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Effect of prompt dissociation of formyl radical on 1,3,5-trioxane and CH_2O laminar flame speeds with CO_2 dilution at elevated pressure

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ABSTRACT

Many studies of the flame speed of hydrocarbon and oxygenated fuels show that flame speed is very sensitive to formyl radical (HCO) reactions with small species, such as $HCO+M=H+CO+M$ (R_1), $HCO+O_2=HO_2+CO$ (R_2) and $HCO+X=CO+XH$ ($X=H$, OH) (R_3). Through comparison among experimental measurements and kinetic model predictions, this paper investigates CH_2O flame speed sensitivities to the effects of HCO prompt dissociation and CO_2 third-body participation in R_1. The conditions considered include atmospheric and elevated pressures as well as lean, ultra lean, and rich fuel mixtures using 1,3,5-trioxane as the CH_2O precursor. The experimental results provide key validation targets for CH_2O and HCO chemistry and the R_1 third-body coefficient of CO_2 in flames. Five mechanisms, GRI Mech 3.0 (Smith et al., 1999), Li Mech (Li et al., 2007), USC Mech II (Wang et al., 2007), HP Mech (Shen et al., 2015), and Aramco Mech 1.3 (Metcalfe et al., 2013) are compared against the experimental data. Model predictions indicate that the prompt reaction pathway has a significant effect on the flame speed. With an increase in pressure or the addition of CO_2, the kinetic between the prompt reaction and R_1 slightly reduces the prompt radical dissociation effect. On the other hand, an increase of O_2 mole fraction enhances the prompt effect on the flame speed. Comparisons among experiments and model predictions show that the HP Mech with the prompt reactions, USC Mech, and Li Mech have better predictions of the flame speed at lean, ultra-lean, rich, and lean with CO_2 conditions than GRI Mech and Aramco Mech. However, the predictions of USC Mech and Li Mech with prompt reactions show increased discrepancy between experiments and predictions. This result indicates that by including a new reaction pathway, an optimized model may fail beyond the validated experimental conditions. On the other hand, an elementary rate-based, non-optimized model like HP Mech can improve the prediction by directly adding the missing prompt reaction pathway.

1. Introduction

At both low and high combustion temperatures, oxidation of virtually all hydrocarbons and oxygenated fuels produces formaldehyde (CH_2O), a key intermediate species, with important pathways to the production of H and HO_2 from formyl radical (HCO), and to the formation of CO and CO_2 subsequently [1,2]. Moreover, CH_2O and CO emissions are harmful to the environment as well as to human health. Thus, it is important to investigate CH_2O and HCO chemistry in combustion processes. Different experimental methods such as flow reactors [3,4], low pressure burner-stabilized flames [5–8], and shock tubes [9–12] have been used to understand CH_2O and HCO chemistry in combustion. However, as CH_2O is difficult to be produced in pure form at high concentrations and is reactive in the gas phase at low temperatures [1,13], its experimental database for kinetic study is relatively limited.

On the other hand, the studies of high temperature flame chemistry of hydrocarbons and oxygenated fuels, such as dimethyl ether [14], diethyl ether [15], and methyl propanoate [16], all indicate that flame speeds for these fuels are very sensitive to CH_2O and HCO chemistry through the following competing reactions for H atom production and consumption,

$$HCO+M=H+CO+M \quad (R_1)$$

$$HCO+O_2=HO_2+CO \quad (R_2)$$

$$HCO+X=CO+XH \ (X=H,\ OH) \quad (R_3)$$

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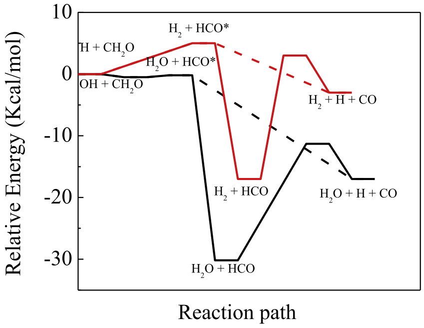

Fig. 1. Schematic of the potential energy surfaces for CH_2O reactions with H and OH atoms [23].

where HCO is mainly produced from CH_2O reactions with H, O, or OH. Unfortunately, although these reaction rates were calculated and optimized in kinetic models to fit the selected target data, there still remains a large uncertainty in the reaction rates (factor of 2–3) [17–22] and in the model predictions of flame speeds [14–16]. Santner et al. [1] have investigated CH_2O and HCO flame chemistry effects on atmospheric pressure flame speed by using 1,3,5-trioxane (henceforth trioxane), which decomposes into CH_2O in the flame preheat zone and serves as an *in situ* precursor of CH_2O in high temperature flames. Computations showed that the characteristic decomposition time of trioxane to three CH_2O molecules in flames was much less than its oxidation reaction time with the O_2 present in the preheat zone, and thus, the flame properties of trioxane were almost completely governed by CH_2O chemistry. The study by Santner et al. [1] showed that the kinetic model predictions varied significantly in comparison with the experimental data and all of the model simulations showed a significant sensitivity to CH_2O and HCO kinetics, and therefore, trioxane flames can serve as a good platform to examine the uncertainty of high temperature CH_2O and HCO combustion kinetics.

More recently, a prompt dissociation reaction pathway of HCO to directly form CO and H atom via CH_2O reactions with radicals has been found by using direct dynamics calculations [23]. This prompt reaction (R_4) provides a new pathway

$$HCO^* = H + CO \text{ or } CH_2O + X = H + CO + HX \ (X = OH,\ H,\ \text{or } O) \quad (R_4)$$

$$P_{diss,X=OH} = 3.308E+3 \times T^{-0.938} \exp(-10426[cal/(mol \cdot K)]/RT)$$
$$P_{diss,X=H} = 8.718E+3 \times T^{-0.948} \exp(-10014[cal/(mol \cdot K)]/RT)$$
$$P_{diss,X=O} = 5.986E+9 \times T^{-2.473} \exp(-19914[cal/(mol \cdot K)]/RT)$$

for the production of H atom to accelerate chain-branching reactions. Here, HCO^* indicates HCO molecules in a non-equilibrium excited state leading to HCO prompt dissociation. The prompt-dissociation probabilities $P_{diss,X}$ for CH_2O reaction with X=OH, H, and O at 1 atm are also listed here. HCO, one of the most common weakly bonded radicals in combustion, has a low dissociation threshold such that time scales for the non-equilibrium dissociation and collisional relaxation become comparable at high temperatures. This permits a significant amount of prompt HCO dissociation to H+CO directly, instead of forming equilibrated HCO that then participates in reactions via R_1–R_3. As shown in Fig. 1, the excited formyl radical, HCO^*, produced from CH_2O, can decompose to H+CO directly through R_4 as an alternative to stepwise reactions of equilibrated HCO through the R_1 reaction channel. It is interesting to note that, with increasing pressure, the prompt reaction pathway will become weaker as collisions are enhanced in the collisional relaxation pathway. By including the HCO prompt reaction, model predictions [23] of trioxane flames [1] showed that flame speeds were increased by 10–15% at 1 atm. However, no experimental studies have been carried out to investigate the effect of the HCO prompt dissociation on the CH_2O flame speed at elevated pressure. Moreover, in practical combustion, CO_2 from exhaust gas recirculation plays a critical role in the collisional energy relaxation of HCO^*, and it is not clear how CO_2 collisional energy transfer will affect the prompt reaction or flames.

Using experimentally measured and model-predicted trioxane flame speeds at ambient and elevated pressures, this paper describes experimental and kinetic modeling investigations of the effects of HCO prompt dissociation and CO_2 collisional energy relaxation on CH_2O/HCO chemistry. At first, the laminar flame speed of trioxane/O_2/N_2 mixtures with varying O_2 mole fraction at atmospheric pressure was measured in a constant pressure spherical bomb to validate Santner's experimental data [1]. Secondly, the trioxane flame speed at elevated pressure was measured at lean, ultra-lean, rich, lean with CO_2 addition, and rich with CO_2 addition conditions. Thirdly, the predictions of different kinetic models with and without including the prompt reaction were used to compare against the experimental data and each other. The effect of radical production via the prompt reaction pathway at different conditions was examined. Finally, the effects of pressure, O_2 content, and CO_2 dilution on the prompt dissociation of HCO were analyzed.

2. Experimental and modeling methods

2.1. Experimental methods

Experiments were conducted in a heated, high-pressure constant-volume spherical chamber (Fig. 2). The chamber was housed in a temperature-controlled oven. Temperature uniformity in the oven was increased by use of two mechanical fans. At first, the chamber was vacuumed and filled with a small amount of inert gas to avoid the trapping of fuel in crevices and pressure gauge lines. Then, gaseous trioxane was prepared by the hot water immersion of an evacuated Pyrex flask containing solid trioxane (99%, Sigma-Aldrich). The flask was heated to 360–370 K to permit trioxane vapor filling into the chamber through electrically heated gas supply lines. According to gas chromatographic analysis, less than 1000 ppm of formaldehyde was detected in the final mixture, indicating a more than 98% purity of trioxane vapor in the gas mixture. The unburned gas reactant mixture was prepared by using the partial pressure method. The validation experiments (trioxane / O_2 / N_2) against previous experimental data [1] were conducted at atmospheric pressure with an initial temperature of 373 K. The fuel loading was fixed at 5% (molar), and O_2 loading varied from 10% to 55% with N_2 as the diluent. As shown in Table 1, high pressure experiments were then conducted at lean, ultra-lean, rich, lean with CO_2 addition and rich with CO_2 addition conditions to examine the effect of pressure, oxygen concentration, and collisional energy transfer of CO_2 on the prompt HCO reaction effect. Helium and nitrogen were added to adjust the mixture Lewis number and the flame temperature to prevent excessive thermal expansion, ignition difficulty, buoyancy effects, cellular instability, and to reduce the extrapolation uncertainty.

After the central ignition of the quiescent combustible mixture, the unsteady flame propagation speed was quantified by using the high-speed schlieren imaging method at a frame rate of 15,000/s. The time history of flame radius data was collected with an automatic flame-edge detection and circle-fitting program of MATLAB. The un-stretched flame speed relative to the burned gas, S_b, was calculated using the nonlinear extrapolation method by Chen [24,25], and this extrapolated burned flame speed was multiplied by the density ratio, calculated in PREMIX [26], to give the flame speed relative to the unburned gas, S_u. Uncertainties in the trioxane flame speeds mainly come from uncertainties in the fuel mole fraction and the trioxane conversion to formaldehyde. The