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High temperature oxidation of formaldehyde and formyl radical: A study of 1,3,5-trioxane laminar burning velocities

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Abstract

Few studies of formaldehyde flames are available, especially at pressures greater than 55 torr, due to the difficulties and hazards associated with producing formaldehyde vapor. This work experimentally and numerically investigates the flame properties of formaldehyde (CH_2O) and formyl radical (HCO) at high O_2 loadings and both atmospheric and reduced pressure by measuring and modeling the laminar burning rates of 1,3,5-trioxane/ O_2/N_2 mixtures. Trioxane is shown to decompose nearly exclusively into high concentrations of formaldehyde early in the flame structure before subsequent flame chemistry reactions occur. Kinetic model predictions show that the flame properties are controlled by CH_2O and HCO kinetics. Laminar burning rate predictions of several combustion kinetic models vary significantly in comparison to experimental data and each other; however, all simulations show that the present observations are particularly sensitive to the competition between reactions $\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$ (R3) and $\text{HCO} + \text{O}_2 = \text{HO}_2 + \text{CO}$ (R4). Monte Carlo optimization of these rate coefficients allows interpretation of the measured flame speeds as indirect rate coefficient measurements at flame relevant temperatures. Although results from simple A-factor optimization agree well with the present measurements, three-parameter optimization is shown to be necessary in order to accurately model kinetics across a wide temperature range, including high temperature flames and low temperature direct rate measurements. A-factor and three-parameter optimization both show that a reduced k_3/k_4 branching ratio over the temperature range from 1100 to 1700 K improves model predictions compared to present measurements.

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Keywords: Laminar flame speed; Formyl chemistry; Formaldehyde chemistry; 1,3,5-Trioxane; Monte Carlo optimization

1. Introduction

Gas phase combustion chemistry may be described by a hierarchical system wherein fuels react to first form a diversity of intermediates, which subsequently react to form the common products CO_2 and H_2O at the oxidation hierarchy base [1]. Oxidation of virtually all hydrocarbon

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and oxygenated fuels produces the key stable intermediate species formaldehyde (methanal, CH_2O), which then reacts to form formyl radical (HCO), CO , and finally CO_2 . Further, CH_2O is also a carcinogenic, regulated hazardous air pollutant. An improved understanding of its formation and destruction chemistry is therefore vital to the study of energy conversion processes involving combustion.

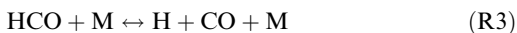
Formaldehyde is toxic, difficult to generate in pure form at high concentrations, oxidatively reactive at low temperatures in the gas phase and on surfaces, and polymerizes to paraformaldehyde at lower temperatures [2]. Thus, its combustion chemistry has been studied principally through low pressure burner-stabilized flame sampling [3–6] or highly diluted flow reactor [7,8] and shock tube [9–13] experiments. 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 CH_2O and HCO flame chemistry.

It has been shown that 1,3,5-trioxane (henceforth “trioxane”) serves as an *in situ* generator of significant quantities of CH_2O since it almost exclusively decomposes unimolecularly to form three formaldehyde molecules [8,14]. Here, premixed laminar burning velocities of trioxane mixtures with different oxygen loadings are measured using outwardly propagating spherical flames. Present computations show that in trioxane flames, decomposition is so rapid that flame properties are almost entirely associated with formaldehyde chemistry. Thus, the use of trioxane permits investigation of CH_2O flame chemistry without the significant difficulties inherent in producing well-defined CH_2O /oxidizer premixtures. Our review of the literature discovered no previous formaldehyde or trioxane burning velocity measurements.

Reactions involving formaldehyde and formyl radicals provide the hierarchical link between hydrocarbon fuels and simpler, well studied fuels such as H_2 and CO . While H_2 and syngas flame chemistry is dominated by competition between R1 and R2 [15],



these reactions are moderated by competition between R3 and R4 in hydrocarbon flames [16],



especially with CO_2 and H_2O dilution typical of exhaust gas recirculation emission control technologies. These two pairs of competing reactions are analogous – both R1 and R3 significantly contribute to reactivity by producing major radical

species H , O , and OH , while both R2 and R4 produce the much less reactive HO_2 radical. 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., [17–19]) validated at flame conditions. However, significantly less progress has been made in the study of the HCO reaction pair, and experimental measurements of R3 and R4 at flame temperatures are generally lacking. The trioxane burning rates at 1 and 0.5 atm offered by the present study provide useful validation data that are highly sensitive to broadly important CH_2O and HCO chemistry at flame conditions.

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 experimental uncertainties are described in detail elsewhere [16,20,21]. From smoothed flame radius *vs.* time history data, the unstretched flame propagation speeds relative to the burned gas $s_{b,0}$ were calculated using the nonlinear extrapolation method (NM I) recommended by Chen [22]. Extrapolation endpoints were determined iteratively by locating the range where the residuals from a nonlinear fit of the data were below a threshold value and using this range to compute a new linear fit. This process was repeated while decreasing the threshold until stable endpoints were found. The extrapolated burning velocity was multiplied by the calculated density ratio [23] to give the flame speed relative to the unburned gas, $s_{u,0}$. The above method excludes measurements affected by transient ignition and flow compression [24], while instabilities and buoyancy effects were negligible.

Preparation of the O_2/N_2 /trioxane 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 R3 and R4. Gaseous trioxane was prepared by hot water immersion of a previously evacuated Pyrex flask containing solid (99%, Sigma-Aldrich) trioxane. Significant vapor pressure is established at ~ 360 K to permit mixture preparation for the experiments by the partial pressure method. Trioxane vapor so produced was conveyed into the spherical combustion chamber through electrically heated lines. Gas chromatographic analysis showed that the final mixtures in the combustion chamber contained less than 1000 ppm of formaldehyde, indicating 98 + % purity of trioxane vapor in the unburned gases. It is worth noting that our preliminary

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