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The discovery of non-equilibrium kinetic sequences important to ammonia/co-fuel and propellant flames

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ABSTRACT

Studies published in the last ~5–10 years have shown that chemically termolecular reactions – first hypothesized in the 1920’s but generally neglected in kinetics models – constitute critical reaction pathways in combustion systems containing high mole fractions of reactive species. These studies have shown that reactions of this type can significantly influence model predictions for many common combustion scenarios, including hydrocarbon flame speed and ignition delay simulations. That said, nearly all published chemical kinetics models do not account for these reactions, which is particularly concerning for flame simulations as these systems often involve significant concentrations of fuels and oxidizers at temperatures and pressures conducive to third-body collisions. Based on a detailed chemical kinetics model developed at the Army Research Laboratory (ARL) to simulate small molecule gas-phase reaction kinetics important to the combustion of gun and rocket propellants, the research presented here utilized an automated screening procedure to identify and estimate rate coefficients for chemically termolecular reactions with the potential to be important to ammonia/co-fuel and propellant flames (as both kinetics systems share similar small molecule chemistry). Changes in ammonia/co-fuel flame speed predictions resulting from the inclusion of these reactions are discussed. Additional ammonium perchlorate/hydroxyl-terminated polybutadiene (AP/HTPB) and nitroglycerin (NG) flame simulations indicate that chemically termolecular reactions significantly impact species mole fractions and temperatures, which supports the notion that these reactions should be considered for ammonia and energetic material kinetics models. Future work will aim to more accurately quantify the rate coefficients of the most influential reactions using high-level theoretical kinetics calculations to further validate the screening procedure and ultimately introduce these reactions into chemical kinetics models.

1. Introduction

Just a few years ago, Burke and Klippenstein [1] demonstrated the significance of chemically termolecular reactions, a class of reactions not previously included in combustion kinetics models. Like termolecular association reactions, chemically termolecular reactions are mediated by an ephemeral collision complex – formed from association of two reactant molecules – which collides with a third molecule. Unlike termolecular association reactions, which involve a collision that only transfers energy to induce stabilization, chemically termolecular reactions involve a collision of the ephemeral complex with a reactive species to induce chemical reaction, such that all three reactants participate in chemical bond transformations. While Burke and Klippenstein showed that chemically termolecular reactions significantly influence predictions of H_2 flame speeds [1], they theorized that many other reacting systems are likely influenced by these reactions, but very few systems [1–4] have been investigated.

An important criterion to assess the relative importance of these reactions is their ability to compete with stabilization processes (i.e., collisions with an inert third body, often depicted in kinetics models as “M”). To compete with these collisional stabilization pathways, high mole fractions of reactive species (generally greater than 1%) are critically important. Of all the chemical kinetics systems that exist today, few produce higher mole fractions of reactive species than

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high temperature flames and energetic material deflagration scenarios, such that chemically termolecular reactions are likely to be especially influential. However, as noted by Burke and Klippenstein [1], "in principle, almost every bimolecular reaction could arise as a chemically termolecular reaction", meaning that, combinatorially, the number of potential chemically termolecular reactions that can exist for a given chemical kinetics system is often staggering, especially for systems that contain many molecular species and bimolecular reaction pathways (as in energetic material combustion). Current computational methods for accurately quantifying rate parameters for chemically termolecular reactions are expensive to the extent that performing high-level theoretical kinetics calculations for all possible reaction pathways is highly impractical.

To address this challenge, an automated screening procedure was leveraged from Barbet et al. [5] to identify and subsequently estimate rate coefficients for all potential reactions that can unfold in a given kinetics system (as represented by an existing chemical kinetics model). This procedure has been shown to accurately identify chemically termolecular reactions of significance, with later *ab initio* master equation calculations [6] confirming the importance of reactions identified by the screening procedure. Considering that many chemically termolecular reactions proven to be important in prior studies [1,5,7] involve small molecules, this evaluation focused on the Army Research Laboratory (ARL) Dark Zone (DZ) mechanism [8], which contains a comprehensive list of small molecule reactions important to energetic material deflagration and ammonia/co-fuel flames (which share a significant amount of small molecule chemistry [9,10]). Ammonia laminar flame speed and burner-stabilized ammonium perchlorate/hydroxyl-terminated polybutadiene (AP/HTPB) and nitroglycerin (NG) flame simulations were explored to identify chemically termolecular reactions potentially important to all scenarios. Simulation results are provided that demonstrate the influence of these reactions on predictions of flame speed, temperature, and species mole fractions. Finally, chemically termolecular reactions most likely to be influential during ammonia and propellant combustion scenarios are identified and recommended for future master equation analysis.

2. Methods

2.1. Analytical approach

The present work leverages the rapid estimation procedure from Barbet et al. [5] which identifies and estimates rate constants for all possible chemically termolecular reactions A + B + C – for which almost no data are available – from available data for other reaction types in current kinetics models. First, the procedure identifies all possible pairs of phenomenological A + B (+M) = AB (+M) (R1) and AB + C = products (R2) reactions. Next, it estimates rate constants for each chemically termolecular reaction, A + B + C, that could arise from reaction of each mediating ephemeral AB** complex with each C based entirely on information available about every R1 and R2 using a simple Lindemann-like scheme. While detailed descriptions of this screening procedure are available elsewhere [5,7], the resulting low- and high-pressure limit expressions used to estimate chemically termolecular reaction rate constants are provided below (Eqs. (1) and (2)). Note the following definitions for all terms in both expressions: from Troe's weak collision theory, Z_c and β_c represent collision frequency and weak collision efficiency, respectively, $k_{R1,0,0}/[\mathrm{M}]$ and $k_{R1,\infty,0}$ represent the low- and high-pressure limit rates of R1, k_{R2} is the R2 constant, and $k_{CTR,0,0}$ and $k_{CTR,\infty,0}[\mathrm{M}]$ represent the low- and high-pressure limit rates of the chemically termolecular reaction.

$$k_{CTR,0,0} = \frac{k_{R2}\left(k_{R1,0,0}/[M]\right)}{\beta_c Z_c} \tag{1}$$

$$k_{CTR,\infty,0}[M] = \frac{k_{R2} k_{R1,\infty,0}}{\beta_c Z_c} \tag{2}$$

A brief description of the uncertainties inherent to this screening procedure is provided in the supplementary material, along with a comparison between estimated (using the screening procedure) and calculated rate constants for the H + O_2 + H and H + O_2 + O reactions — two of the few chemically termolecular reactions for which published rate constant determinations from high-level theoretical kinetics calculations are available.

2.2. Simulation methods

The ARL DZ model used for this study was published in 2011 and contains 60 species and 368 reactions [8]. This model is a critical subset of many larger ARL energetic material models as it contains a comprehensive list of small molecule C/H/N/O reactions that are important to gun and rocket propellant formulations. Considering recent advances in nitrogen chemistry and the significant body of research devoted to ammonia/co-fuel flames generated within the last ~5 years, the recent ammonia kinetics model of Alzueta et al. [11] was included in the analysis for comparative value.

Typical values for collision frequency and efficiency ($Z_c = 5 \times 10^{-10}$ molec cm^3 s^{-1} and β_c = 0.001) [12,13] were used to estimate rate coefficients for all chemically termolecular reactions identified by the Barbet et al. [5] screening procedure. 908 and 688 potential chemically termolecular reactions were identified for the DZ and Alzueta et al. models, respectively.

Ammonia flame speed simulations were run using a 1-D adiabatic freely-propagating flame model that assumed constant pressure, a perfectly premixed reactant mixture, and mixture-averaged transport properties. Kinetic sensitivity analyses of flame speed predictions to reaction rate constants were performed to identify the most influential chemically termolecular reactions.

AP/HTPB (75%/25%) and pure NG flame simulations were run using 1-D adiabatic burner-stabilized flame models that assumed constant pressure, a perfectly premixed reactant mixture, and mixture averaged transport properties. Additionally, the models specified a fixed burner surface temperature of 700 K for both AP/HTPB and NG flame simulations [14] and fixed mass flux values derived from pressure-dependent burn rates (0.83 and 33.25 kg m^{-2} s^{-1} for 1 and 100 atm AP/HTPB simulations, respectively, and 1.76 and 72.00 kg m^{-2} s^{-1} for 1 and 100 atm NG simulations, respectively). A nascent gas-phase mixture was calculated for AP/HTPB simulations from prior condensed-phase correlations [15] to represent typical combustion scenarios. While these values would typically be solved for using a multi-phase flame model, this level of detail was not necessary for an initial evaluation of chemically termolecular reactions and was therefore excluded for simplicity.

To model the chlorine-containing molecular species typically found in AP models, chlorine-containing reaction sets from a reduced Cl/C/H/N/O AP/HTPB model [15] and a recently published Cl/H/N/O AP model [16] were added to the DZ model. Only reactions involving both chlorine- and carbon-containing species were added from the AP/HTPB model. All other chlorine-containing reactions were taken from the AP model as it contains more recent Cl/H/N/O chemistry. To model NG, the authors used a recently published model from ARL containing 1591 reactions and 229 species [17]. It is worth noting that this model contains the same small molecule chemistry captured by the DZ model (as suggested at the start of this section).

Considering that chemically termolecular reactions involving NNH** (which is ephemeral even in its ground state) do not constitute distinct pathways from current reactions in models (discussed further in [5,7]), chemically termolecular reactions mediated by NNH** were excluded in the results shown below. All simulations were run using Cantera 2.6.0 [18].

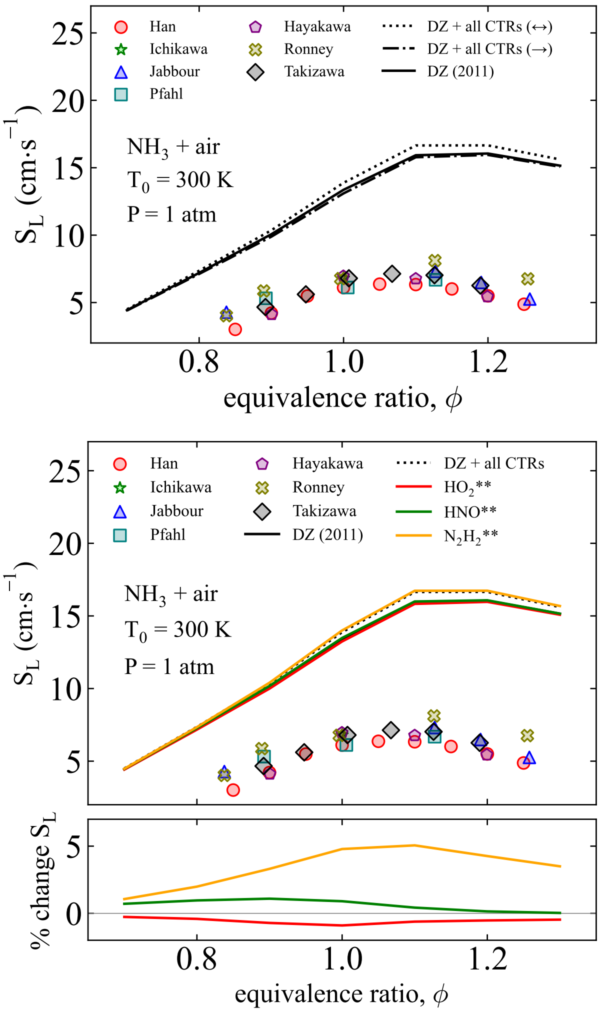

Fig. 1. Laminar flame speed predictions for NH_3 + air mixtures over a range of equivalence ratios. Lines denote model predictions while symbols represent prior experimental measurements [19–25]. The lower plot shows percent changes to flame speed predictions resulting from the inclusion of chemically termolecular reactions (mediated by specific energized complexes and allowed to proceed in both directions).

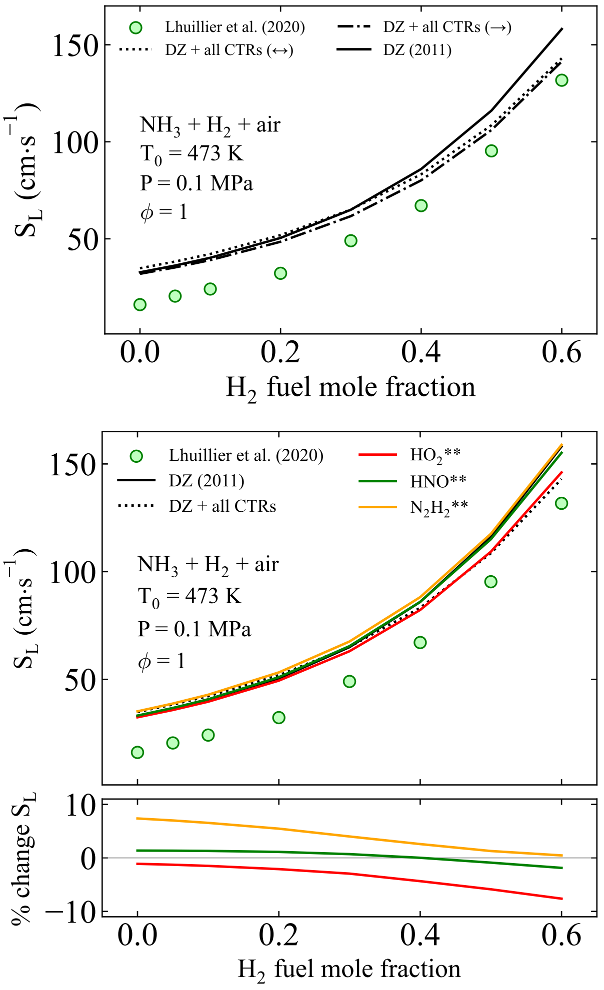

Fig. 2. Laminar flame speed predictions for NH_3 + H_2 + air mixtures over a range of H_2 fuel mole fractions. Lines denote model predictions while symbols represent prior experimental measurements [27]. The lower plot shows percent changes to flame speed predictions resulting from the inclusion of chemically termolecular reactions (mediated by specific energized complexes and allowed to proceed in both directions).

3. Results & discussion

3.1. Ammonia & ammonia/co-fuel flames

Predictions of laminar flame speeds with and without chemically termolecular reactions are provided in Figs. 1–4 for four independent reactant mixtures: NH_3 + air (Fig. 1), NH_3 + H_2 + air (Fig. 2), NH_3 + CH_4 + air (Fig. 3), and NH_3 + syngas (5% H_2, 95% CO) + air (Fig. 4). Models that include chemically termolecular reactions allow them to either proceed in both directions (dotted lines, ↔) or proceed in the forward direction only (dashed–dotted lines, →). Kinetic sensitivity analyses were performed at these conditions to identify the most important chemically termolecular reactions. All reactions identified as influential were further characterized by their ro-vibrationally excited mediating complex — this provides a useful means to bin reaction sets as chemically termolecular reactions that share a mediating complex involve the same potential energy surface. Experimental measurements are provided for comparative value for all four scenarios.

Laminar flame speed predictions for NH_3 + air mixtures (Fig. 1) showed very minor contributions from chemically termolecular reactions over a wide range of equivalence ratios (0.7–1.3). At slightly fuel-rich conditions, a modest increase in flame speed was observed, although these increases were generally limited to ≤5% of the nominal predictions. The lack of participation from chemically termolecular reactions at these conditions was partially attributable to the low reactivity of ammonia. Reactive collisions of rovibrationally excited mediating complexes are unlikely to play an important role in overall reaction kinetics when radical mole fractions drop below a critical threshold (typically ∼1% [1]). Sensitivity analyses performed on these simulations indicated that chemically termolecular reactions mediated by ephemeral HO_2^{**}, $N_2H_2^{**}$, and HNO^{**} were most important (Fig. 1, bottom). Reactions mediated by HO_2^{**} and HNO^{**} slightly decreased and increased flame speed predictions, respectively (changes were generally minor). Reactions mediated by $N_2H_2^{**}$ produced the most significant changes with moderate increases to flame speeds at equivalence ratios near 1.0 – unsurprising, considering that NH_3/air mixtures achieve a maximum adiabatic flame temperature near stoichiometric conditions [26] where mole fractions of radicals (often involved in chemically termolecular reactions as the main reactive colliders) are expected to be highest.

Laminar flame speed predictions for NH_3 + H_2 + air mixtures (Fig. 2) showed increased contributions from chemically termolecular reactions as H_2 fuel mole fractions were increased. The inclusion of chemically termolecular reactions generally resulted in decreased flame speeds with a maximum reduction shown in Fig. 2 at 0.6 H_2 fuel mole

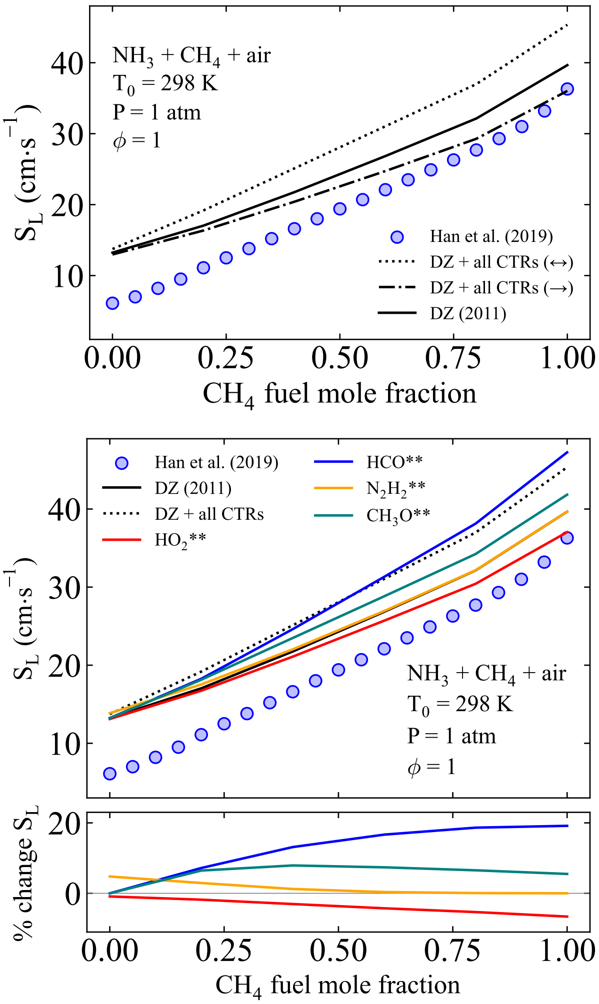

Fig. 3. Laminar flame speed predictions for NH_3 + CH_4 + air mixtures over a range of CH_4 fuel mole fractions. Lines denote model predictions while symbols represent prior experimental measurements [20,28]. The lower plots show percent changes to flame speed predictions resulting from the inclusion of chemically termolecular reactions (mediated by specific energized complexes and allowed to proceed in both directions).

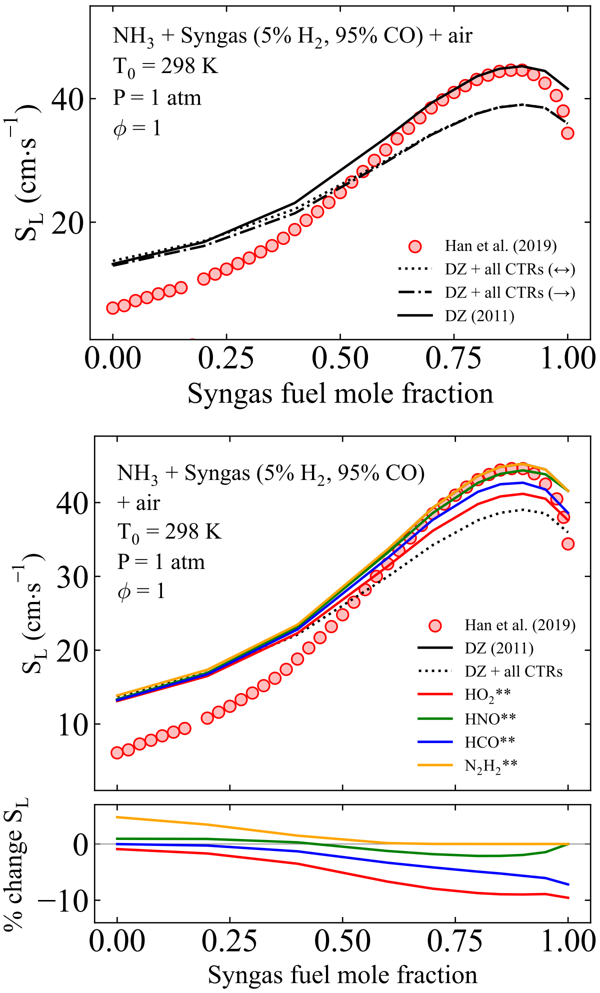

Fig. 4. Laminar flame speed predictions for NH_3 + syngas + air mixtures over a range of syngas fuel mole fractions. Lines denote model predictions while symbols represent experimental measurements [20,28]. The lower plots show percent changes to flame speed predictions resulting from the inclusion of chemically termolecular reactions (mediated by specific energized complexes and allowed to proceed in both directions).

fraction. This observation is in general agreement with prior studies that have shown that H_2 flame speed predictions are significantly reduced when chemically termolecular reactions are included in the kinetics model [1,5]. This is primarily a result of influential chemically termolecular reactions progressing in the forward direction, which typically results in chain terminating reaction pathways that reduce overall reactivity (and, consequently, flame speed). Similar to the results shown in Fig. 1 for NH_3 + air mixtures, chemically termolecular reactions mediated by ephemeral HO_2^{**}, $N_2H_2^{**}$, and HNO^{**} proved to be the most important (Fig. 2, bottom). Reactions mediated by HNO^{**} continued to have limited influence on flame speed predictions. Reactions mediated by $N_2H_2^{**}$ produced moderate increases to flame speeds at lower H_2 fuel mole fractions ($\leq$0.2). Reactions mediated by HO_2^{**} produced the most significant changes to predictions with decreases to flame speeds at elevated H_2 fuel mole fractions.

Laminar flame speed predictions for NH_3 + CH_4 + air mixtures (Fig. 3) showed significant contributions from chemically termolecular reactions. Unlike the NH_3 + H_2 + air predictions (Fig. 2), the inclusion of chemically termolecular reactions *increased* flame speeds. Increases were most significant at elevated CH_4 fuel mole fractions ranging from 0.75–1.00. The opposite trend was observed when chemically termolecular reactions were restricted to forward progression only (dotted–dashed line in Fig. 3, top) – flame speeds *decreased* rather than *increased*. This behavior indicates that some chemically termolecular reactions progressed in the reverse direction, which generally correspond to prompt dissociation reactions [29] that are typically chain-branching (and therefore increase overall reactivity). Additionally, the results of Fig. 3 suggest that chemically termolecular reactions likely play an important role in other co-fuel mixtures that contain significant CH_4 mole fractions, which agrees well with a recent study that investigated the influence of non-thermalized reactions on H_2/CH_4 + air kinetics [4]. Sensitivity analyses indicated that chemically termolecular reactions mediated by ephemeral HO_2^{**}, $N_2H_2^{**}$, HCO^{**}, and CH_3O^{**} were most important (Fig. 3, bottom). Reactions mediated by $N_2H_2^{**}$ continued to exhibit similar trends — they induced modest increases to flame speed predictions when ammonia was the sole fuel but quickly became unimportant in co-fuel scenarios when other hydrocarbon fuels were present at appreciable mole fractions. Reactions mediated by HO_2^{**} continued to produce meaningful decreases in flame speed predictions when hydrocarbon fuel mole fractions were increased. Reactions mediated by HCO^{**} and CH_3O^{**} produced the largest changes to predictions with increases in flame speeds over a wide range of CH_4 fuel mole fractions. Further tests indicated that HCO^{**} and CH_3O^{**} mediated chemically termolecular reactions progressed almost exclusively in the reverse direction, corresponding to prompt dissociation. Interestingly, quantitative studies have proven that the prompt dissociation of HCO

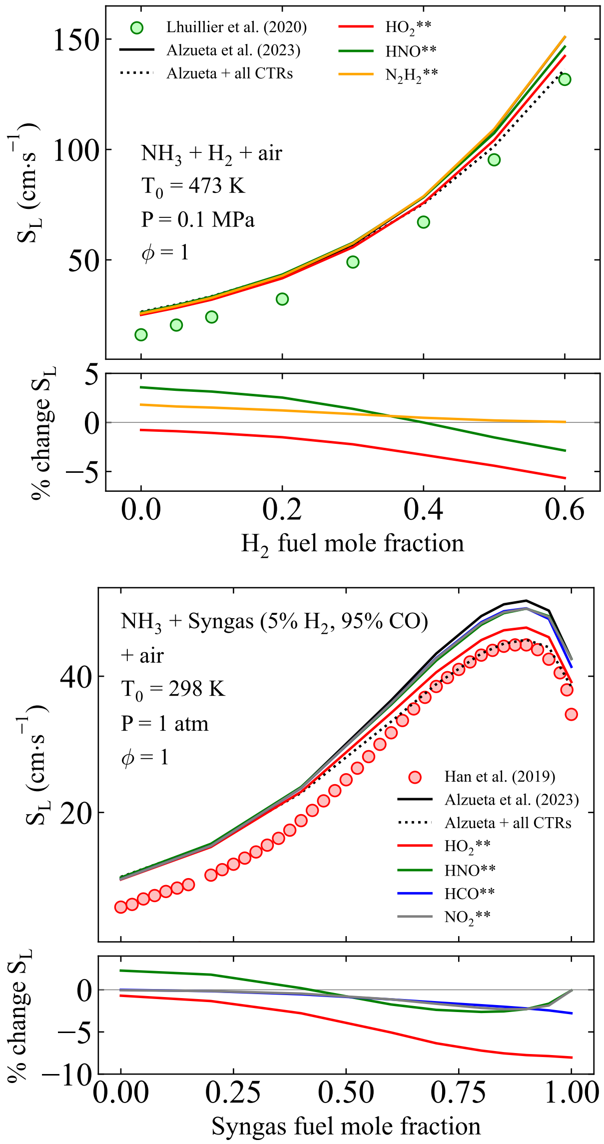

Fig. 5. Laminar flame speed predictions from Alzueta et al. [11] for NH_3 + H_2/syngas + air mixtures over a range of co-fuel mole fractions. Lines denote model predictions while symbols represent prior experimental measurements [20,27,28]. Both plots show percent changes to flame speed predictions resulting from the inclusion of chemically termolecular reactions (mediated by specific energized complexes and allowed to proceed in both directions).

significantly influences CH_2O flame speeds [29,30], indicating that the present estimates are reasonable and yield new insights into other prompt dissociation reactions of potential importance.

Laminar flame speed predictions for NH_3 + syngas (5% H_2, 95% CO) + air mixtures (Fig. 4) showed significant contributions from chemically termolecular reactions. Similar to the NH_3 + H_2 + air predictions (Fig. 2), the inclusion of chemically termolecular reactions decreased flame speed predictions, especially at increased syngas fuel mole fractions. There are no discernible differences between predictions of the two models containing chemically termolecular reactions (Fig. 4, top), indicating that the most influential reactions are progressing almost exclusively in the forward direction. Results from the sensitivity analyses indicated that chemically termolecular reactions mediated by ephemeral HO_2**, N_2H_2**, HNO**, and HCO** were most important (Fig. 4, bottom). Reactions mediated by HO_2** produced their most significant decreases to flame speed predictions compared to the other three scenarios (Figs. 1–3). Once again, reactions mediated by N_2H_2** induced modest increases to flame speed predictions when ammonia fuel mole fractions were high and reactions mediated by HNO** continued to have limited influence. Reactions mediated by HCO** produced moderate decreases in flame speeds at syngas fuel mole fractions ranging from 0.75–1.00. It is interesting to note that reactions mediated by HCO** *increased* flame speed predictions for NH_3 + CH_4 + air mixtures and *decreased* predictions for NH_3 + syngas + air mixtures — likely because HCO** mediated reactions occur in the reverse direction (i.e., prompt dissociation) for NH_3 + CH_4 + air and in the forward direction (i.e., chemically termolecular reactions) for NH_3 + syngas + air.

The combined results of Figs. 1–4 indicate that chemically termolecular reactions are likely unimportant during ammonia combustion when ammonia is the sole fuel. However, ammonia co-fuel applications (where ammonia is mixed with hydrocarbon fuels to increase overall reactivity) generally provide the increased flame temperatures and new molecular species needed to increase the influence of chemically termolecular reactions. This conclusion is particularly important to energetic materials as many generate significant mole fractions of ammonia and other C/H/N/O small molecules during combustion and deflagration.

Considering the important advances in nitrogen chemistry and significant increases in ammonia kinetics research that have occurred over the last ~5–10 years (after publication of the DZ model), the authors thought it prudent to expand the analysis to include a more recent ammonia kinetics model that was engineered for ammonia co-fuel flames and founded on high-level theoretical kinetics calculations (Alzueta et al. [11]). It is important to note that this model already includes four chemically termolecular reactions mediated by HO_2^{**} for which reaction rate coefficients have been previously published [1]. For the purposes of this initial investigation, those four reactions were removed from the Alzueta et al. model and replaced with estimated values provided by the Barbet et al. screening procedure [5] in order to apply the same procedure to the Alzueta et al. model as applied to the DZ model, for consistency.

A sensitivity analysis of flame speed predictions to the rate constants of the Alzueta et al. model [11] for NH_3 + H_2/syngas + air mixtures (Fig. 5) identified many of the same mediating complexes as the DZ model. Additionally, the results using the Alzueta et al. model point to the potential importance of chemically termolecular reactions mediated by NO_2**, although induced reductions to flame speed predictions were relatively minor across all conditions shown in Fig. 5. An interesting conclusion from these results is that the inclusion of chemically termolecular reactions (at their estimated rate coefficients) significantly improves agreement between flame speed predictions and experimental measurements at elevated co-fuel mole fractions — a known shortcoming of Alzueta et al. [11] and other related nitrogen chemistry models [31,32].

Considering that the DZ and Alzueta et al. models identified many of the same mediating complexes as being important to ammonia/co-fuel flame speed simulations, the authors decided to tabulate the reactions from each model that contributed most to changes in predictions (Table 1) as they are likely important to both ammonia/co-fuel and propellant flames and therefore deserving of future master equation analysis.

3.2. AP/HTPB & NG burner-stabilized flames

After identifying the most influential chemically termolecular reactions for ammonia/co-fuel flame speeds, burner-stabilized flame simulations were run for an AP/HTPB mixture and pure NG to explore the influence of these reactions during propellant combustion. All chemically termolecular reactions mediated by HO_2**, N_2H_2**, HNO**, HCO**, and CH_3O** were added to the DZ and NG models [17] to produce the “top CTRs” models identified in Figs. 6 and 7 (note that all chemically termolecular reactions were allowed to progress in both

Table 1
The most influential chemically termolecular reactions identified in ammonia/co-fuel flame simulations ("x" indicates which model was heavily influenced by each listed reaction). DZ: Dark Zone [8], AL: Alzueta et al. [11]. Note that while some tabulated reactions appear to be termolecular association reactions (e.g., H + CO + H = CO + H_2), they represent distinctly different kinetics pathways where all reactants undergo chemical bond transformations (e.g., H + CO + H → HCO^{**} + H → CO + H_2).

Reaction	DZ	AL
CH_3O^{**}		
$H+CH_2O+H \leftrightarrow OH+CH_3$	x	n/a
$H+CH_2O+O \leftrightarrow CH_3+O_2$	x	n/a
$H+CH_2O+OH \leftrightarrow HO_2+CH_3$	x	n/a
HCO^{**}		
$H+CO+H \leftrightarrow CO+H_2$	x	
$H+CO+O \leftrightarrow CH+O_2$	x	
$H+CO+OH \leftrightarrow CH_2+O_2$	x	
$H+CO+OH \leftrightarrow O+CH_2O$	x	
$H+CO+OH \leftrightarrow H_2O+CO$	x	x
$H+CO+O_2 \leftrightarrow CO+HO_2$		x
$H+CO+H_2O \leftrightarrow OH+CH_2O$	x	
$H+CO+CH_3 \leftrightarrow CH_4+CO$	x	
HNO^{**}		
$H+NO+H \leftrightarrow NH_2+O$	x	x
$H+NO+H \leftrightarrow NH+OH$		x
$H+NO+H \leftrightarrow H_2+NO$		x
$H+NO+O \leftrightarrow NH+O_2$		x
$H+NO+O \leftrightarrow NO+OH$		x
$H+NO+NO \leftrightarrow NH+NO_2$		x
$H+NO+H_2O \leftrightarrow NH_2+HO_2$		x
HO_2^{**}		
$H+O_2+H \leftrightarrow OH+OH$	x	x
$H+O_2+H \leftrightarrow H_2+O_2$	x	x
$H+O_2+H \leftrightarrow H_2O+O$		x
$H+O_2+O \leftrightarrow O_2+OH$	x	x
$H+O_2+OH \leftrightarrow O_2+H_2O$		x
$N_2H_2^{**}$		
$NNH+H+H \leftrightarrow NH_2+NH$	x	x
$NNH+H+H_2 \leftrightarrow N_2H_3+H$		x

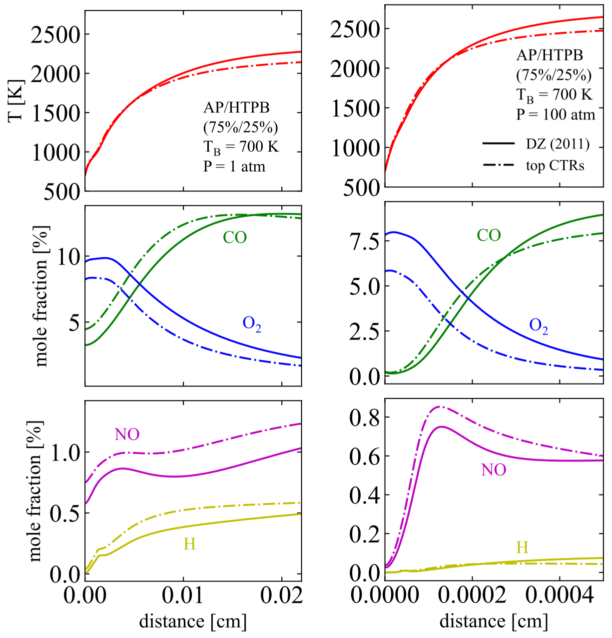

Fig. 6. Burner-stabilized flame predictions for an AP/HTPB mixture (75%/25%) at 1 atm (left) and 100 atm (right) using the DZ model [8,15,16] with (dashed-dotted lines) and without (solid lines) all potentially important chemically termolecular reactions.

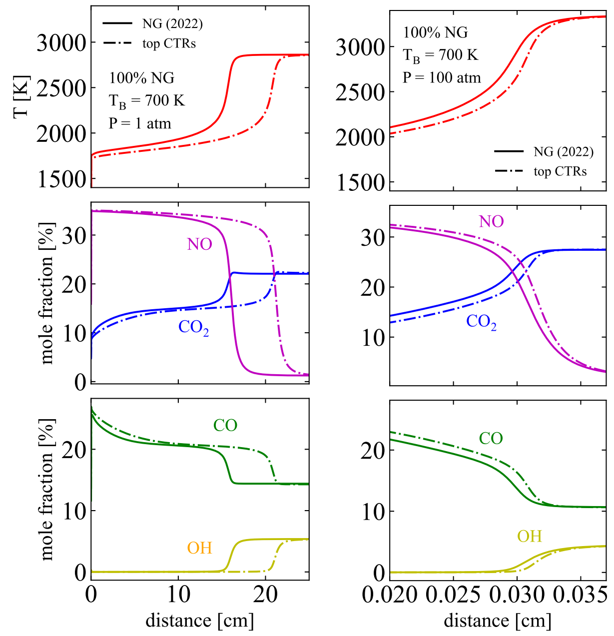

Fig. 7. Burner-stabilized flame predictions for pure NG at 1 atm (left) and 100 atm (right) using the NG model [17] with (dashed-dotted lines) and without (solid lines) all potentially important chemically termolecular reactions.

directions). Simulations were run at 1 and 100 atm to see if an increase in pressure would influence the relative importance of these reactions.

The simulation results shown in Figs. 6 and 7 highlight a few key findings critical to propellant (and ammonia) combustion modeling: (1) temperature, major species (e.g., CO and O_2), and radicals (e.g., H and OH) were all influenced by the inclusion of chemically termolecular reactions for simulations of both AP/HTPB and NG flames; (2) increases in simulation pressure qualitatively and quantitatively altered the influence of these reactions, but significant discrepancies remained at elevated pressures, indicating that chemically termolecular reactions likely remain important at pressures relevant to many propulsion applications (≥100 atm); (3) the ammonia/co-fuel flame simulations explored in the prior section indicated that the most important chemically termolecular reactions identified in this study become more influential when hydrocarbon mole fractions are increased (at least for the limited scenarios investigated). The propellants simulated here have limited hydrogen/carbon content compared to other single-, double-, and triple-base propellants that contain high mole fractions of nitrocellulose, implying that many other formulations may be more heavily influenced than what is highlighted in Figs. 6 and 7.

4. Summary & conclusions

An initial exploration of chemically termolecular reactions was performed for small molecules important to ammonia/co-fuel flames and propellant combustion modeling. Potential chemically termolecular reactions were identified and their respective rate coefficients were estimated using an established screening procedure. Ammonia/co-fuel flame speed simulations were analyzed to identify chemically termolecular reactions important to those predictions and similar energetic material models as many rely heavily on ammonia and hydrocarbon sub-mechanisms. Chemically termolecular reactions identified as potentially important were introduced into AP/HTPB and NG flame simulations and were found to significantly alter predictions of temperature and species mole fractions over a range of pressures. Chemically termolecular reactions mediated by ephemeral HO_2^{**}, $N_2H_2^{**}$, HNO^{**}, HCO^{**}, and CH_3O^{**} have been identified as worthwhile candidates for *ab initio*-based master equation analysis to better quantify their rate coefficients to enable their inclusion in future kinetics models.

CRediT authorship contribution statement

Rodger E. Cornell: Designed simulations, Performed simulations, Analyzed results, Generated figures, Wrote paper. **Michael P. Burke:** Designed simulations, Analyzed results, Reviewed/edited paper.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.proci.2024.105265.

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