



Effect of prompt dissociation of formyl radical on 1,3,5-trioxane and CH₂O laminar flame speeds with CO₂ 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 $\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$ (R₁), $\text{HCO} + \text{O}_2 = \text{HO}_2 + \text{CO}$ (R₂) and $\text{HCO} + \text{X} = \text{CO} + \text{XH}$ (X=H, OH) (R₃). Through comparison among experimental measurements and kinetic model predictions, this paper investigates CH₂O flame speed sensitivities to the effects of HCO prompt dissociation and CO₂ third-body participation in R₁. 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 CH₂O precursor. The experimental results provide key validation targets for CH₂O and HCO chemistry and the R₁ third-body coefficient of CO₂ 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 CO₂, the kinetic between the prompt reaction and R₁ slightly reduces the prompt radical dissociation effect. On the other hand, an increase of O₂ 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 CO₂ 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.

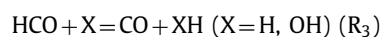
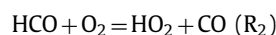
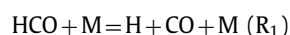
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1. Introduction

At both low and high combustion temperatures, oxidation of virtually all hydrocarbons and oxygenated fuels produces formaldehyde (CH₂O), a key intermediate species, with important pathways to the production of H and HO₂ from formyl radical (HCO), and to the formation of CO and CO₂ subsequently [1,2]. Moreover, CH₂O and CO emissions are harmful to the environment as well as to human health. Thus, it is important to investigate CH₂O 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 CH₂O and HCO chemistry in combustion. However, as CH₂O

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 CH₂O and HCO chemistry through the following competing reactions for H atom production and consumption,



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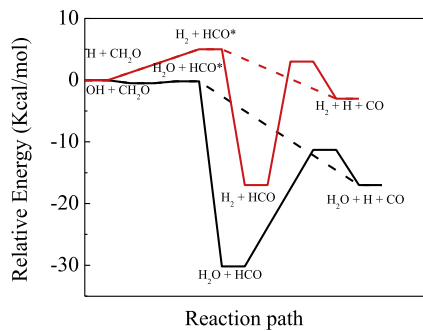
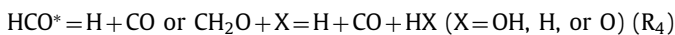


Fig. 1. Schematic of the potential energy surfaces for CH_2O reactions with H and OH atoms [23].

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



$$P_{\text{diss}, \text{X}=\text{OH}} = 3.308\text{E} + 3 \times T^{-0.938} \exp(-10426[\text{cal}/(\text{mol} \cdot \text{K})]/RT)$$

$$P_{\text{diss}, \text{X}=\text{H}} = 8.718\text{E} + 3 \times T^{-0.948} \exp(-10014[\text{cal}/(\text{mol} \cdot \text{K})]/RT)$$

$$P_{\text{diss}, \text{X}=\text{O}} = 5.986\text{E} + 9 \times T^{-2.473} \exp(-19914[\text{cal}/(\text{mol} \cdot \text{K})]/RT)$$

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 $P_{\text{diss}, \text{X}}$ for CH_2O reaction with $\text{X} = \text{OH}, \text{H},$ 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 $\text{H} + \text{CO}$ 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 $\text{H} + \text{CO}$ 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 experi-

mental 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 $\text{CH}_2\text{O}/\text{HCO}$ 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

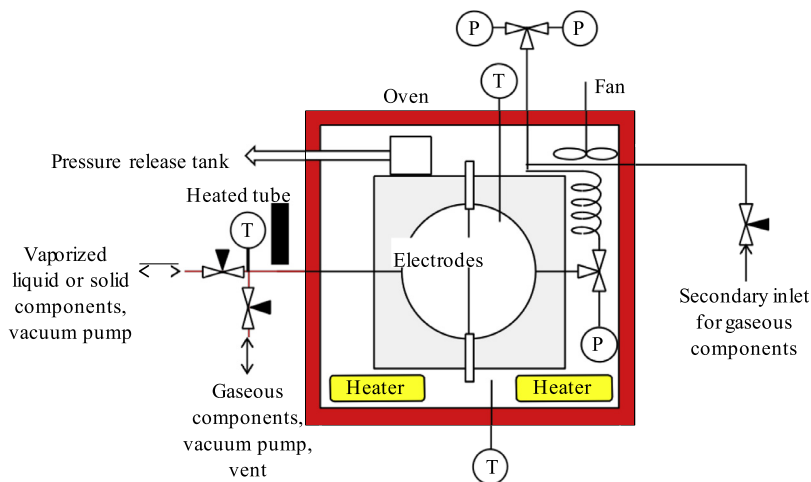


Fig. 2. Schematic of the spherical chamber.

Table 1

Experimental conditions of trioxane flame speed measurement at elevated pressure. T_f is the calculated adiabatic flame temperature at 1 atm.

Case	Equivalence ratio	Trioxane (%)	O ₂ (%)	CO ₂ (%)	N ₂ (%)	He (%)	Pressure range (atm)	T_f (K)
Lean	0.7	0.0454	0.1946	0.0000	0.5846	0.1754	1–9	1900
Ultra-lean	0.34	0.0454	0.4000	0.0000	0.3792	0.1754	1–9	1882
Rich	1.4	0.0889	0.1904	0.0000	0.5544	0.1663	1–5	2000
Lean with CO ₂	0.7	0.0491	0.2103	0.2000	0.2201	0.3206	1–9	1900
Rich with CO ₂	1.4	0.0943	0.2021	0.2000	0.1266	0.3770	1–4	2000

major source of the flame speed uncertainty is the fuel concentration at lean conditions due to the partial pressure method. A fuel mole fraction uncertainty of 1.4% at 1 atm experiments leads to flame speed uncertainties up to 4%. The uncertainty due to 2% formaldehyde content (impurity) in the fuel causes up to 4% biased uncertainty in flame speeds. The total uncertainty, calculated from the root-mean-square sum of the uncertainties from different sources, is around 5–10%. Details of the apparatus, procedures of flame speed extraction, and experimental uncertainties are described elsewhere [1,27,28].

2.2. Kinetic modeling method

Several CH₂O combustion kinetic models, HP Mech [29,30], USC Mech II [31], Aramco Mech 1.3 [32], Li Mech [17], and GRI Mech 3.0 [33] were used to compute the laminar flame speed using PREMIX [26] with an addition of a trioxane kinetic sub-model [1]. Normalized gradient and curvature tolerances for the computational grid refinement were set to 0.03. Using the trioxane decomposition sub-mechanism, it was confirmed that the computed flame speed was insensitive to the rate of the trioxane decomposition reaction as well as its H abstraction reactions as trioxane decomposed to form CH₂O rapidly in the flame preheat zone [1]. Even though the rate coefficients of all the trioxane reactions were simultaneously increased by a factor of 100, the change of the predicted flame speed was less than 1.6%, confirming the low sensitivity to the rates of these reactions and ruling out the coupling uncertainty between trioxane chemistry and CH₂O chemistry. Furthermore, the prompt reaction subsets (CH₂O+H, CH₂O+OH, and CH₂O+O) for 1 and 10 atm [23] were added, respectively, to the mechanisms mentioned above to examine how the prompt reactions affect the flame chemistry and the flame speed at different pressure, oxygen contents, and CO₂ dilution conditions. From our simulation, the prompt effect related to other HCO reactions is negligible. The prompt reactions added to the five models are attached in the Supporting Information.

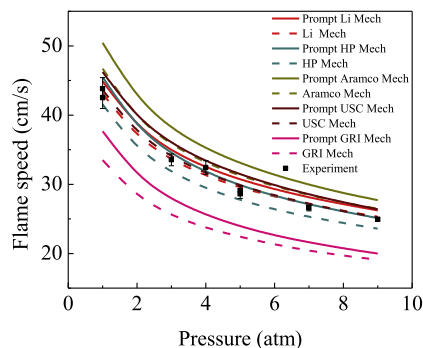


Fig. 3. Laminar flame speed of trioxane with varying pressure at the lean condition ($\phi=0.7$), no CO₂ dilution.

3. Results and discussion

The validation experimental data compared favorably with the results of Santner et al. [1] within, at most, 10% discrepancy (Fig. S1). Given the large difficulty in vaporizing solid fuels, the less than 10% discrepancy at 1 atm indicates a good repeatability for this experimental setup. Notably, since the major uncertainty of flame speed measurements originates from the uncertainty of the fuel mole fraction due to the partial pressure method, the uncertainty of the fuel mole fraction at higher pressure will be proportionally reduced.

The experimental results of measured flame speeds at elevated pressure for the lean condition at equivalence ratio of 0.7 are compared with the modeling results in Fig. 3. With the increase of pressure, the measured flame speed decreases dramatically as expected, and all of the five kinetic models reveal the pressure dependence of the flame speed clearly. Furthermore, it is seen that the prompt reaction has a significant effect on the flame speed predictions using the five models. Specifically, with including the

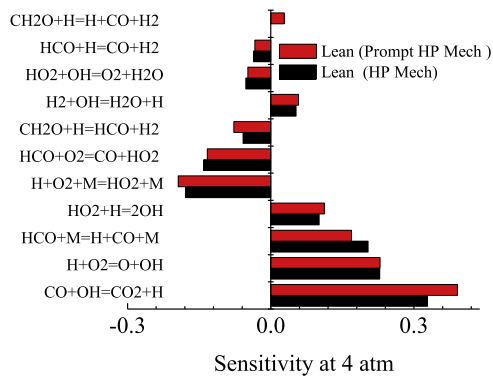


Fig. 4. Trioxane flame speed sensitivity to elementary reaction rate coefficient A-factors at the lean condition ($\varphi=0.7$) and 4 atm, no CO_2 dilution. HP Mech and Prompt HP Mech were used for the calculations.

prompt reaction pathway, the predicted flame speed is increased by 6–10%. To quantitatively examine the effect of the prompt reaction on the flame speed, a parameter, the normalized change of the flame speed between the original model and the prompt model, is defined as,

$$\text{Normalized Change of Flame Speed} = (S_{u,\text{prompt}} - S_u) / S_u = \delta S_u / S_u \quad (1)$$

where, $S_{u,\text{prompt}}$ is the flame speed predicted by the model with the HCO prompt reaction pathway, and S_u is the flame speed predicted by the model without including the prompt reaction pathway. As will be shown below, $\delta S_u / S_u$ decreases slightly with pressure, indicating a decreased effect of prompt reaction pathway on the flame speed with the increase of pressure. That is because R_1 is favored with the increase of pressure, while the increase of pressure deactivates the non-equilibrium HCO^* population more rapidly by collisional energy relaxation. Thus, the relative contribution of H atom production from the prompt HCO reaction becomes smaller with the increase of pressure.

Moreover, it should be noted that while the original Li Mech and USC Mech predict the flame speed very well, the addition of the prompt reaction pathway increases their predicted flame speed. On the other hand, the inclusion of the prompt reaction pathway in the HP Mech improves the prediction of the experimentally measured flame speed. This may be caused by the fact that HP Mech is assembled by choosing the measured and/or calculated elementary reaction rates without any optimization, but the Li Mech and USC Mech have the reaction rates optimized to fit a range of experimental targets. Therefore, when a new reaction pathway is identified, an elementary rate-based model has an opportunity for improving predictions but an optimized model may lose predictive accuracy until it is optimized again. This is an interesting observation. Moreover, Fig. 3 shows that both the original Aramco Mech and Prompt Aramco Mech over-predict the experimental flame speed substantially while both the original GRI Mech and Prompt GRI Mech under-predict the data.

According to the sensitivity analysis of the flame speed at the lean condition and 4 atm (Fig. 4), $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ is the most sensitive reaction as it is the main reaction for chemical heat release in the flame, and the next most sensitive reactions are the $\text{H} + \text{O}_2$ competing pair, $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ and $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$. However, the uncertainties associated with rate coefficients for these three reactions are considered to be low relative to those of the HCO chemistry currently under examination [34]. After these three reactions, the HCO consumption reactions, R_1 and R_2 , to produce active H atom and inactive HO_2 , respectively, in the flame zone are the third most sensitive reaction pair. As stated above,

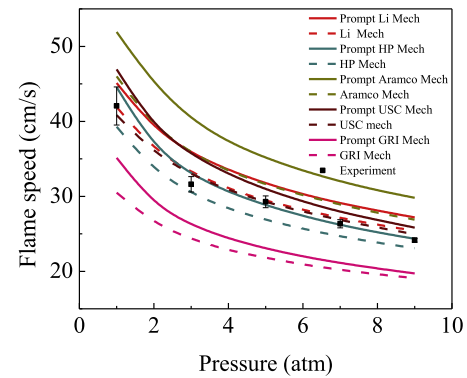


Fig. 5. Laminar flame speed of trioxane with varying pressure at the ultra-lean condition ($\varphi=0.34$), no CO_2 dilution.

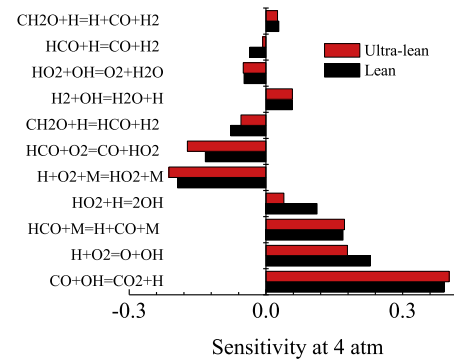


Fig. 6. Trioxane flame speed sensitivity to elementary reaction rate coefficient A-factors at lean ($\varphi=0.7$) and ultra-lean ($\varphi=0.34$) conditions and 4 atm, no CO_2 dilution. Prompt HP Mech was used for the calculations.

the flame speed is very sensitive to HCO kinetics through R_1 – R_3 . Unfortunately, there is a large uncertainty of the rate coefficient for R_1 [17–22] and there are few directly measured rate constants for R_2 and R_3 . Compared to the original model, flame speed sensitivities to R_1 – R_3 decrease when the prompt reaction pathway is included and the sensitivity of the prompt reaction is noticeable in Fig. 4.

The predicted and measured flame speeds at the ultra-lean condition ($\varphi = 0.34$) with varying pressure are shown in Fig. 5. It is seen that the flame speed dependence on pressure in the ultra-lean case is similar to that in the lean case. For both cases, the flame temperature and Lewis number are nearly the same as N_2 and O_2 have similar specific heat and transport properties. The major difference is that the ultra lean case has a higher oxygen concentration such that one of the HCO competing reactions, R_2 , is more favored than R_1 and R_3 , shifting the HCO pathway to produce more HO_2 than H atom (R_1) from HCO. As HO_2 is much less reactive than H atom in high temperature flames, the trioxane flame speed in the ultra-lean case is expected to be slightly lower than that in the lean case and the effect of the prompt reaction pathway will be more important as well. This is confirmed by comparing Fig. 3 and Fig. 5. Similar to the lean case, at the ultra lean condition, Li Mech, USC Mech, and Prompt HP Mech all predict the experimental flame speed well. Once again, both of Aramco Mech and Prompt Aramco Mech over-predict the experimental flame speed to some extent, while both of GRI Mech and Prompt GRI Mech under-predict the experimental data. The A-factor sensitivity analysis presented in Fig. 6 shows clearly that compared with the lean case, in the ultra lean case, the flame speed sensitivity to $\text{HCO} + \text{O}_2$ reaction (R_2) is increased because of

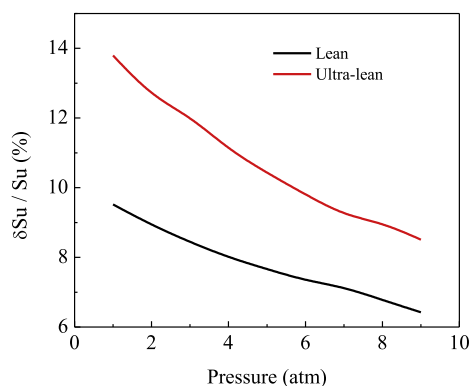


Fig. 7. Normalized Change of Flame Speed, $\delta S_u / S_u$, with varying pressure at lean ($\varphi=0.7$) and ultra-lean ($\varphi=0.34$) conditions, no CO_2 dilution. HP Mech and Prompt HP Mech were used for the calculations.

the increase of O_2 content, but the sensitivity of $\text{HCO} + \text{H}$ reaction (R_3) is decreased due to the reduced concentration of H atom.

It is also interesting to note that the prompt reaction effect is enhanced with increasing O_2 mole fraction in the ultra-lean case by comparing the Normalized Change of Flame Speed. Figure 7 shows the comparison of dependence of $\delta S_u / S_u$ on pressure between the lean and ultra-lean cases. It is seen that the flame speed change due to the prompt effect is much larger in the ultra-lean case than that in the lean case. This change is consistent with the sensitivity analysis in Fig. 6. With more O_2 content in the ultra-lean case, R_2 is more favored than R_1 and R_3 , and the reactivity of the system decreases with more HO_2 formation from R_2 . As a result, the prompt effect on the flame speed from R_4 is more significant as an additional H atom production channel. This statement is also confirmed from the H atom production analysis in Fig. 8. Compared with the lean case, the fraction of the integrated H atom production from HCO through R_1 decreases in the ultra-lean case. However, the fraction of the integrated H atom production from the prompt reaction pathway via CH_2O by reaction R_4 doubles, suggesting a greater contribution of the prompt reaction pathway in increasing the high temperature reactivity at the ultra-lean condition.

Figure 9 shows the variation in peak mole fractions of radicals (H, OH, and O) with pressure for the lean and ultra-lean cases. It is seen that the mole fractions of O and OH in the ultra-lean case are larger than that in the lean case because of the increased forward reaction rate of $\text{H} + \text{O}_2 = \text{O} + \text{OH}$ chain-branching. However, the H atom mole fraction decreases with increasing O_2 content, ultimately decreasing the reactivity of the system in the ultra-lean case.

The measured and predicted flame speeds at the rich case are compared in Fig. 10. Similarly, the prompt effect is reduced with the increase of pressure as seen from the decrease of $\delta S_u / S_u$ with pressure. At the rich condition, Li Mech, Prompt USC Mech, and Prompt HP Mech have good predictions, while the original USC Mech and HP Mech without the prompt reaction subset under-predict the flame speed. Similar to the lean and ultra-lean cases, Aramco Mech and Prompt Aramco Mech still over-predict the experimental flame speed, while GRI Mech and Prompt GRI Mech under-predict the experimental value. In summary, Prompt HP Mech and Li Mech predict the flame speed better in all rich, lean, and ultra-lean cases than HP Mech and Prompt Li Mech, while USC Mech has a good performance in the two lean cases but not for the rich case. Prompt Li Mech increases the over-prediction in all three cases and Prompt USC-Mech has better performance in the rich case. Therefore, it can be concluded that the model optimizations inherent in Li Mech and USC Mech are effective over

validated experimental conditions. However, beyond the validated experimental conditions or by just simply adding a new reaction pathway, an optimized model may fail to predict the flame speed. On the other hand, a non-optimized elementary rate-based model like HP Mech may fail to predict the flame speed if an important reaction pathway is missed. However, by adding the missing reaction pathway, model predictions may improve. These are the two different approaches in model development and users need to be aware of the boundaries of the validity of these approaches.

The flame speed sensitivity analysis of the rich case is plotted in Fig. 11. It is seen that, compared to the original model, flame speed sensitivities to R_1 – R_3 decrease when the prompt reaction pathway is included and the sensitivity of the prompt reaction is significant. Moreover, the flame speed is very sensitive to HCO kinetics mainly through R_1 and R_2 from the sensitivity analysis of the lean case in Fig. 4, while it is very sensitive to R_1 and R_3 in the rich case in Fig. 11. This corresponds to the decrease of O_2 content but increase of H atom in the rich case. In summary, the flame speed is very sensitive to HCO kinetics through R_1 – R_3 for lean and rich conditions.

Figure 12 shows the effect of CO_2 dilution on the flame speed at the lean with 20% CO_2 condition ($\varphi = 0.7$). Compared to the flame speeds at the lean without CO_2 condition, the flame speeds with CO_2 addition are considerably decreased, even at the fixed adiabatic flame temperature (1900 K). This indicates a strong chemical inhibition effect of CO_2 on the flame speed. Although Li Mech, USC Mech, and Aramco Mech predict the flame speed well at lower pressures, the discrepancy becomes much larger at higher pressures. Alternatively, the Prompt HP Mech has a good (within 10% error) prediction of the flame speed both at lower and higher pressures. The comparison of flame speed sensitivities between the fuel lean cases with and without CO_2 is shown in Fig. 13. With CO_2 dilution, the reaction sensitivity of $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ decreases as expected, but the sensitivities of the radical production channels via $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ and $\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$ either increase or remain the same. Moreover, the sensitivity of the prompt reaction slightly decreases.

Therefore, with CO_2 dilution, on the one hand, R_1 is favored as CO_2 has a large third body collision factor to produce H atoms. On the other hand, H atom is consumed by the two reactions, $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$ and $\text{CO}_2 + \text{H} = \text{CO} + \text{OH}$. Overall, considering the flame speed decreases with CO_2 dilution, the inhibition effect of CO_2 from these latter reactions is larger than the enhancement effect from R_1 . It is interesting to note that, different from O_2 , CO_2 addition reduces the prompt effect on the flame speed (Fig. 14). That is because of the reverse shifting equilibrium of R_4 with CO_2 addition.

The measured flame speed at the fuel rich with CO_2 condition is compared to the kinetic modeling results in Fig. 15. Both the Li Mech and HP Mech without prompt reaction pathways fit the flame speed well. However, all the prompt models have over predictions relative to their respective original models. Four aspects may contribute to the discrepancy: radiation, the third-body collision energy transfer by CO_2 , bath gas effect on the prompt dissociation probability, and the CO_2 kinetic effect. 1) For radiation, recent modeling studies of effects of the radiation absorption on the spherical flame propagation showed that the radiation-induced uncertainty in flame speed measurements could be neglected (within 5%) for different CO_2 diluted mixtures (hydrogen, methane, dimethyl ether and iso-octane) at 1–25 atm [35,36]. 2) The third-body effect of R_1 is investigated by varying the "M" factor of CO_2 from 1 to 12 in HP Mech and Prompt HP Mech (the original value is 3) in Fig. 16. It is seen that even though the collision efficiency factor decreases from 3 to 1 in the Prompt HP Mech, the flame speed decreases by less than 3%. Thus, the large discrepancy between the modeling and experimental results is not

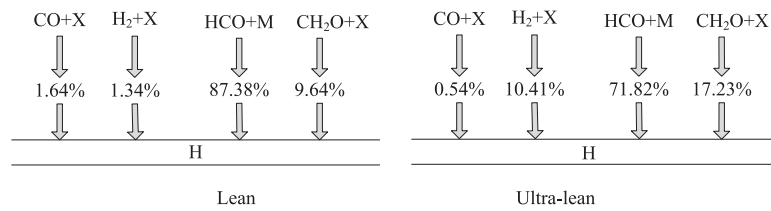


Fig. 8. H atom production analysis on the flame front at lean ($\phi = 0.7$) and ultra-lean ($\phi = 0.34$) conditions and at 4 atm, no CO₂ dilution. Calculations were based on Prompt HP Mech. H atom productions from CO+X, H₂+X, HCO+M, and CH₂O+X are 1.64%, 1.34%, 87.38%, and 9.64%, respectively, at the lean condition, while are 0.54%, 10.41%, 71.82%, and 17.23%, respectively, at the ultra-lean condition. X represents OH and O here.

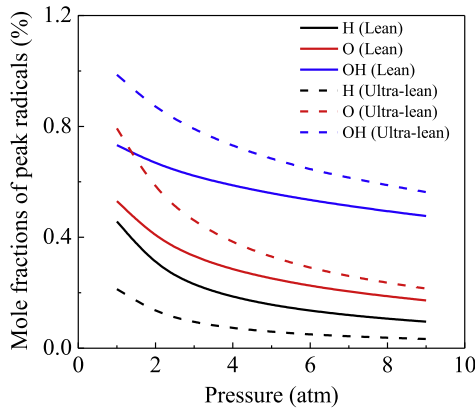


Fig. 9. Mole fractions of peak radicals (H, OH, and O) with varying pressure at lean ($\phi = 0.7$) and ultra-lean ($\phi = 0.34$) conditions, no CO₂ dilution. Prompt HP Mech was used for the calculations.

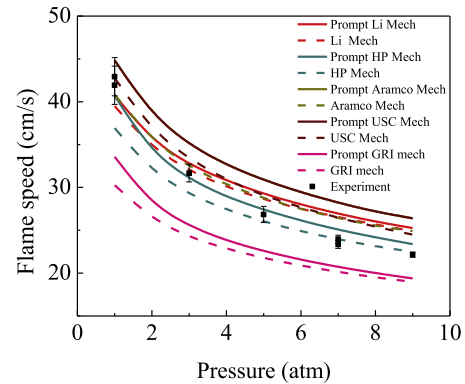


Fig. 12. Laminar flame speed of trioxane with varying pressure at the lean with 20% CO₂ condition ($\phi = 0.7$).

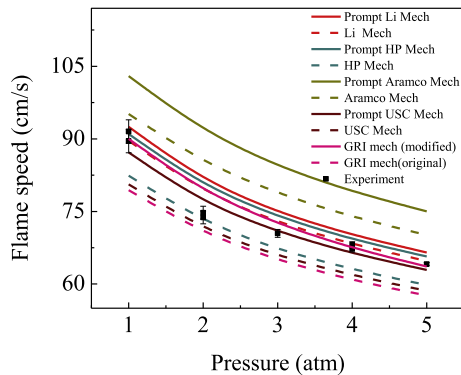


Fig. 10. Laminar flame speed of trioxane with varying pressure at the rich condition ($\phi = 1.4$), no CO₂ dilution.

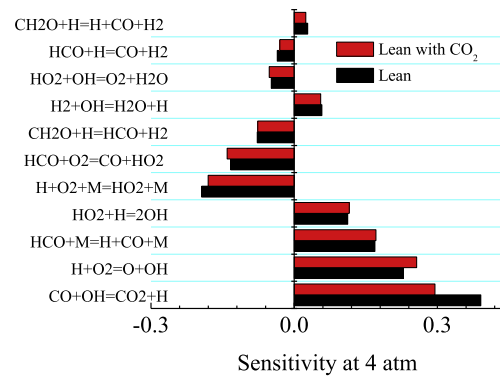


Fig. 13. Trioxane flame speed sensitivity to elementary reaction rate coefficient A-factors at lean and lean with 20% CO₂ conditions ($\phi = 0.7$) and at 4 atm. Prompt HP Mech was used for the calculations.

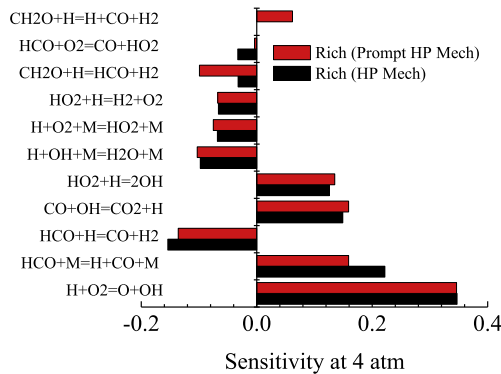


Fig. 11. Trioxane flame speed sensitivity to elementary reaction rate coefficient A-factors at the rich condition ($\phi = 1.4$) and 4 atm, no CO₂ dilution. HP Mech and Prompt HP Mech were used for the calculations.

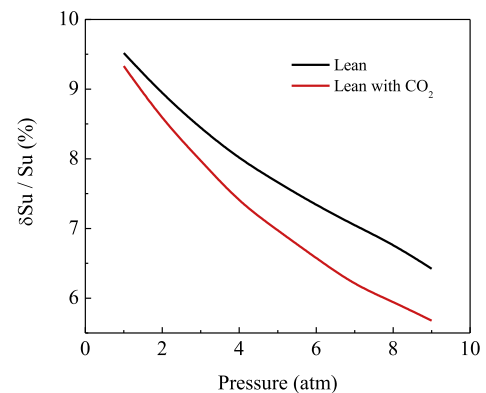


Fig. 14. Normalized Change of Flame Speed, $\delta S_u / S_u$, with varying pressure at the lean and lean with 20% CO₂ conditions ($\phi = 0.7$). HP Mech and Prompt HP Mech were used for the calculations.

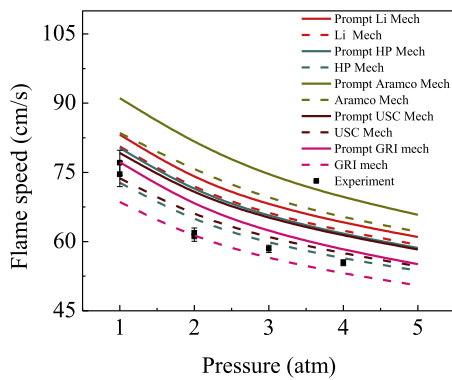


Fig. 15. Laminar flame speed of trioxane with varying pressure at the rich with 20% CO₂ condition ($\phi = 1.4$).

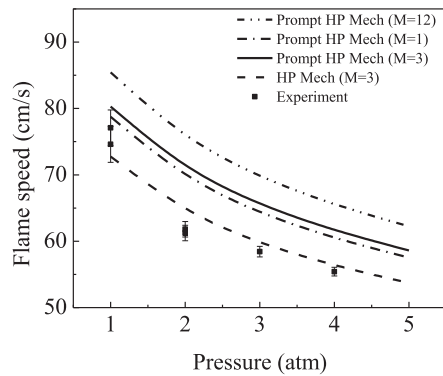


Fig. 16. Laminar flame speed of trioxane with varying pressure and the "M" factor of CO₂ at the rich with 20% CO₂ condition ($\phi = 1.4$). HP Mech and Prompt HP Mech were used for the calculations.

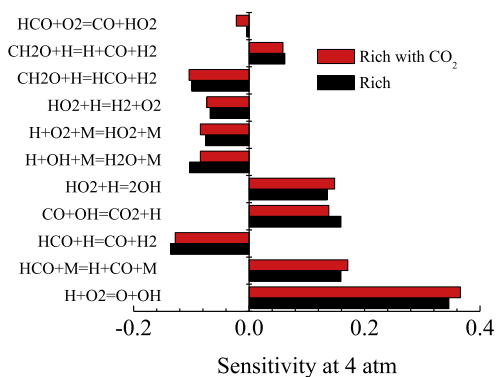


Fig. 17. Trioxane flame speed sensitivity to elementary reaction rate coefficient A-factors at rich and rich with 20% CO₂ conditions ($\phi = 1.4$) and at 4 atm. Prompt HP Mech was used for the calculations.

from the third-body collisional energy transfer effect of CO₂ in R₁. However, from the sensitivity analysis, the CO₂ collisional energy transfer in $H + O_2 + M = HO_2 + M$ ($M = CO_2$) could play an important role to slow down the flame speed. 3) The thermal HCO prompt dissociation probabilities are calculated for N₂ as a bath gas [23], while there are no available rates for CO₂ as a bath gas. Also, when multiple bath gases are used, the prompt reaction rates may also be affected [37] in a non-linear manner. Therefore, changing the bath gas may affect the prompt dissociation rates and then the flame speed predictions. 4) For the CO₂ kinetic effect, the sensitivity analysis is conducted at fuel rich with and without CO₂ conditions (Fig. 17). Sensitivities of R₁, R₃ and R₄ have no significant difference between these two cases, while R₂ sensitivity is too low

to have a significant effect on the flame speed prediction for both cases. Thus, the rate coefficients of R₁, R₃, and R₄, the collisional energy transfer coefficient of CO₂ in $H + O_2 + CO_2 = HO_2 + CO_2$ reaction, and the bath gas effect on the prompt dissociation probability need to be further studied for the rich with CO₂ flame; in the latter case, recent work [34] suggests that at the lower temperatures within the flame structure for which this reaction exerts greatest influence [38], the reaction rate may be slower by ~25–50%. In summary, the trioxane flame speed is well predicted by Prompt HP Mech at lean, ultra-lean, rich, and lean with CO₂ conditions, while there is still a large discrepancy (~15%) at the rich with CO₂ condition. The experimental trioxane flame speeds data at elevated pressures (for all conditions) are included in the Supporting Information.

4. Conclusions

Many studies of hydrocarbon and oxygenated fuel flame speeds indicate that flame speed is sensitive to reactions involving HCO, such as R₁–R₃. This has historically led to targeted experimental measurement, theoretical calculation, and optimization for the rate coefficients of these three reactions. However, a prompt dissociation channel (R₄) for excited formyl radical (HCO*) was recently described [23] as an alternative, competing pathway to R₁–R₃ for formation of CO and/or, importantly, H atoms that feed chain-branching reactions. Save for the present study, no existing experiments have studied the effect of the prompt dissociation of HCO on laminar flame speed, and to date, few kinetic models have considered the prompt reaction in mechanism development and evaluation, particularly at higher pressures relevant to combustion applications. Accordingly, this paper described experimental and kinetic modeling investigations of the effects of HCO prompt dissociation and CO₂ collisional energy relaxation on CH₂O / HCO chemistry by using experimentally measured and model-predicted trioxane flame speeds. In order to demonstrate consistency with the experimental data of Santner et al. [1], the atmospheric pressure laminar flame speeds of trioxane / O₂ / N₂ mixtures were initially measured. Next, flame speeds were measured at elevated pressures for lean, ultra-lean, rich, lean with CO₂ addition, and rich with CO₂ addition conditions. And then, the predictions of several kinetic models with and without including the prompt reaction pathway were used to compare against the experimental data and each other to confirm the necessity of the prompt reaction in kinetic mechanism development. Finally, the effects of pressure, O₂ content, and CO₂ dilution on the prompt dissociation of HCO were analyzed. To further improve the model prediction, in the future, the bath gas effect on the prompt dissociation probability needs to be further studied for CO₂- (and similarly, H₂O-) diluted flames.

It is found that:

- (1) All of the five kinetic models reveal the pressure dependence of the flame speed clearly, and the prompt reaction has a significant effect on the flame speed predictions by the five models.
- (2) There is a decreased effect of the HCO prompt dissociation on flame speed predictions with increasing pressure, while it is enhanced with increasing O₂ mole fraction.
- (3) CO₂ dilution reduces the prompt effect on predicted flame speeds as, in the net, R₄ is directly and indirectly inhibited by CO₂ addition.
- (4) Prompt HP Mech and Li Mech predict the flame speed better in all rich, lean, and ultra-lean cases than HP Mech and Prompt Li Mech, while USC Mech has a good performance in the two lean cases but not for the rich case. Prompt Li Mech increases the over-prediction in all three cases and Prompt USC-Mech has better performance in the rich case.

Aramco Mech and Prompt Aramco Mech still over-predict the experimental flame speed, while GRI Mech and Prompt GRI Mech under-predict the experimental value. From these trends, it can be inferred that model optimization of HCO reaction kinetic parameters can be very effective at conditions coinciding with the experimental optimization. However, beyond the validated experimental conditions or by just simply adding a new reaction pathway, an optimized model may fail to predict the flame speed. On the other hand, a non-optimized elementary rate-based model like HP Mech may fail to predict the flame speed if an important reaction pathway is missed. However, by adding the missing reaction pathway, the model predictions may improve. Kinetic model users should be aware of the valid boundaries for both of these kinetic model approaches.

- (5) Although Li Mech, USC Mech, and Aramco Mech predict the lean flame speed with 20% CO₂ addition well at lower pressures, the discrepancy becomes much larger at higher pressures. Alternatively, Prompt HP Mech has a good (within 10% error) prediction of the flame speed both at lower and higher pressures. Moreover, the prediction of the rich CH₂O flame speed with CO₂ dilution remains challenging.

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Supplementary materials

Supplementary material including the prompt HP mechanism associated with this article can be found, in the online version, at [doi:10.1016/j.combustflame.2017.05.005](https://doi.org/10.1016/j.combustflame.2017.05.005). Any updates of the HP mechanism can be tracked from <http://engine.princeton.edu/mechanism.html>.

Reference

- [1] J. Santner, F.M. Haas, F.L. Dryer, Y. Ju, High temperature oxidation of formaldehyde and formyl radical: A study of 1, 3, 5-trioxane laminar burning velocities, *Proc. Combust. Inst.* 35 (2015) 687–694.
- [2] C.K. Westbrook, F.L. Dryer, Chemical kinetic modeling of hydrocarbon combustion, *Prog. Energy Combust. Sci.* 10 (1984) 1–57.
- [3] S. Hochgreb, R.A. Yetter, F.L. Dryer, The oxidation of CH₂O in the intermediate temperature range (943–995 K), *Symp. (Int.) Combust.*, 23 (1990), pp. 171–177.
- [4] P. Glarborg, M.U. Alzueta, K. Kjaergaard, K. Dam-Johansen, Oxidation of formaldehyde and its interaction with nitric oxide in a flow reactor, *Combust. Flame* 132 (2003) 629–638.
- [5] V. Dias, C. Duynslaegher, F. Contino, J. Vandooren, H. Jeanmart, Experimental and modeling study of formaldehyde combustion in flames, *Combust. Flame* 159 (2012) 1814–1820.
- [6] M.C. Branch, M.E. Sadequ, A.A. Alfarayedhi, P.J. Van Tiggelen, Measurements of the structure of laminar, premixed flames of CH₄/NO₂/O₂ and CH₂O/NO₂/O₂ mixtures, *Combust. Flame* 83 (1991) 228–234.
- [7] A.R. Hall, J.C. McCoubrey, H.G. Wolfhard, Some properties of formaldehyde flames, *Combust. Flame* 1 (1957) 53–59.
- [8] J. Vandooren, L. Oldenhove de Guertchin, P.J. Van Tiggelen, Kinetics in a lean formaldehyde flame, *Combust. Flame* 64 (1986) 127–139.
- [9] V. Vasudevan, D.F. Davidson, R.K. Hanson, Direct measurements of the reaction OH + CH₂O → HCO + H₂O at high temperatures, *Int. J. Chem. Kinet.* 37 (2005) 98–109.
- [10] S. Wang, D.F. Davidson, R.K. Hanson, High-temperature laser absorption diagnostics for CH₂O and CH₃CHO and their application to shock tube kinetic studies, *Combust. Flame* 160 (2013) 1930–1938.
- [11] G. Friedrichs, D.F. Davidson, R.K. Hanson, Direct measurements of the reaction H + CH₂O → H₂ + HCO behind shock waves by means of Vis-UV detection of formaldehyde, *Int. J. Chem. Kinet.* 34 (2002) 374–386.
- [12] G. Friedrichs, D.F. Davidson, R.K. Hanson, Validation of a thermal decomposition mechanism of formaldehyde by detection of CH₂O and HCO behind shock waves, *Int. J. Chem. Kinet.* 36 (2004) 157–169.
- [13] S. Hochgreb, An experimental and numerical study on the oxidation of formaldehyde, Mechanical and Aerospace Engineering Ph.D. Thesis, Princeton University, 1991. T-1910.
- [14] D. Liu, J. Santner, et al., Flame structure and kinetic studies of carbon dioxide-diluted dimethyl ether flames at reduced and elevated pressures, *Combust. Flame* 160 (2013) 2654–2668.
- [15] L. Tran, J. Pieper, H. Carstensen, H. Zhao, et al., Experimental and kinetic modeling study of diethyl ether flames, *Proc. Combust. Inst.* 36 (2017) 1165–1173.
- [16] D. Felsmann, H. Zhao, Q. Wang, et al., Contributions to improving small ester combustion chemistry: Theory, model and experiments, *Proc. Combust. Inst.* 36 (2017) 543–551.
- [17] J. Li, Z. Zhao, A. Kazakov, M. Chaos, F.L. Dryer, J.J. Scire Jr., A comprehensive kinetic mechanism for CO, CH₂O, and CH₃OH combustion, *Int. J. Chem. Kinet.* 39 (2007) 109–136.
- [18] Y. Hidaka, T. Taniguchi, H. Tanaka, T. Kamesawa, K. Inami, H. Kawano, Shock-tube study of CH₂O pyrolysis and oxidation, *Combust. Flame* 92 (1993) 365–376.
- [19] G. Friedrichs, J.T. Herbon, D.F. Davidson, R.K. Hanson, Quantitative detection of HCO behind shock waves: The thermal decomposition of HCO, *Phys. Chem. Chem. Phys.* 4 (2002) 5778.
- [20] W.G. Browne, R.P. Porter, J.D. Verlin, A.H. Clark, A study of acetylene-oxygen flames, *Symp. (Int.) Combust.*, 12 (1969), p. 1035.
- [21] C.T. Bowman, An experimental and analytical investigation of the high-temperature oxidation mechanisms of hydrocarbon fuels, *Combust. Sci. Technol.* 2 (1970) 161.
- [22] R.S. Timonen, E. Ratajczak, D. Gutman, Kinetics of the reactions of the formyl radical with oxygen, nitrogen dioxide, chlorine, and bromine, *J. Phys. Chem.* 92 (1988) 651–655.
- [23] N. Labbe, R. Sivaramkrishnan, et al., Weakly bound free radicals in combustion: “Prompt” dissociation of formyl radicals and its effect on laminar flame speeds, *J. Phys. Chem. Lett.* 7 (2016) 85–89.
- [24] Z. Chen, On the extraction of laminar flame speed and Markstein length from outwardly propagating spherical flames, *Combust. Flame* 158 (2011) 291–300.
- [25] F. Wu, W. Liang, Z. Chen, Y. Ju, C.K. Law, Uncertainty in stretch extrapolation of laminar flame speed from expanding spherical flames, *Proc. Combust. Inst.* 35 (2015) 663–670.
- [26] R.J. Kee, J.F. Grcar, M.D. Smooke, J.A. Miller, Sandia National Laboratory Report SAND 85-8240, 1985
- [27] X. Qin, Y. Ju, Measurements of burning velocities of dimethyl ether and air premixed flames at elevated pressures, *Proc. Combust. Inst.* 30 (2005) 233–240.
- [28] J. Santner, F.L. Dryer, Y. Ju, The effects of water dilution on hydrogen, syngas, and ethylene flames at elevated pressure, *Proc. Combust. Inst.* 34 (2013) 719–726.
- [29] X. Yang, Y. Ju, H. Zhao, X. Shen, S. Yang, Princeton HP-Mech (2017) <http://engine.princeton.edu/mechanism.html>.
- [30] H. Zhao, X. Yang, Y. Ju, Kinetic studies of ozone assisted low temperature oxidation of dimethyl ether in a flow reactor using molecular-beam mass spectrometry, *Combust. Flame* 173 (2016) 187–194.
- [31] H. Wang, X. You, A.V. Joshi, et al., USC Mech Version II, High-Temperature Combustion Reaction Model of H₂/CO/C₁–C₄ Compounds (2007). http://ignis.usc.edu/USC_Mech_II.htm.
- [32] W.K. Metcalfe, S.M. Burke, S.S. Ahmed, H.J. Curran, A hierarchical and comparative kinetic modeling study of C₁–C₂ hydrocarbon and oxygenated fuels, *Int. J. Chem. Kinet.* 45 (2013) 638–675.
- [33] G.P. Smith, D.M. Golden, M. Frenklach, et al. (1999) URL: http://www.me.berkeley.edu/gri_mech/
- [34] F.M. Haas, Studies of small molecule reactions foundational to combustion chemistry, including experimental measurements from a novel high pressure flow reactor, Mechanical and Aerospace Engineering Ph.D. Thesis, Princeton University, 2016. T-3290.
- [35] Z. Chen, Effects of radiation absorption on spherical flame propagation and radiation-induced uncertainty in laminar flame speed measurement, *Proc. Combust. Inst.* 36 (2017) 1129–1136.
- [36] H. Yu, W. Han, J. Santner, X. Gou, C.H. Sohn, Y. Ju, Z. Chen, Radiation-induced uncertainty in laminar flame speed measured from propagating spherical flames, *Combust. Flame* 161 (2014) 2815–2824.
- [37] M.P. Burke, R. Song, Evaluating mixture rules for multi-component pressure dependence: H + O₂ (+ M) = HO₂ (+ M), *Proc. Combust. Inst.* 36 (2017) 245–253.
- [38] Z. Zhao, J. Li, A. Kazakov, F.L. Dryer, Temperature-dependent feature sensitivity analysis for combustion modeling, *Int. J. Chem. Kinet.* 37 (2005) 282–295.