Ignition delay time and multi-speciation measurements of ammonia/C_1 mixtures in shock tube

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1 Abstract

Ignition delay times (IDTs) and time-resolved speciation profiles, including NH_3, NO, and CO were measured for ammonia/C_1 fuel blends (NH_3/CO, NH_3/CH_4, NH_3/CH_3OH) in a shock tube using laser absorption spectroscopy. Experiments covered 15 mixtures across wide equivalence ratios (ϕ = 0.5, 1.0, 1.5) with 5–20% C_1 addition at 1477–2236 K and ~2.5 bar. The PTB-NH_3/C_2 1.1 mechanism showed good agreement with high-temperature trends but showed limitations at lower temperatures and fuel-rich conditions, overpredicting CO and NH_3 mole fractions. Among all three C_1 molecules, CH_3OH showed the strongest enhancement to the ammonia ignition via radical generation while CH_4 showed the weakest enhancement due to some inhibitive pathways. CO demonstrated a clear influence on the carbon-nitrogen kinetics. Key findings highlight NH_2 as a critical intermediate and underscore the need for improved low-temperature kinetic models.

2 Introduction

As combustion technology advances, increasing emphasis is on improving energy efficiency while reducing carbon and pollutant emissions [1]. Combustion devices such as boilers, furnaces, engines, and gas turbines primarily rely on hydrocarbons, emitting carbon dioxide (CO_2), a major greenhouse gas [2]. To achieve decarbonization, alternative fuels like methane, methanol, hydrogen, and ammonia are being explored. Among these, ammonia (NH_3), a carbon-free fuel and hydrogen carrier, is gaining attention as a promising energy source. Ammonia combustion is considered the most efficient method for utilizing NH_3 as an energy carrier, and research suggests its feasibility for combustion applications [3, 4, 5]. However, challenges arise when burning pure ammonia due to its narrow flammability limit (15.5-27.0% by volume in air), high auto-ignition temperature (around 630°C), and low burning velocity (0.05-0.13 m/s) [6].

To enhance the reactivity of NH_3 during combustion, blending it with small amounts of other substances like hydrocarbons has been proposed. This approach helps maintain a carbon-free profile while improving NH_3's combustion characteristics. Research has focused on blending NH_3 with additives like alcohols [7], ethers [8], alkanes [9], and diesel [10] in various experimental setups, including shock tubes, jet-stirred reactors, and constant-volume combustion vessels. While data on global parameters

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like ignition delay times (IDTs) and flame speed have been extensively studied, more detailed species concentration data are necessary for accurate model validation. Such information is critical for designing and optimizing combustion systems that are both efficient and environmentally friendly. Techniques like mass spectrometry (MS), gas chromatography (GC), and optical methods, especially laser absorption spectroscopy (LAS), have been employed to measure species concentration in real-time during combustion. LAS, a non-invasive and sensitive technique [11], has proven invaluable for providing precise and timely data essential for understanding complex chemical processes.

Coupled with shock tubes, LAS has enabled significant advances in studying time-resolved species concentration measurements, aiding in the development and refinement of chemical kinetic models. Research groups like Hanson's [11] have advanced the use of shock tubes and LAS in hydrocarbon combustion studies. Several studies have also explored NH_3 combustion, including work by Li et al. [12], Mathieu et al. [13], and Zhu et al. [14], who employed shock tubes and LAS to investigate NH_3 oxidation and its mixtures with other fuels like C_2H_6, C_2H_5OH, and CH_4. These studies enhance our understanding of NH_3's potential as a fuel and provide valuable data for refining combustion models to reduce emissions. Building on prior research, this study investigates NH_3 oxidation with C_1 molecules (CO, CH_4, and CH_3OH) at high temperatures, generating new datasets for speciation and IDTs while assessing the predictive performance of the PTB-NH_3/C_2 1.1 kinetic mechanism. The findings aim to enhance our understanding of NH_3 combustion chemistry and identify future directions for mechanism improvement.

3 Methodology and experimental setup

The PTB shock tubeis an 8-meter-long stainless-steel facility with a 70 mm overall inner diameter used for the investigation. More details of the shock tube can be found in [14, 15]. Helium serves as the driver gas to achieve the desired conditions. Four piezoelectric pressure sensors (Kistler 603CAB) are spaced 500 mm apart in the last 2 meters of the driven section to measure shock velocities. The fourth sensor, 29 mm from the end wall, records pressure profiles. Reflected shock conditions (P_5, T_5) are calculated using shock equations. ZnSe optical windows near the fourth sensor enable LAS spectrometer coupling (see Fig. 1). The sensors are connected to charge amplifiers (Kistler 5018A), with signals digitized by a Spectrum Instrumentation data acquisition card (M2i.4964-Exp).

Time histories of CO, NH_3, and NO behind reflected shock waves were measured via absorption lines centered at 2059.91 cm^{-1} (CO), 1084.61 cm^{-1} (NH_3), and 1915.76 cm^{-1} (NO) using fixed-wavelength lasers. NH_3 detection employed a CW-DFB quantum cascade laser (Alpes Lasers) with a Thorlabs ITC4005QCL driver. NO and CO were measured using CW-DFB interband cascade lasers (Nanoplus), controlled by ILX Lightwave (LDC-3900) and Thorlabs PRO8000 systems, respectively. Spectroscopic data for these transitions were validated in prior studies [14]. The mixtures shown in Table 1 were prepared based on Dalton's law.

The Beer-Lambert law $\alpha(v) = -\ln\frac{I_t}{I_0} = pS(T)Lx\phi(v) = \sigma(T,p)xn_dL,$ describes the relationship between incident and transmitted beam intensities through absorbing species, allowing for the calculation of mole fractions based on dynamic pressure and temperature profiles. The dynamic parameters, calculated using the PTB-NH_3/C_2 1.1 mechanism and Cantera software, are used to compute the spectroscopic absorption cross-sections and mole fractions. Uncertainty analysis, based on standard error propagation, is applied to the mole fraction calculations, with the maximum uncertainties in NO, CO, and NH_3 mole fractions reaching 23.35%, 10.07%, and 14%, respectively. The uncertainty in IDT is determined using pressure and CO profile analysis, with an IDT uncertainty of 5.92%.

Numerical simulations are performed using the PTB-NH_3/C_2 1.1 mechanism in Cantera, focusing on zero-dimensional constant volume reactors to replicate shock tube conditions. The mechanism incorporates nitrogen sub-mechanisms from Dai et al. [7] and promoter fuel sub-mechanisms from the NUIG 1.1 model [16], validated against autoignition and speciation data for NH_3 fuel mixtures. This study evaluates the mechanism's accuracy in predicting speciation profiles and IDTs for NH_3/C_1 mixtures at high temperatures, extending validation to C_1 chemistry.

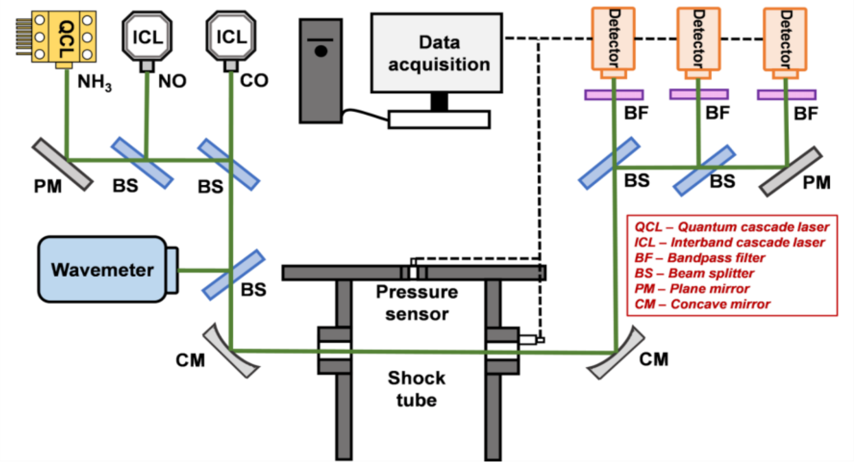

Figure 1: Schematics of the TDLAS setup near the shock tube end-wall [12]. BF – Bandpass filter, BS – Beam Splitter, PM – Plane mirror, CM: Concave Mirror, D: Detector.

Table 1: Detailed mixture compositions and experimental conditions

Mixture	No.	C_1 Percentage	ϕ	NH_3	CO/ CH_4/ CH_3OH	O_2	Ar	T_5 (K)	P_5 (bar)
NH_3/ CO	1	5% CO	1.0	0.05467	0.00288	0.04245	0.9	1662.7 – 2026.6	2.29 – 2.74
	2	10% CO	0.5	0.03674	0.00408	0.05918		1601.8 – 2064.9	2.26 – 2.88
	3		1.0	0.05217	0.00580	0.04203		1721.6 – 2123.3	2.37 – 2.66
	4		1.5	0.06068	0.00674	0.03258		1747.3 – 2101.3	2.45 – 2.76
	5	20% CO	1.0	0.04706	0.01176	0.04118		1579.6 – 2092.3	2.37 – 2.68
NH_3/ CH_4	6	5% CH_4	1.0	0.05241	0.00276	0.04483	0.9	1631.4 – 2236.3	2.34 – 2.65
	7	10% CH_4	0.5	0.03273	0.00364	0.06363		1609.8 – 2146.0	2.42 – 2.92
	8		1.0	0.04800	0.00533	0.04667		1684.0 – 2108.3	2.14 – 2.80
	9		1.5	0.05684	0.00632	0.03684		1680.3 – 2193.5	2.32 – 2.66
	10	20% CH_4	1.0	0.04000	0.01000	0.05000		1607.0 – 2222.8	2.31 – 2.80
NH_3/ CH_3OH	11	5% CH_3OH	0.5	0.0369	0.0019	0.0612	0.9	1535.7 – 1883.4	2.75 – 2.90
	12		1.0	0.0531	0.0028	0.044		1587.4 – 1805.3	2.66 – 2.76
	13		1.5	0.0623	0.0033	0.0344		1601.8 – 1939.3	2.21 – 2.85
	14	10% CH_3OH	1.0	0.0493	0.0055	0.045		1561.8 – 1881.3	2.59 – 3.08
	15	20% CH_3OH	1.0	0.0421	0.0105	0.048		1477.3 – 1750.9	2.77 – 2.80

4 Results and discussion

In this study, IDT is determined from CO profiles, with two definitions based on the fuel mixture: for NH_3/CO, IDT is taken as the minimum rate of CO consumption (d(CO)/dt), while for NH_3/CH_4 and

NH_3/CH_3OH, it is defined by the time of peak CO mole fraction. Representative experimental signals, including pressure, raw laser data, absorbance, and mole fractions, illustrating species evolution during combustion (see Fig. 2). CO and NO are produced in NH_3/CH_3OH and NH_3/CH_4 mixtures, while both NH_3 and CO are consumed in NH_3/CO mixtures, enabling synchronized tracking of reactant depletion and product formation for accurate IDT determination.

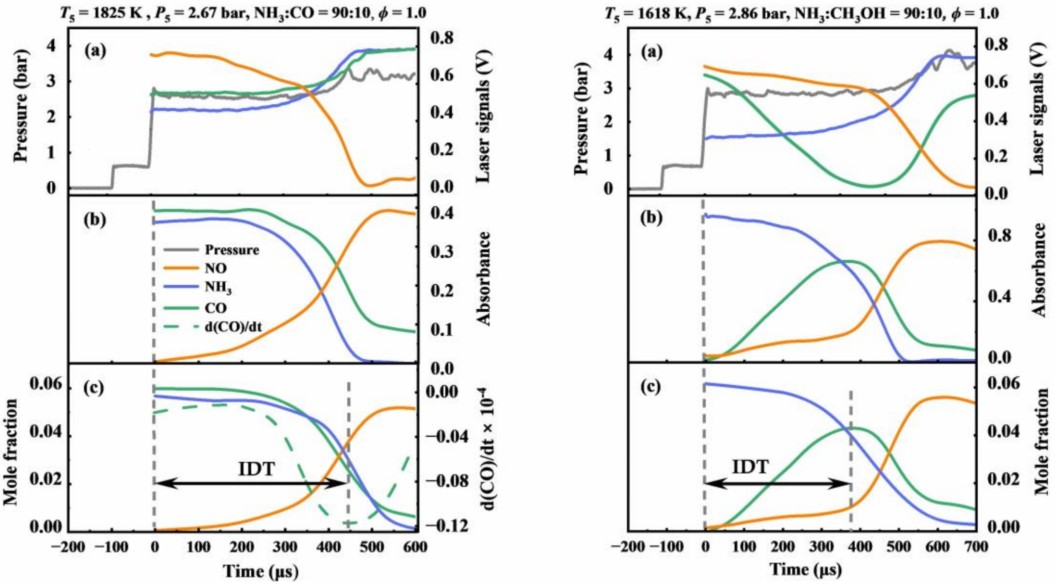

Figure 2: a) Pressure traces alongside corresponding laser signal outputs; b) Measured absorbance data; c) Temporal evolution of species mole fractions for two stoichiometric mixtures - NH_3:CO = 90:10, at T_5 = 1825 K, P_5 = 2.67 bar (left) and $NH_3:CH_3OH$ = 90:10 at T_5 = 1618 K, P_5 = 2.86 bar (right).

The IDTs for NH_3/C_1 fuel blends (CO, CH_4, CH_3OH) exhibit Arrhenius behavior, with IDTs decreasing as temperature increases (see Fig. 3). Adding C_1 fuels to NH_3 reduces IDTs, enhancing reactivity. Among the tested fuels, CH_3OH shows the greatest reactivity promotion, reducing IDTs by a factor of ~2.44 when increasing its content from 10% to 20%. CH_4 and CO exhibit similar but weaker effects, with their IDTs close to each other under identical conditions. Leaner mixtures (ϕ = 0.5) display shorter IDTs, reflecting enhanced reactivity, consistent with previous findings [12]. At high temperatures, radical-mediated reactions dominate ignition, accelerating reactivity. For NH_3/CH_3OH mixtures, methanol addition enhances radical formation pathways, leading to significant IDT reduction. Conversely, NH_3/CH_4 mixtures exhibit enhanced CO and CH_2O formation due to CH_4 oxidation, while NH_3/CO mixtures feature simpler pathways dominated by CO chemistry. Whereas at lower temperatures, intermediate species like peroxy radicals complicate the reaction pathways, leading to slower ignition. This trend is consistent for NH_3/CH_3OH and NH_3/CH_4 mixtures, with the reduction in IDT being more pronounced at higher temperatures. Fuel-rich mixtures (ϕ = 1.5) exhibit longer IDTs because high temperatures hinder rapid chain reactions.

Experimental and simulated IDTs using the PTB-NH_3/C_2 1.1 mechanism generally align well, effectively capturing temperature and equivalence ratio trends. However, at high temperatures (> 1750 K), the mechanism underpredicts chemical reaction rates, causing discrepancies in some cases. Additionally, the IDTs for NH_3/CH_3OH under fuel-rich conditions are underpredicted, particularly at lower temperatures (< 1650 K). Moreover, a comparison of simulated and experimental speciation profiles is carried out (see Fig. 4). All speciation profiles were truncated before the arrival of the contact surface. The mechanism effectively replicates CO formation and NO dynamics across temperature regimes. However, for NH_3 decomposition, simulations lag experiments at low temperatures and fail to capture the two-stage decomposition observed experimentally. NH_3/CH_3OH mixtures show broader CO peaks, distinct from the sharper peaks in NH_3/CO and NH_3/CH_4 mixtures, reflecting unique reaction dynamics successfully captured by the model. In some fuel-rich NH_3/CO mixtures, predicted NO levels are higher than experimental measurements, but otherwise, the model agrees well with experimental trends, within uncertainties. The generation of CO initiates immediately with the oxidation process and persists until it attains a peak value. Due to the conversion of CO into CO_2, CO tends to decrease in most mixtures. But in fuel-rich mixtures, CO reaches its peak and then remains almost unchanged over time. The peak value of CO is less receptive to temperature than that of NO. In comparison to the experimental data, the simulations predict an accelerated consumption of NH_3, which can be attributed to the generation and subsequent consumption of CO - an important reactive intermediate. This process facilitates the production of additional O/H radicals, thereby enhancing the overall reactivity and leading to a faster depletion of NH_3 in the simulated conditions.

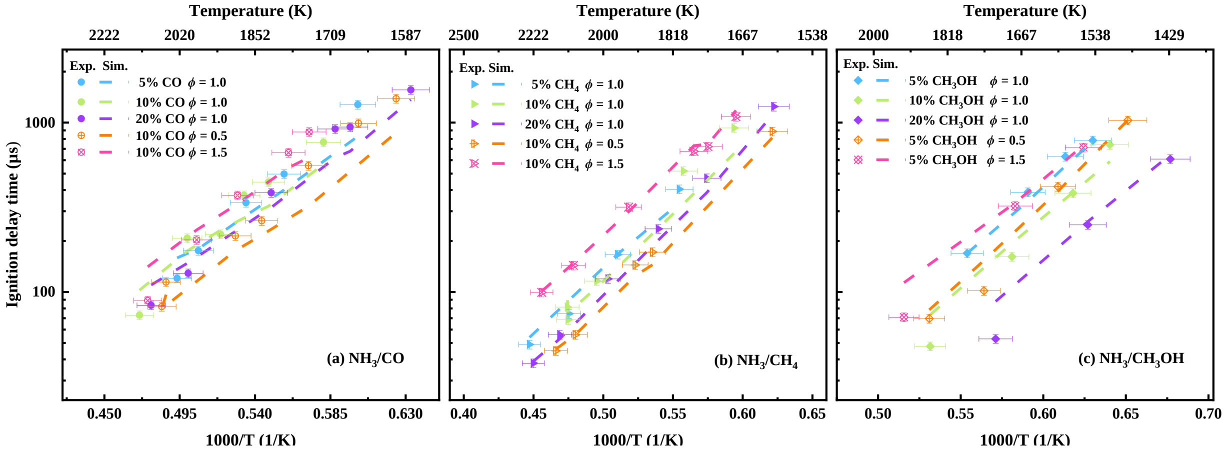

Figure 3: Comparison between experimental and simulated IDTs. The error bars of T_5 (horizontal) and IDT (vertical) are indicated on all mixtures.

In summary, the PTB-NH_3/C_2 1.1 mechanism can reproduce the shapes of speciation profiles as well as the temperature and equivalence ratio dependencies of the experimental results. Nevertheless, addressing observed discrepancies, especially under high-pressure, low-temperature, and fuel-rich conditions. These findings underscore the need for refined kinetic parameters and additional experimental data, particularly at high pressures and for blends with unsaturated hydrocarbons, to improve model accuracy and extend its applicability.

Further, the sensitivity analysis of IDT on NH_3/CO, NH_3/CH_4, and NH_3/CH_3OH reveals that H radicals are key in governing reactivity, with reactions involving NH_3 with O_2, H, OH, and NO exerting significant control over ignition. In NH_3/CO mixtures, hydrogen-nitrogen-oxygen-related reactions dominate, with $NH_2 + NO <=> NNH + OH$ promoting ignition, while $NH_2 + NO <=> N_2 + H_2O$ inhibits it. For NH_3/CH_4, reactions like $CH_3 + O_2 <=> OH + CH_2O$ promote ignition, while $CH_4 + H <=> H_2 + CH_3$ inhibits it. In NH_3/CH_3OH, the CH_3OH dehydrogenation reaction accelerates ignition, while $NH_3 + O_2 <=> HO_2 + NH_2$ becomes inhibitive. At high temperatures (> 1750 K), fuel-rich mixtures exhibit the lowest reactivity due to enhanced nitrogen-carbon interactions, as reactions involving nitrogen species like N_2H_2 become more prominent. This suggests that, under fuel-rich conditions, the formation of key intermediates like HCN or NCO compounds increases, further hindering the reactivity. The reaction pathways highlight the central role of NH_2 in NH_3 oxidation, with significant contributions from CO, CH_4, and CH_3OH chemistry influencing ignition behavior and NO production. Additionally, radical recycling mechanisms, especially involving NH_2 and OH, ensure continued fuel consumption and nitrogen formation, with implications for both energy release and pollutant formation. Understanding these interactions is essential for optimizing combustion strategies in nitrogen-containing fuel mixtures.

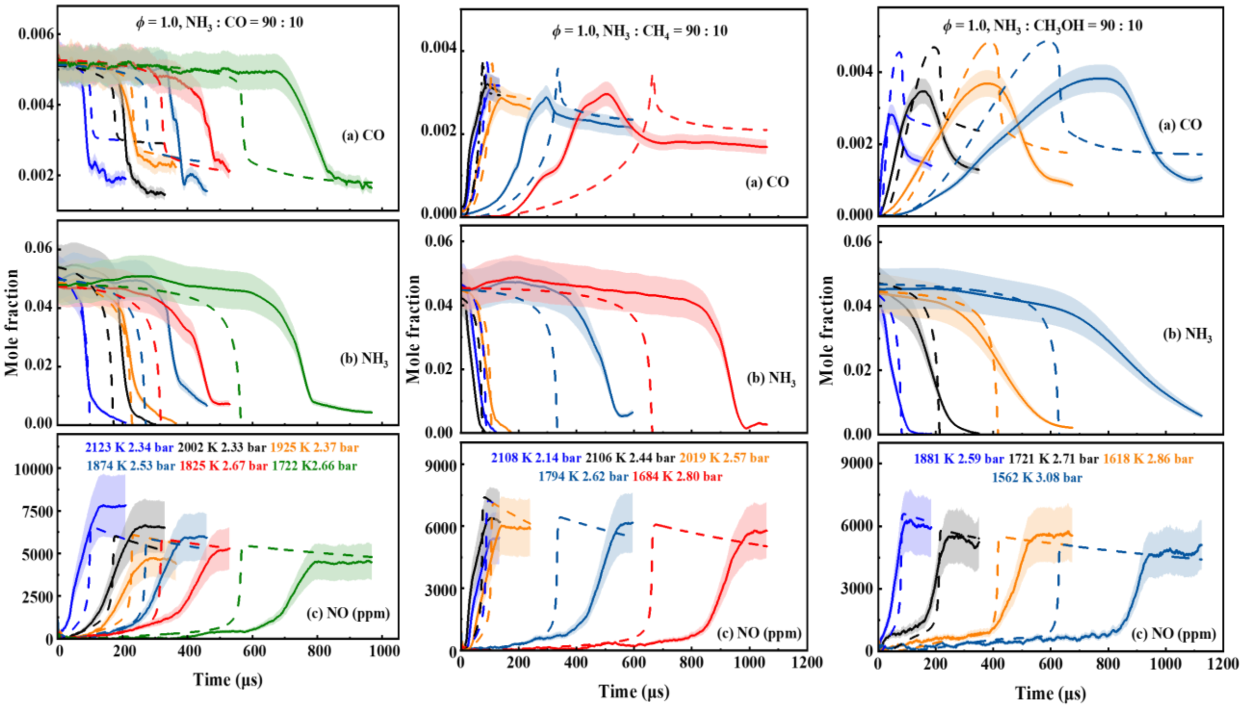

Figure 4: Comparison between experimental and predicted species mole fraction for NH_3/CO, NH_3/CH_4, and NH_3/CH_3OH mixture ($NH_3:C_1 = 90:10$, $\phi = 1.0$, Solid lines: experiments, Dashed lines: simulations, Shadows mark uncertainties).

5 Conclusion

In this study, shock tube experiments combined with multi-species laser absorption spectroscopy (LAS) were performed to investigate the combustion characteristics of NH_3 blended with C_1 fuels (CO, CH_4, and CH_3OH). Experiments were conducted at equivalence ratios of 0.5, 1.0, and 1.5, with temperatures ranging from 1477 to 2236 K and pressures near 2.5 bar. The PTB-NH_3/C_2 1.1 mechanism accurately captured general trends in CO, NO, and NH_3 profiles, including formation, peak, and plateauing behaviors. However, notable discrepancies included underpredictions of NH_3 decomposition rates at low temperatures (< 1650 K) and the absence of two-stage decomposition behaviors in simulations. Additionally, IDTs were underpredicted at certain equivalence ratios and temperatures, and deviations were observed in CO and NO profiles under high-pressure and fuel-rich conditions. The results demonstrated that adding CO, CH_4, or CH_3OH promoted ignition. The promotion of ignition followed the order $CH_3OH > CH_4 > CO$, with CH_3OH displaying unique reaction pathways contributing to broader CO peaks under fuel-rich conditions. These findings highlight the need for refined kinetic parameters and improved modelling of low-temperature and high-pressure reaction pathways. Future work should focus on expanding experimental data to include additional intermediate species, high-pressure conditions, and blends with unsaturated hydrocarbons such as C_2H_2 and C_2H_4. Optimizing the reaction mechanism using advanced tools such as machine learning could further enhance prediction accuracy, advancing the understanding of NH_3/C_1 fuel combustion systems.

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