion of the plasma discharge energy goes into exciting various electronic states of argon, forming metastable Ar^* (see Fig. 6.11). Due to the highly dilute nature of the reactive system, electron-impact reactions are mainly influential in exciting the Ar constituent. Direct electron-impact with the fuel or oxidizer are considered negligible processes since they constitute less than 1% of the mole fraction of the total mixture. From here on, the foremost role of the plasma is to generate Ar^* and the discussion then leads to describe secondary kinetic effects that are influenced by the presence of these plasma generated species.

6.4.1 Kinetics of Plasma-Assisted Ethylene Pyrolysis

Under the influence of the plasma, collisional quenching reactions leading to dissociation dominate the kinetic routes enhancing fuel decomposition. The mechanism assumes the following fuel dissociative pathways with Ar^{*}.

$$C_2H_4 + Ar^* \to C_2H_2 + H + H + Ar \tag{6.60}$$

$$C_2H_4 + Ar^* \rightarrow C_2H_2 + H_2 + Ar \tag{6.61}$$

$$C_2H_4 + Ar^* \to C_2H_3 + H + Ar \tag{6.62}$$

$$C_2H_4 + Ar^* \to CH_2 + CH_2 + Ar \tag{6.63}$$

Hence, the substantial increase in the decomposition of ethylene is expected, as these reactions provide new dissociative pathways independent of temperature with no kinetic equivalency in the thermal reaction. Considering that more than 81% of the product branching ratios of these reactions result in acetylene, the model predicts its formation as the major by-product of fuel decomposition.



Figure 6.20: Path flux analysis of dominate consumption routes in plasma-assisted pyrolysis of ethylene as a function of temperature for P = 1 atm.

Moreover, reactions (6.60) and (6.62) contribute to more than 90% of the H-atom yield under the effects of the plasma and are a major source of enhancing the H-atom radical pool.

Figure 6.20, provides a summary of the path flux analysis derived to elucidate the main kinetic routes involved in the plasma-assisted pyrolysis reaction as a function of temperature. At low- (T= 620 K) and intermediate-temperatures (T = 862 K), addition reactions dominate the kinetic behavior of the system, where more than 60% of the H-atoms produced in the system at these temperatures contribute to increasing the hydrocarbon growth characteristics of the system. Firstly, the plasma-specific reactions (6.60)-(6.63), contribute to only half of the total fuel consumption in the system, with the remaining consumption coming from the neutral chemistry due to the enhancement of H-atoms (see reaction 6.51). As a result of this, the ethyl radical is present in the largest quantity of all the hydrocarbon radicals. Even though reactions (6.62) and (6.63) make up less than 20%of the product branching ratios, vinyl and methylene (CH_2) radicals are present in the established hydrocarbon radical pool, albeit at smaller concentrations. From here, ethyl containing recombination reactions lead to the formation of butane, butene, and ethane. As a secondary effect, the enhancement of H-atoms drive reaction (6.54) to facilitate the formation of methyl radicals, which leads to the observed formation of propane and propene in the results. As temperature increases steadily (intermediate-temperatures), the stabilization of the ethyl radical becomes increasing difficult to sustain and the vinyl and methyl radical chemistry becomes competitive. Product species derivatives of these radicals then reach their maximum extent of formation, namely methane, ethane, and propene. The appearance of propyne, is entirely due to the methylene route, which reacts with the abundant acetylene to form the propargyl radical (C_3H_3) .

At the highest temperature examined (T = 1153 K), the plasma effects begin to diminish, since only 27% of the total fuel consumption routes come from the plasma reactions with close to 70% coming from the neutral chemical effects of reaction (6.48). At this point the hydrocarbon radical pool mainly consists of vinyl radicals and pathways leading to secondary hydrocarbon species formation, other than acetylene, shutoff. However, the 27% contribution of H-atoms from the plasma reactions provide a secondary source to drive the chain-propagating reactions of (6.48)-(6.49), which leads to an enhancement of both ethylene consumption and acetylene formation compared to the thermal reaction under the same high-temperature conditions.

6.4.2 Kinetics of Plasma-Assisted Oxidation

Synonymous to the collisional quenching reactions of (6.60)-(6.63), Ar^{*} also provides new dissociative pathways for molecular oxygen, which has no parallel in a thermal system until relatively high-temperatures (close to the self-ignition temperature).

$$O_2 + Ar^* \to O + O + Ar \tag{6.64}$$

$$O_2 + Ar^* \to O + O(^1D) + Ar$$

$$(6.65)$$

The excited $O(^{1}D)$, is considered a highly reactive species that can enhance a system's reactivity. However, due to the relatively large proportion of Ar in the system, the fate of $O(^{1}D)$ primarily results in de-excitation to form a ground state O-atom.

6.4.2.1 Characteristics of Low-Temperature Kinetics

The path flux analysis for the low-temperature (T = 620 K) plasma-assisted oxidation reaction is shown in Fig. 6.21, and it can be demonstrated that the major fuel decomposition pathways fall into three major categories. The first is the direct collisional quenching with Ar^{*}, identical to the pyrolysis reactions (6.60)-(6.63). Under oxidative conditions these plasma initiated reactions have considerably less influence on the reactivity of the system, as they only account for 12% of the total fuel consumption. The second pathway is through direct oxidation with radical pools enhanced by the plasma, namely O- and H-atoms, which are typical of high-temperature oxidation reactions (see reaction 6.52). More than 90% of the O-atoms generated are provided by reactions (6.64) and (6.65), with reaction (6.60) providing nearly 20% of the total H-atom yield in the system. These channels provide close to 59% of the total fuel consumption routes, resulting in the formation of ethyl radicals $(\sim 33\%$ of fuel consumption), methyl $(\sim 14\%$ of fuel consumption) and vinoxy (CH₂CHO) radicals $(\sim 12\%$ of fuel consumption). The ethyl and methyl routes predominately undergo RO₂ kinetic behavior, and are the main source of the hydroperoxides (C_2H_5OOH , CH_3OOH) produced in the system by way of reactions with HO_2 . It should be made clear that these routes are not associated with the typical internal isomerization kinetics as seen in the low-temperature alkane results (see Chapter 5). In fact, for small molecular sized fuels, it has been argued that a similar chain-branching feature can be achieved by a simpler sequence through the formation and decomposition of a peroxide and hydroperoxide [49, 209].



Figure 6.21: Path flux analysis of dominate consumption routes in plasma-assisted oxidation of ethylene at low temperatures, T = 620 K and P = 1 atm.

$$C_2H_5O_2 + HO_2 \rightarrow C_2H_5OOH + O_2 \tag{6.66}$$

$$C_2H_5O_2 \to C_2H_4 + HO_2 \tag{6.67}$$

$$C_2H_5OOH \to C_2H_5O + OH \tag{6.68}$$

At 620 K, reactions (6.66) and (6.67) are more than 6-orders of magnitude faster than the decomposition reaction (6.68). For this reason the model predicts that ethyl hydroperoxide remains relatively stable at these conditions and is probably not the likely source for enhanced low-temperature reaction. Considering acetaldehyde was a minor intermediate species observed experimentally in the low-temperature regime, the model's inability to accurately predict its formation potentially suggests the kinetics associated with the above scheme needs further validation. This is a prime example of one of the challenges studying PAC kinetics possesses. Already mentioned, RO_2 chemistry is an indicative feature in high-pressure and low-temperature oxidation systems, the applicability, and for that matter, the product channels that these reactions experience at lower pressures can contain considerable uncertainty. With that being said, if the ethyl hydroperoxide chemistry is off, and the experiments are actually forming the ethoxide (C_2H_5O) through reaction (6.68), than reactions (6.69) and (6.70) could be viable routes for acetaldehyde formation.

$$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2 \tag{6.69}$$

$$C_2H_5O \rightarrow CH_3CHO + H$$
 (6.70)

However, the argument can also be extended to assume that the kinetics leading to formation of ethyl hydroperoxide are completely incorrect (which is what the experiments are indicating), other possible arguments need to be made, with reactions (6.71) and (6.72) being likely candidates for correction. Reaction (6.72) is of considerable interest because it has been already demonstrated that the plasma has the capacity to enhance both the ethyl and O-atom radical pools at low-temperature conditions.

$$C_2H_5O_2 \rightarrow CH_3CHO + OH$$
 (6.71)

$$C_2H_5 + O \rightarrow CH_3CHO + H$$
 (6.72)

From here, the methyl and vinoxy routes form a series of oxygenated species that decompose to provide nearly 20% of the total OH yield along with formaldehyde. The last major fuel consuming pathway (~29% of fuel consumption) is through the OH radical to form C_2H_4OH , which undergoes a uniquely similar RO₂ reaction to form an intermediate that further decomposes to form products. This channel results in the formation of two formaldehyde and contributes another 40% to the total OH radical yield. These RO₂ pathways are the main reason why the low-temperature plasmaassisted oxidation experiments do not see C_3 or C_4 hydrocarbon intermediates, since the pyrolysis radical recombination reactions are replaced by O_2 addition reactions.

From the modeling results a major intermediate as result of oxygenated species decomposition is the formation of formaldehyde. More than 62% of the formaldehyde results in HCO (~69% of the HCO produced is through the CH₂O versus ~7% through the C₂H₃ route), which leads to the dominant route for low-temperature CO formation. The second formaldehyde decomposition route provides another major source of H-atoms through formic acid decomposition (~34% of H-atom yield). Both formaldehyde routes are major sinks for OH-radials, accounting for more than 50% of all the OH consumed in the system. A major by-product of CO formation is the formation of HO₂ (~77% of HO₂ produced through HCO+O₂ reaction). An interesting feature of the low-temperature plasma system is that due to the plasma activated enhancement of H-atoms, the inhibiting effect of HO₂ (HO₂ does not actively contribute to the oxidation of fuel, it mainly results in H₂O₂ or C₂H₅OOH) can be counter acted by providing some 20% of the total OH yield by

$$\mathrm{HO}_2 + \mathrm{H} \to \mathrm{OH} + \mathrm{OH}$$
 (6.73)

This is the same kinetic feature seen in the hydrogen oxidation system (see Chapter 4), where a relatively unreactive species is converted into a more reactive radical to facilitate the oxidation process. Despite the plasma's ability to produce acetylene with relative ease, the C_2H_2 -HCCO route to CO formation is of little importance at these low-temperature conditions, but rather acts as a low-temperature CO₂ route. The remaining CO₂ is equally formed through formic acid or CO+OH

reactions.

6.4.2.2 Characteristics of Intermediate-Temperature Kinetics

The path flux analysis for the intermediate temperature (T = 862 K) plasma-assisted oxidation reaction is shown in Fig. 6.22. Firstly, the plasma specific fuel decomposition reactions (6.60)-(6.63) still play a minor role in contributing to the total fuel consumption (~8%), with reactions (6.64) and (6.65) providing more than 80% of the O-atom yield. Approximately 29% of the total fuel consumption comes directly from these O-atom channels due to the enhancement of their radical pool. This leads to the enhancement of methyl and vinoxy radials, with the latter route providing 18% of the total H-atoms in the system. The influence of reaction (6.60) has also decreased slightly compared to the low-temperature reaction, since this reaction now only provides 12% of the total H-atom yield. The greatest kinetic difference at this intermediate temperature comes from the enhancement of the ethyl production route, which has the greatest influence on consuming the fuel at 45%. The fate of C_2H_5 , CH_3 , and CH_2CHO then dictates the various kinetic features of the intermediate temperature reaction. Firstly, RO₂ kinetics are non-existent at this temperature, rather the system reverts to forming stable hydrocarbon intermediate species, including propane, propene, ethane and methane through recombination reactions similar to the pyrolysis system. Apart from fuel fragments, R+OH reactions become competitive and lead to the enhancement of alcohol species, namely ethanol (C_2H_5OH), ethenol (C_2H_3OH) and methanol (CH_3OH). The excessive formation of these more stable by-products are expected to be responsible for the observed inhibition in the rate oxidation for T = 520-750 K, since they do not actively participate in contributing to the oxidation process. Another major source of the inhibiting feature comes from the enhancement of the ethylene reforming reaction (6.53), which accounts for 45% of the consumption of the ethyl radical and provides one of two major sources for the production HO_2 (~34% of HO_2 yield). Unlike the low-temperature reaction, HO_2 plays a more active role in the oxidation process at intermediate temperatures. Firstly, reaction (6.73) contributes to more than 50% of the OH-radical yield in the system, but R+HO₂ reactions leads to the formation of methoxy (CH₃O) and ethoxy (C₂H₅O) radicals. The consequence of these channels are twofold, first they account for more than 50%of the formaldehyde and they also account for the second major source of OH production in the system ($\sim 43\%$ of OH yield). The established formation of OH radicals leads to the last major fuel consumption route to enhance the formation of the vinyl radical, which goes on to produce 22% of the total formaldehyde. Similar to the low-temperature reaction, formaldehyde is one of the major



Figure 6.22: Path flux analysis of dominate consumption routes in plasma-assisted oxidation of ethylene at intermediate temperatures, T = 862 K and P = 1 atm.

sources of HCO (~50%), with nearly 40% coming from either the C_2H_4+O , or $C_2H_3+O_2$ reactions. HCO is then the dominant route for CO production resulting in a major source of H-atoms in the system (~38% of H-atom yield) (i.e., HCO+M=H+CO+M).

6.4.2.3 Characteristics of High-Temperature Kinetics

The path flux analysis for the high temperature (T = 1153 K) plasma-assisted oxidation reaction is shown in Fig. 6.23. At this relatively high-temperature above the self-ignition temperature, the plasma specific reactions have little effect in contributing to the overall oxidation process. Rather the high-temperature chain-branching processes dictate the oxidation process where $H+O_2=O+OH$ provides more than 95% and 70% of both the O-atom and H-atom radicals in the system. From here, more than 85% of the fuel consumption channels occur either through the C_2H_4+O and C_2H_4+OH reactions mainly resulting in the formation of methyl and vinyl radicals. Though these radicals can form hydrocarbon intermediates, they are immediately consumed to form CH₃ fragments. All CH₃ channels end up falling into the CH₂O-HCO-CO pathway and are immediately oxidized. The CO+OH route accounts for 84% of the CO₂ produced in the system, with the remaining 14% provided by the C₂H₂-HCCO route

6.5 Conclusions

The kinetics of plasma-assisted pyrolysis and oxidation of ethylene have been numerically investigated. Combining plasma-specific reactions involving electron-impact reactions leading to the generation of electronically excited species, with a relatively new comprehensive thermal mechanism, a new plasma-specific kinetic mechanism for ethylene has been constructed. The employed model also has the capability of defining a metric to describe the amount of "coupled energy" the plasma is able to deposit into the reactive mixture. The results demonstrated that the coupled energy per unit molecule remains constant independent of number density for all the experiments considered. Generally, the model predicted the experimental results with relatively good agreement. For the pyrolysis experiments all the kinetic trends were appropriately captured for all minor and major species. Direct collisional quenching of fuel and excited states of argon are responsible for the low-temperature enhancement of fuel consumption seen in the plasma-assisted pyrolysis experiments. Due to the plasma's efficient ability to create fuel-fragment, recombination reactions are responsible for the formation of several C_3 - and C_4 -hydrocarbon intermediates. As temperature increases the



Figure 6.23: Path flux analysis of dominate consumption routes in plasma-assisted oxidation of ethylene at intermediate temperatures, T = 1153 K and P = 1 atm.

plasma effects diminish and the plasma chemistry plays a secondary role in the kinetic scheme compared to the neutral chemistry. Comparison of experiments and modeling results of the oxidation system demonstrated relatively good agreement with most major and minor species, however, poor agreement with the fuel and acetaldehyde for T < 750 K. The model also predicted the formation of several oxygenated species not seen in the experimental results. In the oxidation system collisional quenching of excited argon with the initial oxidizer, to enhance O-atom radical pool, complemented the plasma-specific fuel dissociation reactions. The effects of the plasma were found to have differing effects on the total oxidation process at different temperatures. At low-temperatures, $R+O_2$ type chemistry facilities the formation of oxygenated species to enhance oxidation by way of formaldehyde. At intermediate temperatures the formation of hydrocarbon and alcohol intermediates inhibit the oxidation process. Whereas at high-temperatures, plasma effects are unable to compete against the high-temperature chain-branching reactions of the neutral chemistry that dominate and control the overall oxidation process.

Chapter 7

Conclusions

7.1 Summary of Research

This dissertation presents a comprehensive study examining the kinetic enhancement features of plasma-assisted combustion (PAC). A novel plasma flow-reactor (PFR) experimental facility was constructed capable of performing both ex situ and in situ diagnostic techniques to identify and quantify intermediate and product species as a result of reactions. Experiments are performed using highly diluted reactive mixtures in various bath gases (e.g., Ar, He, N₂), at isothermal conditions, where the mixture is perturbed by a nanosecond pulse discharge (non-equilibrium plasma). Kinetic data consists of reactivity maps of intermediate and product species formation for a range of different fuels at atmospheric pressure, and for temperatures ranging from 420-1250 K. In some instances, experimental results are compared to modeling simulations to elucidate the chemistry involved in the enhanced reactions. The present research has shown that the effects of PAC on simple fuels and small alkane hydrocarbons at temperatures below the thermal ignition temperature, enhance the reaction considerably compared to thermal reactions. In most cases, fuel consumption is predominately driven by the onset of plasma effects, initiating reactions with little barrier dependence on temperature and pressure as would be required by a thermal effect. Formation of excited species within the plasma and subsequent collisional quenching with fuel and neutral species, results in significant dissociation leading to radical production to influence the neutral chemistry towards reaction.

7.1.1 Plasma-Assisted Oxidation of Hydrogen

Both *ex situ* and *in situ* techniques were applied in these studies to measure H_2 and O_2 consumption, along with absolute OH formation. Firstly, under the effects of the plasma it was demonstrated that hydrogen oxidation can be extended to temperatures as low as 470 K, opposed to temperatures

greater than 860 K under the pure thermal effects. Both systems exhibit vastly different kinetic characteristics, with the plasma induced system exhibiting slow steady rates of consumption below the explosive regime. Above the ignition temperature, consumption proceeds at an abrupt fast rate, with both thermal and plasma effects contributing to the consumption process. Through OH LIF measurements, it was revealed that the thermal system is dictated by chain-branching chemistry, whereas the slower plasma chemistry is governed by a linear chain-propagating chemistry. The kinetic modeling analysis concluded that the enhanced fuel consumption is attributed to the plasma's ability to enhance the H-atom radical pool through fuel dissociation. As a result of this enhancement, the low temperature neutral chemistry controls the formation of OH through the HO_2 intermediate, an inherently slower reaction than the faster chain-branching chemistry. This neutral chemistry scheme also leads to the recycling of the H-atom that provides the plasma-assisted system with its characteristic propagating feature. As the HO₂ concentration builds up, radicals are removed from this chain and decreases the overall reactivity of the system. However, by adjusting the plasma pulse perturbation frequency, the OH formation in the system can be artificially manipulated to mitigate this unfavorable slow chemistry and induce a higher rate of oxidation independent of system conditions.

7.1.2 Plasma-Assisted Oxidation of Hydrocarbons

These studies began by examining the oxidative characteristics of C_1-C_7 alkane fuels. It was demonstrated once again, that under the effects of the plasma, the rate of oxidation can be extended to temperatures well below the onset of thermal oxidation, while initiating ignition at lower temperatures. Similar to the hydrogen oxidation system, methane and ethane experienced a consistently slow rate of oxidation at temperatures below the self-ignition threshold (T < 800 K). For fuels C_3 and greater, fuel consumption profiles demonstrated multiple transitions in rates of oxidation within the vicinity of T = 600-800 K, with the emergence of an NTC regime in the experimental CO profiles. Based on a phenomenological interpretation of experimental results, it was postulated that the inherently slow chemistry associated with low temperature plasma effects can be mitigated by taking advantage of low temperature degenerate chain-branching reaction synonymous with alkane fuel systems. Typically initiated under high pressure conditions in a thermally constrained system, this chemistry is associated with the R+O₂ = RO₂ kinetic scheme (R being an alkyl radical) that leads to a series of complex internal isomerization pathways resulting in both chain-propagating and chain-branching channels through the formation of oxygenated intermediates (e.g., QOOH being a hydroperoxyalkyl radical). With an understanding of this scheme, the formation of several oxygenated products seen in the experimental results indicated that the plasma's ability to initiate the reaction with relative ease, allows this favorable low temperature chemistry to advance at considerably lower pressures.

Following a hierarchical approach, hydrocarbon studies were extended to investigate the plasmaassisted pyrolysis and oxidation reactions of ethylene, a major intermediate constituent formed in the oxidation of alkane fuel systems. Both these systems experienced enhanced reactivity for all temperatures considered in the presence of the plasma. Experiments demonstrated that the plasmaspecific pyrolysis reactions are responsible for a large proportion of the initial fuel consumption. Also, due the plasma's ability to effectively dissociate the fuel and generate fuel fragments, a plethora of secondary hydrocarbon species were detected as products. At low temperature conditions, pyrolysis product formation favored higher-order hydrocarbons in the appearance of C_4 and C_3 species. When oxygen was added to the system, further enhancement in fuel consumption was observed, along with the enhanced formation of several minor species not seen in the thermal reaction. These experiments ultimately serve as a reliable experimental database to perform plasma-specific kinetic modeling studies. To complement the ethylene investigations, several parametric studies were performed on the oxidation system to characterize the plasma effects of the system. This mainly involved varying the main ionizing constituent of the reactive mixture to induce different plasmas. Comparatively, argon as a plasma source is far more effective than helium in inducing enhancing effects on the reaction, since it requires sufficiently high electron energies to induce electronic excitation and acts as an energy loss mechanism in the system. As for nitrogen, it was found to be the worse, since electron energy energies can be lost in exciting vibrational modes of the gas and have no immediate effect on enhancing the reaction kinetics. This latter statement has consequential implications in practical systems, where air is a predominate oxidizer for combustion systems and brings to light one of the inherent disadvantages PAC can possess.

7.1.3 Plasma-Assisted Kinetic Modeling of Ethylene

The main objective of this part of the dissertation was to construct a new plasma-specific reaction mechanism for ethylene. Numerical predictions were derived using an existing code modified to account for the dynamics of the current PFR experiments in highly dilute reactive mixtures. The constructed mechanism is a hybrid of several sources tailored to describe the pertinent sub-mechanisms of chemistry, including electron-impact reactions, reactions involving interaction of excited species with neutral species, all amended to a relatively recent comprehensive combustion mechanism suited for low temperature combustion up to C_4 and oxygenated species.

Comparison of pyrolysis results indicates that the developed mechanism has good predictive capabilities, since little discrepancy was observed with the experimental results. Enhanced fuel consumption is attributed to collisional quenching reactions between excited states of Ar generated by the plasma with the initial fuel. The different product channels of this reaction leads to the enhancement of both hydrocarbon (e.g., C_2H_3 , CH_2) and H-atom radicals, with acetylene being the major by-product of immediate ethylene decomposition. At low temperatures, addition reactions are favored, leading to a considerable enhancement of the ethyl radical, where recombination reactions dictate the permutation of hydrocarbon intermediates formed. As temperature increases, the growth characteristics of the system become less effective, and fuel fragments predominantly result in smaller order hydrocarbons with the methyl radicals mainly dominating the formation of intermediate species.

In the oxidation system, the overall prediction of the mechanism against the experimental results was satisfactory. The prediction of most major product species and minor species were in relatively good agreement. However, the model's mishandling of some species predictions highlights the current deficiencies in the mechanism. Firstly, the model prediction for fuel decomposition displayed opposite kinetic trends, in fact the model predicts an NTC type phenomena with accelerated reaction as temperature decreases from 750 K. As a result of this, several product species not seen in the experiments are predicted in appreciable amounts, including the formation of hydroperoxides and alcohols. Acetaldehyde was a major intermediate observed in the experimental results at temperatures below 750 K. The model was unable to predict its formation in this regime, and coupled with the low temperature fuel enhancement, the mechanism may be lacking in terms of its kinetic accuracy. This exemplifies one of the challenges in truly understanding the kinetics in these PAC systems. Most of the current combustion mechanisms are relatively well understood and validated under practical combustion environments. Using these mechanisms beyond the realms of where these systems display no reactivity presents a hurdle that needs further investigation to test their applicability.

Similar to excited argon quenching with fuel, excited argon can quench with the initial oxidizer to enhance the O-atom radicals pools of the system and provide enhanced reactivity of the neutral kinetics. Because these quenching reactions are essentially temperature independent, these plasmaspecific reactions are what provide PAC systems their enhancing capabilities, of which there is no equivalent in thermally constrained system. Through a path flux analysis, the inhibition in the rate of oxidation from low to intermediate temperatures is due to the competition between $R+O_2$ and pyrolysis reactions, with the former chemistry leading to oxygenated intermediates that readily decompose to enhance the oxidation process. The plasma's ability to enhance production of OH, H- and O-radicals leads to instigating the high temperature chain-branching process to improve ignition. At relatively high temperatures beyond the self-ignition point, the chain-branching kinetics are comparatively faster than any advantage the plasma is capable of providing and the system is dominated by the thermal neutral kinetic effects.

7.2 Recommendations for Future Work

The conclusions derived from this research leads to several avenues for futures studies. The first aspect involves expanding efforts to better resolve uncertainties in the current understanding of ethylene combustion. Formaldehyde is a stable intermediate that was predicted in appreciable amounts based on the kinetic modeling studies and was readily observed in previous PAC experiments performed by [80,81]. Its detection in the current experiment went without notice, as to whether this issue is due to experimental deficiencies in the current detection limits of the *ex situ* instruments used, or a real kinetic effect due to the enhancement provided by the plasma, a definitive statement to its cause cannot be made at this point in time. The latter reason, suggests that a more direct and explicit detection method is needed, such as in situ LIF. If the modeling studies can provide a lead, it is possible that the kinetics of CH_2O formation and consumption may be entirely coupled to the presence of the plasma discharge, a similar kinetic feature seen in the OH LIF measurements, and may be a reason why the *ex situ* methods were unable to detect its presence. Also, the uncertainty in the acetaldehyde measurement and prediction requires that future investigative efforts be focused on studying the oxidative characteristics of ethylene products and intermediates. This includes specific kinetic studies examining acetaldehyde, formaldehyde and any other oxygenated species and trying to couple those studies into the overall oxidation scheme of ethylene. Essentially, a hierarchical approach needs to be under taken in order to isolate specific sub-mechanisms that lead to the formation of certain species.

It has been conclusively demonstrated in this dissertation that most of the kinetic enhancement that the plasma offers to enhance the combustion process is in the low temperature regime (below the self-ignition threshold). From a fundamental perspective, future kinetic studies should focus on how PAC can benefit other fuels systems in this regime. In the kinetic scheme of cool flame chemistry, the second addition of molecular oxygen to form hydroperoxy-alklyperoxy (OOQOOH) results in significant radical branching when further reacted or decomposed. Enhancing this latter low temperature cool flame sequence and enabling it over a broader range of conditions is desirable for shortening ignition delays of large hydrocarbon fuels. The molecular structure of the fuel (which affects octane number) influences the rates of alkyl-radical and hydroperoxyalkyl-radical (QOOH) formation [197], and how these processes are altered by the plasma chemistry requires further study. Such fuels can include unsaturated hydrocarbons, cycloalkanes, and aromatic hydrocarbons. Of particular interest lies in the aromatic fuels, since there has been experimental evidence suggesting that non-equilibrium plasmas can be used to control soot generation in flames [239]. However, the kinetics associated with this favorable phenomena are not well understood, and it has been postulated that the electron induced chemistry by the plasma can effectively cut-off the reaction pathways to the formation of PAH, which are the precursor to soot particles. Also, the influence of excited $O_2(a^1\Delta_q)$ to promote and instigate the $R+O_2$ isomerization sequence could be of considerable interest. The effects of PAC on biofuels are another important area of future research. Compared to conventional aliphatic based hydrocarbon fuels, biodiesel fuels have larger numbers of carbon double bonds and the presence of an ester group [240]. Because of the variations in CH bond strengths in the vicinity of the C=C double bond, low temperature chemistry can be significantly altered. The ester group can also lead to early CO_2 formation, which will alter the energy release with the fractional conversion of the fuel at low temperatures. Quantification of how the plasma could alter the energy release during fuel conversion at low temperatures could have practical significance.

References

- [1] S. Chu, A. Majumdar, *Nature* 488 (2006) 294-303.
- [2] S.M. Starikovskaya, J. Phys. D: Appl. Phys. 39 (2006) R265–R299.
- [3] A.Yu. Starikovskii, Proc. Combust. Inst. 30 (2005) 2405–2417.
- [4] A.Starikovskiy, N. Aleksandrov, Prog. Energy Combust. Sci. 39 (2013) 61-110.
- [5] S.I. Serbin, A. Mostipanenko, I. Mateev, A. Tropina, AIAA Paper 2011-61, 49th AIAA Aerospace Sciences Meeting including the New Horizons Forum and Aerospace Exposition, Orlando, FL, Jan 2011.
- [6] J.P. Moeck, D.A. Lacoste, C.O. Laux, C.O. Paschereit, AIAA Paper 2013-0565, 51st AIAA Aerospace Sciences Meeting including the New Horizons Forum and Aerospace Exposition, Grapvine, TX, Jan 2013.
- [7] S.I. Serbin, I.B. Matveev, G.B. Mostipanenko, IEEE Trans. Plasma Sci. 39 (2011) 3331-3335
- [8] T. Hammer, T. Kishimoto, J. Verleger, Int. J. Plasma. Envir. Sci. Techno. 4 (2010) 118-122.
- [9] M. Deminsky, I. Chenysheva, A. Napartovich, B. Potapkin, S.G Saddoughi, J. Herbon, T.J. Sommerer, 20th International Symposium on Plasma Chemistry, Philadelphia, PA, Jul. 2011.
- [10] F. Wang, J.B. Liu, J. Sinibaldi, C. Brophy, A. Kuthi, C. Jiang, P. Ronney, M. Gundersen, *IEEE Trans. Plasma Sci.* 33 (2005) 844-849.
- [11] V.H. Rapp, A. DeFilippo, S. Saxena, J.Y. Chen, R.W. Dibble, A. Nishiyama, A. Moon, Y. Ikeda, Journ. Combust. 2012 (2012) 927081.
- [12] Y. Ikeda, A. Nishiyama, M. Kaneko, AIAA Paper 2009-223, 47th AIAA Aerospace Sciences Meeting including the New Horizons Forum and Aerospace Exposition, Orlando, FL, Jan 2009.
- [13] J.K. Lefkowitz, Y. Ju, R. Tsuruoka, Y. Ike AIAA Paper 2012-113, 50th AIAA Aerospace Sciences Meeting including the New Horizons Forum and Aerospace Exposition, Nashville, TN, Jan 2012.
- [14] S.I Serbin, IEEE Trans. Plasma Sci. 34 (2006) 2488-2496.
- [15] D. Singleton, S.J. Pendleton, M.A. Gundersen, J. Phys. D: Appl. Phys. 44 (2011) 022001.
- [16] A. Starikovskiy, A. Rakitin, G. Correale, A. Nikipelov, T. Urushihara, T. Shiraishi, AIAA Paper 2012-0828, 50th AIAA Aerospace Sciences Meeting including the New Horizons Forum and Aerospace Exposition, Nashville, TN, Jan. 2012
- [17] I.V. Adamovich, I. Choi, N. Jiang, J.H. Kim, S. Keshav, W.R. Lempert, E. Mintusov, M. Nishihara, M. Samimy, M. Uddi, *Plasma Sources Sci. Technol.* 18 (2009) 034018.
- [18] H. Do, M.G. Mungal, M.A. Cappelli, *IEEE Trans. Plasma Sci.* 36 (2008) 2898-2923.

- [19] S.B. Leonov, D.A. Yarantsev, A.P. Napartovich, I.V. Kochetov, *IEEE Trans. Plasma Sci.* 34 (2006) 2514-2525.
- [20] L.S. Jacobsen, C.D. Carter, T.A. Jackson, S. Williams, J.Barnett, J. Propulsion Power 24 (2008) 641-654.
- [21] K. Takita, K. Murakami, H. Nakane, G. Masuya, Proc. Combust. Inst. 30 (2005) 2843-2849.
- [22] K. Takita, N. Abea, G. Masuyaa, Y. Ju, Proc. Combust. Inst. 31 (2007) 2489-2496.
- [23] H. Do, S. Im, M.A. Cappelli, M.G. Mungal, Combust. Flame 157 (2010) 2298-2305.
- [24] V.M. Shibkov, A.F. Aleksandrov, V.A. Chernikov, A.P. Ershov, R.S. Konstantinovskij, AIAA Paper 2006-1216, 44th AIAA Aerospace Sciences Meeting and Exhibit, Reno, NV, Jan. 2008
- [25] I.I. Esakov, L.P. Grachev, K.V. Khodataev, V.A. Vinogradov, D.M. Van Wie, AIAA Paper 2006-1212, 44th AIAA Aerospace Sciences Meeting and Exhibit, Reno, NV, Jan. 2008
- [26] A. Gutsol, A. Rabinovich A. Fridman, J. Phys. D: Appl. Phys. 44 (2011) 274001.
- [27] M. Morvova, F. Hanic, I. Morva, J. Therm. Analy. Calori. 61 (2000) 273-287.
- [28] D.E Gildfind, Development of High Total Pressure Scramjet Flow Conditions Using the X2 Expansion Tube, Ph.D Dissertation, School of Mechanical and Mining Engineering, The University of Queensland, 2012.
- [29] D. Dunn-Rankin ed., Lean Combustion: Technology and Control, Academic Press Elesvier Inc., San Diego, CA, 2008.
- [30] J.W. Tester, E.M. Drake, M.J. Driscoll, M.W. Golay, W.A. Peters, Sustainable Energy: Choosing Among Options. The MIT Press, Cambridge, MA, 2005.
- [31] United States Department of Energy (US DOE), "Annual Energy Outlook and Projections to 2040." U.S. Energy Information Administration DOE/EIA-0383, 2013. Retrieved from http://www.eia.gov/forecasts/aeo/pdf/0383(2013).pdf
- [32] J.C.Y Lee, P.C. Malte, M.A Benjamin, ASME Paper 01-GT-0081, 46th ASME International Gas Turbine Institute Conference, Louisiana, LA, Jun. 2001.
- [33] N.A. Cumpsty, Jet Propulsion: A Simple Guide to the Aerodynamics and Thermodynamic, Design and Performance of Jet Engines, Cambridge University Press, New York, NY, 1997.
- [34] T. Lieuwen, V. McDonell, E. Petersen, D. Santavicca, J. Eng. Gas Turb. Power 130 (2008) 011506.
- [35] T. Lieuwen, V. Yang, R.A. Yetter (Eds.), Synthesis Gas Combustion: Fundamentals and Applications, Taylor and Francis Group LLC, Boca Raton, FL, 2010.
- [36] R.S. Fry, J. Propulsion Power 20 (2004) 27-58.
- [37] K. Bowcutt, "Hypersonic Vehicles", Access Science, McGraw-Hill Companies, 2009. Retrieved from http://www.accessscience.com.
- [38] E.T. Curran, J. Propulsion Power 17 (2001) 1138-1148.
- [39] D. Andreadis, "Scramjet Engines Enabling the Seamless Integration of Air and Space Operations", Pratt and Whitney, Hypersonics, West Palm Beach, FL, 2005. Retrieved from http://www.pwrengineering.co/dataresources/TIP_Scramjet_Engines_final.pdf.
- [40] H.L. Beach, E.A. Mackley, R.C. Rogers, W. Chinetz, 17th JANNAF Combustion Meeting, CPIA Pub. 329, (1980) 639-659.

- [41] B. Hidding, M. Pfitzner, D. Simone, C. Bruno, Acta Astronautica 63 (2008) 379–388.
- [42] A. Fridman, *Plasma Chemistry*, Cambridge University Press, New York, NY, 2008.
- [43] M.K. Das, S.T. Thynell, "Corona, Spark, and Electrothermal-Chemical Plasma Ignition Systems", Handbook of Combustion 5 (2010) 53-69.
- [44] Y.P. Raizer, Gas Discharge Physics, Springer, New York, NY, 1991.
- [45] A. Fridman, L.A. Kennedy, Plasma Physics and Engineering, Taylor and Francis Routledge, New York, NY, 2004.
- [46] X. Lu, M. Laoussi, V. Puech, Plasma Sources Sci. Technol. 21 (2012) 034005.
- [47] A. Starikoskiy, N. Aleksandrov, "Plasma-Assisted Ignition and Combustion", M. Mulder (Ed.), Aeronautics and Astronautics (2011) 331-368. Retrieved from http://interchopen.com/books/aeronautics-and-astronautics/plasma-assisted ignition-andcombustion.
- [48] S.M. Starikovskaia, J. Phys. D: Appl. Phys. 47 (2014) 353001.
- [49] I. Glassman, R.A. Yetter, Combustion 4th Ed., Academic Press Elesvier Inc. San Diego, CA, 2008.
- [50] F.R. Gilmore, J. Quant. Spectrose. Radiat. Transfer 5 (1965) 369-390.
- [51] T.E. Sharp, Atomic Data, 2 (1971) 119-169.
- [52] C.M. Ferreira, J. Loureiro, A. Ricard, J. Appl. Phys. 57 (1985) 82-90.
- [53] I.N. Kosarev, N.L. Aleksandrov, S.V. Kindysheva, S.M. Starikovskaia, A.Yu. Starikovskii, *Combust. Flame* 154 (2008) 569-586.
- [54] I.N. Kosarev, N.L. Aleksandrov, S.V. Kindysheva, S.M. Starikovskaia, A.Yu. Starikovskii, *Combust. Flame* 156 (2009) 221-233.
- [55] A.A. Chukalovsky, K.S. Klopovsky, M.A. Liberman, Yu.A. Mankelevich, N.A. Popov, O.V. Proshina, T.V. Rakhimova, *Combust. Sci. Technol.* 184 (2012) 1768-1786.
- [56] S. Vranckx, J. Peeters, S. Carl, Phys. Chem. Chem. Phys. 12 (2010) 9213-9221.
- [57] K. Kohse-Höinghaus, F. Stuhl, J. Chem. Phys. 72 (1980) 3720-3725.
- [58] G. Pilla, D. Galley, D.A. Lacoste, F. Lacas, D. Veynante, C.O. Laux, *IEEE Trans. Plasma. Sci.* 34 (2006) 2471-2477.
- [59] G. Pilla, D. Galley, D.A. Lacoste, F. Lacas, D. Veynante, C.O. Laux, AIAA Paper 2006-3243, 37th AIAA Plasmadynamics and Lasers Conference, San Francisco, CA, June 2006..
- [60] W. Kim, H. Do, M.G. Mungal, M.A. Cappelli, *IEEE Trans. Plasma Sci.* 34 (2006) 2545-2551
- [61] W. Kim, M.G. Mungal, M.A. Cappelli, Combust. Flame 157 (2010) 374-383.
- [62] A.A. Nikipelov, A.E. Rakitin, I.B. Popov, G.Correale, A.Yu. Starikovskii, AIAA Paper 2011-1214, 49th Aerospace Sciences Meeting including the New Horizons Forum and Aerospace Exposition, Orlando, FL, Jan. 2011.
- [63] A. Dutta, Z. Yin, I.V. Adamovich, Combust. Flame 158 (2011) 1564-1576.
- [64] S.V. Pancheshnyi, D.A. Lacoste, A. Bourdon, C.O. Laux. *IEEE Trans. Plasma Sci.* 34 (2006) 2478-2487.

- [65] S.B. Leonov, D.A. Yarantsev, A.P. Napartovich, I.V. Kochetov, AIAA Paper 2006-563, 44th AIAA Aerospace Sciences Meeting and Exhibit, Reno, NV, Jan. 2006.
- [66] S.B. Leonov, A.A. Firsov, D.A. Yarantsev, M.A. Bolshov, Yu.A. Kuritsyn, V.V. Liger, V.R. Mironenko, AIAA Paper 2011-972, 49th AIAA Aerospace Sciences Meeting including the New Horizons Forum and Aerospace Exposition, Orlando, FL, Jan. 2011.
- [67] H. Do, M.A. Cappelli, M.G. Mungal, Combust. Flame 157 (2010) 1783-1794.
- [68] H. Do, S. Im, M.G. Mungal, M.A. Cappelli, Combust. Flame 157 (2010) 2298-2305.
- [69] P.J. Kirby, Proc. R. Soc. Lond. 85 (1911) 151-174.
- [70] S.M. Starikovskaya, N.L. Aleksandrov, I.N. Kosarev, S.V. Kindysheva, A.Yu. Starikovskii, *High Energy Chemistry* 43 (2009) 213-218.
- [71] S.M. Staikovskaia, A.Yu. Starikovskii, D.V. Zatsepin, Combust. Theory Modelling 5 (2001) 97-129.
- [72] N.B. Anikin, S.M. Starikovskaia, A.Yu. Starikovskii, J. Phys. D: Appl. Phys. 39 (2006) 3244-3252.
- [73] N.B. Anikin, S.M. Starikovskaia, A.Yu. Starikovskii, Plasma Physics Reports 30 (2004) 1028-1042.
- [74] S.M. Starikovskaia, E.N. Kukaev, A.Yu. Kuksin, M.M. Nudnova, A.Yu. Starikovskii, Combust. Flame 139 (2004) 177-187
- [75] S.A. Bozhenkov, S.M. Starikovskaia, A.Yu. Starikovskii, Combust. Flame 133 (2003) 133-146.
- [76] I.N. Kosarev, N.L. Aleksandrov, S.V. Kindysheva, S.M. Starikovskaia, A.Yu. Starkoskii, J. Phys. D: Appl. Phys. 41 (2008) 032002.
- [77] N.L. Aleksandrov, S.V. Kindysheva, I.N. Kosarev, S.M. Starikovskaia, A.Yu. Starikovskii, Proc. Combust. Inst. 32 (2009) 205-212.
- [78] A. Bao, Y.G. Utkin, S. Keshav, G. Lou, I.V. Adamovich, *IEEE Trans. Plasma Sci.* 35 (2007) 1628-1638.
- [79] G. Lou, A. Bao, M. Nishihara, S. Keshav, Y.G. Utkin, J.W. Rich, W. R. Lempert, I. V. Adamovich, Proc. Combust. Inst. 31 (2007) 3327-3334.
- [80] E. Mintusov, A. Serdyuchenko, I.Choi, W.R. Lempert, I.V. Adamovich, Proc. Combust. Inst. 32 (2009) 3181-3188.
- [81] M. Uddi, N. Jiang, Mintusov, I.V. Adamovich, W.R. Lempert, Proc. Combust. Inst. 32 (2009) 929-936.
- [82] Y. Zuzeek, I. Choi, M. Uddi, I.V. Adamovich, W.R. Lempert, J. Phys. D-Appl. Phys. 43 (2010) 124001.
- [83] Y. Zuzeek, S. Bowman, I. Choi, I.V. Adamovich, W.R. Lempert, Proc. Combust. Inst. 33 (2011) 3225-3232.
- [84] Z. Yin, K. Takashima, I.V. Adamovich, *IEEE Trans. Plasma Sci.* 35 (2011) 3269-3282.
- [85] I. Choi, Z. Yin, I.V. Adamovich, W.R. Lempert, IEEE Trans. Plasma Sci. 39 (2011) 3288-3299.
- [86] L. Wu, J. Lane, N.P. Cernansky, D.L. Miller, A.A. Fridman, A.Yu. Starikovskii, Proc. Combust. Inst. 33 (2011) 3219-3224.

- [87] W. Sun, M. Uddi, T. Ombrello, S.H. Won, C. Carter, Y. Ju, Proc. Combust. Inst. 33 (2011) 3211-3218.
- [88] W. Sun, M. Uddi, S.H. Won, T. Ombrello, C. Carter, Y. Ju, Combust. Flame 159 (2012) 221-229.
- [89] W. Sun, S.H. Won, T. Ombrello, C. Carter, Y. Ju, Proc. Combust. Inst. 34 (2013) 847-855.
- [90] T. Ombrello, S.H. Won, Y. Ju, S. Williams, Combust. Flame 157 (2010) 1906-1915.
- [91] T. Ombrello, S.H. Won, Y. Ju, S. Williams, Combust. Flame 157 (2010) 1916-1928.
- [92] G.P. Smith, D.M. Golden, M. Frenklach, N.W. Moriarty, B. Eiteneer, M. Goldenberg, C.T. Bowman, R.K. Hanson, S. Song, W.C. Gardiner, Jr., V.V. Lissianski, Z. Qin, GRI-Mech 3.0, http://www.me.berkeley.edu/gri_mech/.
- [93] E.L. Petersen, D.F. Davidson, R.K. Hanson, Combust. Flame 117 (1999) 272-290.
- [94] H.J. Curran, P. Gaffuri, W.J. Pitz, C.K. Westbrook, Combust. Flame 114 (1998) 149–177.
- [95] N.A. Popov, High Temp. 45 (2007) 261-279.
- [96] N.A. Popov, Plasma Sources Sci. Technol. 20 (2011) 045002.
- [97] I.A. Kossyi, A.Yu. Kostinsky, A.A, Matveyev, V.P. Silakov, Plasma Sources Sci. Technolo. 207 (1992) 207.
- [98] H. Wang, X. You, A.V. Joshi, S.G. Davis, A. Laskin, F. Egolfopoulos, C.K. Law, USC Mech Version II. High-Temperature Combustion Reaction Model of H₂/CO/C₁-C₄ Compounds. http://ignis.usc.edu/USC_Mech_II.htm, May 2007.
- [99] A. Starikovskiy, AIAA Paper 2012-0244, 50th AIAA Aerospace Sciences Meeting including the New Horizons Forum and Aerospace Exposition, Nashville, TN, Jan. 2012.
- [100] C.L. Rasmussen, J. Hansen, P. Marshal, P. Glarborg, Int. J. Chem. Kinet. 40 (2008) 454-480.
- [101] J.T. Scanlon, D.E. Willis, J. Chroma. Sci. 23 (1985) 333-340.
- [102] K. Schofield, Prog. Energy Combust. Sci. 34 (2008) 330-350.
- [103] J.C. Lee, R.A. Yetter, F. L. Dryer, A.G. Tomboulides, S.A. Orszag, Combust. Sci. Tech. 159 (2000) 199-212.
- [104] R.V. Poirier, R.W. Carr Jr., J. Phys. Chem. 75 (1971) 1593-1601.
- [105] C.J. Howard, J. Phys. Chem. 83 (1978) 3-9.
- [106] O. Levenspiel, Chemical Reaction Engineering, 3rd Ed., John Wiley and Sons, Inc., New York, NY, 1999.
- [107] R.B. Bird, W.E. Stewart, E.N. Lightfoot, *Transport Phenomena*, 2nd Ed., John Wiley and Sons, Inc., New York, NY, 2002.
- [108] E.L. Cussler, Diffusion:Mass Transfer in Fluid Systems, 3rd Ed., John Wiley and Sons, Inc., New York, NY, 1999.
- [109] S.M. Starikovskaia, A.Yu. Starikovskii, "Plasma-Assisted Ignition and Combustion", Handbook of Combustion 5 (2010) 71-93.
- [110] C.K. Westbrook, F.L. Dryer, Prog. Energy Combust. Sci. 10 (1984) 1-57.
- [111] M.A. Mueller, T.J. Kim, R.A. Yetter, F.L. Dryer, Int. J. Chem. Kinet. 31 (1999) 113-125.

- [112] A.A. Konnov, Combust. Flame 152 (2008) 507-528.
- [113] M. O Conaire, H.J. Curran, J.M. Simmie, W.J. Pitz, C.K. Westbrook, Int. J. Chem. Kinet. 36 (2004) 603-622.
- [114] J. Li, Z. Zhao, A. Kazakov, F.L. Dryer, Int. J. Chem. Kinet. 36 (2004) 566-575.
- [115] Z. Hong, D.F. Davidson, R.K. Hanson, Combust. Flame 158 (2011) 633-644.
- [116] Z. Yin, I.V. Adamovich, W.R. Lempert, Proc. Combust. Inst. 34 (2013) 3249-3258.
- [117] N.A. Popov, Plasma Phys. Repor. 5 (2008) 376-391.
- [118] A.C. Eckbreth, Laser Diagnostics for Combustion Temperature and Species, 2nd Ed., Overseas Publishers Association, Amsterdam, NL, 1996.
- [119] H.F. Dobele, T. Mosbach, K. Niemi, V. Schulz-von der Gathen, Plama Sources Sci. Technol. 14 (2005) S31-S41.
- [120] G. Dilecce, Plasma Sources Sci. Technol. 23 (2014) 015011.
- [121] Y. Teramoto, R. Ono, T. Oda, J. Phys. D: Appl. Phys. 42 (2009) 235205.
- [122] B.H. Bransden, C.J. Joachain, *Physics of Atoms and Molecules*, Pearson Education Limited, Harlow, 1983.
- [123] J. Brzozowski, P. Erman, M. Lyyra, Physica Scripta 17 (1978) 507-511.
- [124] J. Luque, D.R. Crosley, LIFBASE, Database and Spectral Simulation (version 1.5). SRI International Report, MP-99-009, 1999.
- [125] G. Herzberg, Molecular Spectra and Molecular Structure I: Spectra of Diatomic Molecules, 2nd Ed., D. van Nostrand Company, Inc., Toronto, CAN, 1950.
- [126] J. Brown, A. Carrington, Rotational Spectroscopy of Diatomic Molecules, Cambridge University Press, Cambridge, UK, 2003.
- [127] J.A Coxon, Can. J. Phys. 58 (1980) 933-949.
- [128] C. Chan, J.W. Daily, Appl. Opt. 19 (1980) 1357-1367.
- [129] D.E. Heard, D.R. Crosley, J.B. Jeffries, G.P. Smith, A. Hirano, J. Chem. Phys. 96 (1992) 4366-4371.
- [130] Z. Yin, A. Montello, C.D. Carter, W.R. Lempert, I.V. Adamovich, Combust. Flame 160 (2013) 1594-1608.
- [131] Z. Yin, Fuel Oxidation and Ignition by Nanosecond Pulsed Discharges at Elevated Temperatures, Ph.D. Dissertation. The Ohio State University, Columbus, OH, 2013.
- [132] T. Verreycken, R. Mensink, R. van der Horst, N. Sadeeghi, P. Bruggeman, Plasma Sources Sci. Technol. 22 (2013) 055014.
- [133] J. Vorac, P. Dvorak, V. Prochazka, J. Ehlbeck, S. Reauter, Plasma Sources Sci. Technol. 22 (2013) 025016.
- [134] R. Kienle, A. Jorg, K. Kohse-Hoinghaus, Appl. Phys. B 56 (1993) 249-258.
- [135] R. Kienle, M.P. Lee, K. Kohse-Hoinghaus, Appl. Phys. B 62 (1996) 583-599.
- [136] P.H. Paul, J.L. Durant, J.A. Gray, M.R. Furlanetto, J. Chem. Phys. 102 (1995) 8378-8384.
- [137] K. Kohse Hoinghaus, Prog. Energy Combust. Sci. 20 (1994) 203-279.

- [138] J. Luque, D.R. Crosley, J. Chem. Phys. 109 (1998) 439-448.
- [139] K.R. German, J. Chem. Phys. 62 (1975) 2584-2587.
- [140] D.R. Crosley, J. Phys. Chem 93 (1989) 6273-6282.
- [141] P.W. Fairchild, G.P. Smith, D.R. Crosley, J. Chem Phys. 79 (1983) 1795-1807. Eng. Syst. Safe
- [142] R.A. Copeland, D.R Crosley, J. Chem Phys. 84 (1986) 3099-3105.
- [143] R.A. Copeland, M.J. Dyer, D.R Crosley, J. Chem Phys. 82 (1985) 4022-4032.
- [144] J.B. Jeffries, K. Kohse-Hoinghaus, G.P. Smith, R.A. Copeland, D.R. Crosley, Chem. Phys. Lett. 182 (1988) 160-166.
- [145] I.J. Wysong, J.B. Jeffries, D.R. Crosley J. Chem Phys. 92 (1990) 5218-5222.
- [146] B.L. Hemming, D.R Crosley, J.E. Harrington, V. Sick, J. Chem. Phys. 115 (2001) 3099-3104.
- [147] B.L. Hemming, D.R. Crosley, J. Phys. Chem A 106 (2002) 8992-8995.
- [148] P.H. Paul, J. Quant. Spectosc. Radiat. Transfer 51 (1994) 511-524.
- [149] M. Tamura, P.A. Berg, J.E. Harrington, J. Luque, J.B. Jeffries. G.P. Smith, D.R. Crosley, Combust. Flame 114 (1998) 502-514.
- [150] A.E. Bailey, D.E. Heard, D.A. Henderson, P.H. Paul, Chem. Phys. Letter 302 (1999) 132-138.
- [151] A.E. Bailey, D.E. Heard, P.H. Paul, M.J. Pilling, J. Chem. Soc., Faraday Trans. 93 (1997) 2915-2920.
- [152] D.E. Heard, D.A. Henderson, Phys. Chem. Chem. Phys. 2 (2000) 67-72.
- [153] R.K. Lengel, D.R. Crosley, J. Chem. Phys. 68 (1978) 5309-5324.
- [154] R.A. Copeland, M.L. Wise, D.R. Crosley, J. Chem. Phys. 88 (1988) 5710-5715.
- [155] L.R. Williams, D.R. Crosley, J. Phys. Chem. 104 (1996) 6507-6514.
- [156] K.L. Steffens, D.R. Crosley, J. Chem. Phys. 112 (2000) 9427-9432.
- [157] R.J. Cattolica, T.G. Mataga, Chem. Phys. Lett. 182 (1991) 623-631.
- [158] P.H. Paul, J. Chem. Phys. 99 (1995) 8472-8476.
- [159] G.P. Smith, D.R. Crosley, J. Chem. Phys. 85 (1986) 3896-3901.
- [160] P. Hogan, D.D. Davies, J. Chem. Phys. 62 (1975) 4574-4576.
- [161] K.R. German, J. Chem. Phys. 64 (1976) 4065-4068.
- [162] P. Beaud, P.P. Radi, D.Franzke, H. Frey, B. Mischler, A. Tzannis, T. Gerber, Appl. Optics 37 (1998) 3354-3367.
- [163] P. Hogan, D.D. Davies, J. Chem. Phys. 62 (1975) 4574-4576.
- [164] M.A. Linne, Spectroscopic Measurements: An Introduction to the Fundamentals, Elsevier Science Ltd., San Diego, CA, 2002.
- [165] E.C. Rea Jr., A.Y. Chang, R.K. Hanson, J. Quant. Spectosc. Radiat. Transfer 37 (1987) 117-127.
- [166] E.C. Rea Jr., A.Y. Chang, R.K. Hanson, J. Quant. Spectosc. Radiat. Transfer 41 (1989) 29-42.

- [167] M.R. Zaghloul, Mon. Not. R. Astron. 375 (2007) 1043-1048.
- [168] W.P. Partridge, Jr., N.M. Laurendeau, Appl. Optics 35 (1995) 2645-2647.
- [169] J. Luque, D.R. Crosley, Appl. Phys. B 63 (1996) 91-98.
- [170] D.R. Bates, Plane. Space Sci. 32 (1984) 785-790.
- [171] R.B. Miles, W.R. Lempert, J.N. Forkey. Meas. Sci. Technol. 12 (2001) R33-R51.
- [172] A. Bucholtz, Appl. Optics 34 (1995) 2765-2773.
- [173] M. Sneep, W. Ubachs, J. Quant. Spectrosc. Radiat. Transfer 92 (2005) 293-310.
- [174] L.Li, A. Nikiforov, Q. Xiong, N. Britun, R. Snyders, X. Lu, C. Leys, Phys. Plasma 20 (2013) 093502.
- [175] R. Ono, T. Oda, J. Phys. D: Appl. Phys. 41 (2008) 035204.
- [176] P. Bruggeman, G. Cunge, N. Sadeeghi, Plasma Sources Sci. Technol. 21 (2012) 035019.
- [177] S. Yonemori, Y. Nakagawa, R. Ono, T. Oda, J. App. D: Appl. Phy. 45 (2012) 225202.
- [178] A.J. Wheeler, A.R. Ganji, Introduction to Engineering Experimentation, Prentice Hall, Inc., Upper Saddle River, NJ, 1996.
- [179] A.E. Lutz, R.J. Kee, J.A. Miller, Senkin: A Fortran Program for Predicting Homogenous Gas Phase Chemical Kinetics with Sensitivity Analysis, Livermore, CA: Sandia National Laboratories, 1988.
- [180] S. Pancheshnyi, B. Eismann, G.J.M. Hagelaar, L.C. Pitchford, Computer Code ZDPlasKin, Toulouse, France: University of Toulouse, LAPLACE, CNRS-UPS-INP, 2008.
- [181] G.J.M Hagelaar, L.C. Pitchford, Plasma Sources Sci. Technol. 14 (2005) 722-733.
- [182] I.V. Adamovich, M. Nishihara, I. Choi, M. Uddi, W.R. Lempert, Phys. Plasmas 16 (2009) 113505.
- [183] K. Togai, N. Tsolas, R.A. Yetter, "Kinetic Modeling and Sensitivity Analysis of Plasma-Assisted Oxidation in H2/O2/Ar Mixtures" (to be published).
- [184] U. Nowak, J. Warnatz, "Sensitivity Analysis in Aliphatic Hydrocarbon Combustion," Dynamics of Reactive Systems Part I: Flames; Part II: Heterogeneous Combustion and Applications, A.L. Kuhl, J.R. Bowen, J.-C. Leyer, A. Borisov, eds., Washington, D.C.: American Institute of Aeronautics and Astronautics, 1988, pp. 87–103.
- [185] T. Turányi, Reliab. Eng. Syst. Safe. 57 (1997) 41–48.
- [186] J.K. Lefkowitz, M. Uddi, B.C. Windom, G. Lou, Y. Ju, Proc. Combust. Inst. 35 (2015) 3505-3512.
- [187] M.P. Burke, M. Chaos, Y. Ju, F.L. Dryer, S.J. Klippenstein, Int. J. Chem. Kinet. 44 (2012) 444–474.
- [188] A. Sarani, A.Y. Nikiforov, C. Leys, Phys. Plasma 17 (2010) 063504.
- [189] A. Yanguas-Gil, K. Foche, J. Benedikt, A. von Keudell, J. Appl. Phys. 101 (1997) 103307.
- [190] G.T. Linteris, R.A. Yetter, K. Brezinsky, F.L. Dryer, Combust. Flame 86 (1991) 162-170.
- [191] S.A. Stepanyan, M.A. Boumehdi, G. Vanhove, S.M. Starikovskaia, AIAA Paper 2013-1053, 51st AIAA Aerospace Sciences Meeting Including the New Horizons Forum and Aerospace Exposition, Grapevine, TX, Jan. 2013.

- [192] M.A. Boumehdi, S. A. Stepanyan, P. Desgroux, G. Vanhove, S.M. Starikovskaia, Combust. Flame 162 (2015) 1336-1349.
- [193] S.M. Starikovskaia, J. Phys. D: Appl. Phys. 47 (2014) 353001.
- [194] M. Lackner, F. Winter, A. Agarwal (Eds.), Handbook of Combustion, Vol. 1: Fundamentals and Saftey, Wiley-VCH Verlag GmbH and Co. KGaG, Weinheim, GER.
- [195] W.K. Metcalfe, S.M. Burke, S.S. Ahmed, H.J. Curran, Intl. J. Chemical Kinetics 45 (2013) 638-675.
- [196] M.J. Pilling (Ed.), Low Temperature Combustion and Autoignition, Comprehensive Chemical Kinetics Vol. 35, Elsevier, Amsterdam, 1997.
- [197] J. Zádor, C.A. Taatjes, R.X. Fernandes, Prog. Energy Combust. Sci. 37 (2011) 371-421.
- [198] J.D. Savee, E. Papajak, B. Rotavera, H. Huang, A.J. Eskola, O. Welz, L. Sheps, C.A. Taatjes, J. Zádor, D.L. Osborn, *Science* 347 (2015) 643-645.
- [199] D.J. Beere, V.G. McDonell, Proc. Combust. Inst. 33 (2011) 301-307.
- [200] D.C. Horning, D.F. Davidson, R.K. Hanson, J. Prop. Power 18 (2002) 363-371.
- [201] D.N. Koert, D.L. Miller, N.P. Cernansky, Combust. Flame 96 (1994) 34-49.
- [202] M. Uddi, H. Guo, W. Sun, Y. Ju, AIAA Paper 2011-970, 49th AIAA Aerospace Sciences Meeting Including the New Horizons Aerospace Exposition, Orlando, FL, Jan. 2011
- [203] S.M. Villano, L.K. Huynh, H. Carstensen, A.M. Dean, J. Phys. Chem. A 115 (2011) 13425-13442.
- [204] L.K Huynh, H. Carstensen, A.M Dean, J. Phys. Chem. A 114 (2010) 6594-6607.
- [205] M. Cord, B. Husson, J.L. Huerta, O. Herbinet, P. Glaude, R. Fournet, B. Sirjean, F. Battin-Leclerc, M. Ruiz-Lopez, Z. Wong, M. Xie, Z. Cheng, F. Qi, J. Phys. Chem. A 116 (2012) 12214-12228.
- [206] C.F. Goldsmith, W.H. Green, S.J. Klippenstein, J. Phys. Chem. A 116 (2012) 3325-3346.
- [207] J.D. DeSain, S.J. Klippenstein, J.A. Miller, C.A. Taatjes, J. Phys. Chem. A 107 (2003) 4415-4427.
- [208] C.K. Westbrook, Proc. Combust. Inst. 28 (2000) 1563-1577.
- [209] E.A. Filimonova, J. Phys. D: Appl. Phys. 48 (2015) 015201.
- [210] R. Minetti, M. Ribaucour, M. Carlie, C. Fittschen, L.R. Sochet, Combust. Flame 96 (1994) 201-211.
- [211] M.I. Strelkova, A.A. Safanov, L.P. Sukhanov, S.Ya. Umanskiy, I.A. Kirillov, B.V. Potapkin, H.J. Pasman, A.M. Tenter, *Combust. Flame* 157 (2010) 641-652.
- [212] O. Herbinet, F.Battin-Leclerc, S. Bax, H. Le Gall, P. Glaude, R. Fournet, Z. Zhou, L. Deng, H. Guo, M. Xie, F. Qi, Phys. Chem. Chem. Phys. 13 (2011) 296-308.
- [213] M. Cord, B. Sirjean, R. Fournet, A. Tomlin, M. Ruiz-Lopez, F. Battlin-Leclerc, J. Phys. Chem A 116 (2012) 6142-6158.
- [214] A.J. Eskola, O. Welz, J.D. Savee, D.L. Osborn, C.A. Taatjes, J. Chem. A 117 (2013) 12216-12235.
- [215] C.K. Westbrook, F.L. Dryer, K.P. Schug, Proc. Combust. Inst. 19 (1982) 153-166.

- [216] C.K. Westbrook, M.M. Thorton, W.J. Pitz and P.C. Malte, Proc. Combust. Inst. 22 (1988) 863-871.
- [217] P. Dagaut, M. Cathonnet, J.C. Boettner, Int. J. Chem. Kinet. 23 (1991) 437-455.
- [218] N.M. Marinov, P.C. Malte, Int. J. Chem. Kinet. 27 (1995) 957-986.
- [219] T. Carriere, P.R. Westmoreland, A. Kazakov, Y.S. Stein, F.L. Dryer, Proc. Combust. Inst. 29 (2002) 1257-1266.
- [220] J.G. Lopez, C.L. Rasmussen, M.U. Alzueta, Y. Gao, P. Marshall, P. Glarborg, Proc. Combust. Inst. 32 (2009) 367-375.
- [221] Y. Hidaka, T. Nishimori, K. Sato, Y. Henmi, R. Okuda, K. Inami, T. Higashihara, Combust. Flame 117 (1999) 755-776.
- [222] Y. Hayashi, S. Hirao, Y. Zhang, T. Gans, D. O'AConnell, Z. L. Petrovic, T. Makabe, J. Phys. D: Appl. Phys. 42 (2009) 145206 (6pp).
- [223] H. Kiefer, S.A. Kapsalis, M.Z. Al-Alami, K.A. Budach, Combust. Flame 51 (1983) 79-93.
- [224] T. Tanzawa, W.C. Gardiner, Jr. Combust. Flame 39 (1980) 241-253.
- [225] R.D. Wilk, W.J. Pitz, C.K. Westbrook, N.P. Cernansky, Proc. Combust. Inst. 23 (1990) 203-210.
- [226] R.R. Baldwin, I.A. Pickering R.W. Walker, J.C.S. Faraday I 76 (1980) 2374-2382.
- [227] R.P. Linstedt, G. Skevis, Proc. Combust. Inst. 28 (2000) 1801-1807.
- [228] A. Miyosi, J. Yoshida, N. Shiki, M. Koshi, H. Matsui, Phys. Chem. Chem. Phys. 11 (2009) 7318-7323.
- [229] K. Wagatsuma, Spectrochem. Acta Part B 56 (2001) 465-486.
- [230] A. Bao, Ignition of Hydrocarbon Fuels by a Repetitively Pulsed Nanosecond Duration Plasma. PhD Dissertation, The Ohio State University, Columbus, OH, 2008.
- [231] M. Uddi, N. Jiang, I.V. Adamovich, W.R. Lempert, J. Phys. D: Appl. Phys. 42 (2009) 075205.
- [232] I.A. Kossyi, A.Yu. Kostinsky, A.A. Matveyev, V.P. Silakov, Plasma Sources Sci. Technol. 1 (1992) 207- 220.
- [233] G.J.M Hagelaar, L.C. Pitchford, Plasma Sources Sci. Technolo. 14 (2005) 722-733.
- [234] I.V. Adamovich, M. Nishihara, I. Choi, M. Uddi, W.R. Lempert, Phys. Plasmas 16 (2009) 113505.
- [235] K. Takashima, Z. Yin, I.V. Adamovich, Plasma Sources Sci. Technol. 22 (2013) 015013.
- [236] N.J. Mason, W.R. Newell, J. Phys. B. At. Mol. Phys. 20 (1987) 1357-1377.
- [237] E. Mintusov, M. Nishihara, N. Jinag, I. Choi, M. Uddi, A. Dutta, W.R. Lempert, I.V. Adamovich, AIAA Paper 2008-3899, 39th Plasmadynamics and Lasers Conference, Seattle,WA, June 2008.
- [238] W.K. Metcalfe, S.M. Burke, S.S. Ahmed, H.J. Curran, Intl. J. Chemical Kinetics 45 (2013) 638-675.
- [239] M.S. Cha, S.M. Lee, K.T. Kim, S.H. Chung, Combust. Flame 141 (2005) 438-447.
- [240] C.K. Westbrook, Annu. Rev. Phys. Chem. 64 (2013) 201-219, 2013.

Appendix A

Plasma Flow Reactor Technical Drawings


















Appendix B

Plasma-Assisted Ethylene Combustion Mechanism

B.1 Reaction Mechanism

The following mechanism is presented in a format suited specifically to the numerical code implement in this dissertation. The rate constant parameters are given in terms of the Arrhenius form, with the pre-exponential factor A (units cm³/s), the temperature exponent β (unitless) and the activation energy E_a (units K). The electron-impact reactions are defaulted to zero in the mechanism file. The cross-sectional data used to compute their rates is given in Appendix A.2.

*******	*ELECTRON-IMPACT REACTI	ONS**********	******	****	*******	*****
R1.	02+e-=0+0+e-		CRS4.	(see	Appendix	A.2)
R2.	02+e-=0+0(D)+e-		CRS5.	(see	Appendix	A.2)
R3.	02+e-=02(a)+e-		CRS2.	(see	Appendix	A.2)
R4.	02+e-=02(b)+e-		CRS3.	(see	Appendix	A.2)
R5.	AR+e-=AR*+e-		CRS22.	(see	Appendix	A.2)
R6.	AR+e=AR(+)+e		CRS23.	(see	Appendix	A.2)
R7.	C2H4+e-=C2H3+H+e-		CRS8.	(see	Appendix	A.2)
R8.	C2H4+e-=C2H2+H2+e-		CRS9.	(see	Appendix	A.2)
R9.	C2H4+e-=C2H2+H+H+e-		CRS10.	(see	Appendix	A.2)
R10.	C2H4+e-=C2H+H2+H+e-		CRS11.	(see	Appendix	A.2)
R11.	CH4+e-=CH3+H+e-		CRS13.	(see	Appendix	A.2)
R12.	CH4+e-=CH2+H2+e-		CRS14.	(see	Appendix	A.2)
R13.	CH4+e-=CH+H2+H+e-		CRS15.	(see	Appendix	A.2)
R14.	C2H2+e-=C2H+H+e-		CRS17.	(see	Appendix	A.2)
R15.	C2H2+e-=C2+H2+e-		CRS18.	(see	Appendix	A.2)
R16.	C2H2+e-=C+CH2+e-		CRS19.	(see	Appendix	A.2)
R17.	C2H2+e-=CH+CH+e-		CRS20.	(see	Appendix	A.2)
	REACTION		Α		beta	Ea
******	*AR* QUENCHING REACTION	S******	******	****	********	******
R18.	AR*+AR=AR+AR	REF[A.1.1]	2.10E-1	.5	0.00E+00	0.00E+00
R19.	AR*+AR+AR=AR+AR+AR	REF[A.1.1]	1.10E-3	32	0.00E+00	0.00E+00
R20.	AR*+02=AR+0+0	REF[A.1.2]	1.01E-1	.0	0.00E+00	0.00E+00
R21.	AR*+02=AR+0+0(D)	REF[A.1.2]	1.14E-1	.0	0.00E+00	0.00E+00
R22.	AR*+H2=AR+H+H	REF[A.1.3]	6.60E-1	.1	0.00E+00	0.00E+00
R23.	AR*+H2O=AR+OH+H	REF[A.1.3]	4.80E-1	.0	0.00E+00	0.00E+00
R24.	AR*+CO=AR+CO	REF[A.1.4]	1.40E-1	.1	0.00E+00	0.00E+00
R25.	AR*+C02=AR+C0+0	REF[A.1.4]	2.80E-1	.1	0.00E+00	0.00E+00
R26.	AR*+CH4=AR+CH2+H+H	REF[A.1.4-7]	3.19E-1	.0	0.00E+00	0.00E+00
R27.	AR*+CH4=AR+CH+H2+H	REF[A.1.4-7]	5.72E-1	.1	0.00E+00	0.00E+00
R28.	AR*+CH4=AR+CH3+H	REF[A.1.4-7]	5.72E-1	.1	0.00E+00	0.00E+00
R29.	AR*+CH4=AR+CH2+H2	REF[A.1.4-7]	5.72E-1	.1	0.00E+00	0.00E+00
R30.	AR*+C2H4=AR+C2H2+H+H	REF[A.1.3]	3.45E-1	.0	0.00E+00	0.00E+00
R31.	AR*+C2H4=AR+C2H3+H	REF[A.1.3]	6.30E-1	.1	0.00E+00	0.00E+00
R32.	AR*+C2H4=AR+C2H2+H2	REF[A.1.3]	1.89E-1	.0	0.00E+00	0.00E+00
R33.	AR*+C2H4=AR+CH2+CH2	REF[A.1.3]	6.30E-1	.1	0.00E+00	0.00E+00
*******	*O2(a) QUENCHING REACTI	ONS************	******	****	*********	*************
К34. Бог	$U+U+M=U^{2}(a)+M$	KEF[A.1.8]	2./6E-3	52 ·	-1.00E+00	0.008+00
КЗБ. Рос	$U_2(a) + M = U_2 + M$	KEF[A.1.8]	3.00E-1	.Ծ	U.UUE+00	2.00E+02
K36.	$U_2(a) + U + U_2 = U_2 + U + U_2$	KEF[A.1.8]	2.50E-3	52	U.00E+00	0.00E+00
КЗ7.	$U_2(a) + U + AK = U_2 + U + AK$	KEF[A.1.8]	1.57E-3	52	U.UUE+00	0.00E+00
КЗ8.	U2(a)+U2(a)=U2(b)+O2	REFLA.1.9]	7.00E-2	8	3.80E+00	-7.00E+02
R39.	U2(a)+U3=U2+U2+O	REFLA.1.8J	5.20E-1	.1	0.00E+00	2.84E+03

R40.	02(a)+H2=OH+OH	REF[A.1.10]	2.80E-09	0.00E+00	1.79E+04
R41.	02(a)+H=OH+O	REF[A.1.11]	6.39E-14	1.00E+00	2.48E+03
R42.	02(a)+H=OH+O	REF[A.1.11]	1.94E-17	1.56E+00	6.30E+02
R43.	02(a)+H=H+O2	REF[A.1.11]	8.78E-14	6.80E-01	2.82E+03
R44.	02(a)+H=H+O2	REF[A.1.11]	8.90E-18	1.40E+00	8.10E+02
R45.	02(a)+H+M=H02+M	REF[A.1.12]	2.73E-38	2.03E+00	1.69E+03
R46.	H+HO2=H2+O2(a)	REF[A.1.13]	2.72E-16	1.63E+00	7.69E+03
R47.	02(a) + H20 = 02 + H20	REF[A.1.8]	5.00E-18	0.00E+00	0.00E+00
R48.	02(a)+H2O=OH+HO2	REF [A.1.12]	3.40E-10	0.00E+00	2.82E+04
R49.	02(a)+C02=02+C02	REF[A.1.8]	2.00E-20	0.00E+00	0.00E+00
R50.	$\Omega_{2}(a) + CH4 = CH3 + H\Omega_{2}$	REF [A. 1. 14]	1.17E-16	1.97E+00	1.69E+04
R51	$\Omega_2(a) + CH_3 = CH_3\Omega_2$	REF [A. 1. 14]	2.76E-07	-2.71E+00	4.33E+03
R52	$\Omega_2(a) + CH3 = CH2O + OH$	REF[A.1.14]	5.76E-17	1.63E+00	3.47E+03
R53	$D_2(a) + CH_3 = CH_3O + O$	REF [A 1 14]	1 70F-20	2 68F+00	3 35E+03
R54	$D_2(a) + CH_2O = HO_2 + HCO_2$	$REF[\Lambda \ 1 \ 1A]$	1.66F-10	0.00E+00	1 16F+04
1.0 1.			1.001 10	0.001,00	1.101.04
*******	∗O2(Ъ) QUENCHING REACTI	ONS***********	*****	*********	*****
R55.	02(b) + AR = 02(a) + AR	REF[A.1.15]	6.00E-16	0.00E+00	0.00E+00
R56.	02(b)+02=02(a)+02	REF[A.1.15]	3.73E-16	2.40E+00	2.41E+02
R57.	02(b)+03=02(a)+03	REF[A.1.15]	2.20E-11	0.00E+00	0.00E+00
R58.	02(b)+0=02(a)+0	REF[A.1.15]	7.20E-14	5.00E-01	0.00E+00
R59.	02(b) + H = 02(a) + H	REF[A.1.15]	7.20E-14	5.00E-01	0.00E+00
R60.	02(b)+02(b)=02(a)+02	REF[A.1.15]	3.60E-17	5.00E-01	0.00E+00
R61.	02(b)+03=02(a)+02+0	REF [A. 1. 15]	1.00E-14	0.00E+00	0.00E+00
R62	02(b) + 0 = 02 + 0	REF [A. 1. 15]	8.00E-15	5.00E-01	0.00E+00
R63	$D_{2}(b) + D = D_{2} + D(D)$	REF [A. 1. 15]	6.00E-11	-1.00E-01	4.20E+03
R64	02(b)+03=02+03	REF [A. 1. 15]	2.20E-11	0.00E+00	0.00E+00
R65	02(b) + H = 0H + 0(D)	REF [A. 1. 12]	4.38E-10	-3.00E-02	1.62E+04
R66	02(b) + H2 = H + H02	REF[A.1.12]	3.49E-11	0.00E+00	2.05E+04
R67	$D_2(b) + H_2 = D_2(a) + H_2$	$\operatorname{REF}\left[\begin{smallmatrix} A & 1 & 1 \\ A & 1 $	1 00E-12	0.00E+00	0 00E+00
R68	02(b) + H20 = 0H + H02	REF [A 1 12]	3 40F-09	0.00E+00	2.74F+04
R69	02(b) + CH4 = CH3 + H02	$\operatorname{REF}\left[A \ 1 \ 12\right]$	3 69E-10	0.00E+00	2.00E+04
1000.			0.001 10	0.001.00	2.001.01
*******	*O(D) QUENCHING REACTIO	NS***********	******	*********	******
R72.	O(D) + AR = O + AR	REF[A.1.8]	2.09E-11	0.00E+00	3.10E+02
R73.	0(D)+02=0+02	REF[A.1.8]	4.80E-12	0.00E+00	-6.70E+01
R74.	O(D)+O2=O+O2(a)	REF[A.1.8]	1.60E-12	0.00E+00	-6.70E+01
R75.	O(D)+O2=O+O2(b)	REF[A.1.8]	2.56E-11	0.00E+00	-6.70E+01
R76.	0(D)+03=0+0+02	REF[A.1.8]	1.20E-10	0.00E+00	0.00E+00
R77.	O(D)+03=02+02	REF[A.1.8]	1.20E-10	0.00E+00	0.00E+00
R78.	O(D)+H2=OH+H	REF[A.1.8]	1.38E-10	0.00E+00	-2.10E+01
R79.	H+H02=H2O+O(D)	REF[A.1.16]	4.81E-16	1.55E+00	-8.06E+01
R80.	O(D)+CO2=O+CO2	REF[A.1.15]	7.50E-11	0.00E+00	1.15E+02
R81.	0(D)+CO=O+CO	REF[A.1.17]	4.70E-11	0.00E+00	6.24E+01
R82.	O(D)+H2O2=HO2+OH	REF[A.1.18]	5.20E-10	0.00E+00	0.00E+00
R83.	O(D)+H2O=OH+OH	REF[A.1.19]	1.69E-10	0.00E+00	-3.60E+01
R84.	O(D)+CH4=CH3+OH	REF[A.1.17]	1.45E-10	0.00E+00	0.00E+00
R85.	O(D)+CH4=CH2OH+H	REF[A.1.17]	3.42E-11	0.00E+00	0.00E+00
R86.	O(D)+CH4=CH2O+H2	REF[A.1.17]	9.46E-12	0.00E+00	0.00E+00
R87.	0(D)+CH20=C0+H20	REF[A.1.17]	1.66E-10	0.00E+00	0.00E+00
R88.	O(D)+CH3OH=CH2OH+OH	REF[A.1.17]	2.99E-10	0.00E+00	0.00E+00
R89.	О(D)+СНЗОН=НОСНО+Н+Н	REF[A.1.17]	8.97E-11	0.00E+00	0.00E+00

R90.	02+0+AR=03+AR	REF[A.1.8]	1.18E-30	-1.50E+00	0.00E+00
R91.	02+0+AR=03+AR	REF[A.1.8]	1.41E-26	-3.20E+00	0.00E+00
R92.	02+0+M=03+M	REF[A.1.8]	1.80E-30	-1.50E+00	0.00E+00
R93.	02+0+M=03+M	REF[A.1.8]	3.67E-26	-3.30E+00	0.00E+00
R94.	03+0=02+02	REF[A.1.20]	7.68E-12	0.00E+00	2.06E+03
R95.	03+0=02(a)+02	REF[A.1.20]	2.40E-13	0.00E+00	2.06E+03
R96.	03+0=02(b)+02	REF[A.1.20]	8.00E-14	0.00E+00	2.06E+03
R97.	03+H=02+0H	REF[A.1.17]	1.40E-10	0.00E+00	4.70E+02
R98.	03+H=0+H02	REF[A.1.21]	7.50E-13	0.00E+00	0.00E+00
R99.	03+0H=02+H02	REF[A.1.22]	3.07E-13	0.00E+00	4.18E+02
R100.	03+H20=02+H202	REF [A.1.23]	1.10E-22	0.00E+00	0.00E+00
R101.	03+H02=0H+02+02	REF[A.1.17]	1.10E-14	0.00E+00	5.00E+02
R102.	03+CH3=CH30+02	REF [A.1.24]	9.68E-14	0.00E+00	0.00E+00
R103	$0.3+CO=0.2+CO_2$	REF [A. 1. 25]	1.00E-21	0.00E+00	0.00E+00
R104	03+HCO=02+H+CO2	REF [A 1 26]	8 30F-13	0.00E+00	0.00E+00
11104.	00,1100,02,11,002		0.001 10	0.001.00	0.001.00
*******	*SAUDI ARAMCO MECHANISM	V1.3 REF[A.1.2	26] *********	***********	************
R105.	H+U2=U+UH		1.73E-10	0.00E+00	7.69E+03
R106.	U+H2=H+UH		8.44E-20	2.67E+00	3.1/E+03
R107.	0H+H2=H+H20		7.27E-11	0.00E+00	3.52E+03
R108.	0+H20=OH+OH		4.93E-18	2.02E+00	6.74E+03
R109.	H2+M=H+H+M		7.60E-05	-1.40E+00	5.25E+04
R110.	0+0+M=02+M		1.70E-32	-5.00E-01	0.00E+00
R111.	O+H+M=OH+M		1.30E-29	-1.00E+00	0.00E+00
R112.	H+OH+M=H2O+M		9.65E-26	-2.00E+00	0.00E+00
R113.	H+02=H02		7.72E-12	4.40E-01	0.00E+00
R114.	H+02+M=H02+M		1.88E-29	-1.20E+00	0.00E+00
R115.	H02+H=OH+OH		1.18E-10	0.00E+00	1.48E+02
R116.	H2+02=H+H02		8.59E-19	2.43E+00	2.69E+04
R117.	H02+0=0H+02		5.40E-11	0.00E+00	0.00E+00
R118.	H02+0H=H20+02		4.08E-11	0.00E+00	-2.50E+02
R119.	H02+H02=H202+02		2.16E-13	0.00E+00	-8.20E+02
R120.	H02+H02=H202+02		6.07E-10	0.00E+00	6.04E+03
R121.	Н202=0Н+ОН		2.00E+12	9.00E-01	2.45E+04
R122.	H2O2+M=OH+OH+M		4.13E+00	-2.30E+00	2.45E+04
R123.	H2O2+H=H2O+OH		4.00E-11	0.00E+00	2.00E+03
R124.	H202+H=H2+H02		3.57E-14	1.00E+00	3.02E+03
R125.	H202+0=0H+H02		1.59E-17	2.00E+00	2.00E+03
R126.	H202+0H=H20+H02		2.89E-12	0.00E+00	1.60E+02
R127.	H202+0H=H20+H02		1.26E-10	0.00E+00	3.66E+03
R128.	C0+0=C02		2.26E-14	0.00E+00	1.20E+03
R129.	CO+O+M=CO2+M		3.23E-24	-2.79E+00	2.11E+03
R130.	C0+02=C02+0		1.86E-12	0.00E+00	2.40E+04
R131.	CO+OH=CO2+H		1.16E-19	2.05E+00	-1.79E+02
R132.	CO+OH=CO2+H		9.56E-12	-6.64E-01	1.67E+02
R133	CO+HO2=CO2+OH		2.61E-19	2.18E+00	9.03E+03
R134	HCO+M=H+CO+M		9 47E-13	6 60E-01	7 48E+03
R135	HCO+O2=CO+HO2		1 26F-11	0.00E+00	2 06F+02
R136	HCO+H=CO+H2		1 205 11	0 005+00	0 00F+00
R137	HCO+O=CO+OH		5 01F-11	0.00E+00	0.005+00
R138	HCO+O=CO2+H		Δ.ΟΙΈ ΙΙ Λ ΟΩΓ-11	0.005+00	0.005+00
R130.	HCO+OH=CO+H2O		$4.50E^{-11}$	0.005+00	
D140			1.09E-10 1.09E-11		
π14U. D1//1			4.90E-11		0.000000
LI41.			4.90L-12	0.005+00	0.002+00

R143. R144. R145. R146. R147. R148. R149. R150. R151. R152.	CH20+02=HC0+H02 HC0+02=02CH0 CH20+02CH0=HC0+H02CH0 OCH0+0H=H02CH0 H+C02=0CH0 HC0+HC0=CH20+C0 H+0+M=M+0H*	1.34E-08 1.99E-13 3.30E-12 3.32E-11 1.25E-10	0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00	2.69E+04 -5.54E+02 5.87E+03 0.00E+00
R144. R145. R146. R147. R148. R149. R150. R151. R151.	HC0+02=02CH0 CH20+02CH0=HC0+H02CH0 OCH0+0H=H02CH0 H+C02=0CH0 HC0+HC0=CH20+C0 H+0+M=M+0H*	1.99E-13 3.30E-12 3.32E-11 1.25E-10	0.00E+00 0.00E+00 0.00E+00 0.00E+00	-5.54E+02 5.87E+03 0.00E+00
R145. R146. R147. R148. R149. R150. R151. R152.	CH20+02CH0=HC0+H02CH0 OCH0+0H=H02CH0 H+C02=0CH0 HC0+HC0=CH20+C0 H+0+M=M+0H*	3.30E-12 3.32E-11 1.25E-10	0.00E+00 0.00E+00 0.00E+00	5.87E+03 0.00E+00
R146. R147. R148. R149. R150. R151. R152.	OCHO+OH=HO2CHO H+CO2=OCHO HCO+HCO=CH2O+CO H+O+M=M+OH*	3.32E-11 1.25E-10	0.00E+00 0.00E+00	0.00E+00
R147. R148. R149. R150. R151. R152.	H+CO2=OCHO HCO+HCO=CH2O+CO H+O+M=M+OH*	1.25E-10	0.00E+00	
R148. R149. R150. R151. R152.	HCO+HCO=CH2O+CO H+O+M=M+OH*	0 005 11		1.46E+04
R149. R150. R151. R152.	H+O+M=M+OH*	2.99E-11	0.00E+00	0.00E+00
R150. R151. R152.		4.14E-35	0.00E+00	3.01E+03
R151. R152.	0H*+H2O=OH+H2O	9.85E-12	5.00E-01	-4.33E+02
R152.	0H*+H2=OH+H2	4.90E-12	5.00E-01	-2.23E+02
	0H*+N2=0H+N2	1.79E-13	5.00E-01	-6.25E+02
R153.	OH*+OH=OH+OH	9.98E-12	5.00E-01	-3.84E+02
R154.	OH*+H=OH+H	2.18E-12	5.00E-01	-8.40E+01
R155.	OH*+AR=OH+AR	2.81E-12	0.00E+00	2.08E+03
R156.	OH*=OH	1.45E+06	0.00E+00	0.00E+00
R157.	0H*+02=0H+02	3.49E-12	5.00E-01	-2.41E+02
R158.	0H*+C02=OH+C02	4.57E-12	5.00E-01	-4.87E+02
R159.	OH * + CO = OH + CO	5.36E-12	5.00E-01	-3.96E+02
R160.	0H*+CH4=0H+CH4	5.58E-12	5.00E-01	-3.20E+02
R161	CH+02=C0+0H*	6.71E-11	0.00E+00	0.00E+00
R162	C2H+D=CD+CH*	1 03E-11	0 00E+00	0 00E+00
R163	C+H+M=CH*+M	1.00E 11 1.65E-33	0.00E+00	3 49E+03
R164	C2H+D2=CD2+CH*	3 60F-14	0.00E+00	0.00F+00
R165	CH*+AB=CH+AB	6 6/F-13	5 00E-01	0.00E+00
R166	CH*+HOD=CH+HOD	8 80F-11	0.00E+00	0.00E+00
R167	CH*+CD=CH+CD	4 05E-12	5.00E-01	0.00E+00
R168	$CH_{*} + CO_{-} CH_{+} CO_{-}$	4.00E 12 4.00E-25	4 30E+00	-8 52F+02
R160.	CH + 102 - CH + 002	4.00L 20	2.1/E+00	-8 665+02
D170	CII + UZ = CII + UZ	4.12E 10 2 $44E-10$	2.140	6 95E+02
D171	$C_{1} + H_{2} - C_{1} + H_{2}$	2.44E 10 0.97E_11	0.000000	0.00E+02
NI/I.		2.07E-11 1.96E+06	0.00E+00	0.40E+01
N172.		1.00E+00	0.00E+00	-1 00E+00
RI/J.		5.03E-22	3.40E+00	-1.92E+02
R174.		1.81E-12	4.80E-01	-1.31E+02
R175.	HCO+H+M=CH2O+M	3.72E-24	-2.57E+00	7.17E+02
R170.	CU+HZ=CHZU	1.14E-17	1.50E+00	4.01E+04
R1//.	CU+HZ+M=CHZU+M	1.40E-20	-3.42E+00	4.246+04
R178.		1.30E-16	1.63E+00	-5.31E+02
R179.	$CH_2U+H=H_CU+H_2$	9.53E-17	1.90E+00	1.38E+03
R180.	CH2U+U=HCU+UH	1.04E-14	1.15E+00	1.14E+03
R181.	CH2U+CH3=HCU+CH4	6.36E-23	3.36E+00	2.17E+03
R182.	CH2U+HU2=HCU+H2U2	3.12E-20	2.70E+00	5.80E+03
R183.	CH2U+UH=HUCH2U	7.47E-09	-1.10E+00	0.00E+00
R184.	HUCH2U=HUCHU+H	1.00E+14	0.00E+00	7.50E+03
R185.	HUCHU=CU+H2U	2.45E+12	0.00E+00	3.04E+04
R186.	HOCHO=CO2+H2	2.95E+09	0.00E+00	2.44E+04
R187.	0CH0+H02=H0CH0+02	5.81E-14	0.00E+00	-1.65E+03
R188.	HOCHO+OH=H2O+CO2+H	4.35E-18	2.06E+00	4.61E+02
R189.	HOCHO+OH=H2O+CO+OH	3.07E-17	1.51E+00	-4.84E+02
R190.	HOCHO+H=H2+CO2+H	7.04E-18	2.10E+00	2.45E+03
R191.	HOCHO+H=H2+CO+OH	1.00E-10	-3.50E-01	1.50E+03
	HOCHO+CH3=CH4+CO+OH	6.48E-31	5.80E+00	1.11E+03
R192.				
R192. R193.	OCH0+H202=H0CH0+H02	3.99E-12	0.00E+00	5.03E+03
R192. R193. R194.	0CH0+H202=H0CH0+H02 H0CH0+H02=H202+C0+OH	3.99E-12 1.66E-12	0.00E+00 0.00E+00	5.03E+03 6.00E+03

R196.	CH2O+OCHO=HOCHO+HCO	9.30E-12	0.00E+00	6.84E+03
R197.	CH30=CH20+H	6.80E+13	0.00E+00	1.32E+04
R198.	CH3O+M=CH2O+H+M	3.10E+01	-3.00E+00	1.22E+04
R199.	CH30+02=CH20+H02	7.27E-43	9.50E+00	-2.77E+03
R200.	CH20+CH30=CH30H+HC0	1.10E-12	0.00E+00	1.15E+03
R201.	СН3+СНЗОН=СН4+СНЗО	2.39E-23	3.10E+00	3.49E+03
R202.	CH30+CH3=CH20+CH4	1.99E-11	0.00E+00	0.00E+00
R203.	CH30+H=CH20+H2	3.32E-11	0.00E+00	0.00E+00
R204.	CH30+H02=CH20+H202	5.00E-13	0.00E+00	0.00E+00
R205.	CH2O+H=CH2OH	8.97E-13	4.54E-01	1.81E+03
R206.	CH2O+H+M=CH2OH+M	3.50E-16	-4.82E+00	3.29E+03
R207.	CH20H+02=CH20+H02	2.51E-09	-1.00E+00	0.00E+00
R208.	CH20H+02=CH20+H02	4.00E-10	0.00E+00	2.52E+03
R209.	CH20H+H=CH20+H2	9.96E-12	0.00E+00	0.00E+00
R210.	CH20H+H02=CH20+H202	1.99E-11	0.00E+00	0.00E+00
R211	CH20H+HC0=CH20+CH20	2.99E-10	0.00E+00	0.00E+00
R212	CH2OH+CH3O=CH2O+CH3OH	3 99E-11	0 00E+00	0 00E+00
R213		1 60F-20	2 90F+00	6 60F+03
R210.		3 99F-11	0 00F+00	0.00E+00
R214.	0 + C + 2 0 + - 0 + C + 2 0 - 0 + C + 2 0 - 0 + C + 2 0 - 0 + C + 2 0 - 0 + C + 2 0 - 0 + C + 2 0 - 0 + C + 2 0 - 0 + C + 2 0 - 0 + C + 2 0 - 0 + C + 2 0 - 0 + C + 2 0 - 0 + C + 2 0 +	6 97F-11	0.00E+00	0.00E+00
N210.		4 095-10	0.000000	0.00000
NZIU.		$4.90E^{-12}$	0.00E+00	0.00E+00
RZI/.		1.00E-11	0.00E+00	0.00E+00
R210.		2.49E-13	0.00E+00	5.99E+03
R219.		3.00E+11	0.00E+00	4.33E+03
R220.	HUCH2U2+HU2=HUCH2U2H+U2	5.81E-14	0.00E+00	-1.65E+03
R221.	HUCH2U+UH=HUCH2U2H	1.66E-11	0.00E+00	0.00E+00
R222.	CH30H=CH3+0H	2.08E+18	-6.15E-01	4.66E+04
R223.	CH30H+M=CH3+0H+M	2.49E+19	-7.00E+00	4.93E+04
R224.	CH30H=CH2(S)+H20	3.12E+18	-1.02E+00	4.62E+04
R225.	CH30H+M=CH2(S)+H20+M	2.37E+23	-8.23E+00	5.00E+04
R226.	СНЗОН=СН2ОН+Н	7.90E-03	5.04E+00	4.25E+04
R227.	СНЗОН+М=СН2ОН+Н+М	5.63E+18	-7.24E+00	5.30E+04
R228.	CH30H+H=CH20H+H2	5.10E-19	2.55E+00	2.74E+03
R229.	CH30H+H=CH30+H2	3.30E-19	2.56E+00	5.18E+03
R230.	CH30H+0=CH20H+0H	6.44E-19	2.50E+00	1.55E+03
R231.	CH30H+0H=CH20H+H20	5.11E-20	2.65E+00	-4.06E+02
R232.	CH30H+0H=CH30+H20	2.49E-22	3.03E+00	-3.84E+02
R233.	CH30H+02=CH20H+H02	3.40E-11	0.00E+00	2.26E+04
R234.	CH30H+H02=CH20H+H202	1.79E-20	2.55E+00	5.30E+03
R235.	CH3OH+CH3=CH2OH+CH4	5.30E-23	3.17E+00	3.61E+03
R236.	СНЗО+СНЗОН=СН2ОН+СНЗОН	4.98E-13	0.00E+00	2.05E+03
R237.	CH30+CH30=CH30H+CH20	1.00E-10	0.00E+00	0.00E+00
R238.	CH3+H=CH4	2.11E-08	-6.30E-01	1.93E+02
R239.	CH3+H+M=CH4+M	6.83E-15	-4.76E+00	1.23E+03
R240.	CH4+H=CH3+H2	1.02E-18	2.50E+00	4.82E+03
R241.	CH4+OH=CH3+H2O	9.68E-20	2.60E+00	1.10E+03
R242.	CH4+0=CH3+OH	1.69E-15	1.50E+00	4.33E+03
R243.	CH4+H02=CH3+H202	2.81E-23	3.74E+00	1.06E+04
R244.	СН4+СН2=СН3+СН3	4.08E-18	2.00E+00	4.16E+03
R245.	CH3+OH=CH2(S)+H2O	8.77E-07	-1.52E+00	8.92E+02
R246.	CH3+OH=CH2O+H2	2.74E-17	9.73E-01	-1.01E+03
R247.	CH3+OH=CH2OH+H	7.78E-14	8.33E-01	1.79E+03
R248.	CH3+OH=H+CH3O	2.04E-15	1.01E+00	6.01E+03
R249.	CH3+OH=HCOH+H2	2.59E-13	1.56E-01	-6.88E+02
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R250.	HCOH+OH=HCO+H2O	3.32E-11	0.00E+00	0.00E+00
R251.	HCOH+H=CH2O+H	3.32E-10	0.00E+00	0.00E+00
R252.	HCOH+O=CO2+H+H	8.30E-11	0.00E+00	0.00E+00
R253.	HCOH+O=CO+OH+H	4.98E-11	0.00E+00	0.00E+00
R254.	HCOH+02=C02+H+OH	8.30E-12	0.00E+00	0.00E+00
R255.	HCOH+02=C02+H20	4.98E-11	0.00E+00	0.00E+00
R256.	CH3+H02=CH30+OH	1.66E-12	2.69E-01	-3.46E+02
R257.	CH3+H02=CH4+02	1.93E-19	2.23E+00	-1.52E+03
R258.	CH3+0=CH20+H	9.20E-11	5.00E-02	-6.84E+01
R259.	CH3+02=CH30+0	1.25E-11	0.00E+00	1.43E+04
R260.	CH3+02=CH20+0H	4.39E-24	3.28E+00	4.08E+03
R261.	CH3+02=CH302	1.30E-14	9.00E-01	0.00E+00
R262.	CH3+02+M=CH302+M	1.89E-23	-3.00E+00	0.00E+00
R263.	CH302+CH20=CH302H+HC0	3.30E-12	0.00E+00	5.87E+03
R264.	CH4+CH302=CH3+CH302H	1.59E-24	3.77E+00	8.96E+03
R265.	CH30H+CH302=CH20H+CH302H	3.01E-12	0.00E+00	6.90E+03
R266.	CH302+CH3=CH30+CH30	8.44E-12	0.00E+00	-7.10E+02
R267.	CH302+H02=CH302H+02	4.10E-13	0.00E+00	-7.90E+02
R268.	CH302+CH302=CH20+CH30H+02	5.16E-10	-1.61E+00	-5.29E+02
R269.	CH302+CH302=02+CH30+CH30	2.32E-08	-1.61E+00	9.36E+02
R270.	СНЗО2+Н=СНЗО+ОН	1.59E-10	0.00E+00	0.00E+00
R271	CH302+0=CH30+02	5.98E-11	0.00E+00	0.00E+00
R272	CH302+0H=CH30H+02	9 96E-11	0 00E+00	0 00E+00
R272.	CH302H=CH30+0H	6 31F+14	0.00E+00	2 13F+04
R270.	CH2(S)+N2=CH2+N2	2 49F-11	0.00E+00	3 02F+02
R075	CH2(S) + AB = CH2 + AB	1 /QF-11	0.00E+00	3 02E+02
R276	CH2(S) + H = CH + H2	1.49L 11 1 98F-11	0.00E+00	0.005+00
R270.	CH2(S)+H=CH+H2	9.00L 11	0.00E+00	0.00E+00
R078	CH2(S)+0-UC0+H2	2.40L 11 2.40E-11	0.00000	0.00E+00
R270.	CH2(S)+O=HCO+H	2.49L 11 / Q8E_11	0.00000	0.00E+00
N279.	Cn3(g) + n2 - Cn3 + n	4.301 11 1 16F-10	0.000000	0.00E+00
DO01	$Cu_2(g) + n_2 - u_1 - n_1 - c_0$	1.10E 10 4 65E-11	0.000000	0.00E+00
NZOI.	CH2(S) + 02 - CO + U2O	4.05E-11	0.00E+00	0.00E+00
NZOZ.	CH2(S)+U2-CU+H2U	1.99E-11 4 09E-11	0.00E+00	0.00E+00
RZOJ.	$CH_2(S) + H_2U - CH_2 + H_2U$	4.90E-11	0.00E+00	0.00E+00
R204.	$CH_2(S) + CU_2 - CH_2 + CU_2$	1.49E-11 1.16E-11	0.00E+00	0.00E+00
R200.	$CH_2(S) + CU_2 = CH_2 + CU_2$	1.10E-11	0.00E+00	0.00E+00
R286.	CH2(S)+CU2=CH2U+CU	2.32E-11	0.00E+00	0.00E+00
R287.	CH2+H=CH3	4.15E-08	-8.00E-01	0.00E+00
R288.	CH2+H+M=CH3+M	8.82E-21	-3.14E+00	6.19E+02
R289.	CH2+U2=HCU+UH	1.76E-11	0.00E+00	7.55E+02
R290.	CH2+U2=CU2+H+H	4.38E-12	0.00E+00	7.55E+02
R291.	CH2+U=CU+H+H	8.30E-11	0.00E+00	0.00E+00
R292.	CH2+H=CH+H2	1.66E-06	-1.56E+00	0.00E+00
R293.	CH2+UH=CH+H2U	1.88E-1/	2.00E+00	1.51E+03
R294.	CH+U2=HCU+U	5.48E-11	0.00E+00	0.00E+00
R295.	C+OH=CO+H	8.30E-11	0.00E+00	0.00E+00
R296.	C+02=C0+0	8.30E-11	0.00E+00	0.00E+00
K297.	CH+H=C+H2	1.83E-10	0.00E+00	0.00E+00
R298.	CH+U=CO+H	9.47E-11	0.00E+00	0.00E+00
R299.	CH+OH=HCO+H	4.98E-11	0.00E+00	0.00E+00
R300.	CH2+H=CH+H2	4.48E-13	6.70E-01	1.29E+04
R301.	CH+H2O=H+CH2O	2.84E-11	0.00E+00	-3.80E+02
R302.	CH+CO2=HCO+CO	2.82E-12	0.00E+00	3.45E+02
R303.	CH3+CH3=C2H6	3.78E-09	-6.90E-01	8.80E+01

R304	CH3+CH3+M=C2H6+M	2 22F-16	-3 75F+00	4 94F+02
R305	C2H5+H=C2H6	8 65F-07	-9 90F-01	7 95F+02
R306	C2H5+H+M=C2H6+M	5 49F-07	-7 08F+00	3 36F+03
R307	C2H6+H=C2H5+H2	1 Q1F-16	1 90E+00	3 70F+03
R308	C2H6+D=C2H5+D4	5 80F-18	2 405+00	2 03E+03
R300.		0.09E 10	1 005+00	2.95E+03
R309.	C2H0+DH=C2H0+H2D	$2.40E^{-17}$	1.90E+00	4.70E+02
R310.	$C_{2H0+U_{2}=C_{2H0+HU_{2}}}$	1.00E-10	0.00E+00	2.01E+04
R311.		9.10E-25	4.00E+00	4.17E+03
R312.	$C_{2H0+HU2}=C_{2H0+H2U2}$	5.75E-23	3.61E+00	8.51E+03
R313.		3.22E-23	3.64E+00	8.61E+03
R314.	C2H6+CH3U=C2H5+CH3UH	4.00E-13	0.00E+00	3.5/E+03
R315.	C2H6+CH=C2H5+CH2	1.83E-10	0.00E+00	-1.31E+02
R316.	CH2(S)+C2H6=CH3+C2H5	1.99E-10	0.00E+00	0.00E+00
R317.	C2H4+H=C2H5	1.59E-15	1.46E+00	6.82E+02
R318.	C2H4+H+M=C2H5+M	3.91E-09	-6.64E+00	2.90E+03
R319.	Н2+СН302=Н+СН302Н	2.49E-10	0.00E+00	1.31E+04
R320.	H2+C2H5O2=H+C2H5O2H	2.49E-10	0.00E+00	1.31E+04
R321.	C2H4+C2H4=C2H5+C2H3	8.00E-10	0.00E+00	3.60E+04
R322.	CH3+C2H5=CH4+C2H4	1.96E-20	2.45E+00	-1.47E+03
R323.	СНЗ+СНЗ=Н+С2Н5	5.15E-10	-3.62E-01	6.73E+03
R324.	C2H5+H=C2H4+H2	3.32E-12	0.00E+00	0.00E+00
R325.	C2H5+O=CH3CHO+H	1.83E-10	0.00E+00	0.00E+00
R326.	C2H5+H02=C2H50+OH	1.83E-11	0.00E+00	0.00E+00
R327.	CH302+C2H5=CH30+C2H50	1.33E-11	0.00E+00	-5.03E+02
R328.	C2H50+02=CH3CH0+H02	7.11E-14	0.00E+00	5.52E+02
R329.	CH3+CH20=C2H50	4.98E-13	0.00E+00	3.19E+03
R330.	CH3CH0+H=C2H50	7.66E-17	1.71E+00	3.57E+03
R331.	C2H502+CH20=C2H502H+HC0	3.30E-12	0.00E+00	5.87E+03
R332.	CH4+C2H502=CH3+C2H502H	3.01E-13	0.00E+00	9.30E+03
R333.	CH30H+C2H502=CH20H+C2H502H	3.01E-12	0.00E+00	6.90E+03
R334	C2H5D2+HD2=C2H5D2H+D2	2.91E-14	0.00E+00	-1.65E+03
R335	C2H6+C2H5D2=C2H5+C2H5D2H	1.43E-23	3.76E+00	8.66E+03
R336	C2H5O2H=C2H5O+OH	6 31E+14	0 00E+00	2 13E+04
R337	C2H5+D2=C2H5D2	1 55F+36	-1 53F+01	7 17F+03
B338	C2H5+D2=C2H4D2H	8 11F+00	-8 31F+00	3 885+03
R330	C2H5+02=C2H4+H02	3 06F-17	1.13E+00	-3 63E+02
R340	C2H5+02-C2H4+H02	1 10E-23	3 51E+00	7 13E+03
R340.	$C_{2H5+U2} = C_{2H4+HU2}$	1.10E-23	0 19E+00	-2 15E+03
NO41.	$C_{2}H_{2}+D_{2}-C_{2}H_{0}+D_{1}$	4.05E-22	2.105+00	-3.15E+01
R342.		1.13E-25	3.57E+00	1.335+03
R343.		1.06E+41	-1.01E+01	1.31E+04
R344.	C2H5U2=CH3CHU+UH	1.69E+36	-9.22E+00	1.95E+04
R345.	C2H5U2=C2H4+HU2	2.70E+37	-8.47E+00	1.80E+04
R346.	C2H502=C2H401-2+OH	1.92E+43	-1.08E+01	2.13E+04
R347.	C2H402H=C2H401-2+0H	1.22E+37	-8.32E+00	1.08E+04
R348.	C2H4O2H=C2H4+HO2	6.82E+40	-9.61E+00	1.20E+04
R349.	C2H4O2H=CH3CHO+OH	5.52E+34	-9.88E+00	1.32E+04
R350.	C2H401-2=CH3+HC0	3.63E+13	0.00E+00	2.88E+04
R351.	C2H401-2=CH3CH0	7.41E+12	0.00E+00	2.71E+04
R352.	C2H4O1-2+OH=C2H3O1-2+H2O	2.96E-11	0.00E+00	1.82E+03
R353.	C2H4O1-2+H=C2H3O1-2+H2	1.33E-10	0.00E+00	4.87E+03
R354.	C2H401-2+H02=C2H301-2+H2O2	1.88E-11	0.00E+00	1.53E+04
R355.	C2H4O1-2+CH3O2=C2H3O1-2+CH3O2H	1.88E-11	0.00E+00	1.53E+04
R356.	C2H401-2+C2H502=C2H301-2+C2H502H	1.88E-11	0.00E+00	1.53E+04
R357.	C2H401-2+CH3=C2H301-2+CH4	1.78E-12	0.00E+00	5.95E+03

R358.	C2H401-2+CH30=C2H301-2+CH3OH	1.99E-13	0.00E+00	3.40E+03
R359.	C2H301-2=CH3C0	8.50E+14	0.00E+00	7.05E+03
R360.	C2H301-2=CH2CH0	1.00E+14	0.00E+00	7.05E+03
R361.	CH3CH0=CH3+HC0	2.45E+22	-1.74E+00	4.35E+04
R362.	CH3CH0+M=CH3+HC0+M	1.71E+35	-1.13E+01	4.83E+04
R363.	CH3CH0=CH4+C0	2.72E+21	-1.74E+00	4.35E+04
R364.	CH3CH0+M=CH4+C0+M	1.90E+34	-1.13E+01	4.83E+04
R365.	CH3CH0+H=CH3C0+H2	2.18E-19	2.58E+00	6.14E+02
R366.	CH3CH0+H=CH2CH0+H2	4.52E-21	3.10E+00	2.62E+03
R367.	CH3CH0+0=CH3C0+0H	9.86E-12	0.00E+00	9.40E+02
R368.	CH3CH0+0H=CH3C0+H20	5.60E-12	0.00E+00	-3.11E+02
R369.	CH3CH0+02=CH3C0+H02	5.00E-11	0.00E+00	1.97E+04
R370.	CH3CH0+CH3=CH3C0+CH4	1.18E-27	4.58E+00	9.89E+02
R371.	CH3CH0+H02=CH3C0+H202	5.00E-12	0.00E+00	6.00E+03
R372.	CH302+CH3CH0=CH302H+CH3C0	5.00E-12	0.00E+00	6.00E+03
R373.	CH3CH0+CH3CO3=CH3CO+CH3CO3H	5.00E-12	0.00E+00	6.00E+03
R374.		4.98E-09	-1.08E+00	0.00E+00
R375	CH3CH0+0H=CH2CH0+H20	2.86E-19	2.40E+00	4.10E+02
R376	CH3CO=CH3+CO	1.07E+12	6.30E-01	8.50E+03
B377	CH3CO+M=CH3+CO+M	9.38E-06	-9.70E-01	7.35E+03
R378	CH3CO+H=CH2CO+H2	3 32E-11	0 00E+00	0 00E+00
R379	CH3CO+O=CH2CO+OH	3 32F-11	0.00E+00	0.00E+00
R380		8 30F-11	0.00E+00	0.00E+00
R381		1 00F-13	0.00E+00	-5 5/F+02
R301.	CH3CD3+H02-CH3CD3H+D2	1.00L 10 2.01E-1/	0.00E+00	-1 65F+03
D202.		2.91E 14 4 00E-10	0.000000	5 00E+03
n303. D201	n202+0n3003-n02+0n3003n	4.00E-12 2 01E-12	0.00E+00	0 20E+03
N304.		3.01E-13 2.20E-10	0.00E+00	5.30E+03
R303.		3.30E-12	0.00E+00	1 02E+03
R300.		2.02E-11 E_01E+14	0.00E+00	1.036+04
R307.		5.01E+14	0.00E+00	2.02E+04
R300.		7.31E-09	0.00E+00	5.28E+03
R389.	CH2CHU=CH2CU+H	1.43E+15	-1.50E-01	2.29E+04
R390.	CH2CHU+M=CH2CU+H+M	9.96E+05	-3.80E+00	2.19E+04
R391.	CH2CHU=CH3+CU	2.93E+12	2.90E-01	2.03E+04
R392.	CH2CHU+M=CH3+CU+M	1.58E+10	-5.07E+00	2.08E+04
R393.	CH2CHU+U2=U2CH2CHU	1.30E+36	-1.54E+01	8.88E+03
R394.	CH2CHU+U2=CH2CU+HU2	4.17E-19	2.33E+00	1.20E+04
R395.	CH2CH0+02=CH20+C0+0H	2.74E-05	-2.22E+00	5.20E+03
R396.	CH2CH0+02=H02CH2C0	1.10E+25	-1.56E+01	8.79E+03
R397.	02CH2CH0=H02CH2C0	9.03E+19	-2.92E+00	1.12E+04
R398.	02CH2CH0=CH2C0+H02	4.16E+55	-1.58E+01	2.77E+04
R399.	H02CH2CO=CO+CH2O+OH	2.51E+19	-2.95E+00	4.08E+03
R400.	H02CH2CO=CH2CO+H02	9.20E+08	-3.73E+00	1.09E+04
R401.	CH2+CO=CH2CO	1.35E-12	0.00E+00	0.00E+00
R402.	CH2+CO+M=CH2CO+M	7.42E-15	-5.11E+00	3.57E+03
R403.	CH3CO=CH2CO+H	9.41E+07	1.92E+00	2.26E+04
R404.	CH3CO+M=CH2CO+H+M	2.52E+27	-1.03E+01	2.79E+04
R405.	CH2CO+H=HCCO+H2	2.33E-09	-1.71E-01	4.42E+03
R406.	CH2CO+H=CH3+CO	1.28E-10	-1.71E-01	2.11E+03
R407.	CH2C0+0=CH2+C02	2.91E-12	0.00E+00	6.79E+02
R408.	CH2CO+O=HCCO+OH	1.66E-11	0.00E+00	4.03E+03
R409.	CH2CO+OH=HCCO+H2O	1.66E-11	0.00E+00	1.01E+03
R410.	CH2CO+OH=CH2OH+CO	3.32E-12	0.00E+00	-5.08E+02
R411.	CH2C0+CH3=C2H5+C0	7.92E-20	2.31E+00	4.76E+03

R412.	CH2(S)+CH2CO=C2H4+CO	2.66E-10	0.00E+00	0.00E+00
R413.	HCCO+OH=H2+CO+CO	1.66E-10	0.00E+00	0.00E+00
R414.	HCCO+O=H+CO+CO	1.33E-10	0.00E+00	0.00E+00
R415.	HCCO+H=CH2(S)+CO	1.66E-10	0.00E+00	0.00E+00
R416.	HCC0+02=0H+C0+C0	3.17E-13	-2.00E-02	5.13E+02
R417.	HCC0+02=C02+C0+H	7.94E-12	-1.42E-01	5.79E+02
R418.	CH+CO+M=HCCO+M	2.09E-25	-1.90E+00	0.00E+00
R419.	CH+CH2O=H+CH2CO	1.57E-10	0.00E+00	-2.59E+02
R420.	CH+HCCO=CO+C2H2	8.30E-11	0.00E+00	0.00E+00
R421.	C2H3+H=C2H4	1.01E-11	2.70E-01	1.41E+02
R422.	C2H3+H+M=C2H4+M	3.86E-18	-3.86E+00	1.67E+03
R423.	C2H4=H2+H2CC	8.00E+12	4.40E-01	4.47E+04
R424.	C2H4+M=H2+H2CC+M	1.16E+27	-9.31E+00	5.03E+04
R425.	C2H4+H=C2H3+H2	8.42E-17	1.93E+00	6.52E+03
R426.	C2H4+0=CH3+HC0	1.24E-17	1.88E+00	9.21E+01
B427.	C2H4+0=CH2CH0+H	1.01E-17	1.88E+00	9.21E+01
R428	C2H4+OH=C2H3+H2O	3.70E-20	2.75E+00	1.11E+03
R429	C2H4+OH=CH3+CH2O	2 96E-19	1 68E+00	1 04E+03
R430	C2H4+OH=CH3CHO+H	3 95E-26	3 91E+00	8 67E+02
R431	C2H4+OH=C2H3OH+H	5 30F-19	2 19F+00	2 64F+03
R432	C2H4+OH=PC2H4OH	4 25E+12	-7 75E+00	3 50F+03
R/33	C2H30H+02=CH2CH0+H02	9.20E-12 8.80F-13	2 10F-01	2 00E+04
R430.		3 11F-18	1 90F+00	_/ 33E+02
R434.	C2H2OH+OH-CH2CHO+UN	5.115 10	1.30E+00	4.00E102
R433.		0.00E-10 2.27E-20	I.IUE+00	Z.72E+02
R430.	$C_2 H_2 O_1 + C_{H_2} - C_{H_2} C_{H_2} + C_$	5.57E-52	3.90E+00	0.29E+02
R437.		5.05E-21	2.50E+00	4.49E+03
R430.		2.40E-21	3.00E+00	3.03E+03
R439.		4.10E-17	2.03E+00	1.05E+03
R440.		5.00E-16	1.58E+00	1.85E+03
R441.	C2H3UH+HU2=CH3CHU+HU2	2.47E-19	1.67E+00	3.43E+03
R442.		4.42E+42	-9.09E+00	3.38E+04
R443.		1.10E-23	3.70E+00	4.78E+03
R444.	C2H4+U2=C2H3+HU2	7.01E-11	0.00E+00	2.90E+04
R445.	C2H4+CH3U=C2H3+CH3UH	1.99E-13	0.00E+00	3.40E+03
R446.	C2H4+CH3U2=C2H3+CH3U2H	1.43E-23	3.75E+00	1.37E+04
R447.	C2H4+C2H5U2=C2H3+C2H5U2H	1.43E-23	3.75E+00	1.37E+04
R448.	C2H4+CH3CU3=C2H3+CH3CU3H	1.88E-11	0.00E+00	1.53E+04
R449.	C2H4+CH3O2=C2H4O1-2+CH3O	4.68E-12	0.00E+00	8.61E+03
R450.	C2H4+C2H502=C2H401-2+C2H50	4.68E-12	0.00E+00	8.61E+03
R451.	C2H4+H02=C2H401-2+OH	9.26E-13	0.00E+00	8.65E+03
R452.	CH+CH4=C2H4+H	9.96E-11	0.00E+00	0.00E+00
R453.	CH2(S)+CH3=C2H4+H	3.32E-11	0.00E+00	0.00E+00
R454.	C2H2+H=C2H3	2.84E-14	1.27E+00	1.36E+03
R455.	C2H2+H+M=C2H3+M	1.75E-16	-4.66E+00	1.90E+03
R456.	C2H3+O2=CH2O+HCO	2.82E+05	-5.31E+00	3.27E+03
R457.	C2H3+O2=CH2CH0+O	1.16E-09	-6.11E-01	2.65E+03
R458.	C2H3+O2=H+CO+CH2O	8.62E-09	-1.26E+00	1.67E+03
R459.	CH3+C2H3=CH4+C2H2	6.51E-13	0.00E+00	0.00E+00
R460.	C2H3+H=C2H2+H2	1.49E-10	0.00E+00	0.00E+00
R461.	C2H3+H=H2CC+H2	9.96E-11	0.00E+00	0.00E+00
R462.	C2H3+OH=C2H2+H2O	5.00E-11	0.00E+00	0.00E+00
R463.	C2H3+C2H3=C2H2+C2H4	1.59E-12	0.00E+00	0.00E+00
R464.	C2H+H=C2H2	1.66E-07	0.00E+00	0.00E+00
R465.	C2H+H+M=C2H2+M	1.03E-14	-4.80E+00	9.56E+02

R466.	C2H+O=CH+CO	8.30E-11	0.00E+00	0.00E+00
R467.	C2H+OH=H+HCCO	3.32E-11	0.00E+00	0.00E+00
R468.	C2H+02=HC0+C0	8.30E-11	0.00E+00	7.55E+02
R469.	C2H+H2=H+C2H2	8.14E-19	2.50E+00	2.82E+02
R470.	C2H2=H2CC	8.00E+14	-5.20E-01	2.55E+04
R471.	C2H2+M=H2CC+M	4.07E-09	-6.40E-01	2.50E+04
R472.	C2H2+0=CH2+C0	1.23E-15	1.28E+00	1.24E+03
R473.	C2H2+O=HCCO+H	4.91E-15	1.28E+00	1.24E+03
R474.	C2H2+OH=C2H+H2O	4.37E-18	2.14E+00	8.58E+03
R475.	C2H2+OH=HCCOH+H	4.01E-18	2.00E+00	6.40E+03
R476.	C2H2+OH=CH2CO+H	1.25E-17	1.55E+00	1.06E+03
R477.	C2H2+OH=CH3+CO	2.12E-15	7.30E-01	1.30E+03
R478.	C2H2+OH=C2H2OH	2.30E+07	-6.09E+00	3.19E+03
R479.	C2H2+HC0=C2H3+C0	1.66E-17	2.00E+00	3.02E+03
R480.	С2H2+CH2=C3H3+H	1.99E-11	0.00E+00	3.33E+03
R481.	C2H2+CH2(S)=C3H3+H	3.32E-11	0.00E+00	0.00E+00
R482.	C2H2+HCCO=C3H3+CO	1.66E-13	0.00E+00	1.51E+03
R483	$H_2CC+H=C_2H_2+H$	1.66E-10	0.00E+00	0.00E+00
R484	H2CC+DH=CH2CD+H	3.32E-11	0.00E+00	0.00E+00
R485	H2CC+O2=HCO+HCO	1 66E-11	0 00E+00	0 00E+00
R486	H+HCCOH=H+CH2CO	1 66E-11	0 00E+00	0 00E+00
R487	C2H50H=C2H4+H20	5 23F+43	-8 90F+00	4 10F+04
R/88		5 55F+64	-1 45E+01	5 34F+04
R/80	C2H50H=C2H5+0H	4 A6E+65	-1 /9F+01	5.65E+04
R409.		4.40E+03 3.30E-11	0.005+00	2 66F+04
D/01	$C_{2}N_{2}O_{1}O_{2} = C_{2}N_{2}O_{1}O_{2}O_{2}O_{2}O_{2}O_{2}O_{2}O_{2}O_{2$	3.32E 11 2.40E-11	0.000000	2.000104
R491. D/00	C2H50H+02-5C2H40H+H02	2.49E-11 1.46E-10	0.00E+00	2.52E+04
R492.	C2H50H+H=BC2H40H+H2	1.40E-19	2.00E+00	1.40E+03
R493.		0.02E-20	2.01E+00	3.77ETUS
R494. R405		1.57E-21	3.14E+00	4.305+03
R495.		1.19E-19	2.54E+00	-7.72E+02
R496.		9.47E-24	3.38E+00	-1.20E+03
R497.		9.65E-27	4.28E+00	-1.79E+03
R498.		5.81E-29	5.26E+00	3.76E+03
R499.	C2H5UH+HU2=PC2H4UH+H2U2	6.62E-26	4.30E+00	7.72E+03
R500.	C2H5UH+HU2=C2H5U+H2U2	1.07E-30	5.30E+00	5.30E+03
R501.	C2H5UH+CH3U2=PC2H4UH+CH3U2H	2.04E-20	2.55E+00	7.93E+03
R502.	C2H5UH+CH3U2=SC2H4UH+CH3U2H	1.36E-20	2.55E+00	5.41E+03
R503.	C2H50H+CH302=C2H50+CH302H	4.15E-12	0.00E+00	1.21E+04
R504.	C2H5OH+O=PC2H4OH+OH	1.61E-21	3.23E+00	2.34E+03
R505.	C2H5OH+O=SC2H4OH+OH	2.41E-19	2.47E+00	4.41E+02
R506.	C2H50H+0=C2H50+0H	2.42E-27	4.73E+00	8.69E+02
R507.	C2H5OH+CH3=PC2H4OH+CH4	5.48E-22	3.30E+00	6.18E+03
R508.	C2H5OH+CH3=SC2H4OH+CH4	3.31E-23	3.37E+00	3.84E+03
R509.	C2H5OH+CH3=C2H5O+CH4	3.38E-24	3.57E+00	3.89E+03
R510.	C2H5OH+C2H5=PC2H4OH+C2H6	8.30E-14	0.00E+00	6.74E+03
R511.	C2H50H+C2H5=SC2H40H+C2H6	8.30E-14	0.00E+00	5.23E+03
R512.	SC2H4OH=CH3CHO+H	5.36E+55	-1.32E+01	2.61E+04
R513.	SC2H4OH=C2H3OH+H	3.79E+53	-1.25E+01	2.64E+04
R514.	SC2H4OH=C2H5O	1.81E+55	-1.33E+01	2.67E+04
R515.	SC2H4OH=PC2H4OH	5.82E+44	-1.03E+01	2.78E+04
R516.	02C2H4OH=PC2H4OH+02	3.90E+16	-1.00E+00	1.51E+04
R517.	02C2H4OH=OH+CH2O+CH2O	3.13E+09	0.00E+00	9.51E+03
R518.	SC2H40H+02=CH3CH0+H02	8.77E-07	-1.64E+00	4.22E+02
R519.	SC2H4OH+O2=C2H3OH+HO2	1.27E-21	2.45E+00	-1.49E+02

R520.	CH3COCH3=CH3CO+CH3	1.31E+42	-7.66E+00	4.76E+04
R521.	CH3COCH3+OH=CH3COCH2+H2O	2.08E-19	2.48E+00	2.24E+02
R522.	CH3COCH3+H=CH3COCH2+H2	1.63E-18	2.43E+00	2.60E+03
R523.	CH3COCH3+O=CH3COCH2+OH	8.52E-13	2.11E-01	2.46E+03
R524.	CH3COCH3+CH3=CH3COCH2+CH4	6.58E-13	0.00E+00	4.92E+03
R525.	СНЗСОСНЗ+СНЗО=СНЗСОСН2+СНЗОН	7.21E-13	0.00E+00	3.25E+03
R526.	CH3COCH3+02=CH3COCH2+H02	1.00E-10	0.00E+00	2.44E+04
R527.	CH3COCH3+H02=CH3COCH2+H2O2	2.82E-11	0.00E+00	1.03E+04
R528.	CH3COCH3+CH3O2=CH3COCH2+CH3O2H	2.82E-11	0.00E+00	1.03E+04
R529.	CH2CO+CH3=CH3COCH2	2.92E-20	2.48E+00	3.08E+03
R530.	CH3COCH2+02=CH3COCH202	1.99E-13	0.00E+00	-5.54E+02
R531.	CH3COCH3+CH3COCH2O2=CH3COCH2+C3KET21	1.66E-13	0.00E+00	2.52E+03
R532.	CH20+CH3C0CH202=HC0+C3KET21	2.14E-13	0.00E+00	4.53E+03
R533.	H02+CH3COCH202=C3KET21+02	1.66E-12	0.00E+00	0.00E+00
R534.	C2H3+HCO=C2H3CHO	3.01E-11	0.00E+00	0.00E+00
R535.	C2H3CH0+H=C2H3C0+H2	2.23E-11	0.00E+00	1.66E+03
R536.	C2H3CH0+0=C2H3C0+0H	9.86E-12	0.00E+00	9.40E+02
R537.	C2H3CH0+OH=C2H3C0+H20	1.53E-17	1.50E+00	-4.84E+02
R538.	C2H3CH0+02=C2H3C0+H02	1.67E-11	0.00E+00	2.05E+04
R539.	C2H3CH0+H02=C2H3C0+H202	5.00E-12	0.00E+00	6.00E+03
R540.	C2H3CH0+CH3=C2H3C0+CH4	4.33E-18	1.78E+00	2.97E+03
R541.	C2H3CH0+C2H3=C2H3C0+C2H4	2.89E-12	0.00E+00	4.25E+03
R542.	C2H3CHO+CH3O=C2H3CO+CH3OH	1.66E-12	0.00E+00	1.66E+03
R543.	C2H3CH0+CH302=C2H3C0+CH302H	5.00E-12	0.00E+00	6.00E+03
R544	C2H3+CD=C2H3CD	2.51E-13	0.00E+00	2.42E+03
R545	C2H5+HCD=C2H5CH0	3.01E-11	0.00E+00	0.00E+00
R546	C2H5CH0+H=C2H5C0+H2	6.64E-11	0.00E+00	2.11E+03
R547	C2H5CH0+0=C2H5C0+0H	8 30E-12	0.00E+00	9 01E+02
R548	C2H5CH0+0H=C2H5C0+H20	4 47E-14	7 60E-01	-1 71E+02
R549	C2H5CH0+CH3=C2H5C0+CH4	4 33E-18	1 78E+00	2 97E+03
R550	C2H5CH0+H02=C2H5C0+H202	4 65F-12	0.00F+00	6 84F+03
R551	C2H5CH0+CH30=C2H5C0+CH30H	1.66E-12	0.00E+00	1 66F+03
R552	C2H5CH0+CH3O2=C2H5CO+CH3O2H	5 00F-12	0.00E+00	6 00F+03
R553	C2H5CH0+C2H5=C2H5C0+C2H6	1 66F-12	0.00E+00	4 03F+03
R554	C2H5CH0+C2H50=C2H5C0+C2H50H	1.00E 12	0.00E+00	1 66F+03
R555	C2H5CH0+C2H5C2=C2H5C0+C2H5C2H	5 00E-12	0.00E+00	6 00E+03
R556	C2H5CH0+02=C2H5C0+H02	1 67F-11	0.00E+00	2 05F+04
R557	C2H5CH0+CH3CO3=C2H5CO+CH3CO3H	5 00F-12	0.00E+00	6 00F+03
R558	C2H5CH0+C2H3=C2H5C0+C2H4	2 82F-12	0.00E+00	4 25E+03
REEQ	C2H5+C0-C2H5C0	2.02L 12 2.51E - 13	0.000000	2 /2E+03
R560	CH30CH3-CH3+CH30	2.01L 10 / 38F±01	-1 57E+00	2.42L+00
R500.	CH30CH3+M-CH3+CH30+M	4.30E-21	1.57E+00	4.226104
R501. R560		1.25E 00 1 05E-17	2 00E+00	-3 28F+02
R563	CH30CH3+H=CH30CH2+H2	1.03E 17	2.00E+00	1 70F+03
R564		1.20E 17	1 36F+00	1 135+03
N504. R565		1.23E 13 1.44E-21	1.30E+00	6 08F+03
N505.	CH30CH3+H02-CH30CH2+H202	5 10E-00	2 10E+00	6 64E+03
N500.		3.102 22	5.120100	0.04E+03
DECO	CHSUCHS+CHS=CHSUCH2+CH4	2.40E-30	0.00E+00	2.07 E+03
N000.	CH30CH3+CH30-CH30CH2+CH3CH CH30CH3+CH30-CH30CH3+CH3CH	1 00E-10		2.205704
NOUS. DE70		1.00E-12 9 20E-10		2.00E+03
DE71		0.30E-12 7 35E-00	0.00ET00 2 60E±00	0.90ETU3 7 00E±09
R570	CH30CH3+0CH0-CH30CH2+H02CH0 CH30CH3+0CH0-CH30CH2+H02CH0	$1.50E^{-20}$	2.00ET00	1.00ETU3
R572		1 60E±12	0.005+00	0.90ETU3
1010.		1.005-12	0.005-00	1.205-04

R574.	CH30CH2+CH30=CH30CH3+CH20	4.00E-11	0.00E+00	0.00E+00
R575.	CH30CH2+CH20=CH30CH3+HC0	9.12E-21	2.80E+00	2.95E+03
R576.	CH30CH2+CH3CH0=CH30CH3+CH3C0	2.09E-12	0.00E+00	4.28E+03
R577.	CH30CH2+02=CH30CH202	3.32E-12	0.00E+00	0.00E+00
R578.	CH30CH202+CH20=CH30CH202H+HC0	1.66E-12	0.00E+00	5.87E+03
R579.	CH30CH202+CH3CH0=CH30CH202H+CH3C0	4.65E-12	0.00E+00	6.84E+03
R580.	CH30CH202+CH30CH202=02+CH30CH20+CH30C	2.57E-01	-4.50E+00	0.00E+00
R581.	CH30CH20+0H=CH30CH202H	3.32E-11	0.00E+00	0.00E+00
R582.	CH30+CH20=CH30CH20	1.66E-13	0.00E+00	4.01E+03
R583.	CH30CH20+02=CH30CH0+H02	8.30E-14	0.00E+00	2.52E+02
R584.	CH30CH0+H=CH30CH20	1.66E-11	0.00E+00	3.94E+03
R585.	CH30CH202=CH20CH202H	6.00E+10	0.00E+00	1.09E+04
R586.	CH20CH202H=0H+CH20+CH20	1.50E+13	0.00E+00	1.04E+04
R587.	CH20CH202H+02=02CH20CH202H	1.16E-12	0.00E+00	0.00E+00
R588.	02CH20CH202H=H02CH20CH0+0H	4.00E+10	0.00E+00	9.35E+03
R589.	H02CH20CH0=0CH20CH0+0H	2.00E+16	0.00E+00	2.04E+04
R590.		2.08E-13	0.00E+00	5.99E+03
R591		1.00E+11	0.00E+00	7.05E+03
R592		2.49E-13	0.00E+00	2.42E+03
R593	CH20H+CO2=H0CH20CO	2.10E 10 2.49E-13	0 00E+00	1 80E+04
R594		1 66F-10	0.00E+00	0.00F+00
R595		1.66F-10	0.00E+00	0.00E+00
R596		1.00E 10 1.00E+14	0.00E+00	3 15E+04
R507		1 025+37	-1 21E+01	3 705+04
R508		1.02L-07	0.005+00	0.005+00
N590.		4.301 11	0.000000	0.000000
R099.	CH3+0CH0-CH30CH0	1.00E-11 1.66E-11	0.005+00	0.00E+00
R000.		1.00E-11	0.000+00	2.50E+04
ROUI.		3.40E-11	1.00E+00	2.02E+04
ROU2.		2.026-17	1.00E+00	4.70E+02
R603.		8.75E-15	9.70E-01	7.98E+02
R604.		8.00E-21	2.602+00	7.00E+03
R605.		3.95E-20	2.55E+00	8.30E+03
R606.		4.57E-19	2.45E+00	1.42E+03
R607.	CH3UCHU+U=CH2UCHU+UH	1.63E-18	2.43E+00	2.39E+03
R608.	CH3UCHU+H=CH3UCU+H2	1.08E-18	2.40E+00	2.25E+03
R609.	CH3UCHU+H=CH2UCHU+H2	1.10E-18	2.54E+00	3.40E+03
R610.	CH3UCHU+CH3=CH3UCU+CH4	1.25E-24	3.46E+00	2.76E+03
R611.	CH30CH0+CH3=CH20CH0+CH4	7.51E-25	3.65E+00	3.60E+03
R612.	CH30CH0+CH30=CH30C0+CH30H	9.10E-13	0.00E+00	2.52E+03
R613.	CH30CH0+CH30=CH20CH0+CH30H	3.60E-13	0.00E+00	3.25E+03
R614.	CH30CH0+CH302=CH30C0+CH302H	8.00E-21	2.60E+00	7.00E+03
R615.	CH30CH0+CH302=CH20CH0+CH302H	3.95E-20	2.55E+00	8.30E+03
R616.	CH30CH0+HC0=CH30C0+CH20	8.97E-18	1.90E+00	8.56E+03
R617.	CH30CH0+HC0=CH20CH0+CH20	1.70E-19	2.50E+00	9.27E+03
R618.	CH30C0=CH20CH0	1.63E+12	-1.80E-01	2.05E+04
R619.	CH3+CO2=CH3OCO	7.90E-17	1.54E+00	1.75E+04
R620.	CH30+C0=CH30C0	2.57E-18	2.02E+00	2.88E+03
R621.	CH20+HC0=CH20CH0	2.49E-13	0.00E+00	5.99E+03
R622.	C3H8=CH3+C2H5	8.51E+36	-5.84E+00	4.90E+04
R623.	C3H8+M=CH3+C2H5+M	9.37E+50	-1.57E+01	4.97E+04
R624.	NC3H7+H=C3H8	1.66E-10	0.00E+00	0.00E+00
R625.	IC3H7+H=C3H8	1.66E-10	0.00E+00	0.00E+00
R626.	C3H8+O2=IC3H7+HO2	3.32E-11	0.00E+00	2.50E+04
R627.	C3H8+02=NC3H7+H02	9.96E-11	0.00E+00	2.63E+04

R628.	H+C3H8=H2+IC3H7	2.16E-18	2.40E+00	2.25E+03
R629.	H+C3H8=H2+NC3H7	5.80E-19	2.69E+00	3.25E+03
R630.	C3H8+O=IC3H7+OH	9.12E-19	2.50E+00	1.58E+03
R631.	C3H8+O=NC3H7+OH	6.16E-18	2.40E+00	2.77E+03
R632.	C3H8+OH=NC3H7+H2O	1.75E-14	9.70E-01	7.98E+02
R633.	C3H8+OH=IC3H7+H2O	7.75E-17	1.61E+00	-1.76E+01
R634.	C3H8+H02=IC3H7+H2O2	1.05E-22	3.37E+00	6.90E+03
R635.	C3H8+H02=NC3H7+H2O2	6.77E-23	3.59E+00	8.64E+03
R636.	CH3+C3H8=CH4+IC3H7	1.06E-19	2.17E+00	3.78E+03
R637.	CH3+C3H8=CH4+NC3H7	1.50E-24	3.65E+00	3.60E+03
R638.	IC3H7+C3H8=NC3H7+C3H8	4.98E-14	0.00E+00	6.49E+03
R639.	C2H3+C3H8=C2H4+IC3H7	1.66E-13	0.00E+00	5.23E+03
R640.	C2H3+C3H8=C2H4+NC3H7	1.66E-13	0.00E+00	5.23E+03
R641.	C2H5+C3H8=C2H6+IC3H7	1.66E-13	0.00E+00	5.23E+03
R642.	C2H5+C3H8=C2H6+NC3H7	1.66E-13	0.00E+00	5.23E+03
R643	C3H8+C3H5-A=NC3H7+C3H6	1.32E-12	0.00E+00	1.03E+04
R644	C3H8+C3H5-A=TC3H7+C3H6	1 32E-12	0 00E+00	8 15E+03
R645	C3H8+CH3O=NC3H7+CH3OH	4 98F-13	0.00E+00	3 52F+03
R646	C3H8+CH30=TC3H7+CH30H	4.00E 10 4 98F-13	0.00E+00	3 52F+03
R647	CH302+C3H8=CH302H+NC3H7	2 30F-24	3 97E+00	9 20F+03
R648	CH302+C3H8-CH302H+NC3H7	2.50E 24 1 60E-23	3.58E+00	7 /5E+03
R040.	COUEOO + COUEOOU + 1COU	1.09E-23	3.00E+00	0 20E+03
R049.	C2H5U2+C5H6-C2H5U2H+NC5H7	2.30E-24	3.97E+00	9.20E+03
RODU.	C2H5U2+C3H8=C2H5U2H+1C3H7	1.09E-23	3.58E+00	1.45E+03
R051.	NC3H7U2+C3H8=NC3H7U2H+NC3H7	2.82E-11	0.00E+00	1.03E+04
R652.	NC3H/U2+C3H8=NC3H/U2H+1C3H/	3.32E-12	0.00E+00	8.55E+03
R653.	1C3H7U2+C3H8=1C3H7U2H+NC3H7	2.82E-11	0.00E+00	1.03E+04
R654.	1C3H/U2+C3H8=1C3H/U2H+1C3H/	3.32E-12	0.00E+00	8.55E+03
R655.	C3H8+CH3CU3=1C3H7+CH3CU3H	3.32E-12	0.00E+00	8.55E+03
R656.	C3H8+CH3CU3=NC3H7+CH3CU3H	2.82E-11	0.00E+00	1.03E+04
R657.	C3H8+O2CHO=NC3H7+HO2CHO	9.17E-20	2.55E+00	8.29E+03
R658.	C3H8+O2CHO=IC3H7+HO2CHO	2.45E-20	2.60E+00	7.00E+03
R659.	H+C3H6=IC3H7	7.04E-13	5.10E-01	6.19E+02
R660.	IC3H7+H=C2H5+CH3	3.32E-11	0.00E+00	0.00E+00
R661.	IC3H7+02=C3H6+H02	7.47E-43	0.00E+00	2.53E+03
R662.	IC3H7+OH=C3H6+H2O	4.00E-11	0.00E+00	0.00E+00
R663.	IC3H7+O=CH3COCH3+H	8.00E-11	0.00E+00	0.00E+00
R664.	IC3H7+O=CH3CHO+CH3	8.00E-11	0.00E+00	0.00E+00
R665.	CH3+C2H4=NC3H7	2.92E-20	2.48E+00	3.08E+03
R666.	H+C3H6=NC3H7	4.15E-13	5.10E-01	1.32E+03
R667.	NC3H7+02=C3H6+H02	4.98E-43	0.00E+00	1.51E+03
R668.	C2H5CH0+NC3H7=C2H5C0+C3H8	2.82E-12	0.00E+00	4.25E+03
R669.	C2H5CH0+IC3H7=C2H5C0+C3H8	2.82E-12	0.00E+00	4.25E+03
R670.	C2H5CH0+C3H5-A=C2H5C0+C3H6	2.82E-12	0.00E+00	4.25E+03
R671.	C2H3+CH3=C3H6	4.15E-11	0.00E+00	0.00E+00
R672.	C2H3+CH3+M=C3H6+M	1.18E+11	-1.19E+01	4.92E+03
R673.	СЗН5-А+Н=СЗН6	3.32E-10	0.00E+00	0.00E+00
R674.	C3H5-A+H+M=C3H6+M	3.67E+12	-1.20E+01	3.00E+03
R675.	C3H6=C3H5-S+H	7.71E+69	-1.61E+01	7.05E+04
R676.	СЗН6=СЗН5-Т+Н	5.62E+71	-1.66E+01	7.01E+04
R677.	C3H6+0=C2H5+HC0	2.62E-17	1.76E+00	-6.12E+02
R678.	C3H6+0=CH2C0+CH3+H	4.15E-17	1.76E+00	3.82E+01
R679.	C3H6+0=CH3CHCO+H+H	4.15E-17	1.76E+00	3.82E+01
R680.	СЗН6+0=СЗН5-А+ОН	8.70E-13	7.00E-01	2.96E+03
R681.	C3H6+0=C3H5-S+OH	1.99E-13	7.00E-01	4.51E+03
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R682.	C3H6+O=C3H5-T+OH	1.00E-13	7.00E-01	3.84E+03
R683.	C3H6+OH=C3H5-A+H2O	3.27E-18	2.20E+00	2.72E+02
R684.	C3H6+OH=C3H5-S+H2O	3.50E-18	2.00E+00	1.40E+03
R685.	C3H6+OH=C3H5-T+H2O	1.84E-18	2.00E+00	7.30E+02
R686.	C3H6+H02=C3H5-A+H2O2	4.48E-20	2.50E+00	6.21E+03
R687.	C3H6+H02=C3H5-S+H2O2	2.99E-20	2.50E+00	1.39E+04
R688.	C3H6+H02=C3H5-T+H2O2	1.49E-20	2.50E+00	1.19E+04
R689.	СЗН6+Н=СЗН5-А+Н2	2.87E-19	2.50E+00	1.25E+03
R690.	C3H6+H=C3H5-S+H2	1.34E-18	2.50E+00	6.18E+03
R691.	C3H6+H=C3H5-T+H2	6.73E-19	2.50E+00	4.93E+03
R692.	C3H6+H=C2H4+CH3	1.33E-02	-2.39E+00	5.63E+03
R693.	C3H6+02=C3H5-A+H02	6.64E-12	0.00E+00	2.01E+04
R694.	C3H6+02=C3H5-S+H02	3.32E-12	0.00E+00	3.17E+04
R695.	C3H6+02=C3H5-T+H02	2.32E-12	0.00E+00	3.05E+04
R696.	C3H6+CH3=C3H5-A+CH4	3.67E-24	3.50E+00	2.86E+03
R697	C3H6+CH3=C3H5-S+CH4	2.24E-24	3.50E+00	6.47E+03
R698	C3H6+CH3=C3H5-T+CH4	1 39E-24	3 50E+00	5 87E+03
R600	C3H6+C2H5=C3H5-A+C2H6	1.66E-13	0.00E+00	4 93E+03
R700	C3H6+CH3CD3=C3H5-A+CH3CD3H	5 38F-13	0.00E+00	7 50E+03
D701		5.30E 13	0.0000	7.50E+03
R701.	$C_{2}HC_{1}HO_{2}-C_{2}HC_{1}-C_{1}HO_{2}HO_{2}$	0.30E-13	0.00E+00	7.50E+03
R/UZ.		2.14E-12 E 20E 12	0.00E+00	7.506+03
R/U3.		5.38E-13	0.00E+00	7.50E+03
R/04.	C3H0+NC3H7U2=C3H5-A+NC3H7U2H	5.38E-13	0.00E+00	7.50E+03
R/05.	C3H6+1C3H/U2=C3H5-A+1C3H/U2H	5.38E-13	0.00E+00	7.50E+03
R706.	C3H6+UH=C3H6UH	1.65E-12	0.00E+00	-4.83E+02
R707.	C3H6UH+U2=HUC3H6U2	1.99E-13	0.00E+00	-5.54E+02
R708.	HUC3H6U2=CH3CHU+CH2U+UH	1.25E+10	0.00E+00	9.51E+03
R709.	C2H2+CH3=C3H5-A	4.45E+29	-1.28E+01	1.80E+04
R710.	C3H4-A+H=C3H5-A	2.52E+35	-1.35E+01	1.36E+04
R711.	C3H5-A+H02=C3H50+0H	1.16E-11	0.00E+00	-5.03E+02
R712.	C3H5-A+CH302=C3H50+CH30	1.16E-11	0.00E+00	-5.03E+02
R713.	СЗН5-А+Н=СЗН4-А+Н2	2.05E-21	3.04E+00	1.30E+03
R714.	C3H5-A+O=C2H3CHO+H	9.96E-11	0.00E+00	0.00E+00
R715.	C3H5-A+OH=C2H3CHO+H+H	6.97E+08	-5.16E+00	1.52E+04
R716.	C3H5-A+OH=C3H4-A+H2O	9.96E-12	0.00E+00	0.00E+00
R717.	СЗН5-А+СНЗ=СЗН4-А+СН4	4.98E-12	-3.20E-01	-6.59E+01
R718.	C3H5-A+C2H5=C2H6+C3H4-A	6.64E-13	0.00E+00	0.00E+00
R719.	C3H5-A+C2H5=C2H4+C3H6	6.64E-13	0.00E+00	0.00E+00
R720.	C3H5-A+C2H3=C2H4+C3H4-A	1.66E-12	0.00E+00	0.00E+00
R721.	C3H5-A+C3H5-A=C3H4-A+C3H6	1.40E-13	0.00E+00	-1.32E+02
R722.	C3H5-A+O2=C3H4-A+HO2	8.29E-09	-1.40E+00	1.13E+04
R723.	C3H5-A+O2=CH3CO+CH2O	1.98E-09	-1.01E+00	1.01E+04
R724.	C3H5-A+O2=C2H3CHO+OH	3.02E-11	-4.10E-01	1.15E+04
R725.	C3H5-A+HCO=C3H6+CO	9.96E-11	0.00E+00	0.00E+00
R726.	С2Н3+СН3=С3Н5-А+Н	2.49E+00	-2.83E+00	9.37E+03
R727.	СЗН5-А=СЗН5-Т	7.06E+56	-1.41E+01	3.82E+04
R728.	C3H5-A=C3H5-S	5.00E+51	-1.30E+01	3.69E+04
R729.	C2H2+CH3=C3H5-S	5.31E+11	-7.76E+00	6.69E+03
R730.	C3H5-S+02=CH3CH0+HC0	1.66E-13	0.00E+00	0.00E+00
R731.	C3H5-S+H=C3H4-A+H2	5.53E-12	0.00E+00	0.00E+00
R732.	C3H5-S+CH3=C3H4-A+CH4	1.66E-13	0.00E+00	0.00E+00
R733.	C2H2+CH3=C3H5-T	8.29E-02	-4.39E+00	9.49E+03
R734	C3H4-A+H=C3H5-T	1.57E+19	-9.43E+00	5.63E+03
R735	СЗН4-Р+Н=СЗН5-Т	2.012 10 2.76E+23	-1.06E+01	6 89F+03
		2.100.20	1.000.01	0.001.00

R736.	C3H5-S+H=C3H4-P+H2	5.55E-12	0.00E+00	0.00E+00
R737.	C3H5-S+0=C2H4+HC0	9.96E-11	0.00E+00	0.00E+00
R738.	C3H5-S+OH=C2H4+HCO+H	8.30E-12	0.00E+00	0.00E+00
R739.	C3H5-S+H02=C2H4+HC0+0H	3.32E-11	0.00E+00	0.00E+00
R740.	C3H5-S+HC0=C3H6+C0	1.49E-10	0.00E+00	0.00E+00
R741.	C3H5-S+CH3=C3H4-P+CH4	1.66E-13	0.00E+00	0.00E+00
R742.	C3H5-T=C3H5-S	1.50E+48	-1.27E+01	2.71E+04
R743.	C3H4-A+H=C3H5-S	8.97E+05	-6.09E+00	8.20E+03
R744.	СЗН4-А+СЗН4-А=СЗН5-А+СЗНЗ	8.30E-10	0.00E+00	3.26E+04
R745.	C3H5-T+02=C3H4-A+H02	3.14E+06	-5.59E+00	7.82E+03
R746.	C3H5-T+02=CH3C0CH2+0	6.33E-07	-1.36E+00	2.81E+03
B747.	C3H5-T+02=CH3C0+CH20	1.66E-13	0.00E+00	0.00E+00
R748	C3H5-T+H=C3H4-P+H2	5.55E-12	0.00E+00	0.00E+00
R749	C3H5-T+CH3=C3H4-P+CH4	1 66E-13	0 00E+00	0 00E+00
B750	C3H5-T+0=CH3+CH2CO	9 96F-11	0.00E+00	0.00E+00
R751	C3H5-T+0H=CH3+CH2C0+H	8 30E-12	0.00E+00	0.00E+00
R752		3 30E-11	0.00E+00	0.00E+00
R752.	$C_{2}N_{2} = 1 + NC_{2} = C_{1}S + C_{1}C_{2}C_{2} + C_{1}C_{2}$	3.32E-11	0.000+00	0.00E+00
R755.	C3H3 - D - C3H4 - A	1.49E-10	0.00E+00	0.00E+00
R/54.	C3H4-P=C3H4-A	5.15E+60	-1.39E+01	4.59E+04
R/55.	C3H3+HU2=C3H4-A+U2	4.98E-13	0.00E+00	0.00E+00
R/56.	C3H4-A+HU2=CH2CU+CH2+UH	6.64E-12	0.00E+00	9.56E+03
R/5/.	C3H4-A+UH=CH2CU+CH3	5.18E-12	0.00E+00	-2.00E+02
R758.	C3H4-A+UH=C3H3+H2U	8.80E-18	2.00E+00	1.01E+03
R759.	C3H4-A+O=C2H4+CO	3.32E-17	1.80E+00	5.03E+02
R760.	C3H4-A+0=C2H2+CH20	4.98E-27	4.61E+00	-2.14E+03
R761.	СЗН4-А+Н=СЗН3+Н2	2.16E-18	2.00E+00	2.77E+03
R762.	C3H4-A+CH3=C3H3+CH4	2.16E-12	0.00E+00	3.87E+03
R763.	C3H4-A+C3H5-A=C3H3+C3H6	3.32E-13	0.00E+00	3.87E+03
R764.	C3H4-A+C2H=C2H2+C3H3	1.66E-11	0.00E+00	0.00E+00
R765.	C3H4-P=CC3H4	1.20E+44	-9.92E+00	3.48E+04
R766.	СЗН4-Р+Н=СЗН4-А+Н	1.04E-06	-9.10E-01	5.07E+03
R767.	C3H4-P+H=C3H5-S	9.13E+04	-5.74E+00	2.16E+03
R768.	C3H4-P+H=C3H5-A	8.15E+36	-1.44E+01	1.59E+04
R769.	СЗН4-Р+Н=СЗН3+Н2	2.16E-18	2.00E+00	2.77E+03
R770.	СЗН4-Р+СЗН3=СЗН4-А+СЗНЗ	1.02E-17	1.74E+00	5.26E+03
R771.	C3H4-P+0=HCCO+CH3	1.21E-11	0.00E+00	1.13E+03
R772.	C3H4-P+0=C2H4+C0	1.66E-11	0.00E+00	1.13E+03
R773.	C3H4-P+OH=C3H3+H2O	1.66E-18	2.00E+00	5.03E+01
R774.	C3H4-P+C2H=C2H2+C3H3	1.66E-11	0.00E+00	0.00E+00
R775.	C3H4-P+CH3=C3H3+CH4	2.99E-12	0.00E+00	3.87E+03
R776.	C2H2+CH3=C3H4-P+H	4.25E-15	1.10E+00	6.87E+03
B777.	CC3H4=C3H4-A	4.89E+41	-9.17E+00	2.50E+04
B778	C3H3+H=C3H4-P	2.49E-11	0.00E+00	0.00E+00
B779	C3H3+H=C3H4-A	4 15E-12	0.00E+00	0 00E+00
B780	C2H+CH3=C3H4-P	1 33F-10	0.00E+00	0.00E+00
R781	C3H3+H03-C3H4-D+03	1.00L 10	0.00E+00	0.00E+00
B790	$C_{2}N_{-}D_{+}NO_{-}C_{2}N_{+}C_{0}D_{-}D_{0}$	4.136 12	0.000000	0.000000
R/02.	C3H4 - P + HUZ - CZH4 + CU + OH	4.90E-12	0.00E+00	9.00E+00
R/03.		0.30E-20	4.50E+00	-5.03E+02
Л/04. D705		0.01E-1Z	1 505100	1.016+03
л/ ÖD. D706		1.2/E-15	1.506+00	4.33L+U3
K/86. D707	$U_{2}H_{2} + U_{2}H_{3} = U_{3}H_{3} + U_{2}H_{4}$	1.00E-12	0.001+00	3.8/E+03
K/8/.		1.00E-12	U.UUE+00	3.8/E+03
K/88.	C3H3+U=CH2U+C2H	3.32E-11	0.008+00	U.UUE+00
R789.	C3H3+U2=CH2CO+HCO	4.98E-14	0.00E+00	1.44E+03

R790.	C3H3+H02=OH+C0+C2H3	1.33E-12	0.00E+00	0.00E+00
R791.	C3H3+HCO=C3H4-A+CO	4.15E-11	0.00E+00	0.00E+00
R792.	C3H3+HCO=C3H4-P+CO	4.15E-11	0.00E+00	0.00E+00
R793.	C2H5+C2H=C3H3+CH3	3.01E-11	0.00E+00	0.00E+00
R794.	C3H4-A+H02=C2H4+C0+OH	1.66E-12	0.00E+00	7.05E+03
R795.	C3H4-A+H02=C3H3+H202	4.98E-11	0.00E+00	7.05E+03
R796.	С2Н2+СН3=С3Н4-А+Н	8.54E-15	8.60E-01	1.11E+04
R797.	CH3CHC0+0H=C2H5+C02	2.87E-12	0.00E+00	-5.08E+02
R798.	CH3CHCO+OH=SC2H4OH+CO	3.32E-12	0.00E+00	-5.08E+02
R799.	CH3CHCO+H=C2H5+CO	7.31E-12	0.00E+00	7.34E+02
R800.	CH3CHC0+0=CH3CH0+C0	5.31E-12	0.00E+00	-2.20E+02
R801.	NC3H7+HO2=NC3H7O+OH	1.16E-11	0.00E+00	-5.03E+02
R802.	IC3H7+H02=IC3H70+0H	1.16E-11	0.00E+00	-5.03E+02
R803.	CH302+NC3H7=CH30+NC3H70	1.16E-11	0.00E+00	-5.03E+02
R804.	CH302+TC3H7=CH30+TC3H70	1.16E-11	0.00E+00	-5.03E+02
R805.	NC3H7+O2=NC3H7O2	7.51E-12	0.00E+00	0.00E+00
R806	TC3H7+D2=TC3H7D2	1.25E-11	0.00E+00	0.00E+00
R807	NC3H7O2+CH2O=NC3H7O2H+HCO	9 30F-12	0.00E+00	6 84F+03
R808	NC3H7D2+CH3CHD=NC3H7D2H+CH3CD	4 65F-12	0.00E+00	6 84F+03
R800.	TC3H7D2+CH2D=TC3H7D2H+HCD	9 30E-12	0.00E+00	6 84F+03
DQ10		0.00L 12	0.00E+00	6 8/E+03
DO11	NC2UZ02+U02-NC2UZ02U+02	4.00E 12	0.000000	-1 65E+03
DOIL.	102 + 102 - 102 + 102	2.91E-14	0.00E+00	-1.05E+03
RO12.	1C3H/U2+HU2-1C3H/U2H+U2	2.91E-14	0.000000	-1.05E+03
RO13.	C2H4+NC3H7U2=C2H3+NC3H7U2H	1.00E-11	0.002+00	1.53E+04
R814.	C2H4+1C3H7U2=C2H3+1C3H7U2H	1.88E-11	0.00E+00	1.53E+04
R815.	CH3UH+NC3H7U2=CH2UH+NC3H7U2H	1.05E-11	0.00E+00	9.74E+03
R816.	CH3UH+1C3H7U2=CH2UH+1C3H7U2H	1.05E-11	0.00E+00	9.74E+03
R817.	C2H3CHU+NC3H7U2=C2H3CU+NC3H7U2H	4.65E-12	0.00E+00	6.84E+03
R818.	C2H3CHU+1C3H7U2=C2H3CU+1C3H7U2H	4.65E-12	0.00E+00	6.84E+03
R819.	CH4+NC3H7U2=CH3+NC3H7U2H	1.86E-11	0.00E+00	1.24E+04
R820.	CH4+1C3H702=CH3+1C3H702H	1.86E-11	0.00E+00	1.24E+04
R821.	NC3H702+CH302=NC3H70+CH30+02	2.32E-08	-1.61E+00	9.36E+02
R822.	IC3H702+CH302=IC3H70+CH30+02	2.32E-08	-1.61E+00	9.36E+02
R823.	H2+NC3H702=H+NC3H702H	5.00E-11	0.00E+00	1.31E+04
R824.	H2+IC3H702=H+IC3H702H	5.00E-11	0.00E+00	1.31E+04
R825.	IC3H702+C2H6=IC3H702H+C2H5	2.82E-11	0.00E+00	1.03E+04
R826.	NC3H702+C2H6=NC3H702H+C2H5	2.82E-11	0.00E+00	1.03E+04
R827.	IC3H702+C2H5CH0=IC3H702H+C2H5C0	3.32E-13	0.00E+00	4.78E+03
R828.	NC3H702+C2H5CH0=NC3H702H+C2H5C0	3.32E-13	0.00E+00	4.78E+03
R829.	IC3H702+CH3CO3=IC3H70+CH3CO2+O2	2.32E-08	-1.61E+00	9.36E+02
R830.	NC3H702+CH3CO3=NC3H70+CH3CO2+O2	2.32E-08	-1.61E+00	9.36E+02
R831.	IC3H702+C2H502=IC3H70+C2H50+02	2.32E-08	-1.61E+00	9.36E+02
R832.	NC3H702+C2H502=NC3H70+C2H50+02	2.32E-08	-1.61E+00	9.36E+02
R833.	IC3H702+IC3H702=02+IC3H70+IC3H70	2.32E-08	-1.61E+00	9.36E+02
R834.	NC3H702+NC3H702=02+NC3H70+NC3H70	2.32E-08	-1.61E+00	9.36E+02
R835.	IC3H702+NC3H702=IC3H70+NC3H70+02	2.32E-08	-1.61E+00	9.36E+02
R836.	IC3H702+CH3=IC3H70+CH30	1.16E-11	0.00E+00	-5.03E+02
R837.	IC3H702+C2H5=IC3H70+C2H50	1.16E-11	0.00E+00	-5.03E+02
R838.	IC3H702+IC3H7=IC3H70+IC3H70	1.16E-11	0.00E+00	-5.03E+02
R839.	IC3H702+NC3H7=IC3H70+NC3H70	1.16E-11	0.00E+00	-5.03E+02
R840.	IC3H702+C3H5-A=IC3H70+C3H50	1.16E-11	0.00E+00	-5.03E+02
R841.	NC3H702+CH3=NC3H70+CH30	1.16E-11	0.00E+00	-5.03E+02
R842.	NC3H702+C2H5=NC3H70+C2H50	1.16E-11	0.00E+00	-5.03E+02
R843.	NC3H702+IC3H7=NC3H70+IC3H70	1.16E-11	0.00E+00	-5.03E+02

R844.	NC3H7O2+NC3H7=NC3H7O+NC3H7O	1.16E-11	0.00E+00	-5.03E+02
R845.	NC3H702+C3H5-A=NC3H70+C3H50	1.16E-11	0.00E+00	-5.03E+02
R846.	NC3H702H=NC3H70+0H	1.50E+16	0.00E+00	2.14E+04
R847.	IC3H70+0H=IC3H702H	1.66E-09	-8.00E-01	0.00E+00
R848.	C2H5+CH20=NC3H70	1.66E-13	0.00E+00	1.76E+03
R849.	C2H5CH0+H=NC3H70	6.64E-12	0.00E+00	3.15E+03
R850.	CH3+CH3CH0=IC3H70	1.66E-13	0.00E+00	4.66E+03
R851.	CH3COCH3+H=IC3H7O	3.32E-12	0.00E+00	3.66E+03
R852.	IC3H70+02=CH3C0CH3+H02	1.51E-14	0.00E+00	1.96E+02
R853.	NC3H702=C3H600H1-2	6.00E+11	0.00E+00	1.35E+04
R854.	NC3H702=C3H600H1-3	1.13E+11	0.00E+00	1.23E+04
R855.	IC3H702=C3H600H2-1	1.80E+12	0.00E+00	1.48E+04
R856.	TC3H702=C3H600H2-2	1.23E+35	-6.96E+00	2.46E+04
R857	C3H600H1-2=C3H601-2+0H	6.00E+11	0.00E+00	1.11E+04
R858	C3H600H1-3=C3H601-3+0H	7 50E+10	0 00E+00	7 67E+03
R859	C3H600H2-1=C3H601-2+0H	6 00E+11	0.00E+00	1 11E+04
R860	C3H6+H02=C3H600H1-2	1 66F-13	0.00E+00	5 54F+03
R861	$C_{3H6+H02} = C_{3H600H1} - 2$	1.00L 13	0.00000	5 01E+03
R001.	C3H600H1 - 3 - 0H + CH20 + C2H4	1.00E 13 3 0/E+15	-7 90E-01	1 38F±0/
D062.	C_{2}	6 54E+07	-E 1/E+00	1 025+04
DOC1	C_{2}^{2}	0.04E+27	-5.14E+00	1.93E+04
ROO4.	C_{2}	1.31E+33	-7.01E+00	Z.426+04
ROOD.		9.00E+14	0.00E+00	7.55E+02
R000.		8.30E-12	0.00E+00	0.002+00
R867.		7.51E-12	0.00E+00	0.00E+00
R868.	C3H6UUH2-1+U2=C3H6UUH2-1U2	7.51E-12	0.00E+00	0.00E+00
R869.	C3H6UUH1-2U2=C3KET12+UH	6.00E+11	0.00E+00	1.33E+04
R870.	C3H6UUH1-3U2=C3KET13+UH	7.50E+10	0.00E+00	1.08E+04
R871.	C3H6UUH2-1U2=C3KET21+UH	3.00E+11	0.00E+00	1.20E+04
R872.	C3H6U0H2-102=C3H51-2,300H	1.13E+11	0.00E+00	1.23E+04
R873.	C3H6OOH1-202=C3H51-2,30OH	9.00E+11	0.00E+00	1.48E+04
R874.	C3H51-2,300H=AC3H500H+H02	2.56E+13	-4.90E-01	8.94E+03
R875.	СЗН6ООН1-302=СЗН52-1,300Н	6.00E+11	0.00E+00	1.35E+04
R876.	C3H52-1,300H=AC3H500H+H02	1.15E+14	-6.30E-01	8.68E+03
R877.	C3KET12=CH3CH0+HC0+OH	9.45E+15	0.00E+00	2.16E+04
R878.	C3KET13=CH2O+CH2CHO+OH	1.00E+16	0.00E+00	2.16E+04
R879.	C3KET21=CH20+CH3C0+OH	1.00E+16	0.00E+00	2.16E+04
R880.	C3H5O+OH=AC3H5OOH	3.32E-11	0.00E+00	0.00E+00
R881.	C3H5O=C2H3CHO+H	1.00E+14	0.00E+00	1.46E+04
R882.	C2H3+CH2O=C3H5O	2.49E-13	0.00E+00	5.33E+03
R883.	C3H50+02=C2H3CH0+H02	1.66E-12	0.00E+00	3.02E+03
R884.	C2H3OOH=CH2CHO+OH	8.40E+14	0.00E+00	2.16E+04
R885.	C3H601-2=C2H4+CH20	6.00E+14	0.00E+00	3.02E+04
R886.	C3H601-2+0H=CH20+C2H3+H20	8.30E-12	0.00E+00	0.00E+00
R887.	C3H6O1-2+H=CH2O+C2H3+H2	4.37E-17	2.00E+00	2.52E+03
R888.	C3H601-2+0=CH20+C2H3+OH	1.40E-10	0.00E+00	2.62E+03
R889.	C3H601-2+H02=CH20+C2H3+H202	1.66E-11	0.00E+00	7.55E+03
R890.	C3H6O1-2+CH3O2=CH2O+C2H3+CH3O2H	1.66E-11	0.00E+00	9.56E+03
R891.	C3H6O1-2+CH3=CH2O+C2H3+CH4	3.32E-13	0.00E+00	5.03E+03
R892.	C3H6O1-3=C2H4+CH2O	6.00E+14	0.00E+00	3.02E+04
R893.	C3H601-3+OH=CH2O+C2H3+H2O	8.30E-12	0.00E+00	0.00E+00
R894.	C3H601-3+0=CH20+C2H3+OH	1.40E-10	0.00E+00	2.62E+03
R895.	C3H601-3+H=CH20+C2H3+H2	4.37E-17	2.00E+00	2.52E+03
R896.	C3H601-3+CH302=CH20+C2H3+CH302H	1.66E-11	0.00E+00	9.56E+03
R897.	C3H601-3+H02=CH20+C2H3+H202	1.66E-11	0.00E+00	7.55E+03

R898.	C3H601-3+CH3=CH20+C2H3+CH4	3.32E-13	0.00E+00	5.03E+03
R899.	IC3H702=C3H6+H02	1.20E+43	-9.43E+00	2.09E+04
R900.	NC3H702=C3H6+H02	4.31E+36	-7.50E+00	1.99E+04
R901.	C4H10=C2H5+C2H5	1.36E+36	-6.04E+00	4.68E+04
R902.	C4H10+M=C2H5+C2H5+M	7.84E-06	0.00E+00	2.49E+04
R903.	C4H10=NC3H7+CH3	6.60E+52	-1.06E+01	5.05E+04
R904.	C4H1O+M=NC3H7+CH3+M	8.87E-07	0.00E+00	2.16E+04
R905.	PC4H9+H=C4H10	5.99E-11	0.00E+00	0.00E+00
R906.	SC4H9+H=C4H10	5.99E-11	0.00E+00	0.00E+00
R907.	C4H10+02=PC4H9+H02	9.96E-11	0.00E+00	2.63E+04
R908.	C4H10+02=SC4H9+H02	6.64E-11	0.00E+00	2.51E+04
R909.	C4H10+C3H5-A=PC4H9+C3H6	1.32E-12	0.00E+00	1.03E+04
R910.	C4H10+C3H5-A=SC4H9+C3H6	5.25E-13	0.00E+00	8.25E+03
R911	C4H10+C2H5=PC4H9+C2H6	2.62E-13	0.00E+00	6.19E+03
R912	C4H10+C2H5=SC4H9+C2H6	1 66E-13	0 00E+00	5 23E+03
R913	C4H10+C2H3=PC4H9+C2H4	1.00E 10 1.66F-12	0.00E+00	9 06F+03
R010.	C/H10+C2H3-SC/H0+C2H4	1 335-10	0.000000	8 /5F+03
DO15	C4II10+C2II3-DC4II3+C2II4	1.55E 12 1 50E-94	0.00E+00 2.65E+00	2 60E+02
R915.	C4H10+CH3=FC4H9+CH4	1.50E-24 5.01E-24	3.05E+00	2 76E+03
N910.	C4H10+CH3=3C4H9+CH4	5.01E-24	3.40E+00	2.705+03
N917.	C4H10+H=PC4H9+H2	5.00E-19	2.095+00	3.25E+03
R918.	C4H10+H=SC4H9+H2	4.32E-18	2.40E+00	2.25E+03
R919.		1.75E-14	9.70E-01	7.98E+02
R920.	C4H10+UH=SC4H9+H2U	1.55E-16	1.61E+00	-1.76E+01
R921.	C4H10+U=PC4H9+UH	1.88E-10	0.00E+00	3.95E+03
R922.	C4H10+0=SC4H9+0H	9.33E-11	0.00E+00	2.62E+03
R923.	C4H10+H02=PC4H9+H202	6.77E-23	3.59E+00	8.64E+03
R924.	C4H10+H02=SC4H9+H2O2	2.10E-22	3.37E+00	6.90E+03
R925.	C4H10+CH30=PC4H9+CH30H	4.98E-13	0.00E+00	3.52E+03
R926.	C4H10+CH30=SC4H9+CH3OH	9.96E-13	0.00E+00	3.52E+03
R927.	C4H10+C2H50=PC4H9+C2H5OH	4.98E-13	0.00E+00	3.52E+03
R928.	C4H10+C2H50=SC4H9+C2H5OH	9.96E-13	0.00E+00	3.52E+03
R929.	C4H10+PC4H9=SC4H9+C4H10	1.66E-13	0.00E+00	5.23E+03
R930.	C4H10+CH3CO3=PC4H9+CH3CO3H	2.82E-11	0.00E+00	1.03E+04
R931.	C4H10+CH3CO3=SC4H9+CH3CO3H	1.86E-11	0.00E+00	8.91E+03
R932.	C4H10+02CH0=PC4H9+H02CH0	2.79E-11	0.00E+00	1.03E+04
R933.	C4H10+02CH0=SC4H9+H02CH0	1.86E-11	0.00E+00	8.90E+03
R934.	CH302+C4H10=CH302H+PC4H9	2.30E-24	3.97E+00	9.20E+03
R935.	CH302+C4H10=CH302H+SC4H9	3.38E-23	3.58E+00	7.45E+03
R936.	C2H5O2+C4H10=C2H5O2H+PC4H9	6.77E-23	3.59E+00	8.64E+03
R937.	C2H5O2+C4H10=C2H5O2H+SC4H9	2.10E-22	3.37E+00	6.90E+03
R938.	NC3H702+C4H10=NC3H702H+PC4H9	2.82E-11	0.00E+00	1.03E+04
R939.	NC3H702+C4H10=NC3H702H+SC4H9	1.86E-11	0.00E+00	8.91E+03
R940.	IC3H702+C4H10=IC3H702H+PC4H9	2.82E-11	0.00E+00	1.03E+04
R941.	IC3H702+C4H10=IC3H702H+SC4H9	1.86E-11	0.00E+00	8.91E+03
R942.	PC4H902+C3H8=PC4H902H+NC3H7	2.82E-11	0.00E+00	1.03E+04
R943	PC4H9D2+C3H8=PC4H9D2H+TC3H7	3 32E-12	0 00E+00	8 55E+03
R944	PC2HQD2+C2H1D=PC2HQD2H+PC2HQ	2 82F-11	0.00E+00	1 03F+04
RQ15	PC/HQD2+C/H1D=PC/HQD2H+SC/HQD2H	1 86F-11	0.00E+00	8 91F+03
RQ16	CURDD3+C3H8=CUNDOD01+NC3D3	1.00E 11 0 20E-11	0.005+00	1 03510
R0/7		2.02E-11 2.20E-10		2.00ETV4
11341. D010		0.02E-12		1 02E+03
n940. R0/0	$CAHOO_CAHO_CAHO_CAHOO CAHOO $	2.02E-11 1 02E-11		1.U3E+U4
NJ4J. DOFO	DC4U0-CC4U0 DC4U0-CC4U0	1.00E-11 2.565.40		1 000104
RYOU.		3.50E+10	0.00E-01	1.0017.04
K951.	P04N9=504N9	3.80E+10	6./UE-01	1.845+04

R952.	C2H5+C2H4=PC4H9	2.19E-20	2.48E+00	3.08E+03
R953.	C3H6+CH3=SC4H9	2.92E-20	2.48E+00	3.08E+03
R954.	C4H8-1+H=PC4H9	4.15E-13	5.10E-01	1.32E+03
R955.	C4H8-2+H=SC4H9	4.15E-13	5.10E-01	1.32E+03
R956.	C4H8-1+H=SC4H9	7.04E-13	5.10E-01	6.19E+02
R957.	PC4H9+02=C4H8-1+H02	1.39E-24	3.59E+00	6.02E+03
R958.	SC4H9+02=C4H8-1+H02	8.88E-25	3.71E+00	4.69E+03
R959.	SC4H9+02=C4H8-2+H02	1.78E-24	3.71E+00	4.69E+03
R960.	C2H3+C2H5=C4H8-1	1.49E-11	0.00E+00	0.00E+00
R961.	C3H5-A+CH3=C4H8-1	1.66E-10	-3.20E-01	-1.32E+02
R962.	C3H5-A+CH3+M=C4H8-1+M	1.08E+13	-1.28E+01	3.15E+03
R963.	H+C4H71-3=C4H8-1	8.30E-11	0.00E+00	0.00E+00
R964.	C4H8-1+02=C4H71-3+H02	3.32E-11	0.00E+00	1.87E+04
R965	C4H8-1+0=C4H71-3+0H	2 91E-13	7 00E-01	2 96E+03
R966	C4H8-2+0=C4H71-3+0H	2.01E 10 3 64F-13	8 10F-01	3 80F+03
R967	CAH8 - 1 + H = CAH71 - 3 + H2	2 87E-19	2 50E+00	1 25F+03
R068	$C_{4}HS_{1+H} = C_{4}H7_{1-4+H2}$	1 10F-18	2.50E+00	3 /05+03
R900.	C4HO = 1 + H = C4H7 + 1 - 4 + H2	1.10E-10 1.40E-19	2.04E+00	1 06E+03
R909.	C4HO = 1 + 0H = C4H7 1 = 2 + H20	1.49E-10 2.60E-19	2.00E+00	1.20E+03
R970.	C4HO = 1 + 0H = C4H7 1 = 2 + H20	5.09E-10	2.00E+00	1.50E+02
R971.	C4H8 - 1 + 0H = C4H71 - 3 + H20	5.18E-18	2.00E+00	-1.50E+02
R972.	C4H8 - 1 + 0H = C4H71 - 4 + H20	8.75E-15	9.70E-01	7.98E+02
R973.	C4H8 - 1 + CH3 = C4H71 - 3 + CH4	3.67E-24	3.50E+00	2.86E+03
R974.	C4H8-1+CH3=C4H71-4+CH4	7.51E-25	3.65E+00	3.60E+03
R975.	C4H8-1+H02=C4H71-3+H202	4.48E-20	7.00E-01	2.96E+03
R976.	C4H8-1+H02=C4H71-4+H2O2	3.95E-21	2.55E+00	8.30E+03
R977.	C4H8-1+CH3O2=C4H71-3+CH3O2H	4.48E-20	7.00E-01	2.96E+03
R978.	C4H8-1+CH3O2=C4H71-4+CH3O2H	3.95E-21	2.55E+00	8.30E+03
R979.	C4H8-1+CH30=C4H71-3+CH3OH	6.64E-23	2.90E+00	4.33E+03
R980.	C4H8-1+CH3O=C4H71-4+CH3OH	3.60E-13	0.00E+00	3.25E+03
R981.	C4H8-1+CH3CO3=C4H71-3+CH3CO3H	1.66E-13	0.00E+00	4.03E+03
R982.	C4H8-1+C3H5-A=C4H71-3+C3H6	1.31E-13	0.00E+00	6.24E+03
R983.	C4H71-3+C4H71-3=C4H8-1+C4H6	2.66E-12	0.00E+00	0.00E+00
R984.	C4H8-1+C2H5O2=C4H71-3+C2H5O2H	2.32E-12	0.00E+00	7.50E+03
R985.	C4H8-1+NC3H702=C4H71-3+NC3H702H	2.32E-12	0.00E+00	7.50E+03
R986.	C4H8-1+IC3H702=C4H71-3+IC3H702H	2.32E-12	0.00E+00	7.50E+03
R987.	C4H8-1+PC4H902=C4H71-3+PC4H902H	2.32E-12	0.00E+00	7.50E+03
R988.	C4H8-1+SC4H902=C4H71-3+SC4H902H	2.32E-12	0.00E+00	7.50E+03
R989.	C4H8-1+CH3O2=C4H8O1-2+CH3O	1.66E-12	0.00E+00	7.22E+03
R990.	H+C4H71-3=C4H8-2	8.30E-11	0.00E+00	0.00E+00
R991.	C4H8-2+02=C4H71-3+H02	6.64E-11	0.00E+00	1.98E+04
R992.	C4H8-2+H=C4H71-3+H2	7.37E-20	2.81E+00	2.22E+03
R993.	C4H8-2+0H=C4H71-3+H20	8.47E-16	1.40E+00	6.29E+02
R994.	C4H8-2+CH3=C4H71-3+CH4	1.19E-23	3.57E+00	3.85E+03
R995.	C4H8-2+H02=C4H71-3+H202	9.86E-20	2.57E+00	8.12E+03
R996.	C4H8-2+CH302=C4H71-3+CH302H	9.86E-20	2.57E+00	8.12E+03
R997	C4H8-2+CH30=C4H71-3+CH30H	2.99E-23	2.95E+00	6.03E+03
R998	C4H8 - 2 + C2H5O2 = C4H71 - 3 + C2H5O2H	5 31E-12	0 00E+00	7 50E+03
R999	C4H8-2+NC3H7O2=C4H71-3+NC3H7O2H	5 31F-12	0.00E+00	7 50F+03
R1000	C4H8-2+TC3H702-C4H71-3+TC3H702H	5.31E-12	0.00E+00	7.501.03
R1001	СЛН8-2+DСЛН0Л2=САН71-3+DСЛН0Л0Ц	5 215-10	0.005+00	7 505-03
R1001.	CARS-3+2CAR003-CAR11-3+2CAR000R	5.31E-12 5.31E-10		7 EAETOS
R1002.		0.31E-12 1 66E-10		7 00ETU3
R1003.		1.006-12		6 10E+02
R1004.		9.33E-13		0.19E+U3
RI005.	04no-2+0h302=04h802-3+0h30	9.33E-13	0.005+00	p.19F+03

R1006.	C4H8-1+OH=PC4H8OH	7.89E-12	0.00E+00	-3.94E+02
R1007.	C4H8-2+OH=SC4H8OH	7.89E-12	0.00E+00	-3.94E+02
R1008.	PC4H80H+02=C4H80H-102	3.32E-12	0.00E+00	0.00E+00
R1009.	SC4H80H+02=C4H80H-202	3.32E-12	0.00E+00	0.00E+00
R1010.	C4H8OH-102=C2H5CH0+CH2O+OH	1.00E+16	0.00E+00	1.26E+04
R1011.	C4H8OH-202=OH+CH3CH0+CH3CH0	1.00E+16	0.00E+00	1.26E+04
R1012.	C2H2+C2H5=C4H71-1	3.32E-13	0.00E+00	3.93E+03
R1013.	C3H4-A+CH3=C4H71-2	3.32E-13	0.00E+00	3.93E+03
R1014.	C2H4+C2H3=C4H71-4	3.32E-13	0.00E+00	3.93E+03
R1015.	C3H4-P+CH3=C4H72-2	1.66E-13	0.00E+00	3.93E+03
R1016.	C4H6+H=C4H71-3	6.64E-11	0.00E+00	6.54E+02
R1017.	C4H71-3+C2H5=C4H8-1+C2H4	4.30E-12	0.00E+00	-6.59E+01
R1018.	C4H71-3+CH30=C4H8-1+CH20	4.00E-11	0.00E+00	0.00E+00
R1019.	C4H71-3+0=C2H3CH0+CH3	1.00E-10	0.00E+00	0.00E+00
B1020	C4H71-3+H02=C4H70+0H	1.60E-11	0.00E+00	0.00E+00
R1021	C4H71 - 3 + CH302 = C4H70 + CH30	1 60E-11	0 00E+00	0 00E+00
R1021.	C3H5 - A + C4H71 - 3 = C3H6 + C4H6	1.00E 11 1.05E-11	0.00E+00	0.00E+00
R1022.	C/H71 - 3 + 02 = C/H6 + H02	1.000 11	0.00E+00	0.00E+00
R1023.	H + CAH71 - 3 = CAH6 + H2	5 25F-11	0.00E+00	0.00E+00
R1024.		6 61F-10	0.00E+00	0.00E+00
R1025.	$C_{2H3} + C_{4H71} - 3 - C_{4H0} + C_{2H0} + C_{2H0}$	6 61F-12	0.00E+00	0.00E+00
R1020.	$C_{2}H_{3}^{+}C_{4}H_{1}^{-}T_{-}^{-}C_{2}H_{4}^{+}C_{4}H_{0}^{-}C_{1}H_{2}^{-}C_{2}$	0.01E-12 6 21E-12	0.00E+00	-6 04E+00
RIU27.	$C4\pi 7 1 - 3 + C2\pi 302 - C4\pi 7 0 + C2\pi 30$	0.31E-12 6 21E-12	0.00E+00	-6.04E+02
R1020.		0.31E-12	0.00E+00	-0.04E+02
R1029.	NC3H/U2+C4H/I-3=NC3H/U+C4H/U	0.31E-12	0.00E+00	-6.04E+02
R1030.	C4H70=CH3CH0+C2H3	7.94E+14	0.00E+00	9.56E+03
R1031.		7.94E+14	0.00E+00	9.56E+03
R1032.	C4H6=C4H5-1+H	5.70E+36	-6.27E+00	5.65E+04
R1033.	C4H6=C4H5-N+H	5.30E+44	-8.62E+00	6.22E+04
R1034.	C4H6=C4H4+H2	2.50E+15	0.00E+00	4.77E+04
R1035.	C4H6+H=C4H5-N+H2	2.21E-18	2.53E+00	6.16E+03
R1036.	C4H6+H=C4H5-I+H2	1.10E-18	2.53E+00	4.65E+03
R1037.	C4H6+H=C2H4+C2H3	2.42E+06	-4.34E+00	1.09E+04
R1038.	C4H6+H=C3H4-P+CH3	3.32E-12	0.00E+00	3.52E+03
R1039.	С4Н6+Н=СЗН4-А+СНЗ	3.32E-12	0.00E+00	3.52E+03
R1040.	C4H6+O=C4H5-N+OH	1.25E-17	1.90E+00	1.88E+03
R1041.	C4H6+O=C4H5-I+OH	1.25E-17	1.90E+00	1.88E+03
R1042.	C4H6+0=C2H2+C2H401-2	1.66E-16	1.45E+00	-4.33E+02
R1043.	C4H6+D=CH3CHCHCO+H	8.30E-17	1.45E+00	-4.33E+02
R1044.	C4H6+O=CH2CHCHCH0+H	7.47E-16	1.45E+00	-4.33E+02
R1045.	C4H6+OH=C4H5-N+H2O	1.03E-17	2.00E+00	1.73E+03
R1046.	C4H6+OH=C4H5-I+H2O	5.15E-18	2.00E+00	2.16E+02
R1047.	C4H6+H02=C4H6025+OH	1.99E-12	0.00E+00	7.05E+03
R1048.	C4H6+H02=C2H3CH0CH2+OH	7.97E-12	0.00E+00	7.05E+03
R1049.	C4H6+CH3=C4H5-N+CH4	3.32E-10	0.00E+00	1.15E+04
R1050.	C4H6+CH3=C4H5-I+CH4	1.66E-10	0.00E+00	9.96E+03
R1051.	C4H6+C2H3=C4H5-N+C2H4	8.30E-11	0.00E+00	1.15E+04
R1052.	C4H6+C2H3=C4H5-I+C2H4	4.15E-11	0.00E+00	9.96E+03
R1053.	C4H6+C3H3=C4H5-N+C3H4-A	1.66E-11	0.00E+00	1.13E+04
R1054.	C4H6+C3H3=C4H5-I+C3H4-A	8.30E-12	0.00E+00	9.81E+03
R1055.	C4H6+C3H5-A=C4H5-N+C3H6	1.66E-11	0.00E+00	1.13E+04
R1056.	C4H6+C3H5-A=C4H5-I+C3H6	8.30E-12	0.00E+00	9.81E+03
R1057.	C4H71-4=C4H6+H	2.48E+53	-1.23E+01	2.62E+04
R1058.	C2H3+C2H2=C4H4+H	3.32E-06	-1.68E+00	5.33E+03
R1059.	C2H3+C2H2=C4H5-N	1.54E+15	-8.76E+00	6.04E+03

R1060.	C2H3+C2H2=C4H5-I	2.66E+22	-1.10E+01	9.36E+03
R1061.	C2H3+C2H3=C4H6	2.49E+18	-8.84E+00	6.28E+03
R1062.	C2H3+C2H3=C4H5-I+H	1.99E-02	-2.44E+00	6.87E+03
R1063.	C2H3+C2H3=C4H5-N+H	3.99E-04	-2.04E+00	7.73E+03
R1064.	C4H5-N=C4H5-I	1.50E+67	-1.69E+01	2.97E+04
R1065.	C4H5-N+H=C4H5-I+H	5.15E+02	-3.35E+00	8.77E+03
R1066.	C4H5-N+H=C4H4+H2	2.49E-11	0.00E+00	0.00E+00
R1067.	C4H5-N+OH=C4H4+H2O	3.32E-12	0.00E+00	0.00E+00
R1068.	C4H5-N+HC0=C4H6+C0	8.30E-12	0.00E+00	0.00E+00
R1069.	C4H5-N+H02=C2H3+CH2C0+OH	1.10E-11	0.00E+00	0.00E+00
R1070.	C4H5-N+H2O2=C4H6+HO2	2.01E-14	0.00E+00	-3.00E+02
B1071.	C4H5-N+H02=C4H6+02	9.96E-13	0.00E+00	0.00E+00
B1072	C4H5-N+02=CH2CHCHCH0+0	4.98E-13	2.90E-01	5.54E+00
B1073	C4H5-N+O2=HCO+C2H3CHO	1 53E-07	-1 39E+00	5 08E+02
B1074	CAH5-T+H=CAHA+H2	4 98F-11	0.00E+00	0.00E+00
B1075	CAH5-T+H=C3H3+CH3	3 32F-11	0.00E+00	1 01F+03
R1076		6 6/F-10	0.00E+00	0.005+00
R1070.	$C_{4115} = 1 + UCO - C_{4114} + HZO$	0.04E 12 0.04E 12	0.000000	0.00E+00
RI077.	C4H5 - 1 + HC0 - C4H6 + C0	0.30E-12	0.00E+00	0.00E+00
R1078.	C4H5 = 1 + H02 = C2H2 + CH2C0 + 0H	9.90E-13	0.00E+00	0.00E+00
R1079.		1.10E-11	0.00E+00	0.00E+00
R1080.		2.01E-14	0.00E+00	-3.00E+02
R1081.	C4H5-1+U2=CH2CU+CH2CHU	3.59E-14	0.00E+00	1.26E+03
R1082.	C4H5-2=C4H5-1	1.50E+67	-1.69E+01	2.97E+04
R1083.	C4H5-2+H=C4H5-1+H	5.15E+02	-3.35E+00	8.77E+03
R1084.	C4H5-2+H02=OH+C2H2+CH3CO	1.33E-12	0.00E+00	0.00E+00
R1085.	C4H5-2+02=CH3C0+CH2C0	3.59E-14	0.00E+00	1.26E+03
R1086.	C4H612=C4H5-I+H	4.20E+15	0.00E+00	4.66E+04
R1087.	C4H612+H=C4H6+H	3.32E-11	0.00E+00	2.01E+03
R1088.	C4H612+H=C4H5-I+H2	2.82E-19	2.50E+00	1.25E+03
R1089.	C4H612+H=C3H4-A+CH3	3.32E-11	0.00E+00	1.01E+03
R1090.	C4H612+H=C3H4-P+CH3	3.32E-11	0.00E+00	1.01E+03
R1091.	C4H612+CH3=C4H5-I+CH4	1.16E-10	0.00E+00	9.31E+03
R1092.	C4H612+0=CH2C0+C2H4	1.99E-16	1.65E+00	1.65E+02
R1093.	C4H612+0=C4H5-I+OH	2.99E-13	7.00E-01	2.96E+03
R1094.	C4H612+OH=C4H5-I+H2O	5.15E-18	2.00E+00	-1.50E+02
R1095.	C4H612=C4H6	3.00E+13	0.00E+00	3.27E+04
R1096.	C4H6-2=C4H6	3.00E+13	0.00E+00	3.27E+04
R1097.	C4H6-2=C4H612	3.00E+13	0.00E+00	3.37E+04
R1098.	C4H6-2+H=C4H612+H	3.32E-11	0.00E+00	2.01E+03
R1099.	C4H6-2+H=C4H5-2+H2	5.65E-19	2.50E+00	1.25E+03
R1100.	C4H6-2+H=CH3+C3H4-P	4.32E-19	2.50E+00	5.03E+02
R1101.	C4H6-2=H+C4H5-2	5.00E+15	0.00E+00	4.39E+04
R1102.	C4H6-2+CH3=C4H5-2+CH4	2.32E-10	0.00E+00	9.31E+03
R1103.	C2H3CH0CH2=C4H6023	2.00E+14	0.00E+00	2.55E+04
B1104.	С4Н6023=СН3СНСНСНО	1.95E+13	0.00E+00	2.49E+04
B1105	C4H6D23=C2H4+CH2CD	5 75E+15	0 00E+00	3 49E+04
B1106	C4H6D23=C2H2+C2H4D1-2	1 00F+16	0.00E+00	3 81F+04
B1107	CAH6025 = CAHA0 + H2	5 30F+12	0.00E+00	2.44E+04
R1102	C4H40=C0+C3H4-P	1 725+15	0 005+00	3 005+04
R1100.	СЛНАО=СЭНЭ+СНЭСО		0 005-00	3 005+04
R11109.		3.01E+14 3 00E+14	0.005+00	3 /7E±04
R1111		0.90E+14 0 00E-10		1 955±04
D1110		2.02E-19		1 055103
Π1112. D1112		1.00E-19	∠.50E+00	1.20E+U3
к1113.	спзсисисночи=сиз+с2изсио	6.64E-03	-2.39E+00	5.63E+03

R1114.	CH3CHCHCH0+H=C3H6+HC0	6.64E-03	-2.39E+00	5.63E+03
R1115.	CH3CHCHCH0+CH3=CH2CHCHCH0+CH4	3.49E-24	3.50E+00	2.86E+03
R1116.	CH3CHCHCH0+CH3=CH3CHCHC0+CH4	1.83E-24	3.50E+00	2.86E+03
R1117.	CH3CHCHCH0+C2H3=CH2CHCHCH0+C2H4	3.67E-24	3.50E+00	2.36E+03
R1118.	CH3CHCHCH0+C2H3=CH3CHCHC0+C2H4	1.84E-24	3.50E+00	2.36E+03
R1119.	CH3CHCHCO=C3H5-S+CO	1.00E+14	0.00E+00	1.51E+04
R1120.	CH3CHCHCO+H=CH3CHCHCHO	1.66E-10	0.00E+00	0.00E+00
R1121.	CH2CHCHCHO=C3H5-A+CO	1.00E+14	0.00E+00	1.26E+04
R1122.	CH2CHCHCH0+H=CH3CHCHCH0	1.66E-10	0.00E+00	0.00E+00
R1123.	C4H4+H=C4H5-N	2.16E+27	-1.19E+01	8.30E+03
R1124.	C4H4+H=C4H5-I	8.14E+27	-1.19E+01	8.91E+03
R1125.	C4H4+H=C4H3-N+H2	1.10E-18	2.53E+00	6.16E+03
R1126.	C4H4+H=C4H3-I+H2	5.53E-19	2.53E+00	4.65E+03
R1127.	C4H4+OH=C4H3-N+H2O	5.15E-17	2.00E+00	1.73E+03
R1128.	C4H4+0H=C4H3-T+H20	2.57E-17	2.00E+00	2.16E+02
R1129	C4H4+D=C3H3+HCD	9.96E-16	1.45E+00	-4.33E+02
R1130	C3H3+HCCD=C4H4+CD	4 15E-11	0 00E+00	0 00E+00
R1131	СЗНЗ+СН=САНЗ-Т+Н	8 30F-11	0.00E+00	0.00E+00
R1132	C3H3+CH2=C4H4+H	8 30E-11	0.00E+00	0.00E+00
R1133	C3H3+CH3=C4H612	2 49F-12	0.00E+00	0.00E+00
R1134	C3H3+CH3+M=C/H612+M	7 17F+09	-1 19F+01	4 92F+03
R1135	C2H2+C2H=C2H3-N	1 38F-13	8 99F-01	-1 83F+02
R1136	C2H2+C2H+M=CAH3=N+M	2 /0E-17	-4 72E+00	0 /2F+02
D1127		J 10E+42	-0 10E+00	9.420102
NII37.	C4H3-N-C4H3-1 C4H2-N+U-C4H3-1	4.10E+43 4 15E-04	-9.49E+00	2.07E+04
R1130.	C4H3 - N + H - C4H3 - I + H	4.156-04	-1.07E+00	5.43E+03
RI139.	C4H2 - N + H - C2H2 + H2CC	1.05E+02	-3.34E+00	5.04E+03
RI140.	C4H2-N+H-C4H2+H2	3.32E+23	-1.03E+01	0.500+05
RI141.	C4n3 - N + n = C4n2 + n2	4.90E-11	0.00E+00	0.00E+00
RI142.	C4n3-N+Un=C4n2+n2U	3.32E-12	0.00E+00	1.00E+00
RI143.	$C_{2H2+C_{2H}=C_{4H3-1}}$	1.38E-13	8.99E-01	-1.83E+02
R1144.	$C_{2H2+C_{2H}+M=C_{4H3}-1+M}$	3.42E-17	-4.72E+00	9.42E+02
R1145.	C4H3-1+H=C2H2+H2CC	4.65E-01	-2.55E+00	5.42E+03
R1146.	C4H3-1+H=C4H4	5.65E+19	-9.01E+00	6.10E+03
R1147.	C4H3-1+H=C4H2+H2	9.96E-11	0.00E+00	0.00E+00
R1148.	C4H3-1+UH=C4H2+H2U	6.64E-12	0.00E+00	0.00E+00
R1149.	C4H3-1+U2=HCCU+CH2CU	1.31E-07	-1.80E+00	0.00E+00
R1150.	C4H3-1+CH2=C3H4-A+C2H	3.32E-11	0.00E+00	0.00E+00
R1151.	C2H2+C2H=C4H2+H	1.59E-10	0.00E+00	0.00E+00
R1152.	C4H2+H=C4H3-N	1.83E+18	-8.72E+00	7.70E+03
R1153.	C4H2+H=C4H3-1	1.83E+06	-4.92E+00	5.43E+03
R1154.	C4H2+OH=H2C4O+H	1.10E-11	0.00E+00	-2.06E+02
R1155.	H2C40+H=C2H2+HCC0	8.30E-11	0.00E+00	1.51E+03
R1156.	H2C40+OH=CH2CO+HCCO	1.66E-17	2.00E+00	1.01E+03
R1157.	H2CC+C2H2=C4H4	5.81E-19	2.06E+00	-1.21E+03
R1158.	H2CC+C2H2+M=C4H4+M	3.86E+12	-1.26E+01	3.73E+03
R1159.	H2CC+C2H4=C4H6	1.66E-12	0.00E+00	0.00E+00
R1160.	C4H801-2+OH=CH2O+C3H5-A+H2O	8.30E-12	0.00E+00	0.00E+00
R1161.	C4H8O1-2+H=CH2O+C3H5-A+H2	8.30E-12	0.00E+00	0.00E+00
R1162.	C4H8O1-2+O=CH2O+C3H5-A+OH	8.30E-12	0.00E+00	0.00E+00
R1163.	C4H8O1-2+HO2=CH2O+C3H5-A+H2O2	1.66E-11	0.00E+00	7.55E+03
R1164.	C4H8O1-2+CH3O2=CH2O+C3H5-A+CH3O2H	1.66E-11	0.00E+00	9.56E+03
R1165.	C4H8O1-2+CH3=CH2O+C3H5-A+CH4	3.32E-13	0.00E+00	5.03E+03
R1166.	C4H8O1-3+OH=CH2O+C3H5-A+H2O	8.30E-12	0.00E+00	0.00E+00
R1167.	C4H8O1-3+H=CH2O+C3H5-A+H2	8.30E-12	0.00E+00	0.00E+00

R1168.	C4H8O1-3+O=CH2O+C3H5-A+OH	8.30E-12	0.00E+00	0.00E+00
R1169.	C4H801-3+H02=CH20+C3H5-A+H202	1.66E-11	0.00E+00	7.55E+03
R1170.	C4H801-3+CH302=CH20+C3H5-A+CH302H	1.66E-11	0.00E+00	9.56E+03
R1171.	C4H801-3+CH3=CH20+C3H5-A+CH4	3.32E-13	0.00E+00	5.03E+03
R1172.	C4H801-4+OH=CH2O+C3H5-A+H2O	8.30E-12	0.00E+00	0.00E+00
R1173.	C4H801-4+H=CH20+C3H5-A+H2	8.30E-12	0.00E+00	0.00E+00
R1174.	C4H801-4+0=CH20+C3H5-A+OH	8.30E-12	0.00E+00	0.00E+00
R1175.	C4H801-4+H02=CH20+C3H5-A+H202	1.66E-11	0.00E+00	7.55E+03
R1176.	C4H801-4+CH302=CH20+C3H5-A+CH302H	1.66E-11	0.00E+00	9.56E+03
R1177.	C4H801-4+CH3=CH20+C3H5-A+CH4	3.32E-13	0.00E+00	5.03E+03
R1178.	C4H802-3+0H=CH20+C3H5-A+H20	8.30E-12	0.00E+00	0.00E+00
R1179.	C4H802-3+H=CH20+C3H5-A+H2	8.30E-12	0.00E+00	0.00E+00
R1180.	C4H802-3+0=CH20+C3H5-A+0H	8.30E-12	0.00E+00	0.00E+00
R1181	C4H802-3+H02=CH20+C3H5-A+H202	1.66E-11	0.00E+00	7.55E+03
R1182	C4H802-3+CH302=CH20+C3H5-A+CH302H	1 66E-11	0 00E+00	9 56E+03
R1183	C4H802 - 3 + CH3 = CH20 + C3H5 - 4 + CH4	3 32F-13	0.00E+00	5 03F+03
R1100.		7 51F-10	0.00E+00	0.00E+00
D1104.	PC4119+02-PC411902	1 255-11	0.000000	0.00E+00
R1105.	SC4H9+UZ-SC4H9UZ SC4H9+UZ-SC4H9UZ	1.25E-11 0.20E-12	0.005+00	6 9/E+00
RI100.		9.30E-12	0.000000	6.04E+03
RI107.		4.05E-12	0.00E+00	0.84E+03
R1188.	5C4H9U2+HU2=SC4H9U2H+U2	2.91E-14	0.00E+00	-1.65E+03
R1189.		1.16E-11	0.00E+00	-5.03E+02
R1190.	1C3H7U2+SC4H9=1C3H7U+SC4H9U	1.16E-11	0.00E+00	-5.03E+02
R1191.	NC3H7U2+PC4H9=NC3H7U+PC4H9U	1.16E-11	0.00E+00	-5.03E+02
R1192.	NC3H702+SC4H9=NC3H70+SC4H90	1.16E-11	0.00E+00	-5.03E+02
R1193.	SC4H902+SC4H902=02+SC4H90+SC4H90	2.32E-08	-1.61E+00	9.36E+02
R1194.	SC4H902+NC3H702=SC4H90+NC3H70+02	2.32E-08	-1.61E+00	9.36E+02
R1195.	SC4H902+IC3H702=SC4H90+IC3H70+02	2.32E-08	-1.61E+00	9.36E+02
R1196.	SC4H902+C2H502=SC4H90+C2H50+02	2.32E-08	-1.61E+00	9.36E+02
R1197.	SC4H902+CH302=SC4H90+CH30+02	2.32E-08	-1.61E+00	9.36E+02
R1198.	SC4H902+CH3CO3=SC4H90+CH3CO2+O2	2.32E-08	-1.61E+00	9.36E+02
R1199.	H2+PC4H902=H+PC4H902H	5.00E-11	0.00E+00	1.31E+04
R1200.	H2+SC4H9O2=H+SC4H9O2H	5.00E-11	0.00E+00	1.31E+04
R1201.	C2H6+PC4H9O2=C2H5+PC4H9O2H	2.82E-11	0.00E+00	1.03E+04
R1202.	C2H6+SC4H9O2=C2H5+SC4H9O2H	2.82E-11	0.00E+00	1.03E+04
R1203.	PC4H902+C2H5CH0=PC4H902H+C2H5C0	3.32E-13	0.00E+00	4.78E+03
R1204.	SC4H902+C2H5CH0=SC4H902H+C2H5C0	3.32E-13	0.00E+00	4.78E+03
R1205.	SC4H902+CH3=SC4H90+CH30	1.16E-11	0.00E+00	-5.03E+02
R1206.	SC4H902+C2H5=SC4H90+C2H50	1.16E-11	0.00E+00	-5.03E+02
R1207.	SC4H902+IC3H7=SC4H90+IC3H70	1.16E-11	0.00E+00	-5.03E+02
R1208.	SC4H902+NC3H7=SC4H90+NC3H70	1.16E-11	0.00E+00	-5.03E+02
R1209.	SC4H902+PC4H9=SC4H90+PC4H90	1.16E-11	0.00E+00	-5.03E+02
R1210.	SC4H902+SC4H9=SC4H90+SC4H90	1.16E-11	0.00E+00	-5.03E+02
R1211.	SC4H902+C3H5-A=SC4H90+C3H50	1.16E-11	0.00E+00	-5.03E+02
R1212.	PC4H902+CH20=PC4H902H+HC0	9.30E-12	0.00E+00	6.84E+03
R1213.	PC4H902+CH3CH0=PC4H902H+CH3C0	4.65E-12	0.00E+00	6.84E+03
R1214	PC4H902+H02=PC4H902H+02	2.91E-14	0.00E+00	-1.65E+03
R1215	C3H6+PC4H902=C3H5-A+PC4H902H	5 38F-13	0.00E+00	7 50E+03
R1216	C3H6+SC4H9D2=C3H5-A+SC4H9D2H	5 38F-13	0.00F+00	7 505+03
R1217	С2Н4+РС4Н9О2=С2Н3+РС4Н9О2Н	1 88F-11	0 005+00	1 53F+04
R1212	C2H4+SC4H9D2=C2H3+SC4H9D2H	1 885-11	0 005+00	1 535+04
R1210.	СНЗПН+РСДН902-0211313041130211 СНЗПН+РСДН902=СНЭОН+РСИН90ЭН	1 055-11	0.000+00	9 7/F+02
R1220		1 055-11	0.00E+00	0 7/F±03
D1001		1.00E-11 A 65E-10		6 0/E100
RIZZI.	02n30n0+r04n902=02n300+r04n902h	4.006-12	0.005+00	0.045+03

R1222.	C2H3CH0+SC4H902=C2H3C0+SC4H902H	4.65E-12	0.00E+00	6.84E+03
R1223.	CH4+PC4H902=CH3+PC4H902H	1.86E-11	0.00E+00	1.24E+04
R1224.	CH4+SC4H902=CH3+SC4H902H	1.86E-11	0.00E+00	1.24E+04
R1225.	C4H71-3+PC4H902=C4H70+PC4H90	1.16E-11	0.00E+00	-5.03E+02
R1226.	C4H71-3+SC4H902=C4H70+SC4H90	1.16E-11	0.00E+00	-5.03E+02
R1227.	H202+PC4H902=H02+PC4H902H	3.99E-12	0.00E+00	5.03E+03
R1228.	H202+SC4H902=H02+SC4H902H	3.99E-12	0.00E+00	5.03E+03
R1229.	PC4H902+PC4H902=02+PC4H90+PC4H90	2.32E-08	-1.61E+00	9.36E+02
R1230.	PC4H902+SC4H902=PC4H90+SC4H90+02	2.32E-08	-1.61E+00	9.36E+02
R1231.	PC4H902+NC3H702=PC4H90+NC3H70+02	2.32E-08	-1.61E+00	9.36E+02
R1232.	PC4H902+IC3H702=PC4H90+IC3H70+02	2.32E-08	-1.61E+00	9.36E+02
R1233.	PC4H902+C2H502=PC4H90+C2H50+02	2.32E-08	-1.61E+00	9.36E+02
R1234.	PC4H902+CH302=PC4H90+CH30+02	2.32E-08	-1.61E+00	9.36E+02
R1235.	PC4H902+CH3C03=PC4H90+CH3C02+02	2.32E-08	-1.61E+00	9.36E+02
R1236.	PC4H902+CH3=PC4H90+CH30	1.16E-11	0.00E+00	-5.03E+02
R1237.	PC4H902+C2H5=PC4H90+C2H50	1.16E-11	0.00E+00	-5.03E+02
R1238.	PC4H902+IC3H7=PC4H90+IC3H70	1.16E-11	0.00E+00	-5.03E+02
R1239.	PC4H902+NC3H7=PC4H90+NC3H70	1.16E-11	0.00E+00	-5.03E+02
R1240.	PC4H902+PC4H9=PC4H90+PC4H90	1.16E-11	0.00E+00	-5.03E+02
R1241.	PC4H902+SC4H9=PC4H90+SC4H90	1.16E-11	0.00E+00	-5.03E+02
R1242.	PC4H902+C3H5-A=PC4H90+C3H50	1.16E-11	0.00E+00	-5.03E+02
R1243.	PC4H9+H02=PC4H90+0H	1.16E-11	0.00E+00	-5.03E+02
R1244.	SC4H9+H02=SC4H90+0H	1.16E-11	0.00E+00	-5.03E+02
R1245.	CH302+PC4H9=CH30+PC4H90	1.16E-11	0.00E+00	-5.03E+02
R1246	CH302+SC4H9=CH30+SC4H90	1.16E-11	0.00E+00	-5.03E+02
R1247	PC4H902H=PC4H90+0H	1.50E+16	0.00E+00	2.14E+04
R1248	SC4H90+0H=SC4H902H	1.66E-09	-8.00E-01	0.00E+00
R1249	NC3H7+CH20=PC4H90	8.30E-14	0.00E+00	1.74E+03
R1250	CH3+C2H5CH0=SC4H90	8 30E-14	0.00E+00	4 55E+03
R1251	C2H5+CH3CH0=SC4H90	5 53E-14	0.00E+00	3 22E+03
R1252	PC4H9D2=C4H8DDH1-2	2 00E+11	0.00E+00	1 60E+04
R1253	PC4H902=C4H800H1=3	2.50E+11	0.00E+00	1.00E+01
R1250.	PCAH902 = CAH800H1 = A	A 69F+09	0.00E+00	1 12F+04
R1255	SC/H9D2=C/H8DDH2-1	3 00F+11	0.00E+00	1.121.04 1.74F+04
R1256	SC4H9D2=C4H8DDH2-3	2 00E+11	0.00E+00	1.60E+04
R1257	SC4H9D2=C4H8DDH2-4	2.00E-11 3 75F+10	0.00E+00	1 23F+04
R1257	PC/H902=C/H8-1+H02	4 31F+36	-7 50E+00	1 QQF+04
R1250	SC/H9D2=C/H8-1+HD2	5 98F+42	-9 /3E+00	2 09F+04
R1260	SC4H9D2=C4H8-2+HD2	0.00E+42 A 31E+36	-7 50E+00	1 QQE+04
R1261	C4H8-1+H02=C4H800H1-2	1 66F-13	0.00E+00	5 54F+03
R1261.	C4H8-1+H02=C4H800H2-1	1.00E 13	0.00E+00	5 91F+03
R1262	C4H8-2+H02=C4H800H2-3	1.00E 13	0.00E+00	5 91E+03
R1200.	C4H800H1-2=C4H801-2+0H	1 385+10	0.00000	8 00F+03
R1265	C4H800H1-3=C4H801-3+0H	2.04F+11	0.00E+00	9 81F+03
R1266	C4H800H1-A=C4H801-A+0H	5 13F+10	0.00E+00	7 45E+03
R1267	C4H800H2-1=C4H801-2+0H	3 98F+12	0.00E+00	8 55F+03
R1267.	CARSODINZ 1-CARSO2-3+OR	1 385+10	0.00000	8 00F+03
R1260.	C4H800H2-A-C4H801-3+0H	1.00L+12 / /7E+11	0.00000	1 10E+04
R1203.	$C_{11000112} = C_{11001} C_{101}$	9.00E+1/	0.00000	7 555+02
R1071		0 00E-14	0.005+00	7 555-02
R1070	CAH800H1-3=0H+CH00+C3H6	6 6/E+14	-1 605-01	1 505±102
R1073	C4H800H2 - 4 = 0H + CH3CH0 + C3H4	1 QFF+19	-1 63F+00	1 25F+04
R1273.	C4H8DDH1-2+D2=C4H8DDH1-2D2	1 255-11	0 005+00	0 005+04
R1075	C4H8DDH1_3+D2=C4H8DDH1_202	1 255-11	0.005+00	0.005-00
111210.	OTHOUGHT O'UZ-OTHOUUHI JUZ	1.2011 11	0.00000000	0.005.00

R1276.	C4H800H1-4+02=C4H800H1-402	7.51E-12	0.00E+00	0.00E+00
R1277.	C4H800H2-1+02=C4H800H2-102	7.51E-12	0.00E+00	0.00E+00
R1278.	C4H800H2-3+02=C4H800H2-302	1.25E-11	0.00E+00	0.00E+00
R1279.	C4H800H2-4+02=C4H800H2-402	7.51E-12	0.00E+00	0.00E+00
R1280.	C4H8OOH1-202=NC4KET12+OH	2.00E+11	0.00E+00	1.59E+04
R1281.	C4H8OOH1-302=NC4KET13+OH	2.50E+10	0.00E+00	1.08E+04
R1282.	C4H800H1-402=NC4KET14+OH	3.13E+09	0.00E+00	9.74E+03
R1283.	C4H8OOH2-102=NC4KET21+OH	1.00E+11	0.00E+00	1.45E+04
R1284.	C4H800H2-302=NC4KET23+OH	1.00E+11	0.00E+00	1.45E+04
R1285.	C4H800H2-402=NC4KET24+OH	1.25E+10	0.00E+00	8.98E+03
R1286.	NC4KET12=C2H5CH0+HC0+OH	1.05E+16	0.00E+00	2.09E+04
R1287.	NC4KET13=CH3CH0+CH2CH0+OH	1.05E+16	0.00E+00	2.09E+04
R1288.	NC4KET14=CH2CH2CH0+CH20+OH	1.50E+16	0.00E+00	2.11E+04
R1289.	NC4KET21=CH20+C2H5C0+OH	1.50E+16	0.00E+00	2.11E+04
R1290.	NC4KET23=CH3CH0+CH3C0+OH	1.05E+16	0.00E+00	2.09E+04
R1291.	NC4KET24=CH20+CH3C0CH2+OH	1.50E+16	0.00E+00	2.11E+04
R1292.	C2H5COCH3+OH=CH2CH2COCH3+H2O	1.25E-14	9.70E-01	7.98E+02
R1293	С2Н5СОСН3+ОН=СН3СНСОСН3+Н2О	1.40E-12	0.00E+00	-1.15E+02
R1294	C2H5COCH3+OH=C2H5COCH2+H2O	8.47E-13	0.00E+00	6.00E+02
R1295	C2H5COCH3+H02=CH2CH2COCH3+H2O2	3.95E-20	2.55E+00	8.30E+03
R1296	C2H5COCH3+H02=CH3CHCOCH3+H2O2	3 32E-13	0 00E+00	4 38E+03
R1200.	C2H5COCH3+H02=C2H5COCH2+H2O2	3 95F-20	2 55F+00	7 39F+03
R1207.	C2H5CDCH3+D=CH2CH2CDCH3+DH	3 7/F-11	0.005+00	3 87F+03
R1200.	C2H5CDCH3+0-CH3CHCOCH3+0H	5 10F-11	0.005+00	1 71E+03
R1299.		9.10E 11 8.30E-12	0.00E+00	3 00F+03
RISOU.	C2H5CUCH3+U=CU2CU2CUCH2+UH	0.30E - 12	0.00E+00	3.00E+03
R1301.	C2H3CUCH3+H-CH2CH2CUCH3+H2	1.52E-17 7 /1E-19	2.00E+00	1 61E+03
RISUZ.	$C_{2}H_{3}C_{3}C_{4}H_{-}C_{3}C_{4}C_{4}C_{3}H_{2}$	$1.41E^{-10}$	2.00E+00	2 20E+03
RISUS.		1.54E-11	0.00E+00	3.20E+03
RI304.		3.40E-11	0.00E+00	2.50E+04
RI305.		2.57E-11	0.00E+00	2.11E+04
RI300.		3.40E-11	0.00E+00	2.47E+04
RI307.		5.30E-23	3.17E+00	3.61E+03
R1308.		2.89E-24	3.468+00	1.85E+03
R1309.		2.69E-13	0.00E+00	4.85E+03
R1310.	C2H5CUCH3+CH3U=CH2CH2CUCH3+CH3UH	3.60E-13	0.00E+00	3.25E+03
R1311.	C2H5CUCH3+CH3U=CH3CHCUCH3+CH3UH	2.41E-13	0.00E+00	1.39E+03
R1312.	C2H5CUCH3+CH3U=C2H5CUCH2+CH3UH	3.60E-13	0.00E+00	2.35E+03
R1313.	C2H5CUCH3+CH3U2=CH2CH2CUCH3+CH3U2H	5.00E-12	0.00E+00	9.75E+03
R1314.	C2H5CUCH3+CH3U2=CH3CHCUCH3+CH3U2H	3.32E-12	0.00E+00	7.67E+03
R1315.	C2H5CUCH3+CH3U2=C2H5CUCH2+CH3U2H	5.00E-12	0.00E+00	8.85E+03
R1316.	C2H5COCH3+C2H3=CH2CH2COCH3+C2H4	8.30E-13	0.00E+00	5.23E+03
R1317.	C2H5COCH3+C2H3=CH3CHCOCH3+C2H4	4.98E-13	0.00E+00	1.71E+03
R1318.	C2H5C0CH3+C2H3=C2H5C0CH2+C2H4	1.02E-13	0.00E+00	2.15E+03
R1319.	C2H5C0CH3+C2H5=CH2CH2C0CH3+C2H6	8.30E-14	0.00E+00	6.74E+03
R1320.	C2H5C0CH3+C2H5=CH3CHC0CH3+C2H6	4.98E-14	0.00E+00	4.33E+03
R1321.	C2H5C0CH3+C2H5=C2H5C0CH2+C2H6	8.30E-14	0.00E+00	5.84E+03
R1322.	CH3CHCOCH3+02=CH3CH00C0CH3	1.66E-13	0.00E+00	0.00E+00
R1323.	CH3CH00C0CH3=CH2CH00HC0CH3	8.90E+12	0.00E+00	1.49E+04
R1324.	C2H3COCH3+H02=CH2CH0OHCOCH3	1.16E-13	0.00E+00	3.93E+03
R1325.	CH2CH2CH0=C2H4+HC0	3.13E+13	-5.20E-01	1.24E+04
R1326.	CH2CH2COCH3=C2H4+CH3CO	1.00E+14	0.00E+00	9.06E+03
R1327.	C2H5C0CH2=CH2C0+C2H5	1.00E+14	0.00E+00	1.76E+04
R1328.	C2H3COCH3+H=CH3CHCOCH3	8.30E-12	0.00E+00	6.04E+02
R1329.	CH3CHCO+CH3=CH3CHCOCH3	2.04E-13	0.00E+00	3.93E+03

R1330.	NC3H7CH0+02=NC3H7C0+H02	1.99E-19	2.50E+00	1.89E+04
R1331.	NC3H7CH0+OH=NC3H7C0+H2O	3.32E-18	1.80E+00	-6.54E+02
R1332.	NC3H7CHO+H=NC3H7CO+H2	6.87E-15	1.12E+00	1.17E+03
R1333.	NC3H7CH0+0=NC3H7C0+0H	9.86E-12	0.00E+00	9.40E+02
R1334.	NC3H7CH0+H02=NC3H7C0+H202	6.79E-20	2.50E+00	5.13E+03
R1335.	NC3H7CH0+CH3=NC3H7C0+CH4	4.80E-27	4.62E+00	1.62E+03
R1336.	NC3H7CH0+CH30=NC3H7C0+CH30H	1.66E-12	0.00E+00	1.66E+03
R1337.	NC3H7CH0+CH302=NC3H7C0+CH302H	6.79E-20	2.50E+00	5.13E+03
R1338.	NC3H7CH0+OH=C3H6CH0-1+H2O	8.77E-15	9.70E-01	7.98E+02
R1339.	NC3H7CH0+OH=C3H6CH0-2+H2O	7.77E-17	1.61E+00	-1.76E+01
R1340.	NC3H7CH0+OH=C3H6CH0-3+H2O	9.17E-22	3.12E+00	-5.92E+02
R1341.	NC3H7CH0+H02=C3H6CH0-1+H202	3.95E-20	2.55E+00	8.30E+03
R1342.	NC3H7CH0+H02=C3H6CH0-2+H202	1.60E-20	2.60E+00	7.00E+03
R1343.	NC3H7CH0+H02=C3H6CH0-3+H202	5.71E-12	5.00E-02	9.00E+03
R1344	NC3H7CH0+CH302=C3H6CH0-1+CH302H	3.95E-20	2.55E+00	8.30E+03
R1345	NC3H7CH0+CH302=C3H6CH0-2+CH302H	1.60E-20	2.60E+00	7.00E+03
R1346	NC3H7CH0+CH302=C3H6CH0-3+CH302H	5 71E-12	5 00E-02	9 00E+03
R1347	NC3H7CO=NC3H7+CO	1 00F+11	0.00E+00	4 83F+03
R1348	C3H6CH0-1=C2H4+CH2CH0	7 40F+11	0.00E+00	1 11F+04
R1340.		8 30E-12	0.00E+00	6 0/E+02
R1350	C2H3CH0+CH3-C3H6CH0-3	2 0/F-13	0.00E+00	3 035+03
D1251		2.04E 13 9 20E-10	0.000000	1 /6E+02
R1301.	C_{2}	$0.30E^{-12}$	0.00E+00	2 00E+03
RI302.		1.00E-13	0.000000	5.02E+03
R1353.	$C_2H_5CHCU+UH=NC_3H_7+CU_2$	0.19E-12	0.002+00	-5.08E+02
R1354.	$C_{2H5}CHCU+H=NC3H7+CU$	7.31E-12	0.00E+00	7.34E+02
R1355.		5.31E-12	0.00E+00	-2.20E+02
R1356.	SC3H5CHU+UH=SC3H5CU+H2U	4.4/E-14	7.60E-01	-1.71E+02
R1357.		8.30E-12	0.00E+00	4.03E+03
R1358.	SC3H5CHU+HU2=SC3H5CU+H2U2	1.66E-12	0.00E+00	6.00E+03
R1359.	SC3H5CHU+CH3=SC3H5CU+CH4	6.61E-12	0.00E+00	4.38E+03
R1360.	SC3H5CH0+0=SC3H5C0+0H	1.19E-11	0.00E+00	6.99E+02
R1361.	SC3H5CH0+02=SC3H5C0+H02	6.64E-11	0.00E+00	1.89E+04
R1362.	SC3H5CH0+H=SC3H5C0+H2	4.32E-12	0.00E+00	1.31E+03
R1363.	C2H3COCH3+OH=CH3CH0+CH3CO	1.66E-13	0.00E+00	0.00E+00
R1364.	C2H3C0CH3+0H=CH2C0+C2H3+H20	8.47E-13	0.00E+00	6.00E+02
R1365.	C2H3C0CH3+H02=CH2CH0+CH3C0+OH	1.00E-14	0.00E+00	4.00E+03
R1366.	C2H3C0CH3+H02=CH2C0+C2H3+H2O2	1.41E-11	0.00E+00	1.03E+04
R1367.	C2H3C0CH3+CH302=CH2CH0+CH3C0+CH30	6.59E-13	0.00E+00	8.58E+03
R1368.	C2H3C0CH3+CH302=CH2C0+C2H3+CH302H	5.00E-12	0.00E+00	8.85E+03
R1369.	IC4H10=CH3+IC3H7	2.52E+31	-4.10E+00	4.60E+04
R1370.	IC4H10+M=CH3+IC3H7+M	4.00E-05	0.00E+00	2.65E+04
R1371.	IC4H10=TC4H9+H	2.51E+98	-2.38E+01	7.31E+04
R1372.	IC4H10=IC4H9+H	9.85E+95	-2.31E+01	7.43E+04
R1373.	IC4H10+H=TC4H9+H2	1.00E-18	2.40E+00	1.30E+03
R1374.	IC4H10+H=IC4H9+H2	3.01E-18	2.54E+00	3.40E+03
R1375.	IC4H10+CH3=TC4H9+CH4	1.50E-24	3.46E+00	2.31E+03
R1376.	IC4H10+CH3=IC4H9+CH4	2.26E-24	3.65E+00	3.60E+03
R1377.	IC4H10+OH=TC4H9+H2O	4.86E-20	2.53E+00	-8.35E+02
R1378.	IC4H10+OH=IC4H9+H2O	1.10E-19	2.67E+00	-8.50E+01
R1379.	IC4H10+C2H5=IC4H9+C2H6	2.51E-12	0.00E+00	5.23E+03
R1380.	IC4H10+C2H5=TC4H9+C2H6	1.66E-13	0.00E+00	3.98E+03
R1381.	IC4H10+H02=IC4H9+H2O2	1.02E-22	3.59E+00	8.64E+03
R1382.	IC4H10+H02=TC4H9+H2O2	7.19E-22	3.01E+00	6.08E+03
R1383.	IC4H10+0=TC4H9+0H	3.27E-19	2.40E+00	5.79E+02

R1384.	IC4H10+O=IC4H9+OH	6.72E-17	2.03E+00	2.58E+03
R1385.	IC4H10+CH30=IC4H9+CH30H	7.97E-13	0.00E+00	3.52E+03
R1386.	IC4H10+CH30=TC4H9+CH30H	3.16E-14	0.00E+00	1.41E+03
R1387.	IC4H10+02=IC4H9+H02	1.49E-10	0.00E+00	2.63E+04
R1388.	IC4H10+02=TC4H9+H02	1.66E-11	0.00E+00	2.43E+04
R1389.	IC4H10+CH302=IC4H9+CH302H	3.45E-24	3.97E+00	9.20E+03
R1390.	IC4H10+C2H5O2=IC4H9+C2H5O2H	4.23E-11	0.00E+00	1.03E+04
R1391.	IC4H10+CH3CO3=IC4H9+CH3CO3H	4.23E-11	0.00E+00	1.03E+04
R1392.	IC4H10+NC3H702=IC4H9+NC3H702H	4.23E-11	0.00E+00	1.03E+04
R1393.	IC4H10+IC3H702=IC4H9+IC3H702H	4.23E-11	0.00E+00	1.03E+04
R1394.	IC4H10+IC4H902=IC4H9+IC4H902H	4.23E-11	0.00E+00	1.03E+04
R1395.	IC4H10+TC4H902=IC4H9+TC4H902H	4.23E-11	0.00E+00	1.03E+04
R1396.	IC4H10+02CHO=IC4H9+H02CH0	4.18E-11	0.00E+00	1.03E+04
R1397.	IC4H10+02CH0=TC4H9+H02CH0	4.65E-12	0.00E+00	8.06E+03
R1398.	IC4H10+SC4H902=IC4H9+SC4H902H	3.74E-11	0.00E+00	1.03E+04
R1399.	IC4H10+SC4H902=TC4H9+SC4H902H	4.65E-12	0.00E+00	8.05E+03
R1400.	IC4H10+PC4H902=IC4H9+PC4H902H	3.74E-11	0.00E+00	1.03E+04
R1401.	IC4H10+PC4H902=TC4H9+PC4H902H	4.65E-12	0.00E+00	8.05E+03
R1402.	IC4H10+CH302=TC4H9+CH302H	2.27E-22	3.12E+00	6.64E+03
R1403.	IC4H10+C2H502=TC4H9+C2H502H	4.65E-12	0.00E+00	8.05E+03
R1404.	IC4H10+CH3CO3=TC4H9+CH3CO3H	4.65E-12	0.00E+00	8.05E+03
R1405.	TC4H10+NC3H702=TC4H9+NC3H702H	4.65E-12	0.00E+00	8.05E+03
B1406	TC4H10+TC3H702=TC4H9+TC3H702H	4.65E-12	0.00E+00	8.05E+03
R1407	TC4H10+TC4H902=TC4H9+TC4H902H	4.65E-12	0.00E+00	8.05E+03
R1408	TC4H10+TC4H902=TC4H9+TC4H902H	4 65E-12	0 00E+00	8 05E+03
R1409	TC4H10+TC4H9=TC4H9+TC4H10	4 15E-14	0.00E+00	3 98E+03
R1410	TC4H9+HD2=TC4H9D+DH	1.16E-11	0.00E+00	-5.03E+02
R1411	TC4H9+HD2=TC4H9D+DH	1.16E-11	0.00E+00	-5 03E+02
R1412	CH302+TC4H9=CH30+TC4H90	1 16F-11	0.00E+00	-5 03F+02
R1413	CH302+TC4H9=CH30+TC4H90	1 16F-11	0.00E+00	-5 03F+02
R1414		3 56F+10	8 80F-01	1 74F+04
R1415	TC4H8+H=TC4H9	1 04F-12	5 10F-01	1 32F+03
R1416	C3H6+CH3=TC4H9	3 14F-91	2 67F+00	3 45F+03
R1417	H+TC4H8=TC4H9	1 76F-12	5 10F-01	6 19F+02
R1418	тсано-точно тсано+по=тсана+ноо	1 39F-24	3 59F+00	6 02F+03
R1410.	10410 + 02 = 10410 + 102 10410 + 02 = 10410 + 102	1.39L 24	3.71F+00	4 69F+03
R1420	NC3H7O2+TC4H9=NC3H7O+TC4H9O	1.16F-11	0.00F+00	-5 03F+02
R1420.	NC3H7D2+TC4H9=NC3H7D+TC4H9D	1.10L 11 1 16F-11	0.00E+00	-5 03E+02
R1421.	NC3H702 + IC4H7 = NC3H70 + IC4H70	1.10L 11 1 16F-11	0.00E+00	-5 03E+02
R1422.	SCAHOD2+1CAHO=SCAHOD+1CAHOD	1.10L 11 1 16F-11	0.00E+00	-5 03E+02
R1420.	SC4H9D2+TC4H9=SC4H9D+TC4H9D	1.10L 11 1 16F-11	0.00E+00	-5 03E+02
R1425	PCAHQD2+TCAHQ=PCAHQD+TCAHQD	1.10L 11 1 16F-11	0.00E+00	-5 03E+02
R1425.		1.10E 11 1 16E-11	0.00E+00	-5 03E+02
R1420.		1.10E 11 1 16E-11	0.00E+00	-5 03E+02
R1427.		1.10L 11 1.16E_11	0.00E+00	-5 03E+02
R1420.	10411902 104117 - 5041190 - 104117 0	3 75E-10	0.00E+00	0.00E+02
R1429.	TC/HQ+02-TC/HQ02	3.75E 12 3.75E 11	0.00E+00	0.00E+00
D1/21		2.34E 11 1 86E-11	0.00E+00	8 01E+03
D1/20		1.00E 11	0.00E+00	8 01E+03
R1/132		2.80E 11	0.005+00	1 035100
R1/13/		2.025 II 0 80F-11	0.005+00	1 025104
R1435	ТСЗН7О2+ТСАН9=ТСЗН7О+ТСАН9 ТСЗН7О2+ТСАН9=ТСЗН7О+ТСАН9О	2.025 11 1 16F-11	0.005+00	-5 035+04
R1/136	103H7D2+TC/HQ=1C3H7D+TC/HQD	1.10E II 1.16F-11	0.005+00	-5 03E+02
D1/27	103H702+104H9=103H70+104H90	1.10C-11 1.16F-11	0.005+00	-5 02E+02
11437.	10311102+10401-103010+104010	1.106-11	0.005-00	-0.035+02

R1438.	IC4H902+C3H6=IC4H902H+C3H5-A	5.38E-13	0.00E+00	7.50E+03
R1439.	TC4H902+C3H6=TC4H902H+C3H5-A	5.38E-13	0.00E+00	7.50E+03
R1440.	IC4H902+IC4H8=IC4H902H+IC4H7	2.32E-12	0.00E+00	7.50E+03
R1441.	TC4H902+IC4H8=TC4H902H+IC4H7	2.32E-12	0.00E+00	7.50E+03
R1442.	PC4H902+IC4H8=PC4H902H+IC4H7	2.32E-12	0.00E+00	7.50E+03
R1443.	SC4H902+IC4H8=SC4H902H+IC4H7	2.32E-12	0.00E+00	7.50E+03
R1444.	IC3H702+IC4H8=IC3H702H+IC4H7	2.32E-12	0.00E+00	7.50E+03
R1445.	NC3H702+IC4H8=NC3H702H+IC4H7	2.32E-12	0.00E+00	7.50E+03
R1446.	IC4H902+C4H8-1=IC4H902H+C4H71-3	2.32E-12	0.00E+00	7.50E+03
R1447.	TC4H902+C4H8-1=TC4H902H+C4H71-3	2.32E-12	0.00E+00	7.50E+03
R1448.	IC4H902+C4H8-2=IC4H902H+C4H71-3	2.32E-12	0.00E+00	7.50E+03
R1449.	TC4H902+C4H8-2=TC4H902H+C4H71-3	2.32E-12	0.00E+00	7.50E+03
R1450.	CC4H80+0H=CH20+C3H5-A+H20	8.30E-12	0.00E+00	0.00E+00
R1451.	CC4H80+H=CH20+C3H5-A+H2	5.83E-17	2.00E+00	2.52E+03
R1452.	CC4H80+0=CH20+C3H5-A+OH	1.87E-10	0.00E+00	2.62E+03
R1453.	CC4H80+H02=CH20+C3H5-A+H202	1.66E-11	0.00E+00	7.55E+03
R1454.	CC4H80+CH302=CH20+C3H5-A+CH302H	1.66E-11	0.00E+00	9.56E+03
R1455.	CC4H80+CH3=CH20+C3H5-A+CH4	3.32E-13	0.00E+00	5.03E+03
R1456.	C2H4+TC4H9O2=C2H3+TC4H9O2H	1.43E-23	3.75E+00	1.37E+04
R1457.	TC4H902+CH4=TC4H902H+CH3	1.88E-11	0.00E+00	1.03E+04
R1458.	H2+TC4H9O2=H+TC4H9O2H	5.00E-11	0.00E+00	1.31E+04
R1459.	TC4H902+C2H6=TC4H902H+C2H5	2.82E-11	0.00E+00	1.03E+04
R1460.	TC4H902+C3H8=TC4H902H+IC3H7	3.32E-12	0.00E+00	8.55E+03
R1461.	TC4H902+C3H8=TC4H902H+NC3H7	2.82E-11	0.00E+00	1.03E+04
R1462.	TC4H902+CH30H=TC4H902H+CH20H	1.05E-11	0.00E+00	9.74E+03
R1463.	TC4H902+C2H50H=TC4H902H+PC2H40H	1.05E-11	0.00E+00	9.74E+03
R1464.	TC4H902+C2H50H=TC4H902H+SC2H40H	6.97E-12	0.00E+00	7.55E+03
R1465.	IC4H902+CH3CH0=IC4H902H+CH3C0	4.65E-12	0.00E+00	6.84E+03
R1466.	TC4H902+CH3CH0=TC4H902H+CH3C0	4.65E-12	0.00E+00	6.84E+03
R1467.	IC4H902+C2H3CH0=IC4H902H+C2H3C0	4.65E-12	0.00E+00	6.84E+03
R1468.	TC4H902+C2H3CH0=TC4H902H+C2H3C0	4.65E-12	0.00E+00	6.84E+03
R1469.	IC4H902+C2H5CH0=IC4H902H+C2H5C0	4.65E-12	0.00E+00	6.84E+03
R1470.	TC4H902+C2H5CH0=TC4H902H+C2H5C0	4.65E-12	0.00E+00	6.84E+03
R1471.	IC4H902+H02=IC4H902H+02	2.91E-14	0.00E+00	-1.65E+03
R1472.	TC4H902+H02=TC4H902H+02	2.91E-14	0.00E+00	-1.65E+03
R1473.	IC4H902+H202=IC4H902H+H02	3.99E-12	0.00E+00	5.03E+03
R1474.	TC4H902+H202=TC4H902H+H02	3.99E-12	0.00E+00	5.03E+03
R1475.	IC4H902+CH20=IC4H902H+HC0	2.16E-13	0.00E+00	4.53E+03
R1476.	TC4H902+CH20=TC4H902H+HC0	2.16E-13	0.00E+00	4.53E+03
R1477.	IC4H902+CH302=IC4H90+CH30+02	2.32E-08	-1.61E+00	9.36E+02
R1478.	TC4H902+CH302=TC4H90+CH30+02	2.32E-08	-1.61E+00	9.36E+02
R1479.	IC4H902+C2H502=IC4H90+C2H50+02	2.32E-08	-1.61E+00	9.36E+02
R1480.	TC4H902+C2H502=TC4H90+C2H50+02	2.32E-08	-1.61E+00	9.36E+02
R1481.	IC4H902+CH3C03=IC4H90+CH3C02+02	2.32E-08	-1.61E+00	9.36E+02
R1482.	TC4H902+CH3C03=TC4H90+CH3C02+02	2.32E-08	-1.61E+00	9.36E+02
R1483.	IC4H902+IC4H902=02+IC4H90+IC4H90	2.32E-08	-1.61E+00	9.36E+02
R1484.	IC4H902+TC4H902=IC4H90+TC4H90+02	2.32E-08	-1.61E+00	9.36E+02
R1485.	TC4H902+TC4H902=02+TC4H90+TC4H90	2.32E-08	-1.61E+00	9.36E+02
R1486.	IC4H902+PC4H902=IC4H90+PC4H90+02	2.32E-08	-1.61E+00	9.36E+02
R1487.	TC4H902+PC4H902=TC4H90+PC4H90+02	2.32E-08	-1.61E+00	9.36E+02
R1488.	IC4H902+SC4H902=IC4H90+SC4H90+02	2.32E-08	-1.61E+00	9.36E+02
R1489.	TC4H902+SC4H902=TC4H90+SC4H90+02	2.32E-08	-1.61E+00	9.36E+02
R1490.	IC4H902+NC3H702=IC4H90+NC3H70+02	2.32E-08	-1.61E+00	9.36E+02
R1491.	TC4H902+NC3H702=TC4H90+NC3H70+02	2.32E-08	-1.61E+00	9.36E+02

R1492.	IC4H902+IC3H702=IC4H90+IC3H70+02	2.32E-08	-1.61E+00	9.36E+02
R1493.	TC4H902+IC3H702=TC4H90+IC3H70+02	2.32E-08	-1.61E+00	9.36E+02
R1494.	IC4H902+H02=IC4H90+OH+O2	2.32E-08	-1.61E+00	9.36E+02
R1495.	TC4H902+H02=TC4H90+0H+02	2.32E-08	-1.61E+00	9.36E+02
R1496.	IC4H902+CH3=IC4H90+CH30	1.16E-11	0.00E+00	-5.03E+02
R1497.	IC4H902+C2H5=IC4H90+C2H50	1.16E-11	0.00E+00	-5.03E+02
R1498.	IC4H9O2+IC3H7=IC4H9O+IC3H7O	1.16E-11	0.00E+00	-5.03E+02
R1499.	IC4H902+NC3H7=IC4H90+NC3H70	1.16E-11	0.00E+00	-5.03E+02
R1500.	IC4H902+PC4H9=IC4H90+PC4H90	1.16E-11	0.00E+00	-5.03E+02
R1501.	IC4H902+SC4H9=IC4H90+SC4H90	1.16E-11	0.00E+00	-5.03E+02
R1502.	IC4H902+IC4H9=IC4H90+IC4H90	1.16E-11	0.00E+00	-5.03E+02
R1503.	IC4H902+TC4H9=IC4H90+TC4H90	1.16E-11	0.00E+00	-5.03E+02
R1504.	TC4H902+C3H5-A=TC4H90+C3H50	1.16E-11	0.00E+00	-5.03E+02
R1505	TC4H902+C4H71-3=TC4H90+C4H70	1.16E-11	0.00E+00	-5.03E+02
R1506	TC4H902+TC4H7=TC4H90+TC4H70	1 16E-11	0 00E+00	-5 03E+02
R1507		1.10E 11 1 16F-11	0.00E+00	-5 03F+02
R1508	TCAHQO2+C2H5=TCAHQO+C2H5O	1.10E 11 1 16E-11	0.00E+00	-5 03F+02
R1500.		1.10E 11 1.16E_11	0.000000	-5 025+02
R1509.	104H902+103H7-104H90+103H70	1.10E-11 1.16E-11	0.00E+00	-5.03E+02
NIGIU.		$1.10E^{-11}$	0.00E+00	-5.03E+02
RIDII.		1.10E-11	0.00E+00	-5.03E+02
RIDIZ.	TC4H9U2+SC4H9=TC4H9U+SC4H9U	1.10E-11	0.00E+00	-5.03E+02
R1513.		1.16E-11	0.00E+00	-5.03E+02
R1514.	TC4H9U2+TC4H9=TC4H9U+TC4H9U	1.16E-11	0.00E+00	-5.03E+02
R1515.	TC4H9U2+C3H5-A=TC4H9U+C3H5U	1.16E-11	0.00E+00	-5.03E+02
R1516.	TC4H902+C4H71-3=TC4H90+C4H70	1.16E-11	0.00E+00	-5.03E+02
R1517.	TC4H902+IC4H7=TC4H90+IC4H70	1.16E-11	0.00E+00	-5.03E+02
R1518.	IC4H902+C2H4=IC4H902H+C2H3	3.32E-13	0.00E+00	3.02E+03
R1519.	IC4H902+CH4=IC4H902H+CH3	1.88E-11	0.00E+00	1.03E+04
R1520.	H2+IC4H9O2=H+IC4H9O2H	5.00E-11	0.00E+00	1.31E+04
R1521.	IC4H902+C2H6=IC4H902H+C2H5	2.82E-11	0.00E+00	1.03E+04
R1522.	IC4H902+C3H8=IC4H902H+IC3H7	3.32E-12	0.00E+00	8.55E+03
R1523.	IC4H902+C3H8=IC4H902H+NC3H7	2.82E-11	0.00E+00	1.03E+04
R1524.	IC4H902+CH30H=IC4H902H+CH20H	1.05E-11	0.00E+00	9.74E+03
R1525.	IC4H902+C2H50H=IC4H902H+PC2H40H	1.05E-11	0.00E+00	9.74E+03
R1526.	IC4H902+C2H50H=IC4H902H+SC2H40H	6.97E-12	0.00E+00	7.55E+03
R1527.	IC4H9O2H=IC4H9O+OH	1.50E+16	0.00E+00	2.14E+04
R1528.	TC4H902H=TC4H90+0H	5.95E+15	0.00E+00	2.14E+04
R1529.	IC4H90+H02=IC3H7CH0+H2O2	1.66E-12	0.00E+00	0.00E+00
R1530.	IC4H90+0H=IC3H7CH0+H20	3.01E-11	0.00E+00	0.00E+00
R1531.	IC4H90+CH3=IC3H7CH0+CH4	3.99E-11	0.00E+00	0.00E+00
R1532.	IC4H90+0=IC3H7CH0+0H	9.96E-12	0.00E+00	0.00E+00
R1533.	IC4H90+H=IC3H7CH0+H2	3.30E-11	0.00E+00	0.00E+00
R1534.	IC3H7CHO+H=IC4H9O	1.66E-12	0.00E+00	2.95E+03
R1535.	CH20+IC3H7=IC4H90	8.30E-14	0.00E+00	1.17E+03
R1536.	CH3COCH3+CH3=TC4H9O	2.49E-13	0.00E+00	5.99E+03
R1537.	IC4H90+02=IC3H7CH0+H02	3.20E-13	0.00E+00	8.35E+02
R1538.	TC4H90+02=IC4H80+H02	1.35E-12	0.00E+00	2.37E+03
R1539.	IC4H80=IC3H7CH0	4.18E+13	0.00E+00	2.65E+04
R1540.	IC4H80+0H=IC3H6CH0+H20	2.08E-12	0.00E+00	0.00E+00
R1541.	IC4H80+H=IC3H6CH0+H2	2.08E-12	0.00E+00	0.00E+00
R1542.	IC4H80+H02=IC3H6CH0+H202	4.15E-12	0.00E+00	7.55E+03
R1543.	IC4H80+CH302=IC3H6CH0+CH302H	4.15E-12	0.00E+00	9.56E+03
R1544	IC4H80+CH3=IC3H6CH0+CH4	8.30E-14	0.00E+00	5.03E+03
R1545	IC4H80+0=IC3H6CH0+0H	2.08E-12	0.00E+00	0.00E+00

R1546.	TC3H6CHO+H=IC3H7CHO	3.32E-10	0.00E+00	0.00E+00
R1547.	IC3H7+HCO=IC3H7CHO	3.01E-11	0.00E+00	0.00E+00
R1548.	IC3H7CH0+H02=IC3H7C0+H2O2	4.98E-12	0.00E+00	6.00E+03
R1549.	IC3H7CH0+H02=TC3H6CH0+H202	1.33E-13	0.00E+00	6.00E+03
R1550.	IC3H7CH0+CH3=IC3H7C0+CH4	6.61E-12	0.00E+00	4.38E+03
R1551.	IC3H7CH0+0=IC3H7C0+0H	1.19E-11	0.00E+00	6.99E+02
R1552.	IC3H7CH0+02=IC3H7C0+H02	6.64E-11	0.00E+00	1.89E+04
R1553.	IC3H7CH0+OH=IC3H7C0+H20	4.47E-14	7.60E-01	-1.71E+02
R1554.	IC3H7CH0+0H=TC3H6CH0+H20	2.80E-12	0.00E+00	-3.93E+02
R1555.	IC3H7CH0+H=IC3H7C0+H2	4.32E-12	0.00E+00	1.31E+03
R1556.	IC3H7CH0+0H=IC3H6CH0+H20	5.18E-18	2.00E+00	-1.50E+02
R1557.	IC3H7CH0+H02=IC3H6CH0+H202	4.55E-20	2.55E+00	7.80E+03
R1558.	ТСЗН7СНО+СНЗО2=ТСЗН6СНО+СНЗО2Н	7.90E-20	2.55E+00	8.30E+03
R1559	1C3H7+CO=1C3H7CO	2.49E-13	0.00E+00	2.42E+03
R1560		1 66E-13	0 00E+00	3 93E+03
R1561		1.66F-13	0.00E+00	3 935+03
R1562		1.00E 10	0.000000	_/ 83E+00
D1562		1.00E 12	0.00E+00	-5 54E+02
R1505.	103040000+02-102040000	1.99E-13 1.95E+10	0.00E+00	-5.54E+02
R1504.		1.25E+10 7 FOF+10	0.00E+00	9.01E+03
R1505.	1C4H9U2=1C4H8U2H-1	7.50E+10	0.00E+00	1.236+04
R1566.	1C4H9U2=1C4H8U2H-1	9.00E+11	0.00E+00	1.74E+04
R1567.	1C4H9U2=1C4H8U2H-1	1.00E+11	0.00E+00	1.4/E+04
R1568.	1C4H9U2=1C4H8+HU2	2.27E+35	-7.22E+00	1.99E+04
R1569.	TC4H902=IC4H8+H02	7.61E+42	-9.41E+00	2.09E+04
R1570.	IC4H802H-I+02=IC4H800H-I02	3.75E-12	0.00E+00	0.00E+00
R1571.	TC4H802H-I+02=TC4H800H-I02	3.75E-12	0.00E+00	0.00E+00
R1572.	IC4H802H-T+02=IC4H800H-T02	2.34E-11	0.00E+00	0.00E+00
R1573.	IC4H800H-IO2=IC4KETII+OH	5.00E+10	0.00E+00	1.08E+04
R1574.	IC4H800H-TO2=IC4KETIT+OH	4.00E+11	0.00E+00	1.59E+04
R1575.	TC4H800H-IO2=TIC4H7Q2-I	7.50E+10	0.00E+00	1.23E+04
R1576.	IC4H7OOH+HO2=TIC4H7Q2-I	1.66E-13	0.00E+00	5.33E+03
R1577.	IC4H800H-IO2=IIC4H7Q2-I	3.75E+10	0.00E+00	1.23E+04
R1578.	IC4H80OH-IO2=IIC4H7Q2-T	1.00E+11	0.00E+00	1.47E+04
R1579.	IC4H800H-T02=TIC4H7Q2-I	6.00E+11	0.00E+00	1.74E+04
R1580.	AC3H5OOH+CH2O2H=IIC4H7Q2-I	1.41E-13	0.00E+00	5.33E+03
R1581.	IC4H7OOH+HO2=IIC4H7Q2-T	1.66E-13	0.00E+00	3.93E+03
R1582.	CH202H=CH20+0H	9.00E+14	0.00E+00	7.55E+02
R1583.	IC4KETII=CH2O+C2H5CO+OH	1.50E+16	0.00E+00	2.11E+04
R1584.	IC4KETIT=CH3COCH3+HCO+OH	9.50E+15	0.00E+00	2.14E+04
R1585.	IC4H8+H02=TC4H802H-I	6.59E-13	0.00E+00	6.35E+03
R1586.	IC4H8+H02=IC4H802H-T	6.59E-13	0.00E+00	6.35E+03
R1587.	IC4H802H-I=CC4H80+0H	4.47E+11	0.00E+00	1.10E+04
R1588.	TC4H802H-T=TC4H80+0H	3.09E+12	0.00E+00	6.74E+03
R1589.	TC4H802H-T=TC4H80+0H	3.98E+12	0.00E+00	8.55E+03
R1590	TC4H802H-T=0H+CH20+C3H6	8.45E+15	-6.80E-01	1.47E+04
R1591	104H8 = C3H5 - T + CH3	1 92E+66	-1 42E+01	6 45E+04
R1592	10 me 00 me $10 \text$	3 07F+55	-1 15F+01	5 75F+04
R1503		9 /3F+09	-5 72F+00	1 01F+04
R1500.		5.45E-10	2 50E+00	1.01010104
R15054.		5.005-19	2.305+00 1 765+00	1.20E+V3
N1090.		0.00E-17 0.76E-17	1 76E+00	2 00E101
N1090.	TC4R0+0-TC4R2+0R TC4R0+0-TC4R2+0R	2.10E-11 2.00E-12		3.02E+U1
N1091.		Z.UUE-13	7.000-01 2 EARIAA	0.04E+U3
R1090.		1.34E-24	3.50E+00	2.00E+U3
KI599.	104no+HUZ=104H/+H2UZ	3.20E-20	2.005+00	7.00E+03

R1600.	IC4H8+02CH0=IC4H7+H02CH0	3.20E-20	2.60E+00	7.00E+03
R1601.	IC4H8+02=IC4H7+H02	9.96E-12	0.00E+00	2.01E+04
R1602.	IC4H8+C3H5-A=IC4H7+C3H6	1.32E-12	0.00E+00	1.03E+04
R1603.	IC4H8+C3H5-S=IC4H7+C3H6	1.32E-12	0.00E+00	1.03E+04
R1604.	IC4H8+C3H5-T=IC4H7+C3H6	1.32E-12	0.00E+00	1.03E+04
R1605.	IC4H8+OH=IC4H7+H2O	8.63E-18	2.00E+00	-1.50E+02
R1606.	IC4H8+O=IC3H7+HCO	2.62E-17	1.76E+00	-6.12E+02
R1607.	IC4H8+CH3O2=IC4H7+CH3O2H	3.20E-20	2.60E+00	7.00E+03
R1608.	IC4H8+H02=IC4H80+OH	2.14E-12	0.00E+00	6.71E+03
R1609.	IC4H7+02=IC3H5CH0+0H	4.10E-11	-4.50E-01	1.16E+04
R1610.	IC4H7+02=CH3C0CH2+CH20	1.19E-08	-1.21E+00	1.06E+04
R1611.	IC4H7+O2=C3H4-A+CH2O+OH	1.21E+06	-5.71E+00	1.08E+04
R1612.	IC4H7+O=IC3H5CHO+H	1.00E-10	0.00E+00	0.00E+00
R1613.	IC4H7=C3H4-A+CH3	1.23E+47	-9.74E+00	3.74E+04
R1614.	CH302+IC4H7=CH30+IC4H70	1.16E-11	0.00E+00	-5.03E+02
R1615.	TC4H7+H02=TC4H70+0H	1.16E-11	0.00E+00	-5.03E+02
R1616	C3H5-T+CH20=TC4H70	1.66E-13	0.00E+00	6.34E+03
R1617	TC4H70=TC4H60H	1 39E+11	0 00E+00	7 85E+03
R1618	IC4H70=IC3H5CH0+H	5.00E+13	0.00E+00	1.46E+04
R1619	TCAH60H+H2=TCAH70H+H	3 59F-20	2 38F+00	9 56F+03
R1620	104H00H+H2 = 104H00H+H02	9 96F-11	0.00E+00	2 01F+04
R1621		1 05F-15	1 90E+00	9 15F+03
R1021.		7 80F-22	1.90E+00	9.10E+03
R1022.	1040000+10400-1040700+10407	1.60E-22	0.00E+00	9.90E+03
R1023.		1.00E-10		6 92E+00
R1024.		1.50E-10	2.052+00	0.03E+03
R1025.		1.00E-13	0.00E+00	4.03E+03
R1020.		4.98E-14	0.00E+00	8.30E+02
R1027.	104H70+H02=103H50H0+H202	4.98E-13	0.000+00	0.00E+00
R1628.		3.99E-11	0.00E+00	0.00E+00
R1629.		9.96E-12	0.00E+00	0.00E+00
R1630.	1C4H7U+UH=1C3H5CHU+H2U	3.01E-11	0.00E+00	0.00E+00
R1631.	1C4H7U+H=1C3H5CHU+H2	3.30E-11	0.00E+00	0.00E+00
R1632.	1C3H5CH0+0H=1C3H5C0+H20	4.47E-14	7.60E-01	-1.71E+02
R1633.	IC3H5CH0+H02=IC3H5C0+H202	1.66E-12	0.00E+00	6.00E+03
R1634.	IC3H5CH0+CH3=IC3H5C0+CH4	6.61E-12	0.00E+00	4.38E+03
R1635.	IC3H5CH0+0=IC3H5C0+0H	1.19E-11	0.00E+00	6.99E+02
R1636.	IC3H5CH0+02=IC3H5C0+H02	3.32E-11	0.00E+00	2.05E+04
R1637.	IC3H5CH0+H=IC3H5C0+H2	4.32E-12	0.00E+00	1.31E+03
R1638.	IC3H5CO=C3H5-T+CO	1.28E+20	-1.89E+00	1.73E+04
R1639.	ТСЗН60СН0+0Н=ТСЗН6СН0+Н02	3.35E-07	-1.20E+00	1.06E+04
R1640.	TC3H60CH0=CH3C0CH3+HC0	3.98E+13	0.00E+00	4.88E+03
R1641.	IC3H5CH0+H=TC3H6CH0	2.16E-11	0.00E+00	6.04E+02
R1642.	IC3H6CO+H=TC3H6CHO	2.16E-11	0.00E+00	2.42E+03
R1643.	TC3H6CH0+H2=IC3H7CH0+H	3.59E-19	2.38E+00	9.56E+03
R1644.	IC4H70+OH=IC4H70OH	1.66E-13	0.00E+00	0.00E+00
R1645.	IC4H7O+H=IC4H7OH	6.64E-11	0.00E+00	0.00E+00
R1646.	IC4H7OH+H=IC4H8OH	1.66E-11	0.00E+00	6.04E+02
R1647.	IC4H70+H2=IC4H70H+H	1.50E-17	2.00E+00	8.97E+03
R1648.	IC4H7+OH=IC4H7OH	4.98E-11	0.00E+00	0.00E+00
R1649.	IC4H70H+HCO=IC4H70+CH20	5.01E-13	0.00E+00	9.14E+03
R1650.	TC3H6CH0+CH20=IC3H7CH0+HC0	4.18E-16	1.90E+00	9.15E+03
R1651.	TC3H6CH0+IC4H8=IC3H7CH0+IC4H7	7.80E-22	3.30E+00	9.98E+03
R1652.	IC3H6C0+OH=IC3H7+C02	2.87E-12	0.00E+00	-5.08E+02
R1653.	ТСЗН6СН0+ОН=ТСЗН6ОНСНО	8.30E-11	0.00E+00	0.00E+00

R1654.	ТСЗН6ОН+НСО=ТСЗН6ОНСНО	3.01E-11	0.00E+00	0.00E+00
R1655.	СНЗСОСНЗ+Н=ТСЗН6ОН	1.33E-11	0.00E+00	4.78E+03
R1656.	IC3H5OH+H=TC3H6OH	1.04E-12	5.10E-01	2.02E+03
R1657.	C3H5-T+OH=IC3H5OH	8.30E-11	0.00E+00	0.00E+00
R1658.	TC3H6CH0+02=TC3H602CH0	3.30E-07	-2.10E+00	0.00E+00
R1659.	TC3H602CH0=IC3H502HCH0	6.00E+11	0.00E+00	1.50E+04
R1660.	TC3H602CH0=TC3H602HC0	1.00E+11	0.00E+00	1.30E+04
R1661.	IC3H5CH0+H02=IC3H502HCH0	3.70E-13	0.00E+00	5.33E+03
R1662.	TC3H602HCO=CH3C0CH3+CO+OH	4.24E+18	-1.43E+00	2.42E+03
R1663.	TC3H60H+02=CH3C0CH3+H02	3.70E-11	0.00E+00	0.00E+00
R1664.	IC3H6C0+OH=TC3H6OH+C0	3.32E-12	0.00E+00	-5.08E+02
R1665.	TC3H6CH0+H02=IC3H7CH0+02	6.10E-12	0.00E+00	6.59E+02
R1666.	TC3H6CH0+CH3=IC3H5CH0+CH4	5.00E-12	-3.20E-01	-6.59E+01
R1667.	TC4H8CHO=IC3H5CHO+CH3	1.00E+13	0.00E+00	1.32E+04
R1668.	TC4H8CHO=IC4H8+HCO	8.52E+12	0.00E+00	1.01E+04
R1669.	TC4H8CH0+02=02C4H8CH0	3.32E-12	0.00E+00	0.00E+00
R1670.	02C4H8CH0=02HC4H8C0	2.16E+11	0.00E+00	7.73E+03
R1671.	TC4H802H-T+C0=02HC4H8C0	2.49E-13	0.00E+00	2.42E+03
R1672.	IC4H70+IC4H8=IC4H70H+IC4H7	4.48E-13	0.00E+00	2.01E+03
R1673.	TC4H60H+H02=CH2CCH20H+CH20+0H	2.40E-11	0.00E+00	0.00E+00
R1674.	TC4H8+CH2CCH2OH=TC4H7+C3H5OH	1.32E-12	0.00E+00	1.03E+04
R1675	CH2CCH2OH+H2O2=C3H5OH+HO2	5.00E-15	0.00E+00	1.30E+03
R1676	C3H5OH+OH=CH2CCH2OH+H2O	8 40E-12	0 00E+00	3 00E+03
R1677	C3H50H+H=CH2CCH20H+H2	6 48F-19	2 50E+00	2 93F+03
R1678	C3H50H+02=CH2CCH20H+H02	6 64F-11	0.00E+00	3 05F+04
R1670		3 QQF-13	0.00E+00	4 04F+03
R1680		A 98F-11	0.00E+00	0.00F+00
R1681		1.50L 11	0.00E+00	0.00E+00
R1682		7 20E-12	0.00E+00	0.00E+00
R1683		7.20L 12 2 16F+/0	-8 31E+00	2.001+00
D160/		2.10E+40 1 /1E-11	0.005+00	1 01E+02
D1605		1.415 11 1 66E-10	0.000000	2 /65+02
R1000.		1.00E-12		3.40E+03
R1000.	C_{2} L_{1} C_{2} L_{2} C_{2} L_{2} C_{2} L_{2} C_{2} L_{2} L_{2	2.00E+11		9 E4E+04
R1007.		9.30E-04	-2.54E+00	0.04E+02
R1000.		2.32E-12	0.00E+00	5.03E+03
R1009.		8.30E-12	0.000+00	0.00E+00
R1690.		3.32E-12	0.00E+00	0.00E+00
R1691.		9.33E-13	0.00E+00	1.63E+03
R1692.	C4H5-N+C2H2=C6H6+H	2.66E-08	-1.33E+00	2.72E+03
R1693.	C4H5-N+C2H3=C6H6+H2	3.06E-37	7.07E+00	-1.82E+03
R1694.		8.30E-10	0.00E+00	1.26E+04
R1695.	C4H5-2+C2H4=C5H6+CH3	8.30E-10	0.00E+00	1.26E+04
R1696.	С6H2+H=С6H3	1.83E+06	-4.92E+00	5.43E+03
R1697.	C6H3+H=C4H2+C2H2	4.65E-01	-2.55E+00	5.42E+03
R1698.	C6H3+H=L-C6H4	5.65E+19	-9.01E+00	6.10E+03
R1699.	С6Н3+Н=С6Н2+Н2	4.98E-11	0.00E+00	0.00E+00
R1700.	C6H3+OH=C6H2+H2O	6.64E-12	0.00E+00	0.00E+00
R1701.	L-C6H4+H=C6H5	2.82E+54	-1.97E+01	1.58E+04
R1702.	L-C6H4+H=C-C6H4+H	2.32E+30	-1.17E+01	1.74E+04
R1703.	L-C6H4+H=C6H3+H2	2.21E-18	2.53E+00	4.65E+03
R1704.	L-C6H4+OH=C6H3+H2O	5.15E-18	2.00E+00	2.16E+02
R1705.	С-С6Н4+Н=С6Н5	3.99E+36	-1.37E+01	1.48E+04
R1706.	C4H3-N+C2H2=L-C6H4+H	4.15E-10	-5.60E-01	5.33E+03
R1707.	C4H3-N+C2H2=C6H5	1.59E+47	-1.78E+01	1.58E+04

R1708.	C4H3-N+C2H2=C-C6H4+H	1.15E+23	-1.00E+01	1.51E+04
R1709.	C4H3-I+CH3=C5H6	1.66E-12	0.00E+00	0.00E+00
R1710.	C4H2+C2H=C6H2+H	1.59E-10	0.00E+00	0.00E+00
R1711.	C4H2+C2H=C6H3	7.47E+13	-7.68E+00	3.57E+03
R1712.	C4H4+C2H=L-C6H4+H	1.99E-11	0.00E+00	0.00E+00
R1713.	C6H5+H=C6H6	1.66E-10	0.00E+00	0.00E+00
R1714.	C6H5+H+M=C6H6+M	1.82E+28	-1.63E+01	3.52E+03
R1715.	C6H6+O2=C6H5+HO2	1.05E-10	0.00E+00	3.02E+04
R1716.	C6H6+O=C6H5O+H	3.65E-11	0.00E+00	2.28E+03
R1717.	C6H6+O=C6H5+OH	3.32E-11	0.00E+00	7.40E+03
R1718.	C6H6+H=C6H5+H2	4.15E-10	0.00E+00	8.05E+03
B1719.	C6H6+CH3=C6H5+CH4	1.22E-11	0.00E+00	9.52E+03
B1720	С6Н6+Н02=С6Н5+Н202	9.13E-12	0.00E+00	1.45E+04
R1721	С6Н6+ОН=С6Н5+Н2О	1 99E-24	4 10E+00	-1.51E+02
B1722	С6Н6+0Н=С6Н50Н+Н	2 19F-22	3 25F+00	2 81F+03
R1722.	C6H5=H+CAH2+C2H2	2.10E 22 4 30F+12	6 20E-01	3 89F+0/
R1720.		1 /DE-10	0.20E 01 2 10E+00	1 01E+01
R1724.		$1.42E^{-19}$	2.19E+00	1.91E+01
R1725.		1.42E-19 9.20E-10	2.19E+00	1.91E+01
R1720.		0.30E-12	0.00E+00	0.00E+00
R1/2/.		4.32E-11	0.00E+00	3.08E+03
R1728.		4.98E-11	0.00E+00	4.52E+03
R1729.	C6H5+U2=C6H5UU	3.09E-11	-2.20E-01	-3.58E+02
R1730.	C6H5UU=C6H5U+U	1.27E+15	-2.46E-01	1.94E+04
R1731.	C6H5O+OH=C6H5OOH	3.32E-11	0.00E+00	0.00E+00
R1732.	C6H500+C6H50H=C6H500H+C6H50	2.21E-13	0.00E+00	7.05E+03
R1733.	C6H50H+02=C6H50+H02	1.66E-11	0.00E+00	1.95E+04
R1734.	С6Н50Н+О=ОС6Н4ОН+Н	2.66E-11	0.00E+00	1.71E+03
R1735.	C6H5OH+H=C6H5O+H2	1.99E-10	0.00E+00	6.24E+03
R1736.	C6H5OH+O=C6H5O+OH	2.16E-11	0.00E+00	1.46E+03
R1737.	C6H5OH+OH=C6H5O+H2O	2.32E-16	1.40E+00	-4.83E+02
R1738.	C6H5OH+H02=C6H5O+H2O2	1.66E-12	0.00E+00	5.03E+03
R1739.	C6H5OH+CH3=C6H5O+CH4	2.99E-13	0.00E+00	3.87E+03
R1740.	C6H50H+C6H5=C6H50+C6H6	8.14E-12	0.00E+00	2.21E+03
R1741.	C6H5OH+C3H5-A=C6H5O+C3H6	8.14E-13	0.00E+00	4.73E+03
R1742.	C6H5OH+C4H5-I=C6H5O+C4H6	8.14E-13	0.00E+00	4.73E+03
R1743.	C6H50H+H=C6H40H+H2	2.82E-10	0.00E+00	8.05E+03
R1744.	C6H5OH+O=C6H4OH+OH	3.32E-11	0.00E+00	7.40E+03
R1745.	C6H50H+0H=C6H40H+H20	2.32E-11	0.00E+00	2.31E+03
R1746.	C6H50H+H02=C6H40H+H202	6.64E-13	0.00E+00	1.45E+04
R1747.	C6H5OH+CH3=C6H4OH+CH4	3.32E-12	0.00E+00	7.55E+03
R1748.	C6H40H+02=0C6H40H+0	3.49E-11	0.00E+00	3.07E+03
R1749.	C6H40H+H=C6H50H	1.66E-10	0.00E+00	0.00E+00
B1750.	0C6H40H=C5H40H+C0	7.40E+11	0.00E+00	2.20E+04
B1751	С6Н50+Н=С6Н50Н	3.32E-10	0.00E+00	0.00E+00
B1752	С6Н50+Н+М=С6Н50Н+М	2 76E+46	-2 18E+01	6 98E+03
B1753	C6H50H=C5H6+C0	4 31E+15	-6.10E-01	3 73E+04
R1754	C6H50=C0+C5H5	2 00F+11	0.100 01	2.70 ± 04
R1755		2.00E-11 1 66E-11	0.00000	0.005+00
R1756	C6H50+0=C5H5+C02	1.00E-11 1 66E-11	0.005+00	
D1757		1.00E-11 4 20E 14		
N1750		4.32E-14	4./UE-UI	4.U3E+U2
R1/30.		3.32E-12		0.00E+00
R1/59.		0.64E-12	0.001+00	4.90E+03
K1/60.		6.64E-12	U.UUE+00	3.50E+03
R1761.	С6H5U+U=P-C6H4U2+H	7.06E-11	0.00E+00	0.00E+00
R1762.	C6H5O+O=O-C6H4O2+H	1.41E-10	0.00E+00	0.00E+00
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R1763.	0-C6H402=C5H40+C0	1.00E+12	0.00E+00	2.01E+04
R1764.	P-C6H402=C5H40+C0	3.70E+11	0.00E+00	2.97E+04
R1765.	P-C6H402+H=C5H50+C0	4.15E-11	0.00E+00	2.37E+03
R1766.	P-C6H402+H=P-C6H302+H2	3.32E-12	0.00E+00	4.08E+03
R1767.	Р-С6Н402+0=Р-С6Н302+ОН	2.32E-11	0.00E+00	7.40E+03
R1768.	P-C6H402+OH=P-C6H302+H20	1.66E-18	2.00E+00	2.01E+03
R1769.	P-C6H302+H=P-C6H402	1.66E-10	0.00E+00	0.00E+00
R1770.	P-C6H302+H=C2H2+C2H2+C0+C0	1.66E-10	0.00E+00	0.00E+00
R1771.	P-C6H302+0=C2H2+HCC0+C0+C0	1.66E-10	0.00E+00	0.00E+00
R1772.	P-C6H402+0=C0+C0+C2H2+CH2C0	4.98E-11	0.00E+00	2.52E+03
R1773.	C5H5+H=C5H6	4.32E-10	0.00E+00	0.00E+00
R1774.	C5H5+H+M=C5H6+M	1.21E+33	-1.83E+01	6.54E+03
R1775.	C5H6=C3H4-A+C2H2	3.80E+17	0.00E+00	5.23E+04
B1776	C5H6+M=C3H4-A+C2H2+M	1.66E+74	-2.23E+01	6.36E+04
B1777	C5H6+02=C5H5+H02	6.64E-11	0.00E+00	1.87E+04
R1778	C5H6+H02=C5H5+H202	1 83F-20	2 60F+00	6 49F+03
R1770.	C5H6+0H=C5H5+H20	5 11F-18	2.005+00	0.005+00
R1780	C5H6+H=C5H5+H2	1 20F-10	0.00E+00	1 76F+03
R1781	C5H6+H=C2H2+C3H5-A	1.20E 10 1.20E+13	-6 18F+00	1.70E+03
R1701.		1.29E-13 7 97E-20	2.71E+00	5 5/F+02
D1702.		1.97E 20	2.71E+00	0.005+00
R1703.		1.99E-20 E OFE-12	4.00E+00	0.00E+00
R1704.		5.25E-13	0.00E+00	4.03E+03
R1705.		2.99E-25	4.00E+00	0.002+00
R1/80.		1.00E-25	4.00E+00	0.00E+00
R1/8/.	C5H6+C5H5=C6H6+C4H5-N	8.30E-15	0.00E+00	0.00E+00
R1788.		1.98E+68	-1.50E+01	6.29E+04
R1789.	C5H5+U=C4H5-N+CU	5.31E-11	-1.70E-01	2.21E+02
R1790.	C5H5+U=C5H4U+H	9.63E-11	-2.00E-02	1.01E+01
R1791.	C5H5+UH=C5H5UH	1.08E-09	-8.50E-01	-1.37E+03
R1792.	С5H5+0H=С5H50H	1.83E+19	-8.76E+00	9.43E+03
R1793.	С5H5+0H=С5H50H	1.83E+35	-1.31E+01	1.68E+04
R1794.	С5H5+0H=С5H40H+H	5.81E+33	-1.22E+01	2.43E+04
R1795.	C5H5+OH=C4H6+C0	6.64E-10	0.00E+00	2.26E+03
R1796.	С5Н5+Н02=С5Н50+ОН	1.05E+06	-4.69E+00	5.86E+03
R1797.	C5H5+02=C4H40+HC0	9.96E-06	-2.48E+00	5.52E+03
R1798.	C4H4O+H=C3H5-A+CO	1.10E-10	-2.00E-02	1.38E+03
R1799.	C4H4O+H=C3H5-A+CO	9.80E-18	2.00E+00	6.54E+02
R1800.	C4H4O+O=CH2CHO+HCCO	4.98E-16	1.45E+00	-4.33E+02
R1801.	C4H4O+OH=C3H5-A+CO2	4.98E-12	0.00E+00	0.00E+00
R1802.	C3H3+C2H2=C#CC*CCJ	6.82E+48	-1.82E+01	2.28E+04
R1803.	C#CC*CCJ=C5H5	8.00E+13	0.00E+00	1.71E+04
R1804.	C#CC*CCJ+H=C5H6	1.66E-10	0.00E+00	0.00E+00
R1805.	C#CC*CCJ+H=C5H6-L	1.66E-14	0.00E+00	0.00E+00
R1806.	C5H6-L+0=C#CC*CCJ+0H	1.66E-14	0.00E+00	0.00E+00
R1807.	C5H6-L+OH=C#CC*CCJ+H2O	1.66E-14	0.00E+00	0.00E+00
R1808.	C5H5OH+H=C5H4OH+H2	5.31E-12	0.00E+00	0.00E+00
R1809.	C5H5OH+H=C5H5O+H2	6.64E-11	0.00E+00	3.07E+03
R1810.	C5H5OH+OH=C5H4OH+H2O	9.13E-12	0.00E+00	8.71E+02
R1811.	C5H5OH+OH=C5H5O+H2O	1.66E-11	0.00E+00	8.54E+02
R1812.	C5H5OH+O=C5H4OH+OH	7.80E-13	0.00E+00	0.00E+00
R1813.	C5H5OH+O=C5H5O+OH	1.66E-11	0.00E+00	2.36E+03
R1814.	C5H5OH+H02=C5H4OH+H2O2	5.98E-21	2.55E+00	5.30E+03
R1815.	C5H5OH+H02=C5H5O+H2O2	1.66E-11	0.00E+00	7.95E+03

R1816.	С5Н50=С5Н40+Н	2.90E+32	-6.50E+00	1.07E+04
R1817.	C5H5O=C4H5-N+CO	1.10E+79	-1.96E+01	3.33E+04
R1818.	C5H5O=CJ*CC*CC*O	2.00E+13	0.00E+00	7.22E+03
R1819.	CJ*CC*CC*O=C*CC*CCJ*O	4.30E+11	-1.05E+00	2.07E+03
R1820.	C4H5-N+CO=C*CC*CCJ*O	2.51E-13	0.00E+00	2.42E+03
R1821.	CJ*CC*CC*O=C2H2+CJ*CC*O	3.00E+13	0.00E+00	2.20E+04
R1822.	CJ*CC*O=C2H3CO	1.40E+09	9.80E-01	1.62E+04
R1823.	C2H2+HCO=CJ*CC*O	1.29E-17	1.41E+00	3.90E+03
R1824.	C5H4OH+H=C5H5OH	1.66E-10	0.00E+00	0.00E+00
R1825.	C5H4OH+H=C5H4O+H2	3.49E-11	0.00E+00	2.72E+04
R1826.	C5H4OH+O2=C5H4O+HO2	4.98E-11	0.00E+00	2.52E+03
R1827.	C5H40=C0+C2H2+C2H2	5.70E+32	-6.76E+00	3.45E+04
R1828.	C5H40=C0+C2H2+C2H2	6.20E+41	-7.87E+00	4.97E+04
R1829.	C5H40+H=C4H5-N+C0	3.49E+37	-1.33E+01	2.05E+04
R1830.	C5H40+0=C4H4+C02	1.66E-11	0.00E+00	1.01E+03
R1831.	C5H40+H=C5H30+H2	3.32E-12	0.00E+00	4.08E+03
R1832.	C5H40+0=C5H30+0H	2.32E-11	0.00E+00	7.40E+02
R1833.	C5H40+0H=C5H30+H20	1.83E-16	1.42E+00	7.30E+02
R1834.	C5H30+H=C5H40	1.66E-10	0.00E+00	0.00E+00
R1835.	C5H30+02=C02+C2H2+HCC0	1.61E+35	-1.35E+01	1.92E+04
R1836.	C5H30=C2H2+C0+C2H	2.00E+13	0.00E+00	2.57E+04
R1837	C5H7=C*CC.IC*C	3.20E+15	0.00E+00	1.99E+04
R1838	C5H7+H=C5H6+H2	5 98E-12	0 00E+00	0 00E+00
R1839	C5H7+D=C5H6+DH	1 66E-11	0.00E+00	0 00E+00
R1840	C5H7+DH=C5H6+H2D	3 99E-11	0.00E+00	0 00E+00
R1841	C5H7+02=0C5H70	1 48F+01	-3 80F+00	1 01F+04
R1842	C5H6+H=C5H7	3 99F+49	-1 79F+01	1 59F+04
R1843	C5H6+H=C*CC1C*C	1 83F-10	-1.60F-01	1 56F+03
R1844	C5H6+D=C5H5D+H	1.03E 10	-1 50E-01	2 97F+02
R1845	C5H6+0=C5H50+H	9 30F-12	-6 00F-02	1 01F+02
R1045.		1 83F-11	-7 00E-02	1.01E+02
R1040.		2 16E-00	-1 07E + 00	4.300102
R1047.		2.10E 09 1 70E-16	1.07E+00	4.00E+03
R1040.		1.79E 10 3 AOF+A3	-1.61E+01	2.03E+03
R1049.		0 06F-12	0.005+00	2.14E+04
R1050.	C5n0+C4n5-1-C5n5+C4n6	9.90E-12 5 /0E+11	-7 00E+00	3 02E+00
R1051.	C+CC3C+C-C+CC+CC3	3 825-04	-1 60E+00	1 52E+03
R1002.	C*CC*CCJ+H=CAU6+CU2	9.62E-04	-1.64E+00	1.52E+05
R1000.		0.03E+47 1 16E-17	-1.04E+01	2.57 E+04
R1004.		1.10E-17 1 16E-17	2.00E+00	2.52E+05
R1000.		1.10E-17 1.00E+12	2.00E+00	1 COE+00
R1000.		1.99E+12	-7.25E+00	1.09E+04
R100/.	C = C + C + C + D = C + D = C + C + C + C + D = C + D = C + D + C + D = C +	4.82E+02	-2.18E+00	1.85E+04
R1858.		3.32E-10	0.00E+00	0.00E+00
R1859.		2.49E-11	0.00E+00	0.00E+00
R1860.		1.36E-13	1.80E-01	4.60E+03
R1861.	C*CC*CCUH+H=C4H6+CH2UH	4.15E+10	-6.12E+00	8.18E+03
R1862.		1.05E-18	-7.25E+00	1.69E+04
R1863.	C*CCJC*CUH+U2=HUC*CC*U+CH2CHU	1.99E+12	-7.25E+00	1.69E+04
K1864.		4.47E-14	7.60E-01	-1./1E+02
K1865.	HUC*CC*U+HU2=HUC*CCJ*U+H2O2	1.66E-12	U.UUE+00	6.00E+03
K1866.	HUC*CC*U+CH3=HUC*CCJ*0+CH4	6.61E-12	0.00E+00	4.38E+03
K1867.		1.19E-11	U.UUE+00	6.99E+02
K1868.	HUC*CC*U+U2=HUC*CCJ*O+HO2	3.32E-11	0.00E+00	2.05E+04
K1869.	HUC*CC*O+H=HOC*CCJ*O+H2	4.32E-12	0.00E+00	1.31E+03

R1870.	C2H2OH+CO=HOC*CCJ*O	2.51E-13	0.00E+00	2.42E+03		
R1871.	0C4H60+H=0C4H50+H2	3.82E-14	1.05E+00	1.65E+03		
R1872.	0C4H60+0H=0C4H50+H20	5.81E-15	1.18E+00	-2.25E+02		
R1873.	0C4H50+02=02CCH00J+C2H4	2.66E+21	-9.92E+00	1.04E+04		
R1874.	02CCH00J=H0C0+C02	3.00E+13	0.00E+00	2.01E+03		
R1875.	C*CCJC*O=C3H5-A+CO	6.10E+05	9.20E-01	-5.64E+02		
R1876.	C*CCJC*0+02=C2H3CH0+H0C0	1.99E+12	-7.25E+00	1.69E+04		
R1877.	HOCO=CO+OH	1.19E+14	1.30E-01	1.83E+04		
R1878.	HOCO=CO2+H	8.22E+11	4.10E-01	1.78E+04		

- [A.1.1] J.H. Kolts, D.W. Setser, J. Chem. Phys. 68 (1978) 4848-4859.
- [A.1.2] J.T. Gudmundsson, E.G. Thorsteinsson, Plasma Sources Sci. Technol. 16 (2007) 399-413.
- [A.1.3] J.E. Velazco, J.H. Kolts, D.W. Setser, J. Chem. Phys. 69 (1978) 4357-4373.
- [A.1.4] N. Sadeghi, D.W. Sester, A. Francis, U. Czarnetzki, H.F. Dobele, J. Chem. Phys. 115 (2001) 3144-3154.
- [A.1.5] J.L. Jauberteau, L. Thomas, J. Aubreton, I. Jauberteau, A. Catherinot, Plasma Chem. Plasma Proc. 18 (1998) 137-151.
- [A.1.6] J. Balamuta, M.F. Golde, Y. Ho, J. Chem. Phys. 79 (1983) 2822-2830.
- [A.1.7] L.G. Piper, J.E. Velazco, D.W. Setser, J. Chem. Phys. 59 (1973) 3323-3340.
- [A.1.8] R. Atkinson, D.L. Baulch, R.A Cox, N.J. Crowley, R.F Hampson, R.G. Hynes, M.E. Jenkin, M.J. Rossi, J. Troe, Atmos. Chem. Phys. 4 (2004) 1461-1738.
- [A.1.9] R.F. Heidner, C.E. Gardner, T.M. El-Sayed, G.I. Segal, J.V.V. Kasper, J. Chem. Phys. 74 (1981) 5618-5623.
- [A.1.10] N.A. Popov, Plasma Sources Sci. Technolo. 20 (2011) 045002.
- [A.1.11] A.S. Sharipov, A.M. Starik, *Phys. Scr.* 88 (2013) 058305.
- [A.1.12] A. Starik, A. Sharipov, Phys. Chem. Chem. Phys. 13 (2011) 16424-16436.
- [A.1.13] S.H. Mousavipour, V. Saheb, Bull. Chem. Soc. Jpn. 80 (2007) 1901-1913.
- [A.1.14] A.V. Lebedev, M.A. Deminsky, A.V. Zaitzvesky, B.V. Potapkin, Combust. Flame 160 (2013) 530-538.
- [A.1.15] W. Van Gaens, A. Bogaerts, J. Phys. D: Appl. Phys. 47 (2014) 079501.
- [A.1.16] M.A. Blitz, T.J. Dillon, D.E. Heard, M.J. Pilling, I.D. Trought, Phys. Chem. Chem. Phys. 6 (2004) 2162-2171.
- [A.1.17] W.B. DeMore, S.P. Sander, D.M. Golden, R.F. Hampson, M.J. Kurylo, C.J. Howard, A.R. Ravishankara, C.E. Kolb, M.J. Molina, *Chemical Kinetics and Potochemical Data for Use in Stratospheric Modeling - Evaluation No. 12*, JPL Publication 97-4, Jan. 1997.
- [A.1.18] J.A. Davidson, H.I. Schiff, T.J. Brown, C.J. Howard, J. Chem. Phys. 69 (1978) 1216-1217.
- [A.1.19] I.S. Flectcher, D. Husain, Can. J. Chem. 54 (1976) 1765-1770.
- [A.1.20] A.N. Vasiljeva, K.S. Klopovskiy, A.S. Kovalev, D.V. Lopaev, Y.A. Mankelevich, N.A. Popov, A.T. Rakhimov, T.V. Rakhimova, J. Phys. D: Appl. Phys. 37 (2004) 2455-2468.
- [A.1.21] C.J. Howard, B.J. Finlayson-Pitts, J. Chem. Phys. 72 (1980) 3842-3843.
- [A.1.22] A. Mansergas, J.M. Anglada, Chem. Phys. Chem. 8 (2007) 1534-1539.
- [A.1.23] S. Hatakeyama, M.T. Leu, J. Phys. Chem. 93 (1989) 5784-5789.
- [A.1.24] J. Albaladejo, E. Jimenez, A. Notario, B. Cabanas, E. Martinez, J. Phys. Chem. A 106 (2002) 2512-2519.
- [A.1.25] I. Glassman, R.A. Yetter, Combustion 4th Ed., Academic Press-Elesvier Inc. San Diego, CA, 2008.
- [A.1.26] W.K. Metcalfe, S.M. Burke, S.S. Ahmed, H.J. Curran, Intl. J. Chemical Kinetics 45 (2013) 638-675.

B.2 Electron Impact Collisional Cross-sectional Data

Most of the relevant cross-sectional data can be found through the Plasma Data Exchange Project (http://www.fr.lxcat.net), a convenient open-access website for collecting, displaying and downloading a multitude of electron and ion data required for modeling low-temperature plasmas. The following data is presented in the format native to the Boltzmann equation solver, where data is delimited in rows of two. The first row is the electron energy (units eV) followed by the corresponding cross-section (units Å) at that energy.

```
02 + e ^ 02 + e
                                                     CRS1.
                                                                    +1
Transport cross-section
                                                     Ref [A.2.1]
                                                                    +1
0.000e-00 1.000e-01 1.800e-01 2.000e-01 2.300e-01 2.500e-01 3.000e-01+1
1.000e+00 4.600e+00 6.200e+00 6.200e+00 4.500e+00 4.200e+00 4.700e+00+1
4.000e-01 5.000e-01 6.000e-01 8.000e-01 9.500e-01 1.350e+00 1.800e+00+1
5.400e+00 5.700e+00 6.000e+00 5.900e+00 5.900e+00 5.900e+00 6.000e+00+1
2.280e+00 2.600e+00 3.000e+00 4.000e+00 4.830e+00 6.680e+00 8.550e+00+1
6.140e+00 6.250e+00 6.440e+00 6.800e+00 7.060e+00 7.840e+00 8.900e+00+1
1.010e+01 1.180e+01 1.270e+01 1.350e+01 1.550e+01 2.100e+01 3.000e+01+1
9.250e+00 9.070e+00 8.990e+00 8.670e+00 8.160e+00 7.320e+00 6.490e+00+1
4.000e+01 5.000e+01
                                                                    +1
6.030e+00 5.630e+00
                                                                    +1
                                                                    +1
02 + e^{02}(0.98) + e
                                                     CRS2.
                                                                    +1
Electronic excitation (a1Delta, energy=0.98 eV)
                                                     Ref [A.2.1]
                                                                    +1
9.770e-01 1.500e+00 1.980e+00 2.990e+00 3.490e+00 5.050e+00 5.620e+00+1
0.000e+00 9.700e-03 1.620e-02 3.240e-02 3.870e-02 5.890e-02 6.600e-02+1
6.190e+00 6.990e+00 7.610e+00 8.340e+00 1.060e+01 1.220e+01 1.590e+01+1
7.100e-02 7.310e-02 7.130e-02 6.540e-02 5.160e-02 4.450e-02 3.420e-02+1
2.050e+01 2.490e+01 3.090e+01 4.100e+01 4.400e+01 5.000e+01
                                                                    +1
2.590e-02 2.050e-02 1.570e-02 1.100e-02 9.600e-03 8.800e-03
                                                                    +1
                                                                    +1
02 + e^{02(1.63)} + e
                                                      CRS3
                                                                    +1
Electronic excitation (b1Sigma, energy=1.63 eV)
                                                     Ref [A.2.1]
                                                                    +1
1.630e+00 1.990e+00 3.000e+00 3.490e+00 4.000e+00 5.690e+00 7.340e+00+1
0.000e+00 4.570e-03 1.150e-02 1.360e-02 1.580e-02 1.940e-02 1.910e-02+1
8.410e+00 9.260e+00 1.180e+01 1.580e+01 2.070e+01 3.120e+01 4.510e+01+1
1.830e-02 1.740e-02 1.370e-02 1.090e-02 8.560e-03 5.550e-03 3.120e-03+1
5.000e+01
                                                                    +1
2.900e-03
                                                                    +1
                                                                    +1
02 + e^{02(4.8)} + e
                                                      CRS4.
                                                                    +1
Electronic excitation (A3Sigma, energy=4.8 eV)
                                                     Ref [A.2.1]
                                                                    +1
4.800e+00 6.100e+00 6.300e+00 7.000e+00 8.000e+00 1.000e+01 1.200e+01+1
0.000e+00 6.000e-02 5.000e-02 1.000e-02 0.000e+00 0.000e+00 0.000e+00+1
                                                                    +1
02 + e ^ 02(6.1) + e
                                                      CRS5.
                                                                    +1
Electronic excitation (B3Sigma, energy=6.1 eV)
                                                     Ref [A.2.1]
                                                                    +1
6.100e+00 7.000e+00 8.000e+00 9.000e+00 1.000e+01 1.050e+01 1.100e+01+1
0.000e+00 1.530e-01 2.970e-01 3.960e-01 4.320e-01 4.230e-01 4.050e-01+1
1.200e+01 1.300e+01 1.500e+01 2.000e+01 3.000e+01 4.000e+01 5.000e+01+1
3.420e-01 2.790e-01 2.100e-01 9.400e-02 6.000e-02 4.200e-02 3.600e-02+1
1.000e+02
                                                                    +1
2.000e-02
                                                                    +1
                                                                    +1
```

 $02 + e^{0} 02(+) + e + e$ CRS6. +1 Ionization,(energy=12.1 eV) Ref [A.2.1] +1 1.210e+01 1.300e+01 1.350e+01 1.500e+01 1.750e+01 1.900e+01 2.250e+01+1 0.000e+00 4.900e-03 8.700e-03 2.900e-02 7.300e-02 1.140e-01 2.300e-01+1 2.800e+01 3.150e+01 3.700e+01 4.400e+01 4.800e+01 5.150e+01 5.500e+01+1 3.930e-01 4.960e-01 6.400e-01 8.300e-01 9.100e-01 9.900e-01 1.080e+00+1 5.850e+01 6.200e+01 6.600e+01 7.000e+01 8.000e+01 1.000e+02 +1 1.160e+00 1.250e+00 1.320e+00 1.390e+00 1.570e+00 1.700e+00 +1 +1 C2H4 + e ^ C2H4 + e CRS7 +1 Transport cross-section Ref [A.2.2] +1 1.000E-02 8.000E-02 2.540E+00 4.980E+00 9.850E+00 1.720E+01 2.450E+01+1 9.990E+00 1.400E+00 1.200E+01 1.690E+01 1.570E+01 1.460E+01 1.220E+01+1 3.510E+01 4.010E+01 4.510E+01 5.010E+01 5.500E+01 6.000E+01 6.500E+01+1 9.020E+00 7.840E+00 6.850E+00 6.030E+00 5.350E+00 4.780E+00 4.300E+00+1 7.000E+01 7.500E+01 8.000E+01 8.500E+01 9.000E+01 9.500E+01 1.000E+02+1 3.890E+00 3.540E+00 3.240E+00 2.980E+00 2.750E+00 2.550E+00 2.370E+00+1 +1 $C2H4 + e^{C2H4}(d1) + e$ CRS8. +1 Dissociation (C2H3, H) Ref [A.2.2] +1 5.800E+00 6.900E+00 8.400E+00 8.800E+00 9.400E+00 1.000E+01 1.250E+01+1 0.000E+00 0.000E+00 2.133E-02 3.638E-02 6.466E-02 9.771E-02 2.499E-01+1 1.400E+01 1.600E+01 1.800E+01 2.000E+01 2.500E+01 3.000E+01 3.500E+01+1 3.338E-01 4.278E-01 5.016E-01 5.583E-01 6.458E-01 6.854E-01 6.993E-01+1 4.000E+01 4.500E+01 5.000E+01 5.500E+01 6.000E+01 6.500E+01 7.000E+01+1 6.990E-01 6.908E-01 6.784E-01 6.637E-01 6.479E-01 6.317E-01 6.155E-01+1 7.500E+01 8.000E+01 8.500E+01 9.000E+01 9.500E+01 1.000E+02 +1 5.997E-01 5.843E-01 5.695E-01 5.553E-01 5.416E-01 5.286E-01 +1 +1 $C2H4 + e^{C2H4}(d2) + e$ CRS9. +1 Dissociation (C2H2, H2) Ref [A.2.2] +1 5.800E+00 6.900E+00 8.400E+00 8.800E+00 9.400E+00 1.000E+01 1.250E+01+1 0.000E+00 1.327E-02 8.331E-02 1.074E-01 1.448E-01 1.823E-01 3.210E-01+1 1.400E+01 1.600E+01 1.800E+01 2.000E+01 2.500E+01 3.000E+01 3.500E+01+1 3.857E-01 4.518E-01 4.995E-01 5.333E-01 5.781E-01 5.910E-01 5.885E-01+1 4.000E+01 4.500E+01 5.000E+01 5.500E+01 6.000E+01 6.500E+01 7.000E+01+1 5.782E-01 5.643E-01 5.488E-01 5.327E-01 5.167E-01 5.012E-01 4.862E-01+1 7.500E+01 8.000E+01 8.500E+01 9.000E+01 9.500E+01 1.000E+02 +1 4.719E-01 4.583E-01 4.454E-01 4.332E-01 4.216E-01 4.106E-01 +1 +1 $C2H4 + e^{C2H4}(d3) + e$ CRS10. +1 Dissociation (C2H2, H, H) Ref [A.2.2] +1 5.800E+00 6.900E+00 8.400E+00 8.800E+00 9.400E+00 1.000E+01 1.250E+01+1 0.000E+00 4.255E-04 2.167E-02 3.226E-02 5.046E-02 7.031E-02 1.537E-01+1 1.400E+01 1.600E+01 1.800E+01 2.000E+01 2.500E+01 3.000E+01 3.500E+01+1 1.967E-01 2.434E-01 2.789E-01 3.055E-01 3.448E-01 3.608E-01 3.648E-01+1 4.000E+01 4.500E+01 5.000E+01 5.500E+01 6.000E+01 6.500E+01 7.000E+01+1 3.623E-01 3.564E-01 3.487E-01 3.402E-01 3.313E-01 3.224E-01 3.137E-01+1 7.500E+01 8.000E+01 8.500E+01 9.000E+01 9.500E+01 1.000E+02 +1 3.052E-01 2.970E-01 2.892E-01 2.817E-01 2.745E-01 2.677E-01 +1 +1 C2H4 + e ^ C2H4(d4) + e CRS11. +1 Dissociation (C2H, H2, H) Ref [A.2.2] +1 5.800E+00 6.900E+00 8.400E+00 8.800E+00 9.400E+00 1.000E+01 1.250E+01+1 0.000E+00 0.000E+00 0.000E+00 8.486E-05 1.035E-03 3.359E-03 2.452E-02+1 1.400E+01 1.600E+01 1.800E+01 2.000E+01 2.500E+01 3.000E+01 3.500E+01+1 4.095E-02 6.230E-02 8.113E-02 9.690E-02 1.245E-01 1.401E-01 1.483E-01+1 4.000E+01 4.500E+01 5.000E+01 5.500E+01 6.000E+01 6.500E+01 7.000E+01+1 1.520E-01 1.531E-01 1.525E-01 1.509E-01 1.486E-01 1.460E-01 1.432E-01+1 7.500E+01 8.000E+01 8.500E+01 9.000E+01 9.500E+01 1.000E+02 +1 1.402E-01 1.373E-01 1.343E-01 1.314E-01 1.286E-01 1.259E-01 +1 +1 CH4 + e ^ CH4 + e CRS12. +1 Ref [A.2.3] Transport cross-section +1 1.000E-02 1.000E-01 3.000E-01 5.110E+00 1.510E+01 2.010E+01 2.510E+01+1 1.400E+01 2.200E+00 2.000E-01 1.830E+01 1.210E+01 8.650E+00 6.550E+00+1 3.010E+01 3.510E+01 4.010E+01 4.510E+01 5.010E+01 5.510E+01 6.000E+01+1 5.190E+00 4.250E+00 3.570E+00 3.060E+00 2.670E+00 2.350E+00 2.100E+00+1 6.500E+01 7.000E+01 7.500E+01 8.000E+01 8.500E+01 9.000E+01 1.000E+02+1 1.890E+00 1.710E+00 1.570E+00 1.440E+00 1.330E+00 1.230E+00 1.070E+00+1 +1 CH4 + e ^ CH4(d1) + e CRS13. +1 Dissociation (CH3, H) Ref [A.2.3] +1 1.000E+01 1.250E+01 1.400E+01 1.600E+01 1.800E+01 2.000E+01 2.500E+01+1 4.161E-01 1.009E+00 1.217E+00 1.399E+00 1.531E+00 1.636E+00 1.835E+00+1 3.000E+01 3.500E+01 4.000E+01 4.500E+01 5.000E+01 5.500E+01 6.000E+01+1 1.977E+00 2.081E+00 2.156E+00 2.209E+00 2.247E+00 2.271E+00 2.286E+00+1 6.500E+01 7.000E+01 7.500E+01 8.000E+01 8.500E+01 9.000E+01 9.500E+01+1 2.293E+00 2.294E+00 2.289E+00 2.281E+00 2.270E+00 2.257E+00 2.242E+00+1 1.000E+02 +1 2.225E+00 +1 +1 $CH4 + e \cap CH4(d2) + e$ CRS14. +1Dissociation (CH2, H2) Ref [A.2.3] +1 8.800E+00 9.400E+00 1.000E+01 1.250E+01 1.400E+01 1.600E+01 1.800E+01+1 1.000E-10 1.000E-10 1.000E-10 1.000E-10 1.000E-10 1.000E-10 1.000E-10+1 2.000E+01 2.500E+01 3.000E+01 3.500E+01 4.000E+01 4.500E+01 5.000E+01+1 1.000E-10 1.000E-10 1.000E-10 1.000E-10 1.000E-10 1.000E-10 1.000E-10+1 5.500E+01 6.000E+01 6.500E+01 7.000E+01 7.500E+01 8.000E+01 8.500E+01+1 1.000E-10 1.000E-10 1.000E-10 1.000E-10 1.000E-10 1.000E-10 1.000E-10+1 9.000E+01 9.500E+01 1.000E+02 +1 1.000E-10 1.000E-10 1.000E-10 +1 +1 CH4 + e ^ CH4(d3) + e CRS15. +1 Dissociation (CH, H2, H) Ref [A.2.3] +1 8.800E+00 9.400E+00 1.000E+01 1.250E+01 1.400E+01 1.600E+01 1.800E+01+1 1.000E-10 1.000E-10 1.000E-10 1.000E-10 1.000E-10 1.000E-10 1.000E-10+1 2.000E+01 2.500E+01 3.000E+01 3.500E+01 4.000E+01 4.500E+01 5.000E+01+1 1.000E-10 1.000E-10 1.000E-10 1.000E-10 1.000E-10 1.000E-10 1.000E-10+1 5.500E+01 6.000E+01 6.500E+01 7.000E+01 7.500E+01 8.000E+01 8.500E+01+1 1.000E-10 1.000E-10 1.000E-10 1.000E-10 1.000E-10 1.000E-10 1.000E-10+1 9.000E+01 9.500E+01 1.000E+02 +1 1.000E-10 1.000E-10 1.000E-10 +1 +1 C2H2 + e ^ C2H2 + e CRS16. +1 Transport cross-section Ref [A.2.2] +1 1.000E-02 8.000E-02 2.540E+00 4.980E+00 9.850E+00 1.720E+01 2.450E+01+1 9.990E+00 1.400E+00 1.200E+01 1.690E+01 1.570E+01 1.460E+01 1.220E+01+1

3.510E+01 4.010E+01 4.510E+01 5.010E+01 5.500E+01 6.000E+01 6.500E+01+1 9.020E+00 7.840E+00 6.850E+00 6.030E+00 5.350E+00 4.780E+00 4.300E+00+1 7.000E+01 7.500E+01 8.000E+01 8.500E+01 9.000E+01 9.500E+01 1.000E+02+1 3.890E+00 3.540E+00 3.240E+00 2.980E+00 2.750E+00 2.550E+00 2.370E+00+1 +1 C2H2 + e ^ C2H2(d1) + e CRS17. +1 Dissociation (C2H, H) Ref [A.2.2] +1 5.800E+00 6.900E+00 8.400E+00 8.800E+00 9.400E+00 1.000E+01 1.250E+01+1 0.000E+00 0.000E+00 6.080E-03 1.538E-02 3.745E-02 6.763E-02 2.347E-01+1 1.400E+01 1.600E+01 1.800E+01 2.000E+01 2.500E+01 3.000E+01 3.500E+01+1 3.380E-01 4.601E-01 5.603E-01 6.400E-01 7.702E-01 8.358E-01 8.649E-01+1 4.000E+01 4.500E+01 5.000E+01 5.500E+01 6.000E+01 6.500E+01 7.000E+01+1 8.731E-01 8.693E-01 8.584E-01 8.434E-01 8.263E-01 8.080E-01 7.893E-01+1 7.500E+01 8.000E+01 8.500E+01 9.000E+01 9.500E+01 1.000E+02 +1 7.707E-01 7.523E-01 7.344E-01 7.170E-01 7.002E-01 6.841E-01 +1 +1 C2H2 + e ^ C2H2(d2) + e CRS18. +1 Dissociation (C2, H2) Ref [A.2.2] +1 5.800E+00 6.900E+00 8.400E+00 8.800E+00 9.400E+00 1.000E+01 1.250E+01+1 0.000E+00 0.000E+00 0.000E+00 0.000E+00 6.611E-04 3.356E-03 3.636E-02+1 1.400E+01 1.600E+01 1.800E+01 2.000E+01 2.500E+01 3.000E+01 3.500E+01+1 6.467E-02 1.029E-01 1.374E-01 1.669E-01 2.197E-01 2.503E-01 2.670E-01+1 4.000E+01 4.500E+01 5.000E+01 5.500E+01 6.000E+01 6.500E+01 7.000E+01+1 2.753E-01 2.783E-01 2.780E-01 2.757E-01 2.721E-01 2.677E-01 2.628E-01+1 7.500E+01 8.000E+01 8.500E+01 9.000E+01 9.500E+01 1.000E+02 +1 2.577E-01 2.525E-01 2.473E-01 2.422E-01 2.371E-01 2.322E-01 +1 +1 C2H2 + e ^ C2H2(d3) + e CRS19. +1 Dissociation (C, CH2) Ref [A.2.2] +1 5.800E+00 6.900E+00 8.400E+00 8.800E+00 9.400E+00 1.000E+01 1.250E+01+1 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00 7.468E-06 7.972E-03+1 1.400E+01 1.600E+01 1.800E+01 2.000E+01 2.500E+01 3.000E+01 3.500E+01+1 1.967E-02 3.851E-02 5.756E-02 7.500E-02 1.089E-01 1.304E-01 1.435E-01+1 4.000E+01 4.500E+01 5.000E+01 5.500E+01 6.000E+01 6.500E+01 7.000E+01+1 1.511E-01 1.551E-01 1.567E-01 1.568E-01 1.558E-01 1.542E-01 1.521E-01+1 7.500E+01 8.000E+01 8.500E+01 9.000E+01 9.500E+01 1.000E+02 +1 1.498E-01 1.473E-01 1.447E-01 1.421E-01 1.394E-01 1.368E-01 +1 +1 C2H2 + e ^ C2H2(d4) + e CRS20. +1 Ref [A.2.2] +1 Dissociation (CH, CH) 5.800E+00 6.900E+00 8.400E+00 8.800E+00 9.400E+00 1.000E+01 1.250E+01+1 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00 2.273E-03+1 1.400E+01 1.600E+01 1.800E+01 2.000E+01 2.500E+01 3.000E+01 3.500E+01+1 8.537E-03 2.082E-02 3.461E-02 4.803E-02 7.572E-02 9.454E-02 1.066E-01+1 4.000E+01 4.500E+01 5.000E+01 5.500E+01 6.000E+01 6.500E+01 7.000E+01+1 1.141E-01 1.184E-01 1.207E-01 1.216E-01 1.215E-01 1.207E-01 1.196E-01+1 7.500E+01 8.000E+01 8.500E+01 9.000E+01 9.500E+01 1.000E+02 +1 1.181E-01 1.164E-01 1.147E-01 1.128E-01 1.109E-01 1.090E-01 +1 +1 $AR + e^{AR} + e$ CRS21. +1 Ref [A.2.4] Momentum transfer cross-section +1 0.000E+00 1.000E-02 1.500E-02 2.000E-02 3.000E-02 4.000E-02 5.000E-02+1 7.500E+00 4.280E+00 3.810E+00 3.280E+00 2.570E+00 2.050E+00 1.660E+00+1 6.000E-02 7.000E-02 8.000E-02 9.000E-02 1.000E-01 1.500E-01 2.000E-01+1

1.350E+00 1.110E+00 9.160E-01 7.540E-01 6.210E-01 2.320E-01 1.000E-01+1 3.000E-01 4.000E-01 5.000E-01 6.000E-01 7.000E-01 8.000E-01 9.000E-01+1 1.460E-01 3.160E-01 5.040E-01 7.040E-01 8.780E-01 1.050E+00 1.210E+00+1 1.000E+00 1.500E+00 2.000E+00 3.000E+00 4.000E+00 5.000E+00 6.000E+00+1 1.370E+00 2.050E+00 2.700E+00 4.700E+00 7.140E+00 9.410E+00 1.220E+01+1 7.000E+00 8.000E+00 9.000E+00 1.000E+01 1.500E+01 2.000E+01 3.000E+01+1 1.510E+01 1.740E+01 1.840E+01 1.830E+01 1.200E+01 8.320E+00 5.870E+00+1 4.000E+01 5.000E+01 6.000E+01 7.000E+01 8.000E+01 9.000E+01 1.000E+02+1 4.870E+00 4.220E+00 3.390E+00 2.880E+00 2.670E+00 2.480E+00 2.300E+00+1 1.500E+02 2.000E+02 3.000E+02 4.000E+02 5.000E+02 6.000E+02 7.000E+02+1 1.730E+00 1.330E+00 8.890E-01 6.270E-01 4.670E-01 3.660E-01 2.980E-01+1 8.000E+02 9.000E+02 1.000E+03 +1 2.480E-01 2.110E-01 1.820E-01 +1 +1 $AR + e^{AR*} + e$ CRS22. +1 Metastable excitation(3P0,3P2, 11.3 eV threshold) Ref [A.2.4] +1 1.200E+01 1.300E+01 1.400E+01 1.500E+01 1.600E+01 1.700E+01 1.800E+01+1 1.500E-02 7.000E-02 1.000E-01 1.130E-01 1.950E-01 2.600E-01 3.000E-01+1 1.900E+01 2.000E+01 2.100E+01 2.200E+01 2.300E+01 2.400E+01 2.500E+01+1 3.380E-01 3.450E-01 3.500E-01 3.550E-01 3.480E-01 3.380E-01 3.200E-01+1 2.700E+01 2.900E+01 3.100E+01 3.300E+01 3.500E+01 3.700E+01 3.800E+01+1 3.000E-01 2.670E-01 2.350E-01 2.070E-01 1.880E-01 1.750E-01 1.600E-01+1 4.000E+01 4.200E+01 4.400E+01 4.600E+01 4.900E+01 5.500E+01 6.000E+01+1 1.390E-01 1.190E-01 1.000E-01 9.400E-02 8.300E-02 6.000E-02 5.000E-02+1 6.700E+01 7.200E+01 8.200E+01 9.200E+01 1.020E+02 1.220E+02 1.420E+02+1 4.300E-02 4.000E-02 3.900E-02 3.600E-02 3.500E-02 3.100E-02 2.800E-02+1 +1 $AR + e \cap AR(+) + e + e$ CRS23. +1 Ionization, (15.7 eV threshold) Ref [A.2.5] +11.570E+01 1.960E+01 2.450E+01 3.060E+01 3.820E+01 4.780E+01 5.970E+01+1 0.000E+00 9.000E-01 1.730E+00 2.330E+00 2.810E+00 3.060E+00 3.150E+00+1 7.460E+01 9.320E+01 1.160E+02 1.450E+02 1.820E+02 2.270E+02 2.840E+02+1 3.100E+00 2.950E+00 2.750E+00 2.510E+00 2.260E+00 2.010E+00 1.760E+00+1 3.550E+02 4.430E+02 5.540E+02 6.920E+02 8.650E+02 1.080E+03 +1 1.540E+00 1.330E+00 1.140E+00 9.820E-01 8.360E-01 7.090E-01 +1

- [A.2.1] A.A. Ionin, I.V. Kochetov, A.P. Napartovich, N.N. Yuryshev, J. Phys. D: Appl. Phys. 40 (2007) R25-R61.
- [A.2.2] R.K. Janev, D. Reiter, *Phys. Plasmas* 11 (2004) 780-829.
- [A.2.3] S. Motlag, J.H. Moore, J. Chem. Phys. 109 (1998) 432-438.
- [A.2.4] N.J. Mason, W.R. Newell, J. Phys. B. At. Mol. Phys. 20 (1987) 1357-1377.
- [A.2.5] C. Yamabe, S.J. Buckman, A.V. Phelps, Phys. Rev. A 27 (1983) 1345-1352.

B.3 Thermochemical Polynomial Fit Coefficients

The following coefficients for a given species are presented in the format applicable to CHEMKIN. Refer to the CHEMKIN user manual for details on the structure and formatting of the thermodynamic data input file.

```
0
0
                     1
                                          G
                                              200.000 6000.00 1000.00
                                                                             1
2.54363697E+00-2.73162486E-05-4.19029520E-09 4.95481845E-12-4.79553694E-16
                                                                            2
2.92260120E+04 4.92229457E+00 3.16826710E+00-3.27931884E-03 6.64306396E-06
                                                                            3
-6.12806624E-09 2.11265971E-12 2.91222592E+04 2.05193346E+00 2.99687009E+04
                                                                            4
                                          G 0300.00
O(D)
                 0
                                                       5000.00 1000.00
                                                                             1
                     1
0.02542059E+02-0.02755061E-03-0.03102803E-07 0.04551067E-10-0.04368051E-14
                                                                             2
0.02923080E+06 0.04920308E+02 0.02946428E+02-0.16381665E-02 0.02421031E-04
                                                                            3
-0.16028431E-08 0.03890696E-11 0.02914764E+06 0.02963995E+02
                                                                             4
                                              200.000 6000.00 1000.00
N2
                 Π
                     2
                                          G
                                                                            1
3.66096065E+00 6.56365811E-04-1.41149627E-07 2.05797935E-11-1.29913436E-15
                                                                            2
-1.21597718E+03 3.41536279E+00 3.78245636E+00-2.99673416E-03 9.84730201E-06
                                                                            3
-9.68129509E-09 3.24372837E-12-1.06394356E+03 3.65767573E+00 0.00000000E+00
                                                                            4
                                          G 0300.00
                                                       5000.00 1000.00
02(a)
                 Ο
                     2
                                                                            1
0.03697578E+02 0.06135197E-02-0.12588420E-06 0.01775281E-09-0.11364354E-14
                                                                            2
-0.12339301E+04 0.03189165E+02 0.03212936E+02 0.11274864E-02-0.05756150E-05
                                                                            3
0.13138773E-08-0.08768554E-11-0.10052490E+04 0.06034737E+02
                                                                             4
02(b)
                 0
                     2
                                          G 0300.00
                                                       5000.00 1000.00
                                                                            1
0.03697578E+02 0.06135197E-02-0.12588420E-06 0.01775281E-09-0.11364354E-14
                                                                             2
-0.12339301E+04 0.03189165E+02 0.03212936E+02 0.11274864E-02-0.05756150E-05
                                                                            3
0.13138773E-08-0.08768554E-11-0.10052490E+04 0.06034737E+02
                                                                             4
03
                 Ω
                     3
                                          G 0300.00
                                                       5000.00 1000.00
                                                                             1
0.05429371E+02 0.01820380E-01-0.07705607E-05 0.14992929E-09-0.10755629E-13
                                                                             2
0.15235267E+05-0.03266386E+02 0.02462608E+02 0.09582781E-01-0.07087359E-04
                                                                            3
0.13633683E-08 0.02969647E-11 0.16061522E+05 0.12141870E+02
                                                                             4
                                              200.000 6000.00 1000.00
                                                                             1
AR
                 AR 1
                                          G
2.5000000E+00 0.0000000E+00 0.0000000E+00 0.0000000E+00 0.0000000E+00
                                                                             2
-7.45375000E+02 4.37967491E+00 2.50000000E+00 0.0000000E+00 0.0000000E+00
                                                                            3
0.0000000E+00 0.0000000E+00-7.45375000E+02 4.37967491E+00 0.0000000E+00
                                                                             4
AR(+)
                                              200.000 6000.00 1000.00
                 AR 1e -1
                                          G
                                                                             1
2.5000000E+00 0.0000000E+00 0.0000000E+00 0.0000000E+00 0.0000000E+00
                                                                            2
-7.45375000E+02 4.37967491E+00 2.50000000E+00 0.0000000E+00 0.0000000E+00
                                                                            3
0.0000000E+00 0.0000000E+00-7.45375000E+02 4.37967491E+00 0.0000000E+00
                                                                            4
AR*
                                          G 0300.00
                                                       5000.00 1000.00
                 AR 1
                                                                             1
0.02500000E+02 0.0000000E+00 0.0000000E+00 0.0000000E+00 0.0000000E+00
                                                                            2
-0.07453750E+04 0.04366000E+02 0.02500000E+02 0.00000000E+00 0.00000000E+00
                                                                            3
0.0000000E+00 0.0000000E+00-0.07453750E+04 0.04366000E+02
                                                                             4
                 e -1
                                           G 0300.00
                                                       5000.00 1000.00
                                                                             1
e-
0.26152490E+01 0.0000000E+00 0.0000000E+00 0.0000000E+00 0.0000000E+00
                                                                            2
-0.77925980E+03-0.12261360E+02 0.26152490E+01 0.0000000E+00 0.0000000E+00
                                                                            3
0.0000000E+00 0.0000000E+00-0.77925990E+03-0.12261360E+02
                                                                            4
C2
                 С
                                          G 0300.00
                                                       5000.00 1000.00
                                                                             1
                     2
0.40435359E+01 0.20573654E-03 0.10907575E-06-0.36427874E-10-0.34127865E-14
                                                                            2
0.99709486E+05 0.12775158E+01 0.74518140E+01-0.10144686E-01 0.85879735E-05
                                                                            3
0.87321100E-09-0.24429792E-11 0.98911989E+05-0.15845578E+02
                                                                            4
Н
                 Н
                                              200.00
                                                       6000.00 1000.00
                                                                            1
                     1
                                          G
0.25000000E+01 0.0000000E+00 0.0000000E+00 0.0000000E+00 0.0000000E+00
                                                                            2
0.25473660E+05-0.44668285E+00 0.25000000E+01 0.00000000E+00 0.0000000E+00
                                                                            3
0.0000000E+00 0.0000000E+00 0.25473660E+05-0.44668285E+00 0.26219035E+05
                                                                            4
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H2 Η 2 G 200.000 6000.00 1000.00 1 2.93286575E+00 8.26608026E-04-1.46402364E-07 1.54100414E-11-6.88804800E-16 2 -8.13065581E+02-1.02432865E+00 2.34433112E+00 7.98052075E-03-1.94781510E-05 3 2.01572094E-08-7.37611761E-12-9.17935173E+02 6.83010238E-01 0.00000000E+00 4 OH Ο 1H 1 G 200.000 6000.00 1000.00 1 2.83853033E+00 1.10741289E-03-2.94000209E-07 4.20698729E-11-2.42289890E-15 2 3.69780808E+03 5.84494652E+00 3.99198424E+00-2.40106655E-03 4.61664033E-06 3 -3.87916306E-09 1.36319502E-12 3.36889836E+03-1.03998477E-01 4.48613328E+03 4 OH* 0 1H 1 G 300.00 5000.00 1000.00 1 0.02882730E+02 0.10139743E-02-0.02276877E-05 0.02174683E-09-0.05126305E-14 2 5.02650000E+04 0.05595712E+02 0.03637266E+02 0.01850910E-02-0.16761646E-05 3 0.02387202E-07-0.08431442E-11 5.00213000E+04 0.13588605E+01 4 H20 Н 20 1 G 200.000 6000.00 1000.00 1 0.26770389E+01 0.29731816E-02-0.77376889E-06 0.94433514E-10-0.42689991E-14 2 -0.29885894E+05 0.68825500E+01 0.41986352E+01-0.20364017E-02 0.65203416E-05 3 -0.54879269E-08 0.17719680E-11-0.30293726E+05-0.84900901E+00-0.29084817E+05 4 Н 10 200.000 5000.00 1000.00 H02 2 G 1 4.17228741E+00 1.88117627E-03-3.46277286E-07 1.94657549E-11 1.76256905E-16 2 3.10206839E+01 2.95767672E+00 4.30179807E+00-4.74912097E-03 2.11582905E-05 3 -2.42763914E-08 9.29225225E-12 2.64018485E+02 3.71666220E+00 1.47886045E+03 4 H202 Н 20 2 G 200.000 6000.00 1000.00 1 4.57977305E+00 4.05326003E-03-1.29844730E-06 1.98211400E-10-1.13968792E-14 2 -1.80071775E+04 6.64970694E-01 4.31515149E+00-8.47390622E-04 1.76404323E-05 3 -2.26762944E-08 9.08950158E-12-1.77067437E+04 3.27373319E+00-1.63425145E+04 4 CH20 2CG Η 10 1 200.000 6000.00 1000.00 1 3.16952665E+00 6.19320560E-03-2.25056366E-06 3.65975660E-10-2.20149458E-14 2 -1.45486831E+04 6.04207898E+00 4.79372312E+00-9.90833322E-03 3.73219990E-05 3 -3.79285237E-08 1.31772641E-11-1.43791953E+04 6.02798058E-01-1.31293365E+04 4 CO C 10 1 G 200.000 6000.00 1000.00 1 0.30484859E+01 0.13517281E-02-0.48579405E-06 0.78853644E-10-0.46980746E-14 2 -0.14266117E+05 0.60170977E+01 0.35795335E+01-0.61035369E-03 0.10168143E-05 3 0.90700586E-09-0.90442449E-12-0.14344086E+05 0.35084093E+01-0.13293628E+05 4 C02 С 10 2 G 200.000 6000.00 1000.00 1 0.46365111E+01 0.27414569E-02-0.99589759E-06 0.16038666E-09-0.91619857E-14 2 -0.49024904E+05-0.19348955E+01 0.23568130E+01 0.89841299E-02-0.71220632E-05 3 0.24573008E-08-0.14288548E-12-0.48371971E+05 0.99009035E+01-0.47328105E+05 4 HCO С 1H 10 1 G 200.000 6000.00 1000.00 1 3.92001542E+00 2.52279324E-03-6.71004164E-07 1.05615948E-10-7.43798261E-15 2 3.65342928E+03 3.58077056E+00 4.23754610E+00-3.32075257E-03 1.40030264E-05 3 -1.34239995E-08 4.37416208E-12 3.87241185E+03 3.30834869E+00 5.08749163E+03 4 20 HO2CHO С 1H 3 G 300.000 5000.000 1378.00 1 9.87503878E+00 4.64663708E-03-1.67230522E-06 2.68624413E-10-1.59595232E-14 2 -3.80502496E+04-2.24939155E+01 2.42464726E+00 2.19706380E-02-1.68705546E-05 3 6.25612194E-09-9.11645843E-13-3.54828006E+04 1.75027796E+01 4 02CH0 С 1H10 3 G 300.000 5000.000 1368.00 1 7.24075139E+00 4.63312951E-03-1.63693995E-06 2.59706693E-10-1.52964699E-14 2 -1.87027618E+04-6.49547212E+00 3.96059309E+00 1.06002279E-02-5.25713351E-06 3 1.01716726E-09-2.87487602E-14-1.73599383E+04 1.17807483E+01 4 HOCHO Н 2C 10 2 G 200.000 6000.00 1000.00 1 2 0.46138316E+01 0.64496364E-02-0.22908251E-05 0.36716047E-09-0.21873675E-13 -0.47514850E+05 0.84788383E+00 0.38983616E+01-0.35587795E-02 0.35520538E-04 3 -0.43849959E-07 0.17107769E-10-0.46770609E+05 0.73495397E+01-0.45531246E+05 4 HOCO Н 1C 10 2 G 200.000 6000.00 1000.00 1 5.39206152E+00 4.11221455E-03-1.48194900E-06 2.39875460E-10-1.43903104E-14 2

-2.38606717E+04-2.23529091E+00 2.92207919E+00 7.62453859E-03 3.29884437E-06 3 -1.07135205E-08 5.11587057E-12-2.30281524E+04 1.12925886E+01-2.18076591E+04 4 OCHO С 10 2H 1 G 200.000 6000.000 1000.00 1 4.14394211E+00 5.59738818E-03-1.99794019E-06 3.16179193E-10-1.85614483E-14 2 -1.72459887E+04 5.07778617E+00 4.68825921E+00-4.14871834E-03 2.55066010E-05 3 -2.84473900E-08 1.04422559E-11-1.69867041E+04 4.28426480E+00-1.55992356E+04 4 HOCH202H C 1H 40 3 G 300.000 5000.000 1422.000 1 1.16303827E+01 7.15133688E-03-2.39035030E-06 3.65772791E-10-2.10199524E-14 2 -4.31079242E+04-3.24276725E+01 1.85716693E+00 3.23153132E-02-2.69928902E-05 3 1.11694484E-08-1.81284103E-12-4.00314471E+04 1.90917729E+01 4 HOCH2O2 С 1H30 3 G 300.000 5000.000 1412.000 1 2 9.04545938E+00 7.15223373E-03-2.37005676E-06 3.60083481E-10-2.05750228E-14 -2.49414886E+04-1.74210530E+01 2.85441621E+00 2.33663535E-02-1.88115990E-05 3 7.96709515E-09-1.36346618E-12-2.29866196E+04 1.51730565E+01 4 С 1H 30 3 G 300.000 5000.000 1420.000 1 **DCH2D2H** 1.15398246E+01 5.34291432E-03-1.81878917E-06 2.81968625E-10-1.63584348E-14 2 -1.68237489E+04-3.20700633E+01 1.93823075E+00 3.01465730E-02-2.61053152E-05 3 1.09463562E-08-1.78312692E-12-1.38166625E+04 1.85042002E+01 4 1H30 1 HOCH20 С 2 G 300.000 5000.000 1452.000 6.39521515E+00 7.43673043E-03-2.50422354E-06 3.84879712E-10-2.21778689E-14 2 -2.41108840E+04-6.63865583E+00 4.11183145E+00 7.53850697E-03 3.77337370E-06 3 -5.38746005E-09 1.45615887E-12-2.28023001E+04 7.46807254E+00 4 CH3OH С 40 G 200.000 6000.00 1000.00 1H 1 1 3.52726795E+00 1.03178783E-02-3.62892944E-06 5.77448016E-10-3.42182632E-14 2 -2.60028834E+04 5.16758693E+00 5.65851051E+00-1.62983419E-02 6.91938156E-05 3 -7.58372926E-08 2.80427550E-11-2.56119736E+04-8.97330508E-01-2.41746056E+04 4 CH20H C 1H 30 1 G 200.000 6000.00 1 1000.00 5.09314370E+00 5.94761260E-03-2.06497460E-06 3.23008173E-10-1.88125902E-14 2 -4.03409640E+03-1.84691493E+00 4.47834367E+00-1.35070310E-03 2.78484980E-05 3 -3.64869060E-08 1.47907450E-11-3.50072890E+03 3.30913500E+00-2.04462770E+03 4 CH30 C 1H 30 1 G 200.000 6000.00 1000.00 1 4.75779238E+00 7.44142474E-03-2.69705176E-06 4.38090504E-10-2.63537098E-14 2 3 3.78111940E+02-1.96680028E+00 3.71180502E+00-2.80463306E-03 3.76550971E-05 -4.73072089E-08 1.86588420E-11 1.29569760E+03 6.57240864E+00 2.52571660E+03 4 CH302H С 1H40 2 G 200.000 6000.00 1000.00 1 7.76538058E+00 8.61499712E-03-2.98006935E-06 4.68638071E-10-2.75339255E-14 2 -1.82979984E+04-1.43992663E+01 2.90540897E+00 1.74994735E-02 5.28243630E-06 3 -2.52827275E-08 1.34368212E-11-1.68894632E+04 1.13741987E+01-1.52423685E+04 4 CH302 Η 3C 10 2 G 300.00 5000.00 1000.00 1 4.80390863E+00 9.95844638E-03-3.85301026E-06 6.84740497E-10-4.58402955E-14 2 -7.47135460E+02 1.45281400E+00 3.62497097E+00 3.59397933E-03 2.26538097E-05 3 -2.95391947E-08 1.11977570E-11 7.93040410E+01 9.96382194E+00 4 CH202H C 1H 30 2 G 300.000 5000.000 1357.000 1 9.10784249E+00 5.27260434E-03-1.88170543E-06 3.00561364E-10-1.77865959E-14 2 3.77440183E+03-2.11741044E+01 4.47228333E+00 1.33401095E-02-5.92919725E-06 3 4.44481025E-10 2.12699899E-13 5.67413711E+03 4.72608208E+00 4 CH4 С 1H4 G 200.000 6000.00 1000.00 1 2 1.65326226E+00 1.00263099E-02-3.31661238E-06 5.36483138E-10-3.14696758E-14 -1.00095936E+04 9.90506283E+00 5.14911468E+00-1.36622009E-02 4.91453921E-05 3 -4.84246767E-08 1.66603441E-11-1.02465983E+04-4.63848842E+00-8.97226656E+03 4 С 200.000 6000.00 1000.00 CH3 1H 3 G 1 2 0.29781206E+01 0.57978520E-02-0.19755800E-05 0.30729790E-09-0.17917416E-13 0.16509513E+05 0.47224799E+01 0.36571797E+01 0.21265979E-02 0.54583883E-05 3 -0.66181003E-08 0.24657074E-11 0.16422716E+05 0.16735354E+01 0.17643935E+05 4 CH2 С 1H2 G 200.000 6000.00 1000.00 1 3.14631886E+00 3.03671259E-03-9.96474439E-07 1.50483580E-10-8.57335515E-15 2 4.60412605E+04 4.72341711E+00 3.71757846E+00 1.27391260E-03 2.17347251E-06 3 -3.48858500E-09 1.65208866E-12 4.58723866E+04 1.75297945E+00 4.70504920E+04 4 $CH_2(S)$ С 1H 2 G 200.000 6000.00 1000.00 1 3.13501686E+00 2.89593926E-03-8.16668090E-07 1.13572697E-10-6.36262835E-15 2 5.05040504E+04 4.06030621E+00 4.19331325E+00-2.33105184E-03 8.15676451E-06 3 -6.62985981E-09 1.93233199E-12 5.03662246E+04-7.46734310E-01 5.15727280E+04 4 CH С 1H 1 G 200.000 6000.00 1000.00 1 0.25209369E+01 0.17653639E-02-0.46147660E-06 0.59289675E-10-0.33474501E-14 2 0.70946769E+05 0.74051829E+01 0.34897583E+01 0.32432160E-03-0.16899751E-05 3 0.31628420E-08-0.14061803E-11 0.70612646E+05 0.20842841E+01 0.71658188E+05 4 CH* С 1H 1 G 300.00 5000.00 1000.00 1 0.02196223E+02 0.02340381E-01-0.07058201E-05 0.09007582E-09-0.03855040E-13 2 0.10419559E+06 0.09178373E+02 0.03200202E+02 0.02072875E-01-0.05134431E-04 3 0.05733890E-07-0.01955533E-10 0.10393714E+06 0.03331587E+02 4 С 1 C G 200.000 6000.00 1000.00 1 0.26055830E+01-0.19593434E-03 0.10673722E-06-0.16423940E-10 0.81870580E-15 2 0.85411742E+05 0.41923868E+01 0.25542395E+01-0.32153772E-03 0.73379223E-06 3 -0.73223487E-09 0.26652144E-12 0.85442681E+05 0.45313085E+01 0.86195097E+05 4 C2H6 C 2Н G 200.000 6000.00 1000.00 1 6 4.04666411E+00 1.53538802E-02-5.47039485E-06 8.77826544E-10-5.23167531E-14 2 -1.24473499E+04-9.68698313E-01 4.29142572E+00-5.50154901E-03 5.99438458E-05 3 -7.08466469E-08 2.68685836E-11-1.15222056E+04 2.66678994E+00-1.00849652E+04 4 C2H5 С 2H 5 G 300.000 5000.000 1387.000 1 5.88784390E+00 1.03076793E-02-3.46844396E-06 5.32499257E-10-3.06512651E-14 2 1.15065499E+04-8.49651771E+00 1.32730217E+00 1.76656753E-02-6.14926558E-06 3 -3.01143466E-10 4.38617775E-13 1.34284028E+04 1.71789216E+01 4 C2H4 С 2H G 200.000 6000.00 1000.00 1 4 3.99182724E+00 1.04833908E-02-3.71721342E-06 5.94628366E-10-3.53630386E-14 2 4.26865851E+03-2.69081762E-01 3.95920063E+00-7.57051373E-03 5.70989993E-05 3 -6.91588352E-08 2.69884190E-11 5.08977598E+03 4.09730213E+00 6.31426266E+03 4 C2H3 С 2H 3 G 200.000 6000.00 1000.00 1 4.15026763E+00 7.54021341E-03-2.62997847E-06 4.15974048E-10-2.45407509E-14 2 3.38566380E+04 1.72812235E+00 3.36377642E+00 2.65765722E-04 2.79620704E-05 3 -3.72986942E-08 1.51590176E-11 3.44749589E+04 7.91510092E+00 3.56701718E+04 4 C2H2 С 2H 2 G 200.000 6000.00 1000.00 1 4.65878489E+00 4.88396667E-03-1.60828888E-06 2.46974544E-10-1.38605959E-14 2 2.57594042E+04-3.99838194E+00 8.08679682E-01 2.33615762E-02-3.55172234E-05 3 2.80152958E-08-8.50075165E-12 2.64289808E+04 1.39396761E+01 2.74459950E+04 4 2H C2H С 1 G 200.000 6000.00 1000.00 1 3.66270248E+00 3.82492252E-03-1.36632500E-06 2.13455040E-10-1.23216848E-14 2 6.71683790E+04 3.92205792E+00 2.89867676E+00 1.32988489E-02-2.80733327E-05 3 2.89484755E-08-1.07502351E-11 6.70616050E+04 6.18547632E+00 6.83210436E+04 4 CH3CH0 С 2H 40 1 G 200.000 6000.00 1000.00 1 2 0.54041108E+01 0.11723059E-01-0.42263137E-05 0.68372451E-09-0.40984863E-13 -0.22593122E+05-0.34807917E+01 0.47294595E+01-0.31932858E-02 0.47534921E-04 3 -0.57458611E-07 0.21931112E-10-0.21572878E+05 0.41030159E+01-0.19987949E+05 4 200.000 6000.00 1000.00 CH3CO С 2H 30 1 G 1 2 0.53137165E+01 0.91737793E-02-0.33220386E-05 0.53947456E-09-0.32452368E-13 -0.36450414E+04-0.16757558E+01 0.40358705E+01 0.87729487E-03 0.30710010E-04 3 -0.39247565E-07 0.15296869E-10-0.26820738E+04 0.78617682E+01-0.12388039E+04 4 CH2CH0 С 2H 30 1 G 200.000 6000.00 1000.00 1 6.53928338E+00 7.80238629E-03-2.76413612E-06 4.42098906E-10-2.62954290E-14 2

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C2H4O2H С 2H 50 2 G 300.000 5000.000 1397.000 1 1.05228954E+01 9.48091381E-03-3.55727763E-06 6.41445994E-10-4.21232247E-14 2 1.55718322E+03-2.31413632E+01 3.46916874E+00 2.71188626E-02-2.08022550E-05 3 8.44284845E-09-1.40756215E-12 3.89688270E+03 1.43400726E+01 4 CH3CH02H С 2H 50 2 G 300.000 5000.000 1385.000 1 1.06284708E+01 1.01662327E-02-3.34915963E-06 5.07257146E-10-2.89352540E-14 2 -2.15391230E+03-2.60363030E+01 3.91433011E+00 2.52722102E-02-1.62112291E-05 3 5.45591592E-09-7.57965290E-13 2.38044573E+02 1.02327238E+01 4 C2H401-2 С 2H 40 1 G 200.000 6000.00 1000.00 1 0.54887641E+01 0.12046190E-01-0.43336931E-05 0.70028311E-09-0.41949088E-13 2 -0.91804251E+04-0.70799605E+01 0.37590532E+01-0.94412180E-02 0.80309721E-04 3 -0.10080788E-06 0.40039921E-10-0.75608143E+04 0.78497475E+01-0.63304657E+04 4 C2H3O1-2 C 2H 3O 1 G 200.000 6000.00 1000.00 1 5.60158035E+00 9.17613962E-03-3.28028902E-06 5.27903888E-10-3.15362241E-14 2 1.71446252E+04-5.47228512E+00 3.58349017E+00-6.02275805E-03 6.32426867E-05 3 -8.18540707E-08 3.30444505E-11 1.85681353E+04 9.59725926E+00 1.97814471E+04 4 С ЗH 60 1 G 200.000 6000.00 1000.00 CH3COCH3 1 7.29796974E+00 1.75656913E-02-6.31678065E-06 1.02025553E-09-6.10903592E-14 2 -2.95368927E+04-1.27591704E+01 5.55638920E+00-2.83863547E-03 7.05722951E-05 3 -8.78130984E-08 3.40290951E-11-2.78325393E+04 2.31960221E+00-2.58360384E+04 4 CH3COCH2 С 3H 50 1 G 200.000 6000.00 1000.00 1 7.54410697E+00 1.43443222E-02-5.08381081E-06 8.13200521E-10-4.83673315E-14 2 -7.48672286E+03-1.14792587E+01 4.70187196E+00 5.51653762E-03 4.27505858E-05 3 -5.94680816E-08 2.40685378E-11-5.92845491E+03 7.12932590E+00-4.00985747E+03 4 50 С ЗH 3 G CH3COCH2O2 300.000 5000.000 1379.00 1 1.27690342E+01 1.42554828E-02-4.92821461E-06 7.70448921E-10-4.49110534E-14 2 -2.34798669E+04-3.27155799E+01 5.95535468E+00 2.70255205E-02-1.37385031E-05 3 3.53735851E-09-4.03922557E-13-2.06679464E+04 5.21436049E+00 4 CH3COCH2O2H С 3H 6O 3 G 300.000 5000.000 1381.00 1 1.52372810E+01 1.44114651E-02-5.01290009E-06 7.87071229E-10-4.60225784E-14 2 -4.27564444E+04-4.77383784E+01 4.94789761E+00 3.60474432E-02-2.21719933E-05 3 6.98296874E-09-9.21269260E-13-3.88687178E+04 8.49926130E+00 4 CH3COCH2O С ЗH 50 2 G 300.000 5000.000 1370.000 1 1.14637586E+01 1.32124342E-02-4.56580495E-06 7.13897538E-10-4.16281047E-14 2 -2.23833017E+04-3.15127868E+01 3.72927689E+00 2.63943697E-02-1.09796486E-05 3 8.58185303E-10 3.39474590E-13-1.91551565E+04 1.18505335E+01 4 C2H3CH0 С ЗH 40 1 G 300.000 5000.000 1393.000 1 1.04184959E+01 9.48963321E-03-3.29310529E-06 5.16279203E-10-3.01587291E-14 2 -1.49630281E+04-3.07235061E+01 2.92355162E-01 3.54321417E-02-2.94936324E-05 3 1.28100124E-08-2.26144108E-12-1.16521584E+04 2.28878280E+01 4 30 C2H3CO С ЗH 1 G 300.000 5000.000 1402.000 1 9.37467676E+00 7.91296900E-03-2.67198280E-06 4.11115430E-10-2.36978981E-14 2 1.92969514E+03-2.40892696E+01 1.36242013E+00 3.15273972E-02-3.00218935E-05 3 1.48167112E-08-2.87971530E-12 4.25770215E+03 1.72626546E+01 4 C2H5CH0 С ЗH 60 1 G 200.000 6000.00 1000.00 1 7.44085690E+00 1.77301764E-02-6.34081568E-06 1.02040803E-09-6.09461714E-14 2 -2.60055814E+04-1.44195446E+01 4.24529681E+00 6.68296706E-03 4.93337933E-05 3 -6.71986124E-08 2.67262347E-11-2.41473007E+04 6.90738560E+00-2.22688471E+04 4 C2H5CO С ЗH 50 1 G 200.000 6000.00 1000.00 1 2 6.52325448E+00 1.54211952E-02-5.50898157E-06 8.85889862E-10-5.28846399E-14 -7.19631634E+03-5.19862218E+00 6.25722402E+00-9.17612184E-03 7.61190493E-05 3 -9.05514997E-08 3.46198215E-11-5.91616484E+03 2.23330599E+00-3.94851891E+03 4 CH2CH2CH0 С ЗH 50 1 G 300.000 5000.000 1363.000 1 9.96855598E+00 1.61917946E-02-6.64161740E-06 1.15444520E-09-7.21981790E-14 2

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CH20CH0 С 2H 30 2 G 300.000 5000.000 1442.000 1 1.00960096E+01 7.19887066E-03-2.59813465E-06 4.18110812E-10-2.48723387E-14 2 -2.36389018E+04-2.71144175E+01 2.31031671E+00 1.80474065E-02-2.71519637E-06 3 -4.60918579E-09 1.70037078E-12-2.02910878E+04 1.71549722E+01 4 HF. HF. 1 G 200.000 6000.00 1000.00 1 2.5000000E+00 0.0000000E+00 0.0000000E+00 0.0000000E+00 0.0000000E+00 2 -7.45375000E+02 9.28723974E-01 2.50000000E+00 0.0000000E+00 0.0000000E+00 3 0.0000000E+00 0.0000000E+00-7.45375000E+02 9.28723974E-01 0.0000000E+00 4 C3H8 С ЗH 8 G 200.000 6000.00 1000.00 1 6.66919760E+00 2.06108751E-02-7.36512349E-06 1.18434262E-09-7.06914630E-14 2 -1.62754066E+04-1.31943379E+01 4.21093013E+00 1.70886504E-03 7.06530164E-05 3 -9.20060565E-08 3.64618453E-11-1.43810883E+04 5.61004451E+00-1.25900384E+04 4 NC3H7 С 3H 7 G 200.000 6000.00 1000.00 1 6.49636579E+00 1.77337992E-02-6.24898046E-06 9.95389495E-10-5.90199770E-14 2 8.85973885E+03-8.56389710E+00 4.08211458E+00 5.23240341E-03 5.13554466E-05 3 -6.99343598E-08 2.81819493E-11 1.04074558E+04 8.39534919E+00 1.21859256E+04 4 С ЗH 7 200.000 6000.00 1000.00 TC3H7 G 1 5.30597255E+00 1.89854588E-02-6.74315384E-06 1.07993730E-09-6.42785036E-14 2 7.78748910E+03-2.23233935E+00 5.47421257E+00-8.42536682E-03 8.04607759E-05 3 -9.49287824E-08 3.59830971E-11 9.04939013E+03 3.40542323E+00 1.08473019E+04 4 C3H6 С 3H G 200.000 6000.00 1000.00 1 6 6.03870234E+00 1.62963931E-02-5.82130800E-06 9.35936829E-10-5.58603143E-14 2 -7.41715057E+02-8.43825992E+00 3.83464468E+00 3.29078952E-03 5.05228001E-05 3 -6.66251176E-08 2.63707473E-11 7.88717123E+02 7.53408013E+00 2.40543339E+03 4 C3H5-A ЗH С 5 G 300.000 3000.00 1000.00 1 0.65007877E+01 0.14324731E-01-0.56781632E-05 0.11080801E-08-0.90363887E-13 2 0.17482449E+05-0.11243050E+02 0.13631835E+01 0.19813821E-01 0.12497060E-04 3 -0.33355555E-07 0.15846571E-10 0.19245629E+05 0.17173214E+02 4 C3H5-T С ЗH 300.000 3000.00 1000.00 1 5 G 0.54255528E+01 0.15511072E-01-0.56678350E-05 0.79224388E-09-0.16878034E-13 2 0.27843027E+05-0.33527184E+01 0.17329209E+01 0.22394620E-01-0.51490611E-05 3 -0.67596466E-08 0.38253211E-11 0.29040498E+05 0.16568878E+02 4 C3H5-S С ЗH 5 G 300.000 3000.00 1000.00 1 0.53725281E+01 0.15780509E-01-0.59922850E-05 0.93089664E-09-0.36550966E-13 2 0.29614760E+05-0.34186478E+01 0.91372931E+00 0.26432343E-01-0.11758950E-04 3 -0.23035678E-08 0.27715488E-11 0.30916867E+05 0.19989269E+02 4 C3H4-A С ЗH 4 G 200.000 6000.00 1000.00 1 0.63168722E+01 0.11133728E-01-0.39629378E-05 0.63564238E-09-0.37875540E-13 2 0.20117495E+05-0.10995766E+02 0.26130445E+01 0.12122575E-01 0.18539880E-04 3 -0.34525149E-07 0.15335079E-10 0.21541567E+05 0.10226139E+02 0.22962267E+05 4 4C C3H4-P Н 3 G 200.000 6000.00 1000.00 1 0.60252400E+01 0.11336542E-01-0.40223391E-05 0.64376063E-09-0.38299635E-13 2 0.19620942E+05-0.86043785E+01 0.26803869E+01 0.15799651E-01 0.25070596E-05 3 -0.13657623E-07 0.66154285E-11 0.20802374E+05 0.98769351E+01 0.22302059E+05 4 C3H3 С ЗH 3 G 200.000 6000.00 1000.000 1 2 7.14221719E+00 7.61902211E-03-2.67460030E-06 4.24914904E-10-2.51475443E-14 3.95709594E+04-1.25848690E+01 1.35110873E+00 3.27411291E-02-4.73827407E-05 3 3.76310220E-08-1.18541128E-11 4.07679941E+04 1.52058598E+01 4.22762135E+04 4 200.000 6000.00 1000.00 C3H2 С ЗH 2 G 1 2 6.67324762E+00 5.57728845E-03-1.99180164E-06 3.20289156E-10-1.91216272E-14 7.57571184E+04-9.72894405E+00 2.43417332E+00 1.73013063E-02-1.18294047E-05 3 1.02756396E-09 1.62626314E-12 7.69074892E+04 1.21012230E+01 7.83005132E+04 4 C3H50 С ЗH 50 1 G 300.000 5000.000 1380.000 1 1.02551752E+01 1.14983720E-02-3.84645659E-06 5.88910346E-10-3.38557923E-14 2

6.26560810E+03-2.77655042E+01 1.19822582E+00 3.05579837E-02-1.80630276E-05 3 4.86150033E-09-4.19854562E-13 9.58217784E+03 2.15566221E+01 4 C3H600H1 - 3С ЗH 70 2 G 300.000 5000.000 1384.000 1 1.46881564E+01 1.49941200E-02-5.24056505E-06 8.25462711E-10-4.83758952E-14 2 -4.77342863E+03-4.77984492E+01 1.88331465E+00 4.40156051E-02-3.07858462E-05 3 1.13214862E-08-1.75323184E-12-1.68779168E+02 2.14040621E+01 4 3H 70 2 C3H600H1-2 С G 300.000 5000.000 1402.000 1 1.24605763E+01 1.58889526E-02-5.32742106E-06 8.15818791E-10-4.68723250E-14 2 -4.20305196E+03-3.23858947E+01 2.87774562E+00 3.74166999E-02-2.36058063E-05 3 7.79930860E-09-1.06042562E-12-7.82368119E+02 1.93941340E+01 4 C3H600H2-1 С ЗH 70 2 G 300.000 5000.000 1407.000 1 1.42163221E+01 1.43382450E-02-4.78004477E-06 7.29133134E-10-4.17761973E-14 2 -5.67381620E+03-4.35770997E+01 2.09193950E+00 4.69220394E-02-3.90280831E-05 3 1.72381453E-08-3.07968979E-12-1.89377918E+03 2.00178282E+01 4 С 70 2 G 300.000 5000.000 1407.000 1 C3H600H2-2 ЗH 1.42163221E+01 1.43382450E-02-4.78004477E-06 7.29133134E-10-4.17761973E-14 2 -5.67381620E+03-4.35770997E+01 2.09193950E+00 4.69220394E-02-3.90280831E-05 3 1.72381453E-08-3.07968979E-12-1.89377918E+03 2.00178282E+01 4 3H 7O 4 C3H600H1-202 С G 300.000 5000.000 1386.000 1 1.91759159E+01 1.59857013E-02-5.61306378E-06 8.86880495E-10-5.20877040E-14 2 -2.64412115E+04-6.77512936E+01 2.65196584E+00 5.74638149E-02-4.72190867E-05 3 2.05591557E-08-3.68787387E-12-2.08829371E+04 2.01547955E+01 4 С 70 4 G 300.000 5000.000 1382.000 C3H600H1-302 ЗH 1 1.85916698E+01 1.65328553E-02-5.81343626E-06 9.19396939E-10-5.40320702E-14 2 3 -2.39598698E+04-6.42544402E+01 3.14864588E+00 5.33542571E-02-4.08330611E-05 1.67542220E-08-2.89288326E-12-1.85473645E+04 1.86305431E+01 4 C3H600H2-102 C 3H 7O 4 G 300.000 5000.000 1386.000 1 1.91759159E+01 1.59857013E-02-5.61306378E-06 8.86880495E-10-5.20877040E-14 2 -2.64412115E+04-6.77512936E+01 2.65196584E+00 5.74638149E-02-4.72190867E-05 3 2.05591557E-08-3.68787387E-12-2.08829371E+04 2.01547955E+01 4 NC3H70 С 3H 7O 1 G 200.000 6000.00 1000.00 1 8.38041157E+00 1.95206120E-02-6.97374143E-06 1.12144919E-09-6.69467831E-14 2 -8.48625211E+03-1.89916219E+01 4.21934640E+00 7.38556641E-03 6.02825529E-05 3 -8.38680247E-08 3.39623435E-11-6.23491852E+03 8.08139850E+00-4.26576768E+03 4 IC3H70 С 3H 70 G 300.000 5000.000 1393.000 1 1 1.23135031E+01 1.38062606E-02-4.91585531E-06 8.21075632E-10-5.07493001E-14 2 -1.24717023E+04-4.17270532E+01-8.18260771E-01 4.68807147E-02-3.74369377E-05 3 1.55917264E-08-2.64308171E-12-8.15153216E+03 2.79483196E+01 4 NC3H7O2H С 3H 80 2 G 200.000 6000.00 1000.00 1 1.04115631E+01 2.13763889E-02-7.55819870E-06 1.20207180E-09-7.11798090E-14 2 -2.68935445E+04-2.35428789E+01 7.08977756E+00-4.86163264E-03 1.03253531E-04 3 -1.33200956E-07 5.30799252E-11-2.44194556E+04 1.74859215E+00-2.18476548E+04 4 IC3H7O2H С 3H 8O 2 G 300.000 5000.000 1389.000 1 1.57046391E+01 1.65924516E-02-5.77250934E-06 9.06453070E-10-5.30084111E-14 2 -3.23268564E+04-5.71735156E+01 5.19265570E-01 5.32111228E-02-4.05156892E-05 3 1.63346713E-08-2.73751233E-12-2.71048486E+04 2.40815065E+01 4 NC3H702 С ЗH 70 2 G 200.000 6000.00 1000.00 1 2 9.24489759E+00 2.14800809E-02-7.69335773E-06 1.23945160E-09-7.40911693E-14 -9.81187945E+03-2.20401438E+01 6.99488957E+00-7.50355088E-03 1.01250579E-04 3 -1.25012534E-07 4.84675978E-11-7.53004240E+03-2.03740242E+00-5.10764916E+03 4 С 70 G 300.000 5000.000 1388.000 IC3H702 ЗH 2 1 1.32493493E+01 1.64082190E-02-5.67432062E-06 8.87336340E-10-5.17361535E-14 2 -1.44109855E+04-4.29066213E+01 1.49941639E+00 4.43081205E-02-3.22414456E-05 3 1.29687136E-08-2.23370569E-12-1.02587980E+04 2.02336490E+01 4

3H 60 1 200.000 6000.00 1000.00 C3H6O1-3 С G 1 6.80716906E+00 1.88824545E-02-6.79082475E-06 1.09713919E-09-6.57154952E-14 2 -1.36547629E+04-1.35382154E+01 5.15283752E+00-1.86401716E-02 1.29980652E-04 3 -1.58629974E-07 6.20668783E-11-1.13243512E+04 4.73561224E+00-9.75233898E+03 4 C3H601-2 С 3H 60 1 G 200.000 6000.00 1000.00 1 8.01491079E+00 1.73919953E-02-6.26027968E-06 1.01188256E-09-6.06239111E-14 2 -1.51980838E+04-1.88279964E+01 3.42806676E+00 6.25176642E-03 6.13196311E-05 3 -8.60387185E-08 3.51371393E-11-1.28446646E+04 1.04244994E+01-1.11564001E+04 4 C3KET12 С 3H 60 3 G 300.000 5000.000 1388.000 1 1.70756225E+01 1.31013491E-02-4.61949408E-06 7.31991329E-10-4.30788679E-14 2 -4.17008637E+04-5.95778952E+01 1.10507238E+00 5.27396706E-02-4.31805774E-05 3 1.81618292E-08-3.10535568E-12-3.63627536E+04 2.54111636E+01 4 C3KET13 C 3H 6O 3 G 300.000 5000.000 1379.000 1 1.58927479E+01 1.40990923E-02-4.96118851E-06 7.84992198E-10-4.61488928E-14 2 -3.93774829E+04-5.26049341E+01 3.55241022E+00 4.18720270E-02-2.94550370E-05 3 1.09982900E-08-1.75045977E-12-3.48902671E+04 1.42082894E+01 4 С ЗH 60 3 G 300.000 5000.000 1371.000 C3KET21 1 1.56377776E+01 1.44059342E-02-5.08808082E-06 8.07076119E-10-4.75295650E-14 2 -4.30657975E+04-5.13105869E+01 4.55686367E+00 3.57076837E-02-1.94712054E-05 3 4.70695431E-09-3.69753807E-13-3.86710975E+04 9.97761694E+00 4 C3H51-2,300H С 3H 70 4 G 300.000 5000.000 1386.000 1 2.12378169E+01 1.39519596E-02-4.94539222E-06 7.86381389E-10-4.63925564E-14 2 -1.92864584E+04-7.69636561E+01 2.55619708E+00 6.13504487E-02-5.23205391E-05 3 2.28208029E-08-4.02231508E-12-1.31353414E+04 2.21043799E+01 4 3H 7O 4 G C3H52-1,300H С 300.000 5000.000 1379.000 1 2.02817964E+01 1.48155431E-02-5.25503386E-06 8.35963453E-10-4.93308915E-14 2 -1.80085066E+04-7.22688262E+01 4.12253742E+00 5.19553611E-02-3.83733727E-05 3 1.45851637E-08-2.29820536E-12-1.22759164E+04 1.48367359E+01 4 C 3H 70 1 C3H6OH G 300.000 5000.000 1674.000 1 9.31287816E+00 1.67579212E-02-5.75555480E-06 9.00584362E-10-5.26566836E-14 2 -1.20169635E+04-1.95011064E+01 1.20494302E+00 3.30857885E-02-1.63893637E-05 3 3.18103918E-09-6.84229288E-14-9.12961720E+03 2.47155202E+01 4 70 H0C3H602 С ЗH 3 G 300.000 5000.000 1397.000 1 1.42691004E+01 1.71837825E-02-5.83419536E-06 9.00994191E-10-5.20716210E-14 2 -3.14501750E+04-4.15295035E+01 3.06954289E+00 4.43105640E-02-3.18636260E-05 3 1.26409287E-08-2.12751901E-12-2.75893676E+04 1.83891218E+01 4 CH3CHCO C 3H 40 1 G 300.000 5000.000 1400.00 1 1.00219123E+01 9.56966300E-03-3.26221644E-06 5.05231706E-10-2.92593257E-14 2 -1.42482738E+04-2.77829973E+01 1.48380119E+00 3.22203013E-02-2.70250033E-05 3 1.20499164E-08-2.18365931E-12-1.15276540E+04 1.71552068E+01 4 ЗH 60 2 AC3H500H С G 300.000 5000.000 1394.000 1 1.36837693E+01 1.33968049E-02-4.61533631E-06 7.19988958E-10-4.19109988E-14 2 -1.33165248E+04-4.31904193E+01 2.43934647E+00 4.02070638E-02-2.95322679E-05 3 1.14715600E-08-1.85170511E-12-9.43679906E+03 1.70549969E+01 4 C2H300H С 2H 40 2 G 300.000 5000.000 1397.000 1 1.15749951E+01 8.09909174E-03-2.81808668E-06 4.42697954E-10-2.58998042E-14 2 -8.84852664E+03-3.43859117E+01 1.35644398E+00 3.37002447E-02-2.75988500E-05 3 1.14222854E-08-1.89488886E-12-5.49996692E+03 1.98354466E+01 4 C4H10 С 4H 10 G 300.000 5000.000 1392.000 1 1.24940183E+01 2.17726258E-02-7.44272215E-06 1.15487023E-09-6.69712949E-14 2 -2.18403437E+04-4.45558921E+01-4.55756824E-01 4.80323389E-02-2.65497552E-05 3 6.92544700E-09-6.38317504E-13-1.68960904E+04 2.64870966E+01 4 300.000 5000.000 1391.000 PC4H9 C 4H 9 G 1 1.20779744E+01 1.96264778E-02-6.71302199E-06 1.04206424E-09-6.04469282E-14 2

3.22550473E+03-3.87719384E+01 3.20730933E-01 4.34654454E-02-2.40584970E-05 3 6.28245308E-09-5.80113166E-13 7.71490893E+03 2.57301085E+01 4 SC4H9 С 4H 9 G 300.000 5000.000 1381.000 1 1.16934304E+01 1.96402287E-02-6.65306517E-06 1.02631895E-09-5.92826294E-14 2 1.96382429E+03-3.61626672E+01 8.49159986E-01 3.82085320E-02-1.49626797E-05 3 2.04499211E-10 8.24254437E-13 6.38832956E+03 2.44466606E+01 4 C4H8-1 C 4H 8 G 200.000 6000.00 1000.00 1 7.86795262E+00 2.24448843E-02-8.07705438E-06 1.30179988E-09-7.77958472E-14 2 -4.23853340E+03-1.65662549E+01 5.13226136E+00 5.33862838E-03 6.02928960E-05 3 -7.60364685E-08 2.87324693E-11-2.16718358E+03 3.82936810E+00-3.72842176E+00 4 C4H8-2 С 4H8 G 200.000 6000.00 1000.00 1 2 7.89114667E+00 2.24970532E-02-8.12143779E-06 1.31273568E-09-7.84451632E-14 -5.51643171E+03-1.76436027E+01 5.57278967E+00 3.76541017E-03 6.52226708E-05 3 -8.30909522E-08 3.20311342E-11-3.60128327E+03 5.37796708E-01-1.34523863E+03 4 С 4H 7 G 200.000 6000.00 1000.00 C4H71-1 1 8.15646382E+00 1.90308835E-02-6.73262214E-06 1.07333098E-09-6.36886441E-14 2 2.55826427E+04-1.61428872E+01 4.19857522E+00 1.19616999E-02 4.23864923E-05 3 -6.30299109E-08 2.59475110E-11 2.75256555E+04 8.57181248E+00 2.95712937E+04 4 4H 7 200.000 6000.00 1000.00 C4H71-2 С G 1 8.16688868E+00 1.95680375E-02-6.95694878E-06 1.11504166E-09-6.64079384E-14 2 2.37537003E+04-1.77041242E+01 3.77145965E+00 1.46544157E-02 3.70080802E-05 3 -5.72714455E-08 2.36641011E-11 2.58014506E+04 9.11906641E+00 2.78022108E+04 4 С 4H 7 G 200.000 6000.00 1000.00 C4H71-3 1 8.08107449E+00 1.95526544E-02-6.93149115E-06 1.10889183E-09-6.59584410E-14 2 3 1.22822959E+04-1.67137903E+01 4.54746808E+00 4.63771460E-03 6.61340221E-05 -8.97456502E-08 3.61716165E-11 1.43843217E+04 7.30313471E+00 1.63702936E+04 4 C4H71-4 C 4H 7 G 200.000 6000.00 1000.00 1 8.49073768E+00 1.91056974E-02-6.74370664E-06 1.07343267E-09-6.36251837E-14 2 2.04659294E+04-1.74555814E+01 5.07355313E+00 5.27619329E-03 6.23441322E-05 3 -8.54203458E-08 3.45890031E-11 2.24615054E+04 5.60318035E+00 2.46070249E+04 4 C4H72-2 С 4H 7 G 200.000 6000.00 1000.00 1 7.26612168E+00 1.99858497E-02-7.12030976E-06 1.14276142E-09-6.81206632E-14 2 2.31915554E+04-1.09941637E+01 7.61389036E+00-9.06922602E-03 8.28486476E-05 3 -9.61203624E-08 3.59333528E-11 2.44971584E+04-5.90519467E+00 2.69231159E+04 4 C4H6 C 4H G 300.000 3000.00 1000.00 1 6 0.88673134E+01 0.14918670E-01-0.31548716E-05-0.41841330E-09 0.15761258E-12 2 0.91338516E+04-0.23328171E+02 0.11284465E+00 0.34369022E-01-0.11107392E-04 3 -0.92106660E-08 0.62065179E-11 0.11802270E+05 0.23089996E+02 4 PC4H902H С 4H 100 2 G 300.000 5000.000 1387.000 1 1.82687454E+01 2.16940079E-02-7.54629828E-06 1.18484806E-09-6.92818498E-14 2 -3.39441633E+04-6.84816300E+01 6.34644286E-01 6.20007657E-02-4.34477749E-05 3 1.61407616E-08-2.53121507E-12-2.76345805E+04 2.67026090E+01 4 SC4H902H C 4H 100 2 G 300.000 5000.000 1390.000 1 1.88587916E+01 2.11200987E-02-7.33205568E-06 1.14969842E-09-6.71656991E-14 2 -3.64236058E+04-7.20026458E+01 3.40587657E-01 6.52078069E-02-4.84840460E-05 3 1.91011830E-08-3.13833073E-12-3.00007960E+04 2.72835451E+01 4 PC4H902 С 4H90 2 G 300.000 5000.000 1385.000 1 2 1.57845448E+01 2.15210910E-02-7.44909017E-06 1.16558071E-09-6.79885609E-14 -1.60146054E+04-5.40388525E+01 1.94363650E+00 5.15513163E-02-3.28284400E-05 3 1.13064860E-08-1.70118606E-12-1.08358103E+04 2.13503149E+01 4 SC4H902 С 90 2 300.000 5000.000 1389.000 4H G 1 1.64031135E+01 2.09361006E-02-7.23393011E-06 1.13058996E-09-6.58938667E-14 2 -1.85074517E+04-5.77331636E+01 1.32689044E+00 5.62785583E-02-4.01717786E-05 3 1.57120967E-08-2.62948443E-12-1.31557057E+04 2.34069659E+01 4

C 4H 90 1 PC4H90 G 300.000 5000.000 1403.000 1 1.49315588E+01 1.95927054E-02-6.66958265E-06 1.03222635E-09-5.97583630E-14 2 -1.46178979E+04-5.25561919E+01-4.99964924E-01 5.37157310E-02-3.44426650E-05 3 1.08145957E-08-1.29600044E-12-9.11644218E+03 3.09183423E+01 4 SC4H90 C 4H 90 1 G 300.000 5000.000 1679.000 1 1.43323395E+01 2.04542365E-02-7.12271896E-06 1.12545447E-09-6.62697853E-14 2 -1.60006806E+04-5.02030895E+01-4.09000900E-01 5.38573427E-02-3.39105695E-05 3 1.01023834E-08-1.11268025E-12-1.11109627E+04 2.88554742E+01 4 C4H70 С 4H 7O 1 G 300.000 5000.000 1395.000 1 1.53137780E+01 1.43427017E-02-4.81625517E-06 7.39574839E-10-4.26140814E-14 2 -7.29342884E+02-5.52937859E+01-1.60619192E+00 5.58562682E-02-4.35595767E-05 3 1.70589279E-08-2.65635180E-12 4.85090326E+03 3.47112559E+01 4 C4H801-2 C 4H 80 1 G 300.000 5000.000 1399.000 1 1.39197290E+01 1.85551492E-02-6.36014179E-06 9.88844645E-10-5.74274779E-14 2 -2.09452548E+04-5.06788231E+01-2.42033073E+00 5.79308508E-02-4.30236499E-05 3 1.66679793E-08-2.64714350E-12-1.53950880E+04 3.66425242E+01 4 C4H801-3 С 4H 80 1 300.000 5000.000 1371.000 G 1 1.54227092E+01 1.70211052E-02-6.06347951E-06 9.67354762E-10-5.71992419E-14 2 -2.20194174E+04-6.13871862E+01-2.53690104E+00 5.43995707E-02-3.43390305E-05 3 1.01079922E-08-1.10262736E-12-1.52980680E+04 3.67400719E+01 4 C4H801-4 С 4H 80 1 G 300.000 5000.000 1361.000 1 1.42360731E+01 1.81176105E-02-6.46263809E-06 1.03194372E-09-6.10557331E-14 2 -2.99478670E+04-5.52081041E+01-3.28505561E+00 5.04800902E-02-2.51998984E-05 3 3.65743744E-09 3.94863161E-13-2.30067422E+04 4.19349253E+01 4 80 1 С C4H802-3 4H G 300.000 5000.000 1384.000 1 1.58263859E+01 1.64400938E-02-5.80680311E-06 9.21146000E-10-5.42511002E-14 2 $-2.35334573E + 04 - 6.34844562E + 01 - 2.98701197E + 00 \quad 6.32678880E - 02 - 5.20855777E - 05$ 3 2.24064364E-08-3.95416618E-12-1.71957196E+04 3.66920390E+01 4 PC4H8OH C 4H 90 1 G 300.000 5000.000 1503.000 1 1.40357398E+01 1.94173155E-02-6.50230141E-06 9.95481694E-10-5.72034525E-14 2 -1.67631276E+04-4.41162528E+01 1.20329680E+00 4.40218297E-02-2.12295754E-05 3 3.03714993E-09 3.72027554E-13-1.18622440E+04 2.65515175E+01 4 SC4H8OH С 4H90 1 G 300.000 5000.000 1392.000 1 1.48421985E+01 1.78435665E-02-6.16709050E-06 1.00443458E-09-6.10697983E-14 2 -1.81714637E+04-4.96976895E+01-1.04565044E+00 5.72423420E-02-4.43109142E-05 3 1.80944672E-08-3.02843329E-12-1.28718032E+04 3.48383489E+01 4 C4H8OH-102 C 4H 9O 3 G 300.000 5000.000 1396.000 1 1.74383247E+01 2.16778876E-02-7.37772628E-06 1.14128811E-09-6.60391451E-14 2 -3.55892620E+04-5.71247140E+01 2.88497398E+00 5.63287929E-02-3.98403503E-05 3 1.53891643E-08-2.51940787E-12-3.05246721E+04 2.09293355E+01 4 90 3 C4H80H-202 С 4HG 300.000 5000.000 1399.000 1 1.82942871E+01 2.09395389E-02-7.12096934E-06 1.10103094E-09-6.36889768E-14 2 -3.80505855E+04-6.29154326E+01 2.10003504E+00 6.17528218E-02-4.77238541E-05 3 1.99145784E-08-3.44416275E-12-3.26698755E+04 2.30901271E+01 4 C4H800H1-1 C 4H 90 2 G 300.000 5000.000 1379.000 1 1.80477436E+01 1.92137176E-02-6.66503008E-06 1.04468117E-09-6.10170737E-14 2 -1.23069570E+04-6.33580990E+01 4.36087539E+00 4.46153162E-02-2.14784588E-05 3 3.14619957E-09 3.03152649E-13-6.89950326E+03 1.24757248E+01 4 C4H800H1-2 С 4H 90 2 G 300.000 5000.000 1393.000 1 1.58327906E+01 2.07220436E-02-7.09869028E-06 1.10302045E-09-6.40251984E-14 2 -8.53034314E+03-5.04399828E+01 1.51698234E+00 5.44584331E-02-3.84524319E-05 3 1.48145523E-08-2.42809434E-12-3.49728423E+03 2.64916926E+01 4 300.000 5000.000 1377.000 C4H800H1-3 C 4H 90 2 G 1 1.76442170E+01 1.91706536E-02-6.57168641E-06 1.02246571E-09-5.94304735E-14 2

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NC4KET14 С 4H 8O 3 G 300.000 5000.000 1382.000 1 1.90283822E+01 1.86604765E-02-6.53616227E-06 1.03102482E-09-6.04833256E-14 2 -4.34678787E+04-6.80210373E+01 3.40797147E+00 5.37386096E-02-3.72613233E-05 3 4 1.36862855E-08-2.13798779E-12-3.77919233E+04 1.65580190E+01 NC4KET21 С 4H 80 3 G 300.000 5000.000 1376.000 1 1.86231473E+01 1.90969401E-02-6.70745998E-06 1.05994690E-09-6.22564248E-14 2 -4.71929933E+04-6.55477892E+01 4.69785973E+00 4.83859623E-02-3.05576939E-05 3 1.02705744E-08-1.51713483E-12-4.18665528E+04 1.06715264E+01 4 NC4KET23 С 4H80 3 G 300.000 5000.000 1387.000 1 1.99512969E+01 1.79558596E-02-6.31230878E-06 9.98217386E-10-5.86636973E-14 2 -4.95585495E+04-7.43071328E+01 4.50575961E-01 6.48862527E-02-5.04446464E-05 3 2.03085220E-08-3.35952497E-12-4.28779359E+04 3.00153676E+01 4 NC4KET24 C 4H 80 3 G 300.000 5000.000 1380.000 1 1.87707201E+01 1.89490823E-02-6.65182145E-06 1.05080860E-09-6.17069393E-14 2 -4.72319802E+04-6.73335107E+01 2.93007283E+00 5.39296076E-02-3.66164919E-05 3 1.30880106E-08-1.99245456E-12-4.14118815E+04 1.86567511E+01 4 С 4H 80 1 G C2H5COCH3 200.000 6000.000 1000.00 1 9.29655016E+00 2.29172746E-02-8.22048591E-06 1.32404838E-09-7.91751980E-14 2 -3.34442311E+04-2.04993263E+01 6.61978185E+00 8.51847835E-03 5.10322077E-05 3 -6.58433042E-08 2.49110484E-11-3.15251691E+04-1.09485469E+00-2.88403536E+04 4 C2H5COCH2 С 4H 70 1 G 300.000 5000.000 1383.000 1 1.42098738E+01 1.57866459E-02-5.50529183E-06 8.65870540E-10-5.06913329E-14 2 -1.41284951E+04-4.87132911E+01 1.54013856E+00 4.39486258E-02-2.97002421E-05 3 1.05495313E-08-1.58598769E-12-9.50796505E+03 1.99706641E+01 4 С CH2CH2COCH3 4H 70 1 G 300.000 5000.000 1380.00 1 1.24694368E+01 1.71022143E-02-5.92156726E-06 9.26816806E-10-5.40730504E-14 2 -1.01378242E+04-3.62186375E+01 2.40255609E+00 3.67294268E-02-1.97316510E-053 5.07323216E-09-4.99655275E-13-6.15006886E+03 1.93993386E+01 4 CH3CHCOCH3 С 4H 70 1 G 300.000 5000.000 1384.000 1 1.31388032E+01 1.66091073E-02-5.76924215E-06 9.04978165E-10-5.28826527E-14 2 -1.51162098E+04-4.38876580E+01 8.12941079E-01 4.29256944E-02-2.69230252E-05 3 8.59326807E-09-1.13188129E-12-1.05247481E+04 2.32952685E+01 4 C2H3COCH3 С 4H60 1 G 300.000 5000.000 1386.00 1 1.25571995E+01 1.49672645E-02-5.20015351E-06 8.15864365E-10-4.76824406E-14 2 -2.14622958E+04-4.01434299E+01 2.45578501E-01 4.26432049E-02-2.91126822E-05 3 1.03478392E-08-1.53551381E-12-1.70305379E+04 2.64430799E+01 4 СНЗСНООСОСНЗ C 4H 70 3 G 300.000 5000.000 1393.00 1 1.72170832E+01 1.76740453E-02-6.10387321E-06 9.53711693E-10-5.55757409E-14 2 -3.05280370E+04-5.67959657E+01 1.59405312E+00 5.74729487E-02-4.65071459E-05 3 2.01816805E-08-3.61175600E-12-2.53445178E+04 2.60857480E+01 4 70 4HСН2СНООНСОСНЗ С 3 G 300.000 5000.000 1394.00 1 1.93158016E+01 1.56592602E-02-5.45395604E-06 8.57160086E-10-5.01582885E-14 2 -2.47752201E+04-6.70296581E+01 1.55204769E+00 6.08201262E-02-5.04704383E-05 3 2.16347587E-08-3.75674081E-12-1.89563540E+04 2.71011896E+01 4 NC3H7CHO С 4H80 1 G 200.000 6000.000 1000.00 1 1.02351219E+01 2.32201057E-02-8.46144199E-06 1.37589764E-09-8.27046434E-14 2 -3.00345804E+04-2.82583105E+01 5.30068149E+00 5.00213349E-03 8.12219686E-05 3 -1.07815910E-07 4.25781054E-11-2.71198341E+04 4.93592991E+00-2.47924787E+04 4 NC3H7CO С 4H 70 1 G 300.000 5000.000 1380.00 1 2 1.30026331E+01 1.63104877E-02-5.57642899E-06 8.65670629E-10-5.02255667E-14 -1.25523385E+04-4.02608515E+01 2.67256826E+00 3.71198825E-02-2.06862859E-05 3 5.48873888E-09-5.35864183E-13-8.58050888E+03 1.64848950E+01 4 300.000 5000.000 1379.000 C3H6CH0-1 С 4H 70 1 G 1 1.30322954E+01 1.62418373E-02-5.54388124E-06 8.59723685E-10-4.98459726E-14 2

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IC4H8O2H-I C 4H 90 2 G 300.000 5000.000 1388.000 1 1.80246456E+01 1.93668264E-02-6.74676496E-06 1.06040129E-09-6.20506445E-14 2 -1.00858977E+04-6.57629693E+01 9.94784793E-01 5.89212240E-02-4.25202225E-05 3 1.61370574E-08-2.55904902E-12-4.08029057E+03 2.58950880E+01 4 TC4H802H-T С 4H90 2 G 300.000 5000.000 1397.000 1 1.52395012E+01 2.06496983E-02-6.94791927E-06 1.06651097E-09-6.13782754E-14 2 -1.02271199E+04-4.70908585E+01 3.77633001E+00 4.50889269E-02-2.62423875E-05 3 7.74736900E-09-9.11520393E-13-5.98295842E+03 1.53503399E+01 4 IC4H80 С 4H80 1 G 300.000 5000.000 1399.000 1 1.44624830E+01 1.80562860E-02-6.18008791E-06 9.59941341E-10-5.57132297E-14 2 -2.30230616E+04-5.61190165E+01-2.97373741E+00 6.24618637E-02-5.04348211E-05 3 2.13345360E-08-3.67382824E-12-1.73274318E+04 3.62336362E+01 4 CC4H80 C 4H 80 1 G 300.000 5000.000 1401.000 1 1.35131704E+01 1.91666441E-02-6.53902359E-06 1.01366570E-09-5.87546671E-14 2 -2.00311488E+04-5.22146967E+01-5.27768230E+00 6.52482242E-02-5.00209030E-05 3 1.97452179E-08-3.15605813E-12-1.37706522E+04 4.78500688E+01 4 С 4H 90 1 G 200.000 6000.00 1000.00 TC4H90 1 1.27371509E+01 2.33707342E-02-8.50516678E-06 1.38519973E-09-8.34398061E-14 2 -1.66940150E+04-4.53156321E+01 2.77057100E+00 2.68033175E-02 4.12718360E-05 3 -7.22054739E-08 3.02642276E-11-1.27079262E+04 1.21532856E+01-1.04543262E+04 4 IC4H90 С 4H 90 1 G 200.000 6000.00 1000.00 1 1.16309708E+01 2.47981574E-02-9.01550536E-06 1.46714720E-09-8.83214518E-14 2 -1.37854612E+04-3.81956151E+01 3.80297372E+00 1.56874209E-02 6.81105412E-05 3 -9.83346774E-08 3.95261902E-11-1.00832243E+04 9.78963305E+00-7.82602559E+03 4 С G IC4H9O2H 4H 100 2 300.000 5000.000 1388.000 1 1.84308794E+01 2.15337606E-02-7.48623965E-06 1.17499240E-09-6.86890788E-14 2 -3.51483277E+04-7.08030846E+01 2.44181899E-01 6.34027841E-02-4.49162379E-05 3 1.67406877E-08-2.61216478E-12-2.86959808E+04 2.72156229E+01 4 C 4H 100 2 TC4H902H G 200.000 6000.00 1000.00 1 1.52702114E+01 2.56462637E-02-9.02796199E-06 1.43759278E-09-8.52381573E-14 2 -3.58539067E+04-5.44966764E+01 3.96033042E+00 4.06267078E-02 1.85652131E-05 3 -5.72128820E-08 2.73014984E-11-3.20467014E+04 7.55565609E+00-2.89963507E+04 4 IC4H70 С 4H70 1 G 300.000 5000.000 1386.000 1 1.33457615E+01 1.61218588E-02-5.44376403E-06 8.38199374E-10-4.83608280E-14 2 6.11443644E+02-4.36818838E+01 1.74700687E+00 4.07783436E-02-2.44750243E-05 3 7.06502958E-09-7.51570589E-13 4.86979233E+03 1.94535999E+01 4 IC4H8OH С 4H 90 1 G 300.000 5000.000 1376.000 1 1.25605997E+01 2.10637488E-02-7.15019648E-06 1.10439262E-09-6.38428695E-14 2 -1.86203249E+04-3.67889430E+01 3.29612707E+00 3.47649647E-02-1.02505618E-05 3 -2.04641931E-09 1.18879408E-12-1.45627247E+04 1.58606320E+01 4 90 3 4HT02C4H80H С G 300.000 5000.000 1395.000 1 1.79798208E+01 2.13452115E-02-7.29108198E-06 1.13068846E-09-6.55402236E-14 2 -3.85769917E+04-6.23553522E+01 2.88826008E+00 5.80363124E-02-4.26690874E-05 3 1.71759332E-08-2.91842186E-12-3.33881503E+04 1.83381149E+01 4 TC3H7CH0 C 4H 80 1 G 300.000 5000.000 1391.000 1 1.37501656E+01 1.83126722E-02-6.28572629E-06 9.78250756E-10-5.68538653E-14 2 -3.26936771E+04-4.77270548E+01-2.73021382E-01 4.89696307E-02-3.12770049E-05 3 1.00052945E-08-1.27512074E-12-2.76054737E+04 2.83451139E+01 4 TC3H6CH0 С 4H 70 1 G 300.000 5000.000 1389.000 1 1.31013047E+01 1.66391865E-02-5.68457623E-06 8.81808351E-10-5.11290161E-14 2 -1.30638647E+04-4.42705813E+01 1.87052762E+00 4.14869677E-02-2.66815701E-05 3 9.01531610E-09-1.27870633E-12-8.97730744E+03 1.66174178E+01 4 IC3H6CH0 С 4H 70 1 G 300.000 5000.000 1390.000 1 1.33102250E+01 1.62097959E-02-5.57575891E-06 8.69003718E-10-5.05554202E-14 2

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300.000 5000.000 1396.00 ТСЗН6ОНСНО C 4H 8O 2 G 1 1.70788996E+01 1.74005554E-02-5.93008112E-06 9.18860909E-10-5.32512140E-14 2 -5.38730427E+04-6.38638754E+01 2.10033500E-01 5.63086284E-02-3.95158669E-05 3 1.37780428E-08-1.89068805E-12-4.80402638E+04 2.67836070E+01 4 TC3H6OH С 3H 70 1 G 300.000 5000.000 1392.000 1 1.12222277E+01 1.36444398E-02-4.51406709E-06 7.10523275E-10-4.22690392E-14 2 -1.75350136E+04-3.18911926E+01 1.09670360E+00 3.80727565E-02-2.75022497E-05 3 1.07477493E-08-1.74895773E-12-1.40764487E+04 2.22475799E+01 4 IC3H5OH С 3H 60 1 G 300.000 5000.000 1374.00 1 1.07381025E+01 1.31698194E-02-4.41529622E-06 6.77009837E-10-3.89608901E-14 2 -2.47298321E+04-3.13634050E+01 1.58376391E+00 3.16215366E-02-1.73664942E-05 3 4.18927663E-09-2.79899620E-13-2.12643496E+04 1.88313766E+01 4 TC3H602CH0 C 4H 7O 3 G 300.000 5000.000 1386.00 1 1.85534443E+01 1.68774389E-02-5.90752965E-06 9.31518085E-10-5.46345187E-14 2 -2.85447191E+04-6.82486667E+01 2.17883383E+00 5.41595832E-02-3.83435886E-05 3 1.38308104E-08-2.04190147E-12-2.27394154E+04 2.00751264E+01 4 С 4H 70 3 G 300.000 5000.000 1387.00 **ТСЗН602НС0** 1 2.06472678E+01 1.48526500E-02-5.25104875E-06 8.33619219E-10-4.91256069E-14 2 -2.88719869E+04-7.95951389E+01 2.03864428E+00 5.80421003E-02-4.32123528E-05 3 1.58792094E-08-2.32209543E-12-2.24284673E+04 2.03680990E+01 4 IC3H502HCH0 С 4H 70 3 G 300.000 5000.000 1387.00 1 2.06288832E+01 1.48625539E-02-5.25305276E-06 8.33772951E-10-4.91277401E-14 2 -2.27589076E+04-7.82962888E+01 2.05984770E+00 5.82331716E-02-4.37672100E-05 3 1.63249918E-08-2.43462051E-12-1.63496250E+04 2.13687921E+01 4 50 1 С G CH2CCH2OH ЗH 300.000 5000.000 1372.00 1 9.70702027E+00 1.13972660E-02-3.77993962E-06 5.75209277E-10-3.29229125E-14 2 9.13212884E+03-2.25012933E+01 2.88422544E+00 2.42428071E-02-1.14152268E-05 3 1.71775334E-09 1.42177454E-13 1.17935615E+04 1.52102335E+01 4 TC4H8CH0 C 5H 90 1 G 300.000 5000.000 1397.00 1 1.79663933E+01 1.94207117E-02-6.67409451E-06 1.03969221E-09-6.04702651E-14 2 -1.33368585E+04-6.79819424E+01-9.58078294E-01 6.42003258E-02-4.70776827E-05 3 1.75737698E-08-2.64896151E-12-6.86582501E+03 3.33781112E+01 4 02C4H8CH0 С 5H 90 3 G 300.000 5000.000 1395.00 1 2.12629904E+01 2.14072282E-02-7.38342949E-06 1.15281523E-09-6.71508438E-14 2 -3.16854524E+04-7.99828703E+01 1.91847699E+00 6.67245869E-02-4.80871046E-05 3 1.78588690E-08-2.71163880E-12-2.49837984E+04 2.38577867E+01 4 02HC4H8C0 C 5H 90 3 G 300.000 5000.000 1394.00 1 2.38219630E+01 1.91411448E-02-6.67919154E-06 1.05127303E-09-6.15876805E-14 2 -3.23093973E+04-9.42580755E+01 1.82607262E+00 6.93466111E-02-4.93125140E-05 3 1.69848340E-08-2.26117657E-12-2.46578311E+04 2.41167544E+01 4 60 C3H5OH С ЗH 1 G 200.000 6000.00 1000.00 1 8.72477114E+00 1.63942712E-02-5.90852993E-06 9.53262253E-10-5.70318010E-14 2 -1.90496618E+04-1.97198674E+01 3.15011905E+00 1.28538274E-02 4.28438434E-05 3 -6.67818707E-08 2.80408237E-11-1.66413668E+04 1.35066359E+01-1.48710589E+04 4 TIC4H7Q2-I С 4H90 4 G 300.000 5000.000 1400.000 1 2.33848631E+01 1.87070035E-02-6.44021945E-06 1.00428123E-09-5.84468189E-14 2 -2.61180902E+04-8.76610135E+01 4.48426361E+00 6.61225007E-02-5.27349018E-05 3 2.18215585E-08-3.66788946E-12-1.98906586E+04 1.26719614E+01 4 IIC4H7Q2-I С 4H90 4 G 300.000 5000.000 1394.000 1 2.30500244E+01 1.92149194E-02-6.66622576E-06 1.04495725E-09-6.10370520E-14 2 -2.32086881E+04-8.39949885E+01 4.93055661E+00 6.05819201E-02-4.23665566E-05 3 1.49122008E-08-2.10978665E-12-1.68415495E+04 1.36228018E+01 4 IIC4H7Q2-T C 4H 9O 4 G 300.000 5000.000 1377.000 1 2.15070321E+01 2.05359839E-02-7.12383399E-06 1.11655053E-09-6.52112103E-14 2

-2.51117508E+04-7.43379783E+01 8.16274487E+00 4.34463050E-02-1.76972456E-05 3 4.88790666E-10 9.03915465E-13-1.96501749E+04 2.62067299E-01 4 TTC4H7Q2-T С 4H90 4 G 300.000 5000.000 1377.000 1 1.59247008E+01 2.59703101E-02-8.86821278E-06 1.37514707E-09-7.97105419E-14 2 -2.60824218E+04-6.16997349E+01-1.67881131E+00 6.41231428E-02-3.96458285E-053 1.23445155E-08-1.53325385E-12-1.96474971E+04 3.39348804E+01 4 C5H11-1 С 5H 11 G 300.000 5000.000 1396.000 1 1.54992372E+01 2.38273176E-02-8.13845161E-06 1.26220569E-09-7.31730066E-14 2 -1.00988975E+03-5.58563592E+01-9.94216435E-01 5.99860809E-02-3.78318587E-05 3 1.21310895E-08-1.57042863E-12 4.97697538E+03 3.35998032E+01 4 NC5H12 С 5H 12 G 300.000 5000.000 1396.000 1 1.59247008E+01 2.59703101E-02-8.86821278E-06 1.37514707E-09-7.97105419E-14 2 -2.60824218E+04-6.16997349E+01-1.67881131E+00 6.41231428E-02-3.96458285E-05 3 1.23445155E-08-1.53325385E-12-1.96474971E+04 3.39348804E+01 4 С 5H 11 G 300.000 5000.000 1391.000 C5H11-2 1 1.48744992E+01 2.40593799E-02-8.15587903E-06 1.25867109E-09-7.27223868E-14 2 -2.14733945E+03-5.17907576E+01 7.25187788E-01 4.97343569E-02-2.18806076E-05 3 2.09007834E-09 6.62752863E-13 3.46418370E+03 2.67485348E+01 4 C5H11-3 С 5H 11 G 300.000 5000.000 1391.000 1 1.48744992E+01 2.40593799E-02-8.15587903E-06 1.25867109E-09-7.27223868E-14 2 -2.14733945E+03-5.24802393E+01 7.25187788E-01 4.97343569E-02-2.18806076E-05 3 2.09007834E-09 6.62752863E-13 3.46418370E+03 2.60590532E+01 4 300.000 5000.000 1392.000 С 5H 10 G C5H10-1 1 1.45851539E+01 2.24072471E-02-7.63348025E-06 1.18188966E-09-6.84385139E-14 2 -1.00898205E+04-5.23683936E+01-1.06223481E+00 5.74218294E-02-3.74486890E-05 3 1.27364989E-08-1.79609789E-12-4.46546666E+03 3.22739790E+01 4 C5H10-2 C 5H 10 G 300.000 5000.000 1389.000 1 1.41109267E+01 2.28348272E-02-7.78626835E-06 1.20627491E-09-6.98795983E-14 2 -1.14336507E+04-5.01601163E+01-5.41560551E-01 5.39629918E-02-3.23508738E-053 9.77416037E-09-1.18534668E-12-5.98606169E+03 2.97142748E+01 4 C5H81-3 С 5H 8 G 300.000 5000.000 1396.000 1 1.45574490E+01 1.80939266E-02-6.21671892E-06 9.67920254E-10-5.62629326E-14 2 1.22365462E+03-5.43889766E+01-2.32617433E+00 6.38696042E-02-5.57052591E-05 3 2.58049480E-08-4.83405924E-12 6.55183321E+03 3.42036513E+01 4 C5H91-3 C 5H G 300.000 5000.000 1392.000 1 9 1.41860454E+01 2.07128899E-02-7.06960617E-06 1.09607133E-09-6.35322208E-14 2 7.00496135E+03-5.14501773E+01-1.38013950E+00 5.57608487E-02-3.70143928E-05 3 1.26883901E-08-1.78538835E-12 1.25589824E+04 3.26441304E+01 4 C5H91-4 С 5H 9 G 300.000 5000.000 1379.000 1 1.39904314E+01 1.99962562E-02-6.73105937E-06 1.03447598E-09-5.96148983E-14 2 1.36075123E+04-4.58753046E+01 2.07302224E-01 4.75322572E-02-2.55232300E-05 3 5.70570808E-09-2.53926602E-13 1.88300100E+04 2.97527890E+01 4 C5H91-5 C 5H 9 G 300.000 5000.000 1392.000 1 1.41604486E+01 2.02710046E-02-6.90765357E-06 1.06972742E-09-6.19529514E-14 2 1.49795090E+04-4.72301324E+01-3.00352280E-01 5.29029897E-02-3.50199571E-05 3 1.21280172E-08-1.74459793E-12 2.01482388E+04 3.08938514E+01 4 C5H92-4 С 5H 9 G 300.000 5000.000 1389.000 1 2 1.37128284E+01 2.11391857E-02-7.22186145E-06 1.12036442E-09-6.49675872E-14 5.66079366E+03-4.92475603E+01-8.61323386E-01 5.23106875E-02-3.19282664E-05 3 9.73236622E-09-1.17585595E-12 1.10386471E+04 3.00928924E+01 4 С C5H92-5 5H 9 G 300.000 5000.000 1389.000 1 1.36885460E+01 2.06966684E-02-7.05980383E-06 1.09401634E-09-6.33885833E-14 2 1.36345574E+04-4.50306538E+01 2.16350550E-01 4.94614176E-02-2.99438792E-05 3 9.17728978E-09-1.13613754E-12 1.86282306E+04 2.83575279E+01 4

5H 9O 1 G 300.000 5000.000 1393.000 C5H901-3 С 1 1.86270165E+01 1.85189638E-02-6.21111137E-06 9.52916260E-10-5.48704082E-14 2 -4.97349374E+03-7.09678919E+01-2.22532588E+00 6.97271843E-02-5.42285799E-05 3 2.13591167E-08-3.36511599E-12 1.91826163E+03 3.99711270E+01 4 C5H902-4 С 5H 90 1 G 300.000 5000.000 1387.000 1 1.86104516E+01 1.87100216E-02-6.31627652E-06 9.73434030E-10-5.62316246E-14 2 -6.59575918E+03-7.05163465E+01-1.66449167E+00 6.51525448E-02-4.57159226E-05 3 1.55903830E-08-2.04144207E-12 4.10326271E+02 3.84890543E+01 4 C5H110-1 С 5H 11O 1 G 300.000 5000.000 1391.000 1 1.73225378E+01 2.48217999E-02-8.48159842E-06 1.31587304E-09-7.63050620E-14 2 -1.83356880E+04-6.37681611E+01-9.02925873E-02 6.34116550E-02-4.09268668E-05 3 1.36982820E-08-1.89646466E-12-1.20333690E+04 3.05672313E+01 4 C5H110-2 C 5H 110 1 G 300.000 5000.000 1396.000 1 1.78183150E+01 2.44541516E-02-8.36505611E-06 1.29863054E-09-7.53356869E-14 2 -2.06350810E+04-6.67615213E+01-4.94527725E-01 6.73149844E-02-4.72324734E-05 3 1.75936532E-08-2.73651943E-12-1.42372243E+04 3.16370708E+01 4 С 5H 110 1 G 300.000 5000.000 1396.000 C5H110-3 1 1.78183150E+01 2.44541516E-02-8.36505611E-06 1.29863054E-09-7.53356869E-14 2 -2.06350810E+04-6.74510029E+01-4.94527725E-01 6.73149844E-02-4.72324734E-05 3 1.75936532E-08-2.73651943E-12-1.42372243E+04 3.09475892E+01 4 C5H11O2H-1 С 5H 12O 2 G 300.000 5000.000 1387.000 1 2.14180725E+01 2.62251472E-02-9.10691067E-06 1.42824507E-09-8.34473635E-14 2 -3.80401323E+04-8.39746734E+01 4.74596161E-01 7.38808098E-02-5.12216645E-05 3 1.87797149E-08-2.90291870E-12-3.05323779E+04 2.91362231E+01 4 5H 12O 2 G C5H1102H-2 С 300.000 5000.000 1390.000 1 2.21712264E+01 2.55540337E-02-8.86857346E-06 1.39034021E-09-8.12122040E-14 2 $-4.06027396E + 04 - 8.84830959E + 01 - 2.68431172E - 01 \ 7.90975970E - 02 - 5.89751277E - 05 \ 7.907577577E - 05 \ 7.907577577E - 05 \ 7.907577577E - 05 \ 7.9075777E - 05 \ 7.9075777E - 05 \ 7.907577E - 05 \ 7$ 3 2.33029166E-08-3.83794655E-12-3.28329870E+04 3.17836191E+01 4 C 5H 12O 2 G 300.000 5000.000 1390.000 C5H1102H-3 1 2.21712264E+01 2.55540337E-02-8.86857346E-06 1.39034021E-09-8.12122040E-14 2 -4.06027396E+04-8.84830959E+01-2.68431172E-01 7.90975970E-02-5.89751277E-05 3 2.33029166E-08-3.83794655E-12-3.28329870E+04 3.17836191E+01 4 C5H1102-1 С 5H 110 2 G 300.000 5000.000 1386.000 1 1.89702536E+01 2.60355552E-02-9.00706834E-06 1.40888868E-09-8.21618381E-14 2 -2.01253683E+04-6.97477616E+01 1.39788038E+00 6.52788893E-02-4.34224032E-05 3 1.57151743E-08-2.46631324E-12-1.36791222E+04 2.55411824E+01 4 C5H1102-2 C 5H 110 2 G 300.000 5000.000 1389.000 1 1.96655539E+01 2.53946113E-02-8.77477373E-06 1.37145913E-09-7.99350015E-14 2 -2.26521255E+04-7.38934310E+01 7.10786402E-01 7.03521821E-02-5.11565299E-05 3 2.03005197E-08-3.42470585E-12-1.59903126E+04 2.79113132E+01 4 C5H1102-3 С 5H 11O 2 G 300.000 5000.000 1389.000 1 1.96655539E+01 2.53946113E-02-8.77477373E-06 1.37145913E-09-7.99350015E-14 2 -2.26521255E+04-7.38934310E+01 7.10786402E-01 7.03521821E-02-5.11565299E-05 3 2.03005197E-08-3.42470585E-12-1.59903126E+04 2.79113132E+01 4 C5H1000H1-2 С 5H 11O 2 G 300.000 5000.000 1379.000 1 2.09225281E+01 2.34863057E-02-8.03644420E-06 1.24880724E-09-7.25227776E-14 2 -1.43245680E+04-7.79152904E+01 1.66304681E+00 6.42511734E-02-3.94124754E-05 3 1.15348101E-08-1.25128422E-12-7.22288006E+03 2.70063739E+01 4 C5H1000H1-3 С 5H 110 2 G 300.000 5000.000 1379.000 1 2.09225281E+01 2.34863057E-02-8.03644420E-06 1.24880724E-09-7.25227776E-14 2 -1.43245680E+04-7.79152904E+01 1.66304681E+00 6.42511734E-02-3.94124754E-05 3 1.15348101E-08-1.25128422E-12-7.22288006E+03 2.70063739E+01 4 300.000 5000.000 1379.000 C5H1000H1-4 C 5H 110 2 G 1 2.09225281E+01 2.34863057E-02-8.03644420E-06 1.24880724E-09-7.25227776E-14 2

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C5H1000H1-202 C 5H 110 4 G 300.000 5000.000 1387.000 1 2.55478814E+01 2.50385111E-02-8.74243938E-06 1.37611416E-09-8.06073182E-14 2 -3.46345151E+04-9.91022020E+01 2.53072834E+00 8.12167401E-02-6.33054798E-05 3 2.63900700E-08-4.58739612E-12-2.67337637E+04 2.39105049E+01 4 C5H1000H1-302 С 5H 110 4 G 300.000 5000.000 1387.000 1 2.55478814E+01 2.50385111E-02-8.74243938E-06 1.37611416E-09-8.06073182E-14 2 -3.46345151E+04-9.91022020E+01 2.53072834E+00 8.12167401E-02-6.33054798E-05 3 2.63900700E-08-4.58739612E-12-2.67337637E+04 2.39105049E+01 4 C5H1000H1-402 С 5H 110 4 G 300.000 5000.000 1387.000 1 2.55478814E+01 2.50385111E-02-8.74243938E-06 1.37611416E-09-8.06073182E-14 2 -3.46345151E+04-9.91022020E+01 2.53072834E+00 8.12167401E-02-6.33054798E-05 3 2.63900700E-08-4.58739612E-12-2.67337637E+04 2.39105049E+01 4 C5H1000H1-502 C 5H 110 4 G 300.000 5000.000 1385.000 1 2.48666576E+01 2.56688838E-02-8.97169324E-06 1.41315614E-09-8.28158711E-14 2 -3.21479218E+04-9.51211738E+01 2.81997434E+00 7.72690504E-02-5.67282509E-05 3 2.23236523E-08-3.71501383E-12-2.43447483E+04 2.35135259E+01 4 С 5H 110 4 G 300.000 5000.000 1387.000 C5H1000H2-102 1 2.55478814E+01 2.50385111E-02-8.74243938E-06 1.37611416E-09-8.06073182E-14 2 -3.46345151E+04-9.91022020E+01 2.53072834E+00 8.12167401E-02-6.33054798E-05 3 2.63900700E-08-4.58739612E-12-2.67337637E+04 2.39105049E+01 4 C5H1000H2-302 С 5H 110 4 G 300.000 5000.000 1389.000 1 2.62850175E+01 2.43678422E-02-8.50101950E-06 1.33736519E-09-7.83075048E-14 2 -3.71537284E+04-1.03435286E+02 2.08935173E+00 8.57156954E-02-7.04986902E-05 3 3.07497216E-08-5.51132533E-12-2.90970365E+04 2.50297599E+01 4 C5H1000H2-402 С 5H 110 4 G 300.000 5000.000 1389.000 1 2.62850175E+01 2.43678422E-02-8.50101950E-06 1.33736519E-09-7.83075048E-14 2 -3.71537284E+04-1.03435286E+02 2.08935173E+00 8.57156954E-02-7.04986902E-05 3 3.07497216E-08-5.51132533E-12-2.90970365E+04 2.50297599E+01 4 C5H1000H2-502 С 5H 110 4 G 300.000 5000.000 1387.000 1 2.55478814E+01 2.50385111E-02-8.74243938E-06 1.37611416E-09-8.06073182E-14 2 -3.46345151E+04-9.91022020E+01 2.53072834E+00 8.12167401E-02-6.33054798E-05 3 2.63900700E-08-4.58739612E-12-2.67337637E+04 2.39105049E+01 4 C5H1000H3-102 С 5H 110 4 G 300.000 5000.000 1387.000 1 2.55478814E+01 2.50385111E-02-8.74243938E-06 1.37611416E-09-8.06073182E-14 2 -3.46345151E+04-9.91022020E+01 2.53072834E+00 8.12167401E-02-6.33054798E-05 3 2.63900700E-08-4.58739612E-12-2.67337637E+04 2.39105049E+01 4 C5H1000H3-202 С 5H 110 4 G 300.000 5000.000 1389.000 1 2.62850175E+01 2.43678422E-02-8.50101950E-06 1.33736519E-09-7.83075048E-14 2 -3.71537284E+04-1.03435286E+02 2.08935173E+00 8.57156954E-02-7.04986902E-05 3 3.07497216E-08-5.51132533E-12-2.90970365E+04 2.50297599E+01 4 5H 10O 3 NC5KET12 С G 300.000 5000.000 1389.000 1 2.34427049E+01 2.21540692E-02-7.74817880E-06 1.22107095E-09-7.15883644E-14 2 -4.99350593E+04-9.09970812E+01 5.64845658E-01 7.74889690E-02-6.00818427E-05 3 2.42432817E-08-4.02329880E-12-4.21262314E+04 3.12910774E+01 4 NC5KET13 С 5H 10O 3 G 300.000 5000.000 1387.000 1 2.27897549E+01 2.26387719E-02-7.89832354E-06 1.24260309E-09-7.27609759E-14 2 -5.00526193E+04-8.71676166E+01 2.53945153E+00 7.08645319E-02-5.32266350E-05 3 2.12906293E-08-3.56676536E-12-4.29988725E+04 2.14543054E+01 4 NC5KET14 С 5H 10O 3 G 300.000 5000.000 1387.000 1 2.27897549E+01 2.26387719E-02-7.89832354E-06 1.24260309E-09-7.27609759E-14 2 -5.00526193E+04-8.71676166E+01 2.53945153E+00 7.08645319E-02-5.32266350E-05 3 2.12906293E-08-3.56676536E-12-4.29988725E+04 2.14543054E+01 4 300.000 5000.000 1383.000 NC5KET15 С 5H 10O 3 G 1 2.21776239E+01 2.31939864E-02-8.09797899E-06 1.27464047E-09-7.46625107E-14 2

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C4H4 С 4HG 300.000 3000.00 1000.00 4 1 0.66507092E+01 0.16129434E-01-0.71938875E-05 0.14981787E-08-0.11864110E-12 2 0.31195992E+05-0.97952118E+01-0.19152479E+01 0.52750878E-01-0.71655944E-04 3 0.55072423E-07-0.17286228E-10 0.32978504E+05 0.31419983E+02 4 C4H3-T С 4H 3 G 300.000 3000.00 1000.00 1 0.90978165E+01 0.92207119E-02-0.33878441E-05 0.49160498E-09-0.14529780E-13 2 0.56600574E+05-0.19802597E+02 0.20830412E+01 0.40834274E-01-0.62159685E-04 3 0.51679358E-07-0.17029184E-10 0.58005129E+05 0.13617462E+02 4 C4H612 С 4H6 G 300. 3000. 1000.0 1 0.1781557E 02 -0.4257502E-02 0.1051185E-04 -0.4473844E-08 0.5848138E-12 2 0.1267342E 05 -0.6982662E 02 0.1023467E 01 0.3495919E-01 -0.2200905E-04 3 0.6942272E-08 -0.7879187E-12 0.1811799E 05 0.1975066E 02 0.1950807E+05 4 C6H5 С 6H 5 G 200.000 6000.000 1000. 1 1.08444762E+01 1.73212473E-02-6.29233249E-06 1.02369961E-09-6.16216828E-14 2 3.55598475E+04-3.53735134E+01 2.10306633E-01 2.04745507E-02 5.89743006E-05 3 -1.01534255E-07 4.47105660E-11 3.95468722E+04 2.52910455E+01 4.08610970E+04 4 С 4H C4H2 2 G 300.000 3000.000 1 0.91576328E+01 0.55430518E-02-0.13591604E-05 0.18780075E-10 0.23189536E-13 2 0.52588039E+05-0.23711460E+02 0.10543978E+01 0.41626960E-01-0.65871784E-04 3 0.53257075E-07-0.16683162E-10 0.54185211E+05 0.14866591E+02 4 C4H3-N C 4H 3 G 300.000 3000.00 1000.00 1 0.54328279E+01 0.16860981E-01-0.94313109E-05 0.25703895E-08-0.27456309E-12 2 0.61600680E+05-0.15673981E+01-0.31684113E+00 0.46912100E-01-0.68093810E-04 3 0.53179921E-07-0.16523005E-10 0.62476199E+05 0.24622559E+02 4 C4H5-N С 4H- 5 G 300.000 3000.00 1000.00 1 0.98501978E+01 0.10779008E-01-0.13672125E-05-0.77200535E-09 0.18366314E-12 2 0.38840301E+05-0.26001846E+02 0.16305321E+00 0.39830137E-01-0.34000128E-04 3 0.15147233E-07-0.24665825E-11 0.41429766E+05 0.23536163E+02 4 С 4H300.000 3000.00 1000.00 1 C4H5-I 5 G 0.10229092E+02 0.94850138E-02-0.90406445E-07-0.12596100E-08 0.24781468E-12 2 0.34642812E+05-0.28564529E+02-0.19932900E-01 0.38005672E-01-0.27559450E-04 3 0.77835551E-08 0.40209383E-12 0.37496223E+05 0.24394241E+02 4 CH3CHCHCO С 4H50 1 G 200.000 6000.000 1000.0 1 8.90967920E+00 1.34364140E-02-7.62977390E-07-1.69114810E-09 2.95540440E-13 2 1.48898740E+03-1.79662460E+01-1.08199860E+00 3.64929760E-02-1.52255950E-05 3 -5.62607170E-18 2.16113750E-21 3.56713230E+03 3.27142550E+01 4.73074990E+03 4 CH2CHCHCHO С 4H50 1 G 200.000 6000.000 1000.0 1 8.90967920E+00 1.34364140E-02-7.62977390E-07-1.69114810E-09 2.95540440E-13 2 1.48898740E+03-1.79662460E+01-1.08199860E+00 3.64929760E-02-1.52255950E-05 3 -5.62607170E-18 2.16113750E-21 3.56713230E+03 3.27142550E+01 4.73074990E+03 4 60 C4H6025 С 4H 1 G 200.000 5000.000 1000.0 1 8.60658242E+00 2.08310051E-02-8.42229481E-06 1.56717640E-09-1.09391202E-13 2 -1.76177415E+04-2.32464750E+01 2.67053463E+00 4.92586420E-03 8.86967406E-05 3 $-1.26219194E-07 \hspace{0.1in} 5.23991321E-11-1.46572472E+04 \hspace{0.1in} 1.45722395E+01-1.30831522E+04$ 4 C2H3CH0CH2 C 4H 60 1 G 300. 3000 1000.0 1 2 -4.72093360E+00 3.91413780E-02-6.52872650E-06-7.68209500E-09 2.51473310E-12 1.75352252E+03 5.17190420E+01 7.97985440E-01 3.44034320E-02-1.24598510E-05 3 -5.18062790E-18 1.99359540E-21-6.48927540E+02 2.18896980E+01 1.00654250E+03 4 C4H5-2 С 4H 5 G 300.000 3000.00 1000.00 1 2 1.45381710E+01-8.56770560E-03 2.35595240E-05-1.36763790E-08 2.44369270E-12 3.32590950E+04-4.53694970E+01 2.96962800E+00 2.44422450E-02-9.12514240E-06 3 -4.24668710E-18 1.63047280E-21 3.55033160E+04 1.20360510E+01 3.73930550E+04 4 C4H6-2 С 4H 6 G 300. 3000. 1000.0 1 9.0338133E+00 8.2124510E-03 7.1753952E-06 -5.8834334E-09 1.0343915E-12 2

1.4335068E+04 -2.0985762E+01 2.1373338E+00 2.6486229E-02 -9.0568711E-06 3 -5.5386397E-19 2.1281884E-22 1.5710902E+04 1.3529426E+01 1.7488676E+04 4 C4H6023 С 4H 60 1 G 200.000 5000.000 1000.0 1 8.60658242E+00 2.08310051E-02-8.42229481E-06 1.56717640E-09-1.09391202E-13 2 -1.32392815E+04-2.32464750E+01 2.67053463E+00 4.92586420E-03 8.86967406E-05 3 -1.26219194E-07 5.23991321E-11-1.02787872E+04 1.45722395E+01-1.30831522E+04 4 CH3CHCHCHO C 4H 60 1 G 298.150 3000.0 1000.0 1 1.98794540E+01-2.09130550E-02 4.45360508E-05-2.60374870E-08 4.86836120E-12 2 -1.95278768E+04-6.87200320E+01-1.55577660E+00 4.09640630E-02-1.69868810E-05 3 -6.00928140E-18 2.31368530E-21-1.41394920E+04 3.74707580E+01-1.29340710E+04 4 C4H40 С 4H40 1 G 200.000 6000.0 1000.0 1 2 9.38935003E+00 1.40291241E-02-5.07755110E-06 8.24137332E-10-4.95319963E-14 -8.68241814E+03-2.79162920E+01 8.47469463E-01 1.31773796E-02 5.99735901E-05 3 -9.71562904E-08 4.22733796E-11-5.36785445E+03 2.14945172E+01-4.17166616E+03 4 H2CC Η 2C 2 G 200.000 6000.000 1000.000 1 0.42780340E+01 0.47562804E-02-0.16301009E-05 0.25462806E-09-0.14886379E-13 2 0.48316688E+05 0.64023701E+00 0.32815483E+01 0.69764791E-02-0.23855244E-05 3 -0.12104432E-08 0.98189545E-12 0.48621794E+05 0.59203910E+01 0.49887266E+05 4 40 2C G 0300.00 1 H2C40 Н 1 4000.00 1000.00 0.01026888E+03 0.04896164E-01-0.04885081E-05-0.02708566E-08 0.05107013E-12 2 0.02346903E+06-0.02815985E+03 0.04810971E+02 0.01313999E+00 0.09865073E-05 3 -0.06120720E-07 0.01640003E-10 0.02545803E+06 0.02113424E+02 4 2 C6H2 С 300.000 3000.00 1000.00 6H G 1 0.13226281E+02 0.73904302E-02-0.22715381E-05 0.25875217E-09-0.55356741E-14 2 0.80565258E+05-0.41201176E+02-0.15932624E+01 0.80530145E-01-0.14800649E-03 3 0.13300031E-06-0.45332313E-10 0.83273227E+05 0.27980873E+02 4 C6H3 С 6H 3 G 300.000 3000.00 1000.00 1 0.58188343E+01 0.27933408E-01-0.17825427E-04 0.53702536E-08-0.61707627E-12 2 3 0.85188250E+05-0.92147827E+00 0.11790619E+01 0.55547360E-01-0.73076168E-04 0.52076736E-07-0.15046964E-10 0.85647312E+05 0.19179199E+02 4 L-C6H4 С 6H 4 G 300.000 3000.00 1000.00 1 0.12715182E+02 0.13839662E-01-0.43765440E-05 0.31541636E-09 0.46619026E-13 2 3 0.57031148E+05-0.39464600E+02 0.29590225E+00 0.58053318E-01-0.67766756E-04 0.43376762E-07-0.11418864E-10 0.60001371E+05 0.22318970E+02 4 C-C6H4 С 6H G 300.000 3000.00 1000.00 1 4 0.13849209E+02 0.78807920E-02 0.18243836E-05-0.21169166E-08 0.37459977E-12 2 0.47446340E+05-0.50404953E+02-0.30991268E+01 0.54030564E-01-0.40839004E-04 3 0.10738837E-07 0.98078490E-12 0.52205711E+05 0.37415207E+02 4 C6H5OH С 6H 60 1 G 300.000 5000.000 1000. 1 0.14912073E+02 0.18378135E-01-0.61983128E-05 0.91983221E-09-0.49209565E-13 2 -0.18375199E+05-0.55924103E+02-0.16956539E+01 0.52271299E-01-0.72024050E-05 3 -0.35859603E-07 0.20449073E-10-0.13284121E+05 0.32542160E+02-0.11594207E+05 4 C6H50 С 6H 5O 1 G 200.000 6000.000 1000. 1 1.37221720E+01 1.74688771E-02-6.35504520E-06 1.03492308E-09-6.23410504E-14 2 2.87274751E+02-4.88181680E+01-4.66204455E-01 4.13443975E-02 1.32412991E-05 3 -5.72872769E-08 2.89763707E-11 4.77858391E+03 2.76990274E+01 6.49467016E+03 4 P-C6H402 С 6H 40 2 G 270.000 3000.000 1370.00 1 2 1.23423732E+01 2.40612690E-02-1.16565184E-05 2.71393504E-09-2.47643065E-13 -2.06185312E+04-4.08244024E+01-2.43170113E+00 6.87937608E-02-6.41382837E-05 3 3.08126855E-08-5.99832072E-12-1.65696994E+04 3.48309430E+01 4 С 30 2 270.000 3000.000 1290.00 P-C6H302 6H G 1 2 1.22963699E+01 2.15055142E-02-1.07516136E-05 2.57528163E-09-2.41023652E-13 1.15428998E+04-3.72584002E+01-1.57852347E+00 6.55376473E-02-6.50308721E-05 3 3.32026554E-08-6.86665555E-12 1.51750093E+04 3.31518638E+01 4

G 270.000 3000.000 1370.00 0-C6H4O2 С 6H 4O 2 1 1.23614349E+01 2.40491397E-02-1.16529057E-05 2.71332785E-09-2.47593219E-13 2 -1.67079717E+04-4.00310857E+01-2.36179712E+00 6.86058343E-02-6.39129516E-05 3 3.06903009E-08-5.97357785E-12-1.26704431E+04 3.53724482E+01 4 C5H5 C 5H 5 G 298.150 3500.000 969.35 1 1.33675715E+00 3.24793912E-02-1.67587774E-05 4.03514137E-09-3.70739036E-13 2 3.00730524E+04 1.60315806E+01-3.97555452E+00 7.41370991E-02-1.11803345E-04 3 9.04628776E-08-2.80999747E-11 3.01769405E+04 3.67153636E+01 4 C5H6 С 5H 6 G 200.000 6000.000 1000. 1 0.99757848E+01 0.18905543E-01-0.68411461E-05 0.11099340E-08-0.66680236E-13 2 0.11081693E+05-0.32209454E+02 0.86108957E+00 0.14804031E-01 0.72108895E-04 3 -0.11338055E-06 0.48689972E-10 0.14801755E+05 0.21353453E+02 0.16152485E+05 4 C5H5OH C 5H 6O 1 G 300.000 5000.000 1398.000 1 1.53433477E+01 1.50754059E-02-5.13553582E-06 7.95807816E-10-4.61311517E-14 2 -1.19645453E+04-5.85204430E+01-4.26822012E+00 6.62446749E-02-5.68494038E-05 3 2.46858526E-08-4.26820696E-12-5.75581338E+03 4.47962850E+01 4 С 5H 40 G 200.000 6000.000 1000. C5H40 1 1 1.00806824E+01 1.61143465E-02-5.83314509E-06 9.46759320E-10-5.68972206E-14 2 1.94364771E+03-2.94521623E+01 2.64576497E-01 3.34873827E-02 1.67738470E-06 3 -2.96207455E-08 1.54431476E-11 5.11159287E+03 2.35409513E+01 6.64245999E+03 4 C5H50 С 5H 50 1 G 300.000 5000.000 1392.000 1 1.48322894E+01 1.40483376E-02-4.92302051E-06 7.77041219E-10-4.56103939E-14 2 1.45523665E+04-5.73228191E+01-2.83112840E+00 5.67277287E-02-4.44757303E-05 3 1.74924447E-08-2.76004847E-12 2.04992154E+04 3.69634411E+01 4 50 1 C5H4OH 5H G С 200.000 6000.000 1000. 1 1.33741248E+01 1.51996469E-02-5.45685046E-06 8.80944866E-10-5.27493258E-14 2 2.20358027E+03-4.59569069E+01-1.28398054E+00 4.90298511E-02-1.35844414E-05 3 -2.92983743E-08 1.90820619E-11 6.37364803E+03 3.08073591E+01 8.00114499E+03 4 50 2 C6H5OO С 6H G 300.000 5000.000 1403.000 1 1.67078262E+01 1.62326229E-02-5.47969630E-06 8.43510060E-10-4.86562431E-14 2 8.14242915E+03-6.08346973E+01-2.99164672E+00 7.03857150E-02-6.34400574E-05 3 2.91548920E-08-5.30706938E-12 1.41320240E+04 4.20142955E+01 4 C6H500H С 6H 60 2 G 300.000 5000.000 1404.000 1 1.92317474E+01 1.63154699E-02-5.53448904E-06 8.55059974E-10-4.94583790E-14 2 -1.01971012E+04-7.61674471E+01-4.03105975E+00 7.96101888E-02-7.21655013E-05 3 3.27610696E-08-5.85584239E-12-3.10973017E+03 4.54324978E+01 4 C6H4OH С 6H 50 1 G 300.000 5000.000 1402.000 1 1.73187560E+01 1.36366984E-02-4.68316332E-06 7.29071204E-10-4.23805358E-14 2 1.14990276E+04-6.89986593E+01-5.99875435E+00 8.59063379E-02-9.12525636E-05 3 4.72275890E-08-9.35576749E-12 1.78621926E+04 4.99931427E+01 4 С 6H 60 2 HOC6H4OH G 300.000 5000.000 1405.000 1 2.31394847E+01 1.31873680E-02-4.49072464E-06 6.95268891E-10-4.02643108E-14 2 -4.25885990E+04-1.02692352E+02-8.68529064E+00 1.17282933E-01-1.33754802E-04 3 7.16697462E-08-1.44385730E-11-3.44903827E+04 5.77087257E+01 4 0C6H40H С 6H 50 2 G 300.000 5000.000 1403.000 1 2.22718210E+01 1.21038561E-02-4.18429526E-06 6.54475399E-10-3.81746504E-14 2 -2.34827539E+04-9.61035467E+01-8.02205657E+00 1.09403210E-01-1.23489276E-04 3 6.56286805E-08-1.31527870E-11-1.55949156E+04 5.72175202E+01 4 P-0C6H50J С 60 2H 5 G 300.000 5000.000 1400.000 1 1.82799770E+01 1.59280974E-02-5.50765220E-06 8.61649836E-10-5.02677539E-14 2 -6.25907994E+01-7.25809444E+01-3.29683290E+00 7.27365977E-02-6.36158220E-05 3 2.80683553E-08-4.92279426E-12 6.73402222E+03 4.09349895E+01 4 300.000 5000.000 1400.000 0-0C6H50J С 60 2H 5 G 1 1.84625733E+01 1.57607263E-02-5.44671499E-06 8.51765760E-10-4.96759541E-14 2

-1.72770226E+02-7.28742484E+01-2.65459198E+00 7.17179095E-02-6.31552372E-05 3 2.81132946E-08-4.97463333E-12 6.45283150E+03 3.81123139E+01 4 C#CC*CCJ С 5H 5 G 300.000 5000.000 1396.000 1 1.41230912E+01 1.14233190E-02-3.95851276E-06 6.20128961E-10-3.62097887E-14 2 4.25158384E+04-5.02942871E+01-6.16143558E-01 5.06466579E-02-4.48561743E-05 3 2.02459419E-08-3.64542145E-12 4.71532377E+04 2.71623299E+01 4 C5H6-I. C 5H 6 G 300.000 5000.000 1372.000 1 1.29600892E+01 1.48953758E-02-5.23622902E-06 8.27916389E-10-4.86464523E-14 2 2.38180800E+04-4.25312093E+01 3.58448213E+00 3.24459626E-02-1.70150991E-05 3 4.22715914E-09-4.18452556E-13 2.76514681E+04 9.60644208E+00 4 CJ*CC*CC*O С 5H 50 1 G 300.000 5000.000 1396.000 1 2 1.62360823E+01 1.18297101E-02-4.11454219E-06 6.46026823E-10-3.77767639E-14 1.93499885E+04-5.83498817E+01-5.06628841E-01 6.04671965E-02-5.97396749E-05 3 2.96804228E-08-5.76240010E-12 2.42765544E+04 2.82994148E+01 4 С 50 1 G 300.000 5000.000 1399.000 C*CC*CC.I*O 5H 1 1.53178248E+01 1.27352911E-02-4.35882964E-06 6.76912763E-10-3.92771371E-14 2 7.60582726E+03-5.43599625E+01-2.18492198E-01 5.92100223E-02-5.89241174E-05 3 2.97411920E-08-5.85244770E-12 1.20600764E+04 2.55968530E+01 4 30 С ЗH C.J*CC*O1 G 300.000 5000.000 1402.000 1 1.07482537E+01 6.19822688E-03-2.06130981E-06 3.14418872E-10-1.80309517E-14 2 1.51410162E+04-3.01266033E+01 1.46654466E+00 3.23390476E-02-3.05588208E-05 3 1.44081861E-08-2.65600505E-12 1.78850058E+04 1.80850321E+01 4 C5H30 С G 300.000 3500.000 1500.00 5H 30 1 1 1.19961781E+01 1.34287065E-02-5.90045309E-06 1.22553862E-09-9.86114716E-14 2 2.89592010E+04-4.07548249E+01-3.03242604E+00 5.43937201E-02-4.95018348E-05 3 2.25523751E-08-4.10727920E-12 3.35644081E+04 3.78374823E+01 4 C5H7 C 5H 7 G 300.000 5000.000 1377.000 1 1.36630213E+01 1.68061358E-02-5.98746539E-06 9.55341072E-10-5.64951981E-14 2 $1.27238941E + 04 - 5.46331286E + 01 - 6.75118368E + 00 \quad 6.06461693E - 02 - 4.01260152E - 05$ 3 1.22051562E-08-1.33459844E-12 2.01365277E+04 5.62694938E+01 4 0C5H70 С 5H 7O 2 G 300.000 5000.000 1375.000 1 1.65416953E+01 1.86677673E-02-6.44836048E-06 1.00787611E-09-5.87521858E-14 2 -2.82017168E+04-5.47258181E+01 4.88394767E+00 4.03401300E-02-1.97774150E-05 3 3.68903501E-09-3.40202384E-14-2.35295942E+04 9.97070337E+00 4 C*CCJC*COH C 5H 70 G 300.000 5000.000 1397.000 1 1 1.67465815E+01 1.58357240E-02-5.44954706E-06 8.49881387E-10-4.94743246E-14 2 -4.30972870E+03-6.19378748E+01-2.91175436E+00 6.69362484E-02-5.71603047E-05 3 2.48753749E-08-4.33243894E-12 1.96441523E+03 4.17454344E+01 4 C*CC*CCJ С 5H 7 G 300.000 5000.000 1386.000 1 1.47302883E+01 1.59030900E-02-5.57729508E-06 8.80604825E-10-5.16963733E-14 2 1.74050791E+04-5.42670706E+01-1.60087476E+00 5.38764703E-02-3.96302225E-05 3 1.49599474E-08-2.31995284E-12 2.31199746E+04 3.35492960E+01 4 C*CC*CC C 5H 8 G 300.000 5000.000 1395.000 1 1.41303131E+01 1.81877961E-02-6.19208788E-06 9.58333792E-10-5.54785472E-14 2 2.25907168E+03-5.11705577E+01-1.19376866E+00 5.65474329E-02-4.39472481E-05 3 1.82341266E-08-3.12226566E-12 7.36084709E+03 3.02808980E+01 4 C*CC*CCOH С 5H 80 1 G 300.000 5000.000 1396.000 1 2 1.63079670E+01 1.79957763E-02-6.03115896E-06 9.23992259E-10-5.31254053E-14 -1.58204603E+04-5.84137244E+01-5.31488384E-01 6.06983915E-02-4.81499862E-05 3 2.00308244E-08-3.38987282E-12-1.03301302E+04 3.07961436E+01 4 С 50 C*CCJC*O 4H 1 G 300.000 5000.000 1385.000 1 1.22833215E+01 1.26428506E-02-4.31034879E-06 6.68415867E-10-3.87693974E-14 2 1.86818728E+03-3.84807909E+01-4.83886977E-01 4.23431670E-02-3.05389089E-05 3 1.11441978E-08-1.63863920E-12 6.28635090E+03 3.00860103E+01 4

C 4H 6O 2 G 0C4H60 300.000 5000.000 1382.000 1 1.41894774E+01 1.53345510E-02-5.24594862E-06 8.14655154E-10-4.72759368E-14 2 -4.10001835E+04-4.43771751E+01 4.21628848E+00 3.57422725E-02-2.04226185E-05 3 5.63821367E-09-5.88888993E-13-3.72055911E+04 1.02814620E+01 4 OC4H50 C 4H 50 2 G 300.000 5000.000 1388.000 1 1.32138775E+01 1.37339051E-02-4.62639517E-06 7.10941370E-10-4.09538499E-14 2 -2.16535271E+04-3.64185255E+01 4.60550978E+00 3.30498712E-02-2.13102363E-05 3 7.37021089E-09-1.08289438E-12-1.85460831E+04 1.01599453E+01 4 HOC*CC*O C 3H 40 2 G 300.000 5000.000 1413.000 1 1.66505478E+01 6.11745137E-03-2.09080785E-06 3.24985683E-10-1.88875073E-14 2 -3.82179939E+04-6.36794754E+01-2.01837189E+00 6.26539783E-02-6.73359280E-05 3 3.39430425E-08-6.48917648E-12-3.31367523E+04 3.18162860E+01 4 C 3H 3O 2 HOC*CCJ*O G 300.000 5000.000 1414.000 1 1.52720985E+01 5.02586331E-03-1.68408578E-06 2.58390706E-10-1.48849424E-14 2 -1.98506828E+04-5.54641734E+01 6.07270082E-01 4.96011303E-02-5.32300885E-05 3 2.68392951E-08-5.13094510E-12-1.58814562E+04 1.94817133E+01 4 C2H2OH 3C 20 G 300.00 1 Н 1 5000.00 1000.00 6.81339897E+00 8.05827723E-03-3.11728612E-06 5.54590896E-10-3.71804255E-14 2 1.31583034E+04-1.09863525E+01 5.62397968E-01 2.64598620E-02-2.28453705E-05 3 9.14478695E-09-1.06711936E-12 1.48374643E+04 2.10439544E+01 4 02CCHOOJ С 2H 10 4 G 300.000 5000.000 1682.000 1 1.09910849E+01 7.46985861E-03-2.75568271E-06 4.51353051E-10-2.72108652E-14 2 -3.51335323E+04-2.11652231E+01 8.91497688E+00 8.60571847E-03 5.24416766E-07 3 -2.79301331E-09 7.62963051E-13-3.40867754E+04-8.72978273E+00 4 300. HCOH C 1H 2O 1 G 5000. 1398. 1 9.18749272E+00 1.52011152E-03-6.27603516E-07 1.09727989E-10-6.89655128E-15 2 7.81364593E+03-2.73434214E+01-2.82157421E+00 3.57331702E-02-3.80861580E-05 3 1.86205951E-08-3.45957838E-12 1.12956672E+04 3.48487757E+01 4 C 2H 4O 1 G 300.000 5000.000 1410.000 1 C2H3OH 8.32598158E+00 8.03387281E-03-2.63928405E-06 3.98410726E-10-2.26551155E-14 2 -1.83221436E+04-2.02080305E+01-1.27972260E-01 3.38506073E-02-3.30644935E-05 З 1.64858739E-08-3.19935455E-12-1.59914544E+04 2.30438601E+01 4 02CH2CH0 С 2H 30 3 G 300.000 5000.000 1393.000 1 1.11807543E+01 9.14479256E-03-3.15089833E-06 4.91944238E-10-2.86639180E-14 2 -1.55790331E+04-2.87892740E+01-1.29465843E+00 4.44936393E-02-4.26577074E-05 3 2.07391950E-08-3.96828771E-12-1.18275628E+04 3.60778797E+01 4 H02CH2CO C 2H 3O 3 G 300.000 5000.000 1386.000 1 1.04146322E+01 1.12680116E-02-5.17494839E-06 1.00333285E-09-6.68165911E-14 2 -1.40955672E+04-2.27894400E+01 2.22681686E+00 3.56781380E-02-3.26401909E-05 3 4 1.47651988E-08-2.64794380E-12-1.18735095E+04 1.91581197E+01
VITA

Nicholas Tsolas

Nicholas Tsolas was born on July 4th, 1986 in Toronto, Ontario, Canada as the offspring of Julie and Athanasios Tsolas. He attended secondary school at Silverthorne Collegiate Institute, from which he graduated in June of 2004. That same year Nicholas began studying at the University of Toronto towards his Bachelors of Applied Science in Mechanical Engineering. During his last year, he would dedicate part of his time as a research assistant at the Toronto Rehabilitation Institute -Lyndhurst Spinal Cord Center, while working towards his minor in Bioengineering. He graduated in June of 2008 and would continue on to graduate school within the Mechanical and Industrial Engineering Department, under the mentorship of Dr. Sanjeev Chandra. He earned his Masters of Applied Science in July of 2010 by investigating the heat-transfer enhancement features of metalfoam heat exchangers. From here, he decided to take his talents to State College, PA, USA, after being accepted into the the Mechanical and Nuclear Engineering Department at the Pennsylvania State University. Here he would work under the guidance of his advisor Dr. Richard Yetter, undertaking research examining the combustion kinetics associated with plasma-assisted combustion, which is the focus of his PhD dissertation.