Ramifications of Including Non-equilibrium Effects for HCO in Flame Chemistry

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ABSTRACT

The formation and destruction pathways of the formyl radical (HCO) occupy a pivotal role in the conversion of fuel molecules (and their intermediates) to eventual products CO and CO₂, and therefore, HCO has been a prescient indicator for heat release in combustion. In this work, we have characterized the impact of including non-equilibrium effects for HCO, i.e. “prompt” dissociation of HCO to H + CO, in simulations of laminar flame speeds for archetypal hydrocarbon and oxygenated molecules relevant to combustion. Prompt dissociation probabilities for HCO were systematically applied to all elementary reactions that included this radical (as either a product or reactant) in literature combustion kinetics models. Simulations with the prompt HCO dissociation corrected models predicted a 7-13% increase in laminar flame speeds at 1 atm for the fuels characterized here (CH₄, n-C₇H₁₆, CH₃OH, CH₃OCH₃) relative to the predictions using the original models. It is evident that simulations of other fuel-air flames at 1 atm will be similarly impacted, suggesting the indispensability of incorporating these non-equilibrium effects for predictive flame modeling. Simulations of higher pressure (10 atm) heptane-air flames predicted a more modest effect (< 5%) of incorporating these non-equilibrium effects. Additionally, species profiles in low-pressure (0.03 atm) flames of CH₂O and auto-ignition delay simulations (1.4 atm) for CH₂O-O₂-Ar mixtures were also impacted to a noticeable extent. Lastly, it is also worth noting that prompt dissociations are a ubiquitous feature of all weakly-bound radicals; the kinetics of many of which (C₂H₃, C₂H₅, CH₃O, CH₂OH, etc.) are central to our current understanding of combustion chemistry. Theory/modeling studies are in progress to address the relevance of prompt dissociations in these weakly-bound radicals to combustion modeling.

KEYWORDS

Chemical Kinetics, Prompt Dissociation, CH₂O, Combustion Modeling, Laminar Flame Speed

1. INTRODUCTION

Formyl radical, HCO, is a critical species that plays a substantial role in the oxidation of hydrocarbons. The combustion mechanism for oxidation of simple hydrocarbon fuels to CO/CO₂ is well known [1] and proceeds through formaldehyde, CH₂O, often through the oxidation of methyl radical, i.e. CH₃ + O₂/O/OH. In turn, CH₂O is primarily destroyed through the highly exothermic reactions,

resulting in HCO formation. Flame simulations by Najm et al. [2] and in recent work by Nikolaou et al. [3], have highlighted the particular importance of these two CH₂O destruction reactions, observing that the main product of reactions (1) and (2), HCO, had strong correlations with local heat release rates in CH₄ flames.

HCO, in turn, is often destroyed through three major competing pathways,

Reaction (3) is a chain propagating reaction, producing a reactive H-atom, which fuels perhaps the most important reaction in combustion, the chain branching reaction $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$. Reaction (4) creates the more stable HO₂ radical and competes with the H-atom producing reaction (3). On the other hand, H-atoms are quenched in a facile manner by reaction (5). This competition between the propagation reaction (3), and terminating reactions (4) and (5), determines the net rate of production of H-atoms and thus impacts predictions of hydrocarbon laminar flame speeds [4]. While the rate constant for reaction (5) is well characterized [5], there are larger uncertainties in k_3 and k_4 . Experimental and modeling studies have therefore been initiated, particularly by Dryer and co-workers, on CH₂O and CH₃OH combustion [6,7] to characterize this competition between reactions (3) and (4) and to understand the discrepancies in their kinetics.

Numerous theoretical, experimental, and modeling studies have been performed to determine the rates of these two reactions. For example, Hsu et al. [8] calculated the rate constant for reaction (4) using variational transition state theory and RRKM theory for a temperature range of 300-3500 K. Colberg and Friedrichs [9] performed a combined study of room temperature photolysis of glyoxal, a thermal source for HCO radicals, in the presence of O₂ and shock tube experiments (739-1108 K) of glyoxal decomposition in the presence of O₂ to measure k_4 by monitoring HCO concentrations. They found that their [9] experimentally determined rate constants differed from those of Hsu et al. [8] by up to a factor of 2.5. More recently, Faßheber et al. [10] performed additional high temperature shock tube experiments (1285 K < T < 1760 K) on glyoxal pyrolysis and oxidation by monitoring HCO decay combined with a modeling study to determine k_4 . The results from these higher temperature experiments supported the conclusions of Colberg and Friedrichs [9].

Given its importance in hydrocarbon combustion, reaction (3) has also been the subject of numerous experimental studies spanning wide temperature (600-1250 K) and pressure ranges (10 Torr – 100 atm). The laser photolysis-photoionization, mass-spectrometry experimental results of Timonen et al. [11] and the accompanying theoretical results formed the basis for k_3 in numerous combustion modeling efforts for a long time. Subsequent laser-photolysis shock tube experiments by Friedrich et al. [12] at higher temperatures (835-1230 K) and pressures (0.25-1.9 atm) assumed that k_3 was in the low-pressure limit and their results were in discord with Timonen et al. [11]. Discrepancies in the thermal rate constant and the extent of fall-off for reaction (3) persisted despite two subsequent higher pressure studies by Hippler et al. [13] and Krasnoperov et al. [14]. The sparsity of the density of states for HCO, due to it being a small, weakly-bound radical, leads to difficulties in theoretical analyses for the thermal kinetics of reaction (3). Uncertainties in these two competing rate constants significantly influences flame propagation as observed in the recent study by Santner et al. [15]. Santner et al. [15] performed laminar burning velocity experiments on 5% mixtures of 1,3,5-trioxane, a CH₂O trimer, with varying O₂/N₂ ratios to probe this competition between k_3 and k_4 . Monte Carlo optimization, using a modified

version of the USC Mech II [16] model, was employed to constrain k_3 and k_4 , since these were the most sensitive (and had the largest uncertainties) for flame speed predictions.

Further complicating the chemistry of HCO, as studied in recent work from our group [17], weakly-bound radicals with low-dissociation thresholds dissociate so rapidly at high temperatures that the dissociation process interferes with the collisional internal energy relaxation process as it occurs within vibrational-rotational relaxation time scales. Under such conditions some dissociation naturally occurs as part of the vibrational-rotational relaxation process regardless of the initial conditions. In our recent work [17] on the HCO radical, which has a weak C-H bond energy of 14.5 kcal/mol, we calculated that there is a significant amount of such “prompt” dissociation of HCO to H + CO at $T > 1000$ K. Furthermore, in this work [17], we have calculated that when HCO is formed through exothermic reactions such as reactions (1) and (2), this prompt dissociation probability is enhanced. As a result, simulations of the Santner et al. [15] 1,3,5-trioxane flame and literature acetylene flames were shown to be impacted by inclusion of HCO prompt dissociation.

In this work, we highlight the impact of including HCO prompt dissociation in simulations of laminar flame speeds for a variety of simple hydrocarbon and oxygenated fuels of relevance to the combustion community. Additionally, HCO prompt dissociation is shown to also affect simulations of species profiles in CH₂O low-pressure flames and CH₂O auto-ignition at high-temperatures. It is evident that the effects of including these non-equilibrium effects for HCO persist across widely used combustion kinetics models, including USC Mech II [16], Aramco Mech 1.3 [18], Zhao et al. dimethyl ether (DME) model [19], and the Chaos et al. primary reference fuel mechanism [20] for flame simulations of a variety of common combustion fuels. Lastly, the present results also imply the need to characterize prompt dissociations in other common weakly-bound radicals (C₂H₃, C₂H₅, CH₃O, CH₂OH etc.) and include their role in combustion modeling.

2. THEORY AND SIMULATIONS

The derivation of the probability of prompt dissociation, P_{diss} , for a thermal distribution of a given weakly-bound radical is described in detail in our previous paper [17] and will not be repeated in detail here. In brief, the fraction of the radical concentration that dissociates during its internal-energy relaxation stage may generally be written as

$$P_{diss}(T, P) = \int_0^\infty x(E, 0) g_{diss}(E) dE \quad (6)$$

where $x(E, 0)$ is the initial population distribution of the dissociating radical and $g_{diss}(E)$ is the probability that a radical at energy E dissociates to products during the vibrational-rotational relaxation timescale. The quantity $g_{diss}(E)$ is given by Eq. (38) of [21] when a delta function is used for the $f_{0,\lambda}$ there. In the case of a single-well, single-product radical such as HCO born with an initial thermal distribution $x(E, 0)$, Eq. 6 simplifies to

$$P_{diss}(T, P) = 1 - f_{ne}(T, P) \quad (7)$$

where f_{ne} is the non-equilibrium factor, which is a convenient and useful measure of the degree to which dissociation interferes with internal energy relaxation, and has been previously calculated for several combustion relevant radicals [22-26]. With this simplification, $P_{diss,HCO}(T)$ was easily calculated and fit to an Arrhenius-type expression for specific pressures of interest [17] (cf. Supplemental Material).

For reactions where direct dynamics results for $x(E, 0)$ are not available, Eq. (7), assuming an initially thermal distribution of HCO, offers an adequate approximation for $P_{diss,HCO}$ that can be easily incorporated into large combustion models that include a multitude of elementary reactions involving HCO as a product (or reactant). However, this may not be a good representation for highly exothermic reactions forming HCO, such as reactions (1) and (2). Therefore, in the previous paper [17] we have also determined $P_{diss,HCO}$ for these two exothermic reactions using direct dynamics calculations of $x(E, 0)$, and these results were used exclusively for reactions (1) and (2). Arrhenius fits to $P_{diss,HCO}$ for reactions (1) and (2) are also provided in the Supplemental Material. There may be additional exothermic reactions that directly form HCO in large combustion chemistry models, but only $H/OH + CH_2O$ were considered

for direct dynamics here since they are often the predominant pathways that lead to HCO, and therefore, are also pertinent to the heat-release process in combustion.

To test the impact of including prompt HCO dissociations on combustion model predictions, the fits for $P_{diss,HCO}$ were applied to every reaction for several widely-used combustion mechanisms (Aramco Mech 1.3 [18], USC Mech II [16], Chaos et al. PRF model [20], and the Zhao et al. DME model [19]). An in-house code was utilized to generate versions of these combustion kinetics models automatically that include HCO prompt dissociation. In general, $P_{diss,HCO}$ was applied for a single pressure of interest, i.e. $P_{diss,HCO}$ for 1 atm was applied to make a 1 atm combustion mechanism. For Aramco Mech 1.3 [18], $P_{diss,HCO}$ was already included for the reaction $C_2H_3 + O_2 \rightarrow HCO + CH_2O$ based on preliminary estimates from Klippenstein [27], so the application of Eq. (6) was not considered for this reaction. The single-pressure prompt HCO version of these mechanisms lead to an additional 184 reactions for Aramco Mech 1.3 [18], 140 reactions for USC Mech II [16], 98 reactions for the PRF model [20], and 82 reactions for the DME model [19]. These altered models accounting for prompt HCO are provided in the Supplemental Material.

In the case of variable-pressure simulations, or in conditions other than pressures of 30 Torr, 1 atm, or 10 atm, $P_{diss,HCO}$ was applied as PLOGs to capture the pressure dependence of $P_{diss,HCO}$. The variable pressure model has three main drawbacks: 1) the time for simulation is dramatically increased with numerous PLOG expressions included, 2) for reactions where fall-off is included (e.g., Troe fits), rate constants have to be refit to PLOGs, introducing small errors, and 3) effects of collision partners are lost as a result of using this PLOG formulation. Comparisons of 1 atm flame speed simulations showed no discernable difference when using either the single-pressure or multi-pressure mechanism formulations. As such, when applicable, the single-pressure formulation was preferred, particularly for the 1 atm flame speed simulations described below.

Simulations of flame speeds, low-pressure flames, and ignition delay times were all performed using the Chemkin [28] suite of programs. Flame speeds were calculated with mixture averaged

transport properties and with the inclusion of thermal diffusion (Soret). Converged results were obtained with > 700 grid points for the flames computed here. Sample flame simulations with the inclusion of multicomponent diffusion led to flame speeds that differed by $0.5 - 1$ cm/s from the mixture averaged transport solutions. However, the differences between flame speeds with the original models and the modified models with HCO prompt dissociation were similar with computations that used either mixture-averaged transport or multicomponent transport properties. The majority of the flame results reported in this work utilized results from mixture-averaged transport to facilitate flame simulations with some of the larger kinetic models used here. Simulations for the CH_2O low-pressure flame utilized the reported measured temperature profile with multicomponent transport. CH_2O auto-ignition delays measured in shock tubes were simulated assuming constant volume, homogeneous, adiabatic conditions behind reflected shock waves.

3. RESULTS AND DISCUSSIONS

As already stated, to test the impact of including HCO prompt dissociation on combustion model predictions, the fits for $P_{diss,HCO}$ for pressures of interest were applied to every elementary reaction (including HCO as a product or reactant) for several commonly used combustion mechanisms. Here, we compare the modeling results of the original, unaltered models with the modeling results of the altered models containing prompt HCO decompositions. It is not the intent of this study to analyze the discrepancies that arise between literature mechanisms/models and experiment, which may be indicative of shortcomings in either or both, but rather merely to present the impact of a hitherto unaccounted for phenomenon in combustion modeling, the “prompt” dissociation of HCO. In our previous work [17], we demonstrated the effects of including hot HCO dissociation on 1,3,5-trioxane (a trimer of CH_2O) and acetylene flame speeds. We expand upon that work here to highlight the effects of prompt HCO dissociation on flame propagation for a wide variety of core fuels relevant to combustion model applications at 1 atm, and also in some instances at higher pressures.

3.1 Oxygenated-fuel flame speeds

Oxygen-containing fuels are obvious targets for including prompt HCO decomposition in combustion models. Because they contain C-O bonds, fuel-decomposition pathways proceed directly through formaldehyde, giving an immediate link from fuel to HCO. Flame speeds are also good targets to probe the competition between chain-branching (radical generating) reactions and chain-terminating (radical sequestering) reactions. The largest effects of incorporating prompt HCO dissociations are to be expected with CH_2O as a fuel, which was the reason for our prior simulations [17] of flame speeds of 1,3,5-trioxane [15]. The combustion of simple oxygenated fuels such as methanol, dimethyl ether, acetone, etc. all lead to appreciable levels of CH_2O formation, and consequently it is expected that these flames will be impacted. Here we show simulations for methanol and dimethyl ether flames at 1 atm. Methanol flame speeds have been studied extensively in the past at a wide variety of conditions including three recent studies with an inlet temperature, T_u , of 298 K for methanol-air mixtures at 1 atm [29-31]. Methanol decomposition almost entirely proceeds through formaldehyde formation, which is the only stable product from dissociation of CH_2OH and CH_3O . As a result, there are significant effects on simulations of methanol flame speeds when prompt HCO decomposition is included, as shown in Figure 1. Including prompt HCO dissociation increases flame speeds by up to 10.5% (2.5 cm/s) for Aramco Mech 1.3 [18] and 12.5% (4.8 cm/s) for USC Mech II [16].

Figure 1: Methanol-air flames, $T_u = 298$ K, $P = 1$ atm. Experimental data from Sileghem et al. [30], Vancoillie et al. [29], and Egolfopoulos et al. [31] in symbols. Aramco Mech 1.3 [18] results in red. USC Mech II [16] results in blue. Solid lines - Original models. Dotted lines - Prompt HCO dissociation corrected models.

Dimethyl ether (DME) was also studied as another important oxygen-containing fuel. Like methanol and other oxygenated fuels, DME combustion also proceeds largely through CH_2O chemistry, since it is also the only stable product of the CH_3OCH_2 radical (formed through abstractions from DME). Due to DME's importance as a fuel/fuel-additive, several flame speed studies have been reported for DME in air laminar flames at 1 atm and with $T_u = 298$ K [32-37]. In Figure 2, we compare the model results for the Zhao et al. DME model [19] with and without inclusion of prompt HCO dissociation with the experimental studies [32-37]. By including prompt HCO dissociation, flame speed predictions with the Zhao et al. [19] model are increased by up to 9.7% (4.3 cm/s).

Figure 2: Dimethyl ether-air flames, $T_u = 298$ K, $P = 1$ atm. Experimental data from Daly et al. [32], Zhao et al. [33], Qin et al. [34], Wang et al. [35], Chen et al. [36], and Huang et al. [37] in symbols. Simulations with Zhao et al. DME model [19]. Solid line - Original model. Dotted line - Prompt HCO dissociation corrected model.

3.2 Hydrocarbon-fuel flame speeds

While oxygen-containing fuels have direct pathways to formaldehyde through fuel breakdown chemistry, in hydrocarbon fuels, CH_2O formation primarily occurs through reactions involved in the oxidation of CH_3 radical. In our previous work [17], we have shown that including hot HCO decomposition increases flame speeds of acetylene by as much as 9%. This is primarily due to the increase of heat release by providing a prompt source of H-atoms, effectively promoting chain branching through $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$ and subsequent CO_2 formation from $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$. In Figure 3, we illustrate this effect of an increase in net heat release by including prompt HCO dissociation for simulations of an acetylene-air flame using Aramco Mech 1.3 [18] and USC Mech II [16]. Of course, in this case, there are prompt pathways to CO_2 [38] through $\text{HCCO} + \text{O}_2$ and $\text{CH}_2 + \text{O}_2$ that also influence heat release apart from the traditional heat release pathway proceeding through CH_2O .

Figure 3: Net heat release for a C_2H_2 -air flame, $T_u = 298$ K, $P = 1$ atm. Simulations with Aramco Mech 1.3 [18] and USC Mech II [16]. Solid lines – original models, Dotted lines – models updated with prompt HCO dissociation.

Also of considerable interest to the combustion community are methane-air flames. As the primary component of natural gas and the simplest hydrocarbon fuel, there have been extensive studies on methane flame propagation, with numerous laminar flame speed measurements at $P = 1$ atm and $T_u = 298$ K [39-46]. Again, we find significant differences with the inclusion of prompt HCO dissociation as shown in Figure 4, with predicted flame speeds increasing by up to 9.9% (2.6 cm/s) for Aramco Mech 1.3 [18] and by 8.0% (2.4 cm/s) for USC Mech II [16].

Figure 4: Methane-air flames, $T_u = 298$ K, $P = 1$ atm. Experimental data from Lowry et al. [46], Aung et al. [45], Hassan et al. [42], Vagelopoulos et al. [39], Gu et al. [43], Rozenchan et al. [41], Bosschaart et al. [40], and Tahtouh et al. [44] in symbols. Aramco Mech 1.3 [18] results in red. USC Mech II [16] results in blue. Solid lines - Original models. Dotted lines - Prompt HCO dissociation corrected models.

3.3 Flame speed pressure dependence

Heptane has been rigorously studied as a real fuel and is often considered a surrogate for diesel fuels. As a result, primary reference fuel (PRF) models such as the one by Chaos et al. [20] have been developed to simulate n-heptane combustion. Kelley et al. [47] performed a study on the flame speeds of C₅-C₈ n-alkanes in air, observing the trends of flame speeds with increasing chain length and also variations with pressures ranging from 1 to 10 atm. In this work, we have simulated not only the 1 atm heptane flame speeds of Kelley et al. [47], but also the higher pressure flame speeds. As observed for the other two hydrocarbon fuels (methane and acetylene), including prompt HCO decomposition pathways has a net increase up to 7.0%, 3.0 cm/s for n-heptane 1 atm flame speeds (black lines in Figure 5).

Figure 5: n-Heptane-air flames, $T_u = 353$ K, $P = 1, 2, 5,$ and 10 atm. Experimental data from Kelley et al. [47] in symbols. Simulations with Chaos et al. PRF model [20]. Solid lines - Original model. Dotted lines - Prompt HCO dissociation corrected model.

Perhaps more interesting is the effect of pressure on these simulations. As outlined in our previous paper [17], the probability of prompt dissociation of HCO decreases with increasing pressure, and this effect is reflected in the higher pressure flame simulations. As pressure is increased, the total differences between the two models decrease, from 7.0% (3.0 cm/s max) at 1 atm, to 6.7% (2.0 cm/s

max) at 2 atm. This trend continues at 5 atm (max differences of 6.4%, 1.2 cm/s) and finally at 10 atm the changes are much more modest with only a net change of 5.4% (0.7 cm/s) at lean conditions. Additional flame simulations (C_2H_4 , C_2H_6 , preheated- CH_4) are provided in the Supplemental Material.

3.4 Low-pressure flame speciation

The results for n-heptane in Figure 5 suggest that prompt HCO dissociation should have a greater impact on lower pressure experiments such as laminar flame speciation experiments. Vandooren et al. [48] studied a laminar flat flame of formaldehyde at 0.03 atm. The flame was a lean flame, with 18% CH_2O in 82% O_2 . They measured not only the major species concentration profiles as a function of distance from the burner using MBMS techniques, but they also measured several intermediate species including H, O, OH, and HO_2 radicals. In this work, we simulated the H, O, OH, and HO_2 profiles with the Aramco Mech 1.3 [18] with and without prompt HCO dissociation using their measured temperature profile and these results are shown in Figure 6. Perhaps the most significant effect on these flame simulations is the net shift of these radical profiles toward the burner. While the unperturbed Aramco Mech 1.3 [18] was able to capture OH, H, and HO_2 profiles quite well, the predicted profile for O-atom was shifted away from the data set. With the inclusion of prompt HCO dissociation, the opposite is true. The modified model captures O-atom and H-atom profiles better. However, OH and HO_2 profiles are shifted towards the burner. Maximum shifts observed are as large as 1.5 mm.

Figure 6: Radical species profiles in a formaldehyde (18% CH_2O in O_2) low-P ($P = 0.03$ atm), laminar flame. Experimental data from Vandooren et al. [48] in symbols. Simulations with Aramco Mech 1.3 [18]. Solid lines - Original model. Dotted lines - Prompt HCO dissociation corrected model.

Because of the critical role of HCO in flames as an important source of H-atoms, inclusion of prompt HCO dissociation in a kinetic mechanism affects the predicted radical concentration profiles. As demonstrated with the formaldehyde flame in Figure 6, addition of prompt HCO pathways not only affects the peak concentrations of radicals, but also shifts profiles towards the burner. For oxygenated fuels such as dimethyl ether and methanol, where large concentrations of HCO would be produced, similarly noticeable effects are expected. An example of prompt HCO effects on a low-pressure dimethyl ether flame is included in the Supplemental Material.

3.5 Ignition delay times

Prompt HCO dissociation also has consequences for ignition delay time predictions. Eiteneer et al. [49] measured the ignition delay times for CH_2O by measuring the concentrations of CO. Ignition was defined as the delay times to 25%, 50%, and 75% of $[\text{CO}]_{\text{max}}$. Here we simulate ignition defined as the time delays to 50% $[\text{CO}]_{\text{max}}$ profiles for 1.00% CH_2O and 5.96% O_2 mixtures dilute in Ar at $P = 1.4$ atm. Figure 7 shows the results of simulating these ignition delay times with Aramco Mech 1.3 [18] and USC Mech II [16] with and without prompt HCO effects. As one can see, the effect becomes more pronounced with increasing temperature, ultimately having a 33% (91 μs) change for Aramco Mech 1.3

[18] and a 36% (47 μ s) change for USC Mech II [16]. This correlates well with the increase in $P_{diss,HCO}$ with temperature. Ignition delay times for formaldehyde as a fuel are noticeably shortened when including $P_{diss,HCO}$ since HCO is the fuel radical. For other fuels such as methane, effects of including $P_{diss,HCO}$ on predicted ignition delay times are less pronounced.

Figure 7: Formaldehyde ignition. Ignition delays defined as the time to 50% maximum CO production. Experimental data from Eiteneer et al. [49] in symbols. Aramco Mech 1.3 [18] results in red. USC Mech II [16] results in blue. Solid lines - Original models. Dotted lines - Prompt HCO dissociation corrected model.

4. CONCLUSIONS

In this work we have analyzed the impact of including HCO prompt dissociation in laminar flame speed simulations for a variety of common hydrocarbon and oxygenated fuels. This phenomenon was systematically included for all reactions involving HCO (as a reactant or product) in current widely-used combustion kinetics models. Simulations indicated that laminar flame speed predictions were increased by approximately 10% in the prototype hydrocarbon and oxygenated fuels (CH_4 , $n\text{-C}_7\text{H}_{16}$, CH_3OH and CH_3OCH_3) simulated here at 1 atm when including prompt HCO dissociation. It is very likely that simulations of other fuel-air flames at 1 atm will be influenced to a similar extent given the central role of HCO in the heat release process. Simulations of higher-pressure heptane-air flames (2 atm, 5 atm, and 10 atm) indicated a more minor effect of including these non-equilibrium effects for

HCO. Additionally, species profiles in low-pressure flames of CH₂O and auto-ignition delay simulations for CH₂O-O₂-Ar mixtures were impacted to a noticeable extent. The present results indicate the need to include non-equilibrium effects for HCO for predictive simulations of flame chemistry. Lastly, it is worth noting that prompt dissociations are a common feature for a variety of key combustion radicals (C₂H₃, C₂H₅, CH₃O, CH₂OH, etc.) and we have initiated theory/modeling efforts to characterize their relevance to combustion modeling.

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LIST OF FIGURE CAPTIONS

Figure 1: Methanol-air flames, $T_u = 298$ K, $P = 1$ atm. Experimental data from Sileghem et al. [30], Vancoillie et al. [29], and Egolfopoulos et al. [31] in symbols. Aramco Mech 1.3 [18] results in red. USC Mech II [16] results in blue. Solid lines - Original models. Dotted lines - Prompt HCO dissociation corrected models.

Figure 2: Dimethyl ether-air flames, $T_u = 298$ K, $P = 1$ atm. Experimental data from Daly et al. [32], Zhao et al. [33], Qin et al. [34], Wang et al. [35], Chen et al. [36], and Huang et al. [37] in symbols. Simulations with Zhao et al. DME model [19]. Solid line - Original model. Dotted line - Prompt HCO dissociation corrected model.

Figure 3: Net heat release for a C_2H_2 -air flame, $T_u = 298$ K, $P = 1$ atm. Simulations with Aramco Mech 1.3 [18] and USC Mech II [16]. Solid lines – original models, Dotted lines – models updated with prompt HCO dissociation.

Figure 4: Methane-air flames, $T_u = 298$ K, $P = 1$ atm. Experimental data from Lowry et al. [46], Aung et al. [45], Hassan et al. [42], Vagelopoulos et al. [39], Gu et al. [43], Rozenchan et al. [41], Bosschaart et al. [40], and Tahtouh et al. [44] in symbols. Aramco Mech 1.3 [18] results in red. USC Mech II [16] results in blue. Solid lines - Original models. Dotted lines - Prompt HCO dissociation corrected models.

Figure 5: n-Heptane-air flames, $T_u = 353$ K, $P = 1, 2, 5,$ and 10 atm. Experimental data from Kelley et al. [47] in symbols. Simulations with Chaos et al. PRF model [20]. Solid lines - Original model. Dotted lines - Prompt HCO dissociation corrected model.

Figure 6: Radical species profiles in a formaldehyde (18% CH_2O in O_2) low-P ($P = 0.03$ atm), laminar flame. Experimental data from Vandooren et al. [48] in symbols. Simulations with Aramco Mech 1.3 [18]. Solid lines - Original model. Dotted lines - Prompt HCO dissociation corrected model.

Figure 7: Formaldehyde ignition. Ignition delays defined as the time to 50% maximum CO production. Experimental data from Eiteneer et al. [49] in symbols. Aramco Mech 1.3 [18] results in red. USC Mech II [16] results in blue. Solid lines - Original models. Dotted lines - Prompt HCO dissociation corrected model.