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An Experimental and Modeling Study of Formaldehyde and 1,3,5-Trioxane Flame Chemistry

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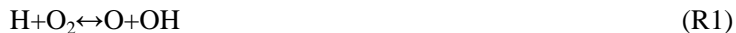
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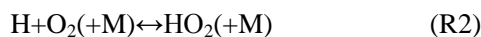
Formaldehyde is a key species produced during oxidation of virtually all hydrocarbon and oxygenated fuels, and it is also a regulated hazardous air pollutant. An improved understanding of its formation and destruction chemistry is therefore vital to the study of many energy conversion processes. To this end, this work experimentally and numerically investigates the flame chemistry of formaldehyde (CH₂O) at atmospheric pressure. The laminar burning rate of 1,3,5-trioxane/O₂/N₂ mixtures is measured in outwardly propagating spherical flames, where high concentrations of formaldehyde are generated early in the flame structure from decomposition of 1,3,5-trioxane. Though laminar burning rate predictions of several combustion kinetic models vary significantly, simulations agree that observables measured at the present experimental conditions are particularly sensitive to the competition between reactions HCO+O₂=CO+HO₂ and HCO(+M)=H+CO(+M). The present experimental measurements provide accurate data sensitized to these important HCO reactions, and are a valuable constraint for small molecule kinetic models.

1. Introduction

Gas phase combustion chemistry may be described by a hierarchical system, wherein fuels react to form intermediates on the way to formation of product CO₂ and H₂O at the base of the oxidation hierarchy [1]. Formaldehyde is a simple fuel/intermediate near the base of this hierarchy, and it is an important stable intermediate species observed in the combustion of larger fuels. However, formaldehyde is toxic and difficult to generate, so many experimental studies of formaldehyde chemistry are performed at low pressure in burner stabilized flame sampling systems [2-4] or at very dilute concentrations in flow reactors [5, 6] and shock tubes [7-11]. Our review of the literature found no formaldehyde flame speed measurements. The present study aims to expand the available database of kinetic model validation targets to include the first (to our knowledge) flame speed measurements specifically targeting formaldehyde and HCO flame chemistry. In order to achieve this goal, premixed laminar flame speeds of 1,3,5-trioxane (henceforth referred to as “trioxane”) are measured in outwardly propagating spherical flames. Trioxane serves as an *in situ* generator of significant quantities of formaldehyde since it decomposes unimolecularly to form three formaldehyde molecules within the early part of the flame structure. Consequently, trioxane flames share their governing chemistry with formaldehyde flames. This allows investigation of formaldehyde flame chemistry without the significant difficulties inherent in producing well-defined formaldehyde/oxidizer premixtures.

Reactions involving formaldehyde and formyl (HCO) provide the hierarchical link between hydrocarbon fuels and simpler, well studied fuels such as H₂ and CO. While H₂ and syngas flame chemistry is dominated by competition between R1 and R2 [12],





these reactions are moderated by competition between R3 and R4 in hydrocarbon flames,



especially with CO_2 and H_2O dilution found in modern exhaust gas recirculation systems [17].

These two pairs of competing reactions are analogous – both R1 and R3 significantly contribute to radical branching by producing the major radical species H, O, and OH, while both R2 and R4 produce the less reactive HO_2 radical and essentially behave as radical termination reactions. Elementary reactions R1 and R2 have enjoyed significant study over the past several decades, and the continual refinement of their rate coefficients has contributed to reasonably

predictive kinetic models (*e.g.*, [18-20]) validated at flame conditions. However, significantly less progress has been made in the study of the HCO reaction pair, and measurements at flame conditions sensitized to R3 and R4 are generally lacking. Thus, in the present study we measure flame speeds of trioxane at 1 atm in order to provide useful validation data that are highly sensitive to formaldehyde and formyl radical chemistry.

2. Experimental and modeling methods

2.1. Acquisition of experimental measurements

Experiments were conducted in a spherical, heated high pressure constant volume chamber. The apparatus, general experimental method, and associated uncertainties are described in significant detail elsewhere [17, 21]. From the smoothed measured flame radius *vs.* time history, the unstretched flame propagation speed $s_{b,0}$ was calculated using the nonlinear extrapolation method (NM I) recommended by Chen [22] for mixtures with Lewis numbers greater than unity (positive Markstein length). The extrapolated burning velocity was multiplied by the calculated density ratio [23] to give the flame speed relative to the unburned gas, $s_{u,0}$. Measurements apparently affected by instabilities, buoyancy, and/or transient or non-linear response of flame speed to stretch rate have been excluded.

Preparation of the $\text{O}_2/\text{N}_2/\text{fuel}$ unburned gas mixtures merits specific description due both to the inherent complications in handling the fuel, as well as the desired sensitization of the competing HCO reactions. Gaseous trioxane was prepared from the solid (99%, Sigma-Aldrich) by heating it in a previously evacuated Pyrex flask immersed in a hot water bath. Significant vapor pressure is established at ~ 360 K and permits mixture preparation by the partial pressure method. Trioxane vapor so produced was conveyed into the spherical chamber through electrically heated lines to preclude condensation. Gas chromatographic analysis showed that the final mixtures in the combustion chamber contained less than 1000 ppm of formaldehyde (less than 2% of the fuel), indicating some impurity and/or decomposition of trioxane. It is worth noting that our preliminary trioxane vaporization attempts using a stainless steel vaporization flask found substantial ($\sim 40\%$) trioxane decomposition to CH_2O .

Experiments were conducted at an initial pressure of 1 ± 0.003 atm and initial temperature of 373 ± 1 K for a fixed 5% (molar) fuel loading. In order to sensitize the flame speed to the competition of the HCO reactions as a function of temperature while maintaining a single characteristic transport environment and

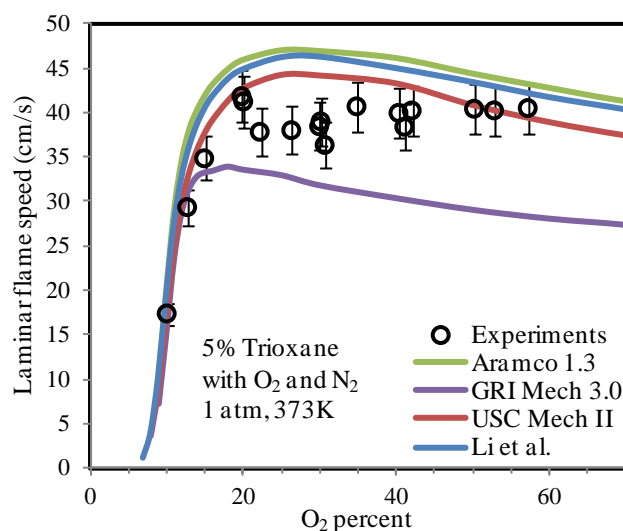


Figure 1: Laminar flame speed of 1,3,5-trioxane at 1 atm and 373 K with varying O_2 content. Experimental measurements are compared to predictions of several base kinetic models [13-16].

adiabatic flame temperature, the oxygen/nitrogen ratio was varied for this study. Provided there is sufficient O_2 to oxidize the fuel (lean conditions), the Lewis number and flame temperature will remain nearly constant for these mixtures since O_2 and N_2 have similar transport properties and specific heats. Control of these transport and enthalpic considerations permits a more direct interpretation of the HCO kinetics subsequently discussed.

2.2. Kinetic modeling approach

Laminar flame speed predictions of several base kinetic models [13-16] sharing a common trioxane kinetic submodel have been computed using the PREMIX code [23] to simulate planar, adiabatic flames with multi-component transport and Soret diffusion. Gradient and curvature tolerances were set to 0.05 or lower. The trioxane submodel employed includes one additional species (trioxane) and seven

additional reactions involving abstraction of H atoms and thermal decomposition of trioxane. Additional reaction parameters are taken from the literature where available ([6, 24]), or estimated by analogy with H abstraction reactions from formaldehyde [16, 24]. The 1,3,5-trioxan-2-yl produced by abstraction of H atoms from trioxane is assumed to spontaneously decompose into $2 CH_2O + HCO$ following the mechanism considered in the study of Curioni *et al.* [25]. Thermodynamic and transport properties for trioxane are taken from [26, 27]. Computed flame speeds are found to be insensitive to the H abstraction reactions since the fuel decomposes to form CH_2O early in the flame before significant abstraction reactions with trioxane can occur. Predicted flame speeds were found to change by no more than 1.6% when the H abstraction reaction rates were increased by a factor of 100, confirming the extremely low sensitivity to these reactions.

3. Results and Discussion

3.1. Experimental and modeling results

Experimental results are compared to kinetic modeling results in Figure 1. The measured flame speed rises sharply as the oxygen content increases to a slightly fuel-lean equivalence ratio of 20% O_2 . At yet leaner conditions, with oxygen contents above 20%, the flame speed appears unaffected by the oxygen concentration within experimental uncertainty bounds. None of the models investigated [13-16] *qualitatively* reproduce the observed experimental behavior at fuel-lean conditions; all models predict a slightly decreasing flame speed with increasing oxygen content. The models do *quantitatively* agree with the few measurements for fuel rich conditions ($< 15\% O_2$), but predictions deviate from results for lean conditions, with all models overpredicting the flame speed except for GRI Mech 3.0 [14], which predicts much slower flame speeds. It is worth noting that the GRI Mech 3.0 optimization increased the ratio $R4/R3$ by a factor of 1.78 from the Timonen *et al.* [28, 29] recommendations employed by earlier releases of the GRI kinetic models. This alteration favors reaction of HCO by R4, which tends to slow predicted flame speeds. Interestingly, the relative difference between GRI 3.0 and the predictions of other kinetic models provides an indication of the constraining value of the present experiments and the importance of the rate ratio between the competing HCO reactions.

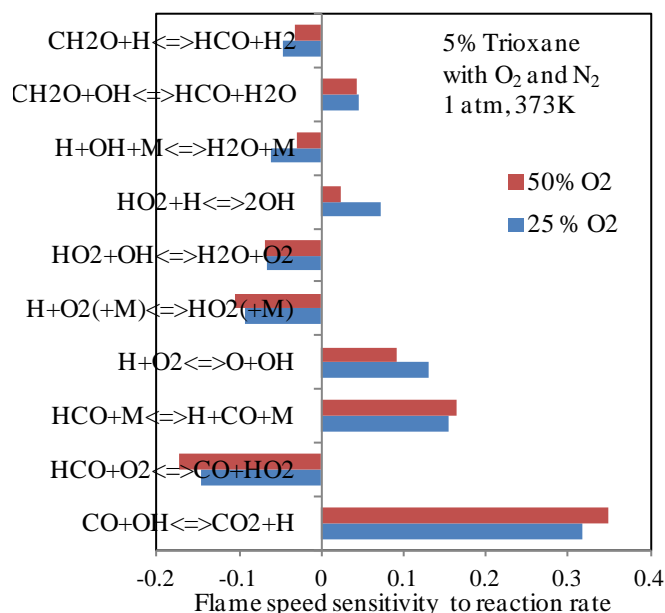


Figure 2: Flame speed sensitivity to elementary reaction rate A-factors. Calculated using the Li *et al.* model [16].

3.2. Flame chemistry

The model predictions of a significantly decreasing flame speed with increasing oxygen content may appear counterintuitive since this is a unique phenomenon, not seen in simulations for other fuels at similar conditions; however, this behavior results directly from competition between the HCO reactions. Reaction path flux analysis of the kinetic model predictions for fuel lean conditions shows a direct, primary oxidation path from trioxane \rightarrow $\text{CH}_2\text{O} \rightarrow \text{HCO} \rightarrow \text{CO} \rightarrow \text{CO}_2$. In all cases, trioxane decomposes unimolecularly to form 3 CH_2O with minimal additional flux through radical reactions. As oxygen is added above the 15% stoichiometric requirement, the fluxes through parallel competing pathways along this straight oxidation route are altered. With increasing oxygen, radical attack by OH on CH_2O is favored over attack by H, leading to decreased branching, as H_2O is formed rather than OH. However, this is somewhat moderated by increased attack by O atoms, forming OH radicals. The major change with O_2 addition is in the $\text{HCO} \rightarrow \text{CO}$ pathways. With increasing oxygen loading, R4 is increasingly favored over R3. Because H radicals are significantly more reactive than HO_2 radicals, the shift to HO_2 formation leads to a decreased branching rate and consequently, a lower flame speed at high oxygen content. When changing from 25% O_2 to 50% O_2 , the ratio of fluxes of the HO_2 pathway to the H pathway increases from 1.6 to 2.5.

However, there is a mechanism to counteract the decreased branching at high O_2 content. A major source of radical chain branching is the reaction $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ (R1). While this reaction competes with R2, increasing O_2 content does not directly affect the competition between these two reactions – it only increases the rates of both relative to other H consumption reactions, which are often chain-carrying or terminating. It appears that predictions of several of the kinetic models could be improved if the rates of the HCO reactions were decreased relative to the rates of the $\text{H} + \text{O}_2$ reaction pair, so that the increased branching with higher O_2 content caused by R1 would counteract the overall inhibiting effects of O_2 on the HCO reaction pair. Though the rate coefficient ratio of the $\text{H} + \text{O}_2$ reaction pair is reasonably well established over a large range of temperatures and pressures, present uncertainties in the rate coefficients of both HCO reactions may permit the adjustment recommended above. In fact, a recent recommendation for the reaction rate of R4 [30] is slower than the rates used in the models investigated here.

A sensitivity analysis (Fig. 2) reveals that the most sensitive reaction is $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$. This is frequently a highly sensitive reaction in

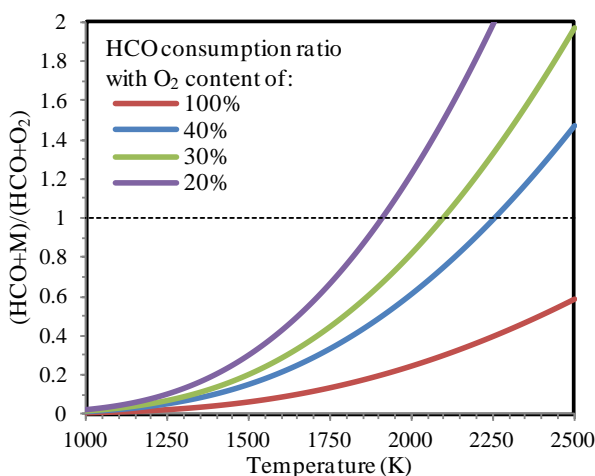


Figure 3: Reaction rate ratio of $\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$ to $\text{HCO} + \text{O}_2 = \text{HO}_2 + \text{CO}$ with varying oxygen content. Calculated using the Li *et al.* model [16].

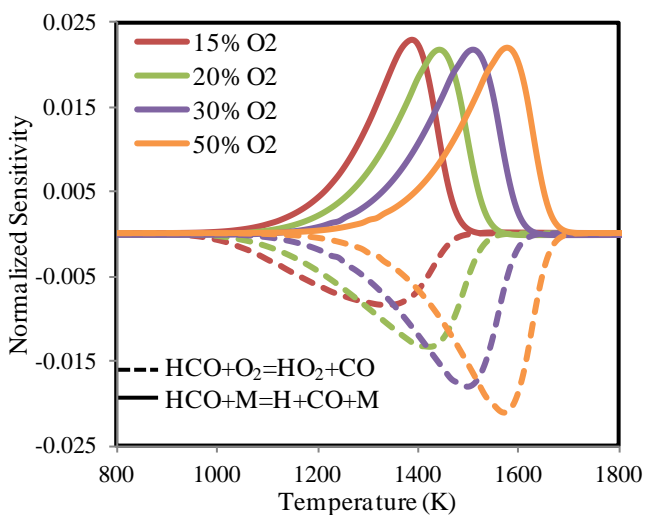


Figure 4: Temperature window sensitivity of flame speed to the major HCO consumption reactions with varying oxygen content. Calculated using the Li *et al.* model [16].

flames, as it is the major source of heat release, and the vast majority of carbon in the system proceeds through this reaction to form CO_2 . Despite its sensitivity, the rate coefficient for this reaction has very low uncertainty – generally considered to be better than chemical accuracy [31]. The next most sensitive reactions are the two HCO consumption reactions. These two reactions are particularly sensitive as a consequence of the present experimental design. Simulations show that ~90% of fuel carbon passes through these reactions, and these pathways control radical chain branching. These HCO consumption reactions are likely the cause of predictive discrepancy due to their relatively high uncertainties and sensitivities.

The varied oxygen content in the present experiments alters the temperature dependence of the HCO reaction rate ratio R3/R4 (Fig. 3), such that the HCO reactions are co-sensitized at varying temperatures depending on the O_2 loading. Increasing oxygen linearly increases the rate of R4, decreasing the overall radical branching rate and increasing the crossover temperature for HCO radical (Fig. 3). Due to this changing temperature window, experimental mixtures are sensitive to HCO reactions at different temperatures within the flame. Figure 4 shows the results of a temperature window sensitivity analysis based on the methodology developed in [32] and used extensively in developing the Li *et al.* model [16]. Unlike a conventional sensitivity analysis where each reaction rate is perturbed uniformly over the entire temperature range, this analysis results from perturbing individual elementary reaction rates by a temperature-dependent Gaussian function in order to determine the temperature range where the flame speed is most sensitive to each reaction. Figure 4 clearly shows that altering the oxygen content allows the HCO consumption pathways access to different temperature ranges. Based solely on this analysis, the temperature dependence of the branching ratio between R3 and R4 should be altered to decrease the radical branching rate at lower temperatures (~1200-1500 K, or ~20-30% O_2) relative to the chain branching rate above ~1500 K in order to improve predictions, if there is further support from calculations or other sensitized experiments. Towards integrating these specific temperature-dependent results into the general sensitivity/uncertainty analysis presented earlier, further application of this temperature window sensitivity analysis for reactions other than those involving HCO consumption is warranted in extension of the present work.

4. Conclusions

Flame speeds of 5% 1,3,5-trioxane blended with varying mole fractions of N_2 and O_2 were measured at atmospheric pressure using the outwardly propagating spherical flame technique. At lean conditions (O_2 loadings exceeding ~20%), measured flame speeds appear to be unaffected by increasing O_2 content in the unburned gas. This trend is counter to predictions of several base literature kinetic models [13-16], which uniformly show reductions in flame speed as O_2 loading increases. These predictions result from strong co-sensitization of the competing HCO reactions $\text{HCO}+\text{M}=\text{H}+\text{CO}+\text{M}$ (R3) and $\text{HCO}+\text{O}_2=\text{HO}_2+\text{CO}$ (R4), which suggest the value of the present data in constraint of kinetic models.

Systematic discrepancies between experimental measurements and the predictions of several unoptimized kinetic models are likely due to the rate coefficients used to describe the competing HCO consumption reactions, R3 and R4. Combined sensitivity/uncertainty analysis suggests that the net radical chain branching ratio through both HCO reactions apparently needs to be reduced relative to the better characterized rate coefficients of the $\text{H}+\text{O}_2$ reaction pair.

Acknowledgements

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