Plasma Flow Reactor Studies of H₂/O₂/Ar Kinetics

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Abstract

In the present study, a plasma flow reactor (PFR) facility designed to perform both *ex situ* and *in situ* experiments of stable (H_2 and O_2) and intermediate (OH radicals) species detection was used to examine the plasma-assisted characteristics of hydrogen oxidation at 1 atm pressure for temperatures ranging from 420 K to 1100 K. Experiments were performed at nearly isothermal conditions, by heavily diluting reactive mixtures in argon, in an attempt to mitigate temperature changes from exothermic chemical reactions. This technique allows experimental results to be interpreted from a perspective that plasma and thermal (neutral) heat release effects are decoupled, essentially isolating the effects of the plasma-chemistry and its influence on the neutral-chemistry. Results showed no thermal reaction until 860 K, at which point hydrogen was rapidly consumed within the flow residence time associated with the reactor. With the plasma discharge, the onset of oxidation was extended to lower temperatures ($T < 860$ K), while exhibiting a steady increase in the rate of oxidation starting from 470 K, and eventually consuming all the initial hydrogen by 800 K. Absolute measurements of OH mole fraction reveal that at conditions well below the dominance of the thermal chain-branched chemistry (at $T = 668$ K), the plasma induced a chain-propagating effect on OH formation, which was entirely confined to the boundaries of the plasma discharge section of the reactor. Furthermore, temporal measurements were also performed, showing that the extent of OH formation and subsequently its global effect on the fuel consuming chemistry can be manipulated based on the plasma perturbation timescale (i.e., the time scale at which the high-voltage pulses are administered to the reactive flow to generate the plasma discharge). Experimental results are compared to modeling calculations and show relatively good agreement, with the model predicting similar kinetic trends as a function of temperature. These results demonstrate new insight into the kinetics governing plasma-assisted combustion, and provide new experimental data to facilitate the development and validation of PAC-specific kinetic mechanisms.

Keywords: plasma-assisted combustion, non-equilibrium plasmas, flow reactor, hydrogen oxidation

1 Introduction

The investigation into plasma-assisted combustion (PAC) is an ongoing and active research initiative that has gained some notoriety in recent years. Specifically, non-equilibrium plasmas generated through high-peak-voltage nanosecond pulsed-discharges, have experimentally demonstrated reduced ignition delay [1–9] and enhanced flame stabilization [10–13] in fuel-air mixtures. The inherent advantage of generating such repetitively pulsed plasmas over other conventional methods (e.g., DC, RF and microwave discharges) are their capability to generate relatively high reduced field (E/N) strengths [14, 15]. Under such conditions, a large portion of the deposited energy is spent to excite electronic states and enhance dissociation of gas molecules [16]. This in turn, facilitates the production of radicals that readily react with the fuel and oxidizer to induce combustion. Moreover, such plasmas exhibit improved stability at higher pressures (0.1–1.0 atm), where high pulse repetition-rates combined with nanosecond pulse durations reduce the propensity of ionization instabilities, while preventing substantial plasma decay between pulses [14].

The potential advantages of incorporating PAC systems into practical applications are numerous, ranging from more fuel efficient engines [10, 17] to the realization of hypersonic propulsion systems [17–21]. However, a major deterrent in moving ahead in developing such future technologies is the lack of understanding in the indicative chemical processes that lead to the observed enhancements. One of the immediate goals the PAC community has been collectively working towards is developing a predictive kinetic model for non-equilibrium plasmas sustained in fuel-air mixtures. Thus far, kinetic modeling calculations have demonstrated that existing “thermal” combustion mechanisms coupled with known plasma chemistry show good agreement with experimental results at conditions close to the “self-ignition” threshold ($T > 800$ K) and for simple fuels (e.g., H_2 and hydrocarbons less than C_3). Moving into low temperature applications where PAC has considerable potential, the kinetic mechanism is not fully understood. To embark on elucidating such a task, several issues need to be addressed. First, combustion mechanisms are typically validated at high temperatures, and their use at low temperatures common to PAC needs to be rigorously assessed to prove their applicability. The lack of data on plasma generated species and their interaction with neutral species calls for further investigation. This becomes particularly challenging when considering that the plasma kinetics (nanosecond time scales, low temperatures) and the combustion chemistry (micro- and millisecond time scales, high temperatures) occur at vastly different time scales and conditions. Lastly, experimental data on reaction products (including excited species, radicals, and intermediates) in well-characterized PAC experiments needs to be made available to validate any future mechanistic development efforts.

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 [22]. 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 the system behavior dominated by chain-branching reactions. Such mechanisms include those of Mueller et al. [23] and Konnov [24]. 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 [25–27]). However, 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 ($T = 850\text{--}1300$ K, $P = 0.3\text{--}0.6$ atm [6]) and flow reactor studies with initial preheating of non-dilute reactants ($T = 473\text{--}500$ K, $P = 0.1\text{--}0.2$ atm [1, 2, 14, 28]). The latter work was intended to be an extension of the shock tube studies, where low temperature plasma-assisted ignition data could be obtained at temperatures significantly lower than thermal ignition. In both instances, experimental data comprises of *in situ* measurements of the ignition delay time through OH emission spectroscopy, time-resolved OH concentration using LIF (Laser-Induced Fluorescence) and time-resolved temperature measurements using CARS (Coherent Anti-Stokes Raman Spectroscopy - in N_2 containing mixtures) or OH LIF thermometry. Several years after the work of Ref. [6] was completed, Popov [29] developed a PAC specific hydrogen-air kinetic mechanism to describe the experimental results. The same mechanism was also used to model the experiments of Refs. [1, 2, 14]. All these studies demonstrated that the enhanced generation of radicals below the ignition threshold (number densities much greater than their equilibrium densities in combustible mixtures) would result in significant additional heating due to low temperature fuel oxidation reactions with radicals. At this point, the significance of the plasma chemical reactions diminishes and the high temperature chain-branching reactions would cause the ignition threshold to shift towards lower temperatures. 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 (slow-oxidation) have not been thoroughly explored and could provide particular insight to the mechanism driving the ignition process under the effect of a non-equilibrium plasma discharge.

In the current study, a previously constructed plasma flow reactor (PFR) is used to investigate the thermal and plasma-assisted kinetics associated with hydrogen oxidation at atmospheric pressure. Experiments are performed under highly diluted conditions in argon for temperatures ranging from 420 K to 1010 K, using both *ex situ* and *in situ* experimental diagnostic techniques to measure hydrogen and oxygen consumption, along with OH radical production as a result of any observed reactions. Also, experimental data presented in this paper are complemented with numerical modeling results obtained from a newly developed kinetic model by Togai et al. [30]. The culmination of these results will help elucidate the kinetics of the system, while corroborating their validity.

2 Experimental Methods

Details of the plasma flow reactor (PFR) and the accompanying experimental facility used in this study can be found in Tsolas et al. [31]. Briefly, the PFR is a continuous flow experiment, where the reactive mixture passes through a quartz tube comprising of both circular and rectangular cross-sections. Mounted on the quartz reactor, a ceramic electrode housing assembly is positioned to hold in place two copper electrodes in a plane-to-plane orientation around the rectangular tube section. In between the contact surfaces of the quartz tube and electrodes, two thin ceramic dielectrics are inserted to produce a uniform, volume-filling plasma discharge. The entire PFR assembly is placed into a three-zone tube furnace, generating a quasi-isothermal reaction zone of approximately 45 cm in length, with the discharge section positioned at the beginning (inlet) of this reaction zone and accounting for 11% of the reaction zone length. The reactive mixtures were prepared by premixing the reactants H_2 (99.999% purity, Praxair) and O_2 (99.993% purity, Praxair) and heavily diluting them in Ar (99.999% purity, Praxair) before entering the reactor. For all experiments performed in this study, a reactive mixture of 2000 ppm H_2 / 3000 ppm O_2 / balanced in Ar for a total flow rate of 1 SLPM ($T = 298$ K, $P = 1$ atm) was used at 1 atm pressure, producing residence times as a function of reaction zone temperature equivalent to $\tau = 510.3 \text{ s}\cdot\text{K}/T$. Unlike previous PFR studies where gas chromatography was conducted offline by way of sample storage, in the current study, *ex situ* measurements are extended to measure H_2 and O_2 concentrations using an online micro gas chromatograph (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- μm 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 known H_2 /Ar and O_2 /Ar samples on a mass flow basis to obtain a linear calibration curve. Overall uncertainty in *ex situ* 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 H_2O formation to ensure minimal degradation of the GC column.

A schematic of the PFR facility expanded to perform *in situ* OH laser-induced fluorescence (LIF) studies is shown in Fig.1. A pulsed Nd:YAG laser (Continuum, PR 8010) equipped with a second-harmonic generator crystal outputting at 532 nm, is used to pump a tunable dye laser (Continuum, ND6000) and generate a fundamental output near 566 nm (Rhodamine 590 as the dye). From here, a frequency doubling unit (Continuum, 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 $\sim 10 \mu\text{J}$). 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. 1) 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 allow the laser beam to pass 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. Measurements made using a thermocouple, verify that keeping the tube furnace open during the course of an experiment has minimal effect on the steady-state temperature profiles (refer to Ref. [31] for typical PFR temperature profiles).

For relative OH measurements, excitation of the ($A^2\Sigma^+$, $v' = 1 \leftarrow X^2\Pi$, $v'' = 0$) OH band is made through the $Q_1(4)$ transition at 282.522 nm. Fluorescence images are 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 from plasma emission and scattered light by bandpass filters attached to the lens, to allow high transmittance of the ($v' = 1$, $v'' = 1$) band at $\sim 312\text{-}322$ nm and the ($v' = 0$, $v'' = 0$) band at $\sim 306\text{-}316$ nm. This particular excitation scheme is usually employed to discriminate against inherent scattered laser light that may undermine the fluorescence signal [15]. 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 is adjusted to enclose the entire plasma discharge region with a spatial resolution of approximately 5 cm in length. To discriminate between the OH LIF signal and the background emission, final LIF images were created as follows: $S_{\text{LIF}} = I_{\text{on}} - (I_{\text{off}}) * E_{\text{on}}/E_{\text{off}}$. Here, the on-resonance image (I_{on}) contained the LIF signal on top of the background emission, while the off-resonance image (I_{off}) had only the background emission (combination of plasma afterglow emission, ambient emission and the off-transition laser emission). This method also accounts for any variation in laser energy between the two measurements (E_{on} and E_{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 camera and plasma discharge can be synchronized, such that LIF signal can be captured at various time delays in the afterglow generated by a high-voltage discharge pulse. Relative OH measurements are calibrated using the Rayleigh scattering technique at the wavelength identical to the ($v' = 1$, $v'' = 0$) excitation scheme. This technique is discussed in greater detail in Yin et al. [32]. All the experimental data in the present paper are compared to kinetic modeling results. Details about the kinetic model development, assumptions, mechanism and results are discussed in a companion paper by Togai et al. [30].

3 OH LIF Data Reduction and Calibration

3.1 Laser Induced Fluorescence 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. [15]. With an understanding of the relevant collisional processes that dictate the excitation dynamics of OH LIF, a quantitative mole fraction measurement can ultimately be deduced from the experimentally captured relative LIF signals. Usually a simple two-level model is sufficient to characterize OH LIF under low pressure conditions, since the frequency of collisional processes leading to the population redistribution of the excited state is lower than the frequency of laser excitation. At atmospheric pressure however, the frequency of such processes increases significantly, thus requiring the use of a more complex model to account for their influence [33]. Such processes include rotational energy transfer (RET), vibrational energy transfer (VET) and collisional (electronic) quenching (see Fig. 2a).

In this study, a three-level model is employed assuming (i) negligible upward VET to higher vibrational levels ($v' > 1$, $v' = 1 \leftarrow 0$), which only acts to populate the excited state $v' = 0$ from $v' = 1$ [34], and (ii) at all times the rotational distribution in all vibrational levels is in equilibrium with the gas temperature (the rotational manifold is fully thermalized) [33,34]. 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 rate of OH ($A^2\Sigma^+$, $v' = 1$, $N' = 5$, F_1) with argon as the collider medium has been reported by Kienle et al. [35] and under the present conditions can be inferred to be on the order of $2 \times 10^9 \text{ s}^{-1}$. This rate is considered 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 O_2 and H_2O will further facilitate the increase of RET since they have considerably higher RET rate coefficients compared to argon [35,36]. The typical pumping rate in the present 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 rate of laser excitation and fluorescence. It can then be assumed that complete rotational relaxation towards gas temperature is achieved, and will not change appreciably between laser pulses. This is expected to hold greater relevance at higher temperatures, where argon is known to be an inefficient quencher and very efficient collisional partner for RET [37]. Both the excited state ($v' = 0$) and ground state can also be assumed thermalized, since RET rate coefficients for the $v' = 1$ are generally the same for $v' = 0$ state [35], while RET rates for the ground state tend to always be higher than the excited state [38]. The latter statement imposes that if the laser energy is kept low, negligible perturbation in the ground state can be assumed, such that its population remains constant for the entire laser pulse.

The physical description of the LIF process can be translated into a mathematical description as shown in Fig.

2b, with the following system of rate equations describing the population of each level:

$$\frac{dN'_1}{dt} = N''W_{12} - N'_1(A_1 + Q_1 + Q_{10}) \quad (1)$$

$$\frac{dN'_0}{dt} = N'_1Q_{10} - N'_0(A_0 + Q_0) \quad (2)$$

$$\frac{dN''}{dt} = N'_0(A_0 + Q_0) + N'_1(A_1 + Q_1) - N''W \quad (3)$$

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 the 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 populate separate vibrational levels in the ground state.

The fluorescence transition is actually composed of many rovibronic transitions from the excited state and with the inclusion of the thermalized rotational manifold assumption, the determination of $A_{v'}$ can be expressed as a weighted average:

$$A_{v'} = \sum_{J'} f_B(v', J') \cdot \sum_{v'', J''} A_{v'', J''}^{v', J'} \quad (4)$$

such that the $A_{v'', J''}^{v', J'}$ transitions are taken from LIFBASE [38] and are evaluated separately for the ($v' = 1, v'' = 1$) and ($v' = 0, v'' = 0$) bands. In rotational thermal equilibrium the Boltzmann fraction, f_B , is given by Eq.(5) and the rotational energy term values, $E_{J'}$, in the excited state are taken from Coxon [40] (k_B is the Boltzmann constant):

$$f_B(v', J') = \frac{(2J' + 1) \exp\left(\frac{-E_{J'}}{k_B T}\right)}{\sum_{J'} (2J' + 1) \exp\left(\frac{-E_{J'}}{k_B T}\right)} \quad (5)$$

The determination of the quenching and VET rates are obtained using available literature values, and rescaled for differences in temperature and mixture composition based on the present experimental conditions. It is expected that the greatest inherent source of error in the derived measurements is due to the uncertainty of these rates. Most combustion applications of OH LIF are found in high temperature regimes and have only been experimentally verified at such conditions. Recently, some attempts have been made to gather quenching data at lower temperatures. These results have been used here, when applicable and available. The quenching rate of a particular collisional process is generally given by [14]:

$$Q = \sum_i n_i k_i = \sum_i n_i \sigma_{Q_i} \left[\frac{8k_B T}{\pi \mu_i} \right]^{\frac{1}{2}} \quad (6)$$

Here, n_i is the number density of the quencher, σ_{Q_i} is the thermally-averaged cross-section of a particular collisional

process with a known collider, μ_i is the reduced mass of given collisional pair, k_i is the rate coefficient, and T is the gas temperature. The collisional partners considered are Ar, H₂, O₂ and H₂O, with their respective collisional cross-sections taken from Refs. [41–52]. It was assumed that the mixture composition for a given temperature condition was equal to the composition measured at the exit of the flow reactor as reported in Fig. 5. This is considered to be 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 quenching rates with Ar dominate, and the overall rates become essentially independent of any uncertainty in inferring mixture composition during the LIF measurement.

3.2 Determining Absolute OH Density

The number density of laser-induced OH($A^2\Sigma^+$) is dependent on a proportionality between the fluorescence signal intensity, S_{LIF} (number of photons), and the number density in the lower laser-coupled energy state, described by the following expression:

$$S_{\text{LIF}} = N_{\text{OH}} f_B b_{12} E_L \Phi g(\nu) \frac{l\Omega\beta}{4\pi} \quad (7)$$

where $b_{12} = B_{12}/c$ is the Einstein absorption coefficient ($\text{cm}^2\text{cm}^{-1}\text{J}^{-1}$) for the specified transition taken from LIFBASE [39]; E_L is the measured laser pulse energy (J); and N_{OH} is the number density of the OH radical (cm^{-3}). The Boltzmann factor correlates the number density of the absorbing state OH ($X^2\Pi$, $v'' = 0$, $J'' = 4.5$, f_1) to the OH ($X^2\Pi$, $v'' = 0$) population in the ground vibronic level ($E_{J''}$ taken from [40]).

$$f_B = \frac{N_{\text{OH}(X, v''=0)}}{N''_{(X, J''=4.5)}} = \frac{\sum_{J''} (2J'' + 1) \exp\left(\frac{-E_{J''}}{k_B T}\right)}{(2J'' + 1) \exp\left(\frac{-E_{J''}}{k_B T}\right)} \quad (8)$$

The population of the lower state, N'' , is obtained by solving the system of rate equations given in Eqs. (1)-(3), resulting in the appearance of the fluorescence quantum yield, Φ :

$$\Phi = \frac{\epsilon_0 A_0 Q_{10} + \epsilon_1 A_1 (A_0 + Q_0)}{(A_0 + Q_0) (A_1 + Q_1 + Q_{10})} \quad (9)$$

Here, ϵ_0 and ϵ_1 are the collection efficiencies of the optical system for the ($v' = 0$, $v'' = 0$) and ($v' = 1$, $v'' = 1$) transitions, respectively.

The overlap integral, $g(\nu_L)(1/\text{cm}^{-1})$, is the convolution of the laser lineshape, L_L , and the absorption lineshape, Y_A , defined as [53]:

$$g(\nu_L) = \int_{-\infty}^{+\infty} L_L(\nu_L - \nu) Y_A(\nu) d\nu \quad (10)$$

Both lineshape functions are normalized to unity in this expression. The absorption line was assumed to have a Voigt profile, whose Doppler and collisional broadening linewidths were calculated based on known correlations taken from [54]. From here the value of $g(\nu_L)$ is calculated assuming a Gaussian profile for a laser beam with a linewidth at FWHM of 0.6 cm^{-1} . This value was determined by deconvoluting a Gaussian profile from an experimental excitation spectrum, obtained by scanning across the $Q_1(4)$ transition and fitting it to a Voigt profile. Calculations of the overlap integral reveal minimal variation with changes in temperature. This can be attributed to the relatively wide laser lineshape compared to the combined linewidths of both the Doppler and collisional broadening effects (less than 0.2 cm^{-1}). Due to this, in the present work a constant value of the overlap integral is used to reduce all OH LIF data.

3.3 LIF Calibration: Rayleigh Scattering Measurements

All that remains in Eq. (7) is the determination of the calibration factor of the optical collection system ($l\Omega\beta$). Here, l is the path length of the laser beam 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 its origin from Luque and Crosley [55], who used it to obtain absolute CH measurements. Since then, it has been demonstrated as an applicable technique for OH LIF in plasma systems [15, 33, 34]. The calibration is performed using the same optical setup and laser beam alignment as the LIF measurements, to ensure that the Rayleigh scattering beam occupies the same path as the fluorescence beam. Pure N_2 (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:

$$S_{\text{Rayleigh}} = \frac{\epsilon_R}{h\nu_L} \left(\frac{\partial\sigma}{\partial\Omega} \right) l\Omega\beta \cdot (NE_L) \quad (11)$$

$$= D_{\text{Rayleigh}} \cdot (NE_L) \quad (12)$$

where ϵ_R is the collection efficiency of the Rayleigh scattering signal; $h\nu_L$ is the photon energy at the laser wavelength (J); $N = P/k_B T$ 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 (cm^2/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:

$$\frac{\partial\sigma}{\partial\Omega} = \frac{9\pi^2\nu^4}{N_o^2} \left[\frac{n_o^2 - 1}{n_o^2 + 2} \right]^2 \frac{3}{3 - 4\rho_p} (1 + \rho_p) \quad (13)$$

Here n_o is the index of refraction, and N_o is the number density evaluated at reference conditions. The depolarization ratio of polarized light, ρ_p , is taken from dispersion formulations found in [56]. For $\nu_L = 282.522$ nm, the differential cross-section was determined to be 8.76×10^{-27} cm²/sr. Rayleigh scattering measurements were made by varying either the pressure of the calibration gas or the laser pulse energy in the plasma reactor and collecting the corresponding signal. Plotting S_{Rayleigh} vs. (NE_L) reveals a linear relationship, from which the slope, D_{Rayleigh} , can be used to calculate the unknown calibration factor in Eq. (11). Calibration measurements are performed independently after each set of LIF measurements to account for any inherent drift in the optical setup. Combining Eqs. (7) and (11), the final expression for the absolute number density of the ground state OH is:

$$N_{OH} = \frac{4\pi S_{\text{LIF}} \epsilon_R \left(\frac{\partial \sigma}{\partial \Omega} \right)}{f_B b_{12} E_L \Phi g(\nu) h c \nu_L D_{\text{Rayleigh}}} \quad (14)$$

Based on standard error propagation analysis, 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 number density is approximately $\pm 30\%$. OH measurements are presented as a mole fraction with respect to the total number density of the reactive mixture at the given experimental condition.

3.4 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-induced systems [14, 32, 33, 54], fluorescence based thermometry has been applied as a reliable technique when using linear LIF. The method is based on the premise that the collected fluorescence intensity across several transitions scales linearly with the rotational level population of the ground state. Thus, LIF signals can be fitted to a Boltzmann expression (Eq.15) by manipulating Eq.(7).

$$\ln \left[\frac{S_{\text{LIF}}}{b_{12} (2J'' + 1)} \right] = - \frac{E_{J''}}{k_B T} + \text{const} \quad (15)$$

An example of temperature inference based on a Boltzmann plot is shown in Fig. 3, with measurements corresponding to excitation transitions $Q_1(2)$ up to $Q_1(7)$. The slope of the linear fit through the experimental points is equal to $1/k_B T$, providing temperature. Accurate temperature inference based on OH thermometry can only be determined when good signal-to-noise ratio (S/N) is achieved. Signal obtained across the field of view of the camera extended beyond the regions of the discharge section. At certain transitions, the S/N at these extremities was determined to be poor (~ 1). For this reason, the temperature profiles were cropped to include measurement portions having Boltzmann fits with fit uncertainty within $\pm 10\%$. The uncertainty in the inferred temperature is about $\pm 15\%$.

4 Results

4.1 Gas Temperature and Plasma Uniformity

A qualitative analysis of plasma uniformity similar to Yin et al. [15] was carried out in the current plane-to-plane plasma discharge experiment. Figure 4 shows single-shot broadband images of plasma emission at different pulse repetition rates, at the same experimental conditions ($T = 668$ K, $P = 1$ atm, $Q = 1$ SLPM) intended for plasma OH LIF measurements. These images were taken after the discharge had been in operation for some elapsed time and are representative of the discharge 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 pulse (pulse duration ~ 250 nsec). Previous measurements [57] indicate that 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 results of Refs. [58,59]. Images show that the plasma remains diffuse and occupies the entire volume between the electrodes, before it rapidly decays within 300 ns after the pulse (not shown in Fig. 4). From this, it can be inferred that the excited species leading to light emission generated in the plasma are present only during the high-voltage pulse, and quench rapidly in the afterglow. Plotted below each image (all on the same relative scale) are emission intensity profiles along the centerline of the discharge to demonstrate the degree of axial uniformity through the discharge. At all plasma conditions, the emission intensity profiles are smooth and relatively constant, reaffirming that under the present experimental conditions the plasma is void of any significant well-defined filamentary structures. This fact is particularly important to show, since the formation of filament structures can lead to localized “hot-spots” inducing undesired thermal effects [15]. 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. [1], suggesting somewhat higher discharge power densities exist at the boundaries of the electrodes. Increasing the pulse repetition rate increases the emission intensity of the profiles, as expected, since energy coupled into the reactive mixture increases with the number of pulses, and hence increases the number density of excited radiating species being generated.

To quantify thermal effects, centerline temperature distribution measurements were also performed using OH thermometry (Fig. 4). These measurements were taken a few nanoseconds after the high-voltage pulse, when the maximum temperature influence from the discharge is expected. Axial temperature profiles indicate that the temperature distribution is nearly uniform through the bulk of the discharge section of the reactor, with temperature deviating from the average value by a maximum of ± 44 K. Increasing the discharge coupled energy by increasing the pulse repetition rate has some effect on the temperature, with average temperature values of 624 K, 638 K and 647 K for 1, 3 and 5 kHz, respectively. These measurements have a maximum deviation of $\pm 7\%$ from previous measurements of isothermal temperature profiles along the reactor length using a thermocouple without the plasma.

The boundaries of the discharge regions exhibit localized temperature rise of approximately 70 K, which correlates with higher plasma emission intensity as mentioned previously. Based on these results, it can be concluded that the axial uniformity of the plasma is modest, and temperature rise induced by the discharge and the oxidation reaction may be considered minimal (within the uncertainty of the experimental measurements). This suggests that the pure thermal effects of the plasma that may influence the experimental results are likely to be weak.

4.2 Hydrogen Oxidation

Figure 5 shows a comparison of H_2 oxidation between the thermal and plasma-assisted systems between 420K to 1010 K. In the thermal system (i.e., without the plasma), hydrogen oxidation is not observed at temperatures lower than 860 K, for the given flow residence times of 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 [23]. With the application of the plasma discharge (see Fig. 5b), the oxidation characteristics of the system extend to temperatures lower than the 860 K threshold, 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 induced chemistry has managed to consume all the fuel, nearly 40 K below the onset of any thermal chemistry effects. For $T > 840$ K both the plasma and thermal effects are driving the oxidation process to full completion. The lines in the plots are kinetic modeling predictions, described in detail in a companion paper [30]. The modeling results display similar experimental trends for both the plasma chemistry and thermal chemistry, with the plasma-assisted system predicting 50% fuel consumption shifted towards higher temperatures by approximately 80 K.

4.3 Behavior of OH Formation

For a reactor temperature within the explosive regime ($T = 921$ K, Fig. 6a), the thermal kinetics induce an OH axial profile experiencing both exponential growth and decay characteristics. This profile is consistent with the flow reactor experimental results of Linteris et al. [60], which is indicative of chain-branched 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 occurs, which further facilitates the chain-branching reactions. At a reactor temperature well below the thermal explosive regime ($T = 668$ K, Fig. 6b), the extent of the OH axial profile is entirely confined to the boundaries

of the discharge. Once the reactive mixture enters the discharge, OH displays rapid growth, linearly increases, and finally decays rapidly once the flow exits the discharge. 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 at higher pulse repetition rates at the same reactor temperature ($T = 668$ K), the effect on the plasma induced OH axial profiles are shown in Fig. 7. Here, the linear propagating feature of the OH profile persists, while the overall OH mole fraction increases proportionally to the pulse repetition rate. Although peak OH mole fraction increases by nearly a factor of 5, the plasma-assisted system is still unable to transition to a fast, chain-branched system. In Fig. 8, the temporal effects within the plasma are examined for a given axial position within the discharge. Maximum OH mole fraction is achieved rapidly near the end of the high-voltage pulse, and OH is predominately consumed in the afterglow of the discharge, albeit at a relatively slower rate compared to its formation in the discharge. The absence of chain-branching processes in the low temperature plasma and OH temporal behavior within the plasma, are experimentally comparable and consistent to the observations made by Choi et al. [14] for a single-pulse discharge in a hydrogen-air plasma ($T = 300\text{-}400$ K, $P = 54\text{-}94$ torr). The kinetic model is observed to capture both the trend and the absolute magnitude of the OH axial profiles, for both different temperatures (Fig. 6b) and different pulse repetition rates (Figs. 7 and 8).

5 Discussion

Initiation of thermal oxidation is usually related to H_2 dissociation (i.e., $\text{H}_2 + \text{M} = \text{H} + \text{H} + \text{M}$), due to its relatively lower bond energy compared to that required for O_2 dissociation [61] at relatively high temperatures, and to the bimolecular reaction between H_2 and O_2 at lower temperatures (i.e., $\text{H}_2 + \text{O}_2 = \text{HO}_2 + \text{H}$). Regardless, the thermal experiments indicate that the system still requires sufficient temperature ($T > 860 \text{ K}$) to induce a reaction on the available time scales of the experiments. In the presence of the plasma, this high temperature reaction rate dependence is no longer a constraint, but more importantly, it can be assumed that both H_2 and O_2 dissociation act as initiation steps. The low temperature oxidation of H_2 can be attributed to unique plasma chemical processes that enhance molecular dissociation. These include direct electron-impact (i.e., $\text{H}_2 + e = \text{H} + \text{H} + e$ [1, 14]) and collisional quenching with excited species (i.e., $\text{Ar}^* + \text{O}_2 = \text{Ar} + \text{O} + \text{O}$, where Ar^* is a metastable state formed via an electronic collision [8, 9]). In the case of O_2 , an added benefit potentially arises considering that electronically excited states can be readily formed (i.e., $\text{O}_2 (a^1\Delta_g)$, $\text{O}_2 (b^1\Sigma_g)$ [8]), which react considerably faster than their ground state counterpart at lower than normal combustion temperatures. The enhancement of these processes with temperature is evident and expected, since E/N (reduced electric field, a metric widely used to characterize the discharge energy fraction going to electronic excitation of atoms and molecules by electron-impact in the discharge) scales proportionally to temperature, which in turn increases the rate of electron-impact reactions and subsequently H_2 and O_2 dissociation. Based on these qualitative assertions, the forthcoming discussion assumes that H-atom and O-atom reservoirs are in abundance within the plasma and the underlying thermal (neutral) chemistry marks the behavioral differences between the two systems.

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 (i.e., H, O, OH) are regenerated and provided as surplus by the following reactions [23]:

The first two chain-branching reactions kinetically dominate the system and accelerate the global rate of reaction at sufficiently high temperatures [23], with reaction (18) contributing the most to the exothermicity of the system ($\sim 68 \text{ kJ/mol}$). Early on in the reaction, reactions (16) and (17) are the main source of OH production, out-competing reaction (18) leading to excess OH formation. As the extent of reaction progresses, fuel and oxidizer consumption continues. At this point, the production rates of reactions (16) and (17) establish a partial equilibrium, and the main

consumption route is through reaction (18), which causes the system to consume OH faster than it can produce it (see Fig. 6a).

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 below the self-ignition threshold limit. This can be attributed to the low temperature and high pressure behavior of the $\text{H} + \text{O}_2$ reaction, which favors the production of the hydroperoxyl radical, HO_2 , a stable and essentially less reactive species [23]. From a kinetics perspective, HO_2 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 16) and consequently decreases the overall reactivity of the system. As such, radical fluxes reach a balance, leading to the straight-chain propagation given by reactions [23]:

with reaction (18) remaining as the primary consumption route for OH. 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 radical through the system.

These reactions are mainly sustained due to the continual generation of O-atoms by the plasma and are an excellent example of how the effects of the plasma may be used to facilitate the neutral chemistry. Reaction (23) occurs due to super equilibrium of O and OH concentrations 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 terminating reaction routes (21) and (23). Despite reaction (22) being a branching step, the reaction rate of (21) dominates over reaction (22) due to the abundance of HO_2 driving reaction (21), but also due to the low rate constant reaction (22) has at 668 K. This competition effectively makes the reaction system (21)-(23) net radical terminating. Though the plasma alleviated the temperature constraint in initiating the reaction, the importance of temperature on the secondary kinetics limits

the chain length, preventing 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. 7, the profiles show the accumulation of OH through the discharge region of the flow reactor at a given instant in time with respect to the high-voltage pulse. Considering a particle element traveling in the reactor for a fixed flow residence time, the same element will experience more perturbations due to individual discharge pulses, as the pulse repetition rate is increased. Thus, the observed enhancement of OH mole fraction as pulse repetition rate increases, can be correlated to the acceleration of reactions (19) to (21), due to the proportional increase in H- and O-atom radical pools. As far as OH production is concerned, these reactions are considered to be the most dominant [30]. Moreover, 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 (18) (see Fig. 8). These results demonstrate that for a given set of conditions (T and $P = \text{constant}$), the neutral chemistry can be manipulated by changing the perturbation timescale of the plasma. This holds a particular significance because the intrinsically disadvantageous slow chemistry inherent to the low temperature 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. 7 is that a gradual rise in the tail of the OH axial profiles is observed as pulse repetition rate increases. In tandem with the above enhancement, for a given pulse repetition rate, the rate of consumption from reaction (18) declines as the amount of remaining H_2 decreases proportionally, as the oxidation process proceeds. More strictly speaking, the decline in both $k_{R20}[\text{HO}_2][\text{H}]$ and $k_{R21}[\text{HO}_2][\text{O}]$ are both less significant than the reduction in $k_{R18}[\text{H}_2][\text{OH}]$. Subsequently, the production fluxes from reactions (20) and (21) dominate over the consumption fluxes resulting in a net build up of OH. As a secondary minor effect, the proportional accumulation of H_2O suggests that new production channels leading to the formation of OH become more relevant, such as [30]:

6 Conclusion

The plasma-assisted oxidation characteristics of hydrogen were studied experimentally under highly dilute conditions using a 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 mole fraction of OH. Qualitative image analysis and OH thermometry were also performed to characterize the physical attributes of the plasma discharge at low temperature conditions, for different 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 distribution along the discharge. This provides further evidence that the plasma does not contain well pronounced filamentary structures that may induce undesirable thermal effects and potentially affect the interpretation of the chemical kinetic features of the system. Oxidation of H_2 under the effect of the plasma extends to lower temperatures ($T < 860$ K) and occurs at a slow steady rate, compared to that of the thermal system, where oxidation does not proceed until $T > 860$ K (for the residence time studied) with an abrupt fast reaction. Insight into the dynamics of OH formation reveals that at low temperatures the plasma induces a linear chain-propagation effect, with HO_2 as an active intermediate. Temporal studies within the plasma show that peak OH formation occurs near the end of the high-voltage pulse and that OH consumption kinetics dominate the afterglow event. Furthermore, the experiments demonstrated that the plasma system is capable of accelerating the slow kinetics to enhance oxidation by increasing the frequency of discharge pulse excitation.

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Figure 1: Schematic of *in situ* LIF experimental setup with the plasma flow reactor.

Figure 2: Excitation dynamics of OH LIF (a) physical description and (b) mathematical description: three-level model with infinitely fast RET assumed in all levels.

Figure 3: Example of temperature inference based on Boltzmann plot. The best fit temperature is 626 ± 37 K, with $R^2 = 0.9945$.

Figure 4: ICCD single-shot broadband images of plasma emission, axial centerline emission intensity (bottom curves) and centerline temperature distributions (top curves) at pulse repetition rates of (a) 5 kHz (b) 3 kHz (c) 1 kHz. Initial conditions: $X(\text{H}_2) = 2000$ ppm, $X(\text{O}_2) = 3000$ ppm, $X(\text{Ar}) = 0.995$, $P = 1$ atm, $T = 668$ K, $Q = 1$ SLPM. Plasma conditions: pulse peak voltage of 10 kV. The uncertainty in the inferred temperature is $\pm 15\%$.

Figure 5: H₂ (solid square marks) and O₂ (hollow circle marks) mole fractions from (a) thermal oxidation and (b) plasma-assisted oxidation experiments as a function of isothermal reactor temperature. Initial conditions: $X(\text{H}_2) = 2000$ ppm, $X(\text{O}_2) = 3000$ ppm, $X(\text{Ar}) = 0.995$, $P = 1$ atm, $Q = 1$ SLPM ($\tau = 510.3 \text{ s}\cdot\text{K}/T$). Plasma conditions: pulse peak voltage of 10 kV at pulse repetition rate of 1 kHz. Symbols are experimental data; lines are model predictions.

Figure 6: Axial OH mole fraction profiles at (a) $T = 921$ K for thermal oxidation and (b) $T = 668$ K for plasma-assisted oxidation at $10 \mu\text{s}$ delay after the high-voltage pulse. Initial conditions: $X(\text{H}_2) = 2000$ ppm, $X(\text{O}_2) = 3000$ ppm, $X(\text{Ar}) = 0.995$, $P = 1$ atm, $Q = 1$ SLPM. Plasma conditions: pulse peak voltage of 10 kV at pulse repetition rate of 1 kHz. Symbols are experimental data; lines are model predictions.

Figure 7: Comparison of axial OH mole fraction profiles for different pulse repetition rates of 1, 3, 5 kHz (with the total number of pulses the reactive mixture experiences through the discharge) at $T = 668$ K at $150 \mu\text{s}$ delay after the high-voltage pulse. Initial conditions: $X(\text{H}_2) = 2000$ ppm, $X(\text{O}_2) = 3000$ ppm, $X(\text{Ar}) = 0.995$, $P = 1$ atm, $Q = 1$ SLPM. Plasma conditions: pulse peak voltage of 10 kV. Symbols are experimental data; lines are model predictions.

Figure 8: For a given axial location, $x = 45$ mm in Fig. 7 (or for a given pulse), in the discharge region, the local OH mole fraction as a function of pulse delay after the high-voltage pulse. Initial conditions: $X(\text{H}_2) = 2000$ ppm, $X(\text{O}_2) = 3000$ ppm, $X(\text{Ar}) = 0.995$, $T = 668$ K, $P = 1$ atm, $Q = 1$ SLPM. Plasma conditions: pulse peak voltage of 10 kV. Symbols are experimental data; lines are model predictions.