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Laser-absorption-spectroscopy-based temperature and NH_3 -concentration time-history measurements during the oxidation processes of the shock-heated reacting NH_3/H_2 mixtures



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ARTICLE INFO

Article history: Received 15 May 2022 Revised 15 August 2022 Accepted 22 August 2022 Available online 5 September 2022

Keywords: NH₃ oxidation Shock tube Laser absorption spectroscopy Temperature Kinetics mechanism

ABSTRACT

As a carbon-free fuel, NH₃ has been considered as a potential and promising alternative energy carrier in the future transportation system. This study simultaneously measured the temperature and NH₃concentration time histories during the oxidation processes of the shock-heated NH₃/H₂ mixtures by combining laser absorption techniques. The v'' = 0, P8 and v'' = 1, R21 lines in the fundamental vibrational band of CO were selected for temperature time-history measurements. Nine transition lines in the v_2 fundamental vibrational band of NH₃ near 8.91 um were selected for NH₃-concentration time-history measurements. The temperature- and pressure-dependent NH₃ absorption cross-section highly diluted in argon was measured at 1000-2200 K and 0.8-3.9 bar, respectively. The time-dependent temperature and NH₃ concentration were then measured and compared with the predictions based on four mechanisms (Mathieu & Petersen, 2015; Glarborg et al., 2018; Wang et al., 2020; Shrestha et al., 2021). The four mechanisms were substantially slow in predicting the NH₃-concentration time histories for the stoichiometric NH₃/H₂ mixtures. The Glarborg et al. mechanism and the Shrestha et al. mechanism showed very good agreements with the experiments for the fuel-rich NH₃/H₂ mixtures, especially in predicting the NH₃concentration time-history profiles in the burnout state. Comprehensive kinetics analyses illustrated that the NH₃ addition evidently changed the mixture reactivity and formation and consumption processes of H and OH radicals. This study updated the rate coefficients of $NH_3 + OH = NH_2 + H_2O$ in the Glarborg et al. mechanism and the modified mechanism showed improved performances in predicting the NH₃-concentration profiles.

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1. Introduction

The increasing global warming motivated the world to find alternative fuels with limited or no greenhouse-gas emissions. NH_3 is a promising engine alternative fuel for future transportation systems because of its unusual characteristics like zero carbon emission and no soot formation. NH_3 has a higher energy density in the liquid phase than H_2 and has similar thermal properties (e.g., boiling temperature and condensation pressure) to propane [1]. Moreover, when compared to H_2 , compressing NH_3 in liquid phase is far more convenient for safe transport. Therefore, a good strategy is to convert H_2 into NH_3 by reacting with N_2 for safe energy transportation. The detailed technical and economic evaluations can be found in the studies reported by Kobayashi et al. [2] and

* Corresponding author. *E-mail address:* apspect@tsinghua.edu.cn (Z. Peng). Valera-Medina et al. [3]. NH₃ can also be derived from renewable sources using the concept of power-to-gas, such as biomass gasification processes. NH₃ is widely used as an effective agent to decrease NO_x emissions in coal power plant. Shu et al. [4] numerically demonstrated the potential capability of NH₃/air to be free from NO_x emission under specific conditions. Therefore, it is critical to investigate the combustion properties of NH₃ under engine-relevant conditions by measuring key parameters, such as ignition delay times [5], laminar flame speeds [6], and pollution emission [7]. These experimental results are crucial for future engine design and optimization. In addition, the combustion performance of NH₃ has been reported to differ from that of common hydrocarbon fuels [1]. Mixing NH₃ with other fuels is an appropriate way to improve the combustion performance.

As an "ideal" high-temperature reactor, the shock tube can heat and compress the gas mixtures in the driven section instantaneously and homogeneously by the incident and reflected shock waves. In addition, the "stable" environment behind re-

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flected shock waves can be sustained for a certain time scale (e.g., 1–3 ms), making it an ideal environment for high-temperature reaction kinetics studies. Many research groups have used shock tubes to measure the ignition delay times of hydrocarbon and blended fuels. Mathieu and Petersen [8] measured the ignition delay times of NH₃/O₂/Ar mixtures under high-temperature conditions behind the reflected shock waves. Shu et al. [4] also measured the ignition delay times of NH₃/air mixtures under high-ressure conditions.

When compared with the global parameters like ignition delay times and laminar flame speeds, the time-resolved measurements of temperature and species concentration during fuel oxidation can give insights into fuel reaction processes and provide valuable data for mechanism developments and optimization. Laser absorption spectroscopy (LAS) is a highly-selective, non-intrusive, and highly-sensitive technique for measuring multiparameters transient processes with microsecond time-resolution. LAS techniques for temperature and species concentration measurements have been developed by several research groups [9–16]. The time-resolved temperature measurements provide detailed insights into the real thermo-kinetic states during fuel reaction processes considering the influences of non-ideal effects inside shock tubes and heat release/sink [17-19]. Furthermore, the measured temperature helps in accurate conversion of the species absorbance profiles into the concentration profiles, especially for the transition lines with strong temperature dependence. Notably, when developing LAS techniques for high-temperature measurements during fuel oxidation, it is critical to consider potential absorption interferences from other species. He et al. [10] and Mulvihill and Petersen [20] measured the CO₂ broadband absorbance near 4.56 µm over a wide range of temperatures and subtracted the CO₂ interferences for accurate CO concentration measurements during the hydrocarbon oxidation. However, the above-mentioned measurements still need mechanism-dependent temperature and CO₂ concentration predictions to subtract the interferences from CO₂ absorbance. Zheng et al. [21] developed the LAS technique for simultaneous temperature, CO-, and CO₂-concentration time-history measurements during the oxidation processes of n-heptane blended with diethyl ether. The measured results were independent of the predictions of mechanisms. The multi-parameter measurements during hydrocarbon oxidation provide valuable information for mechanism development and optimization.

Time-dependent fuel-concentration measurements are also important for mechanism developments. Several research groups [22-24] have measured and reported the absorption cross-section of hydrocarbons near 3.39 µm. NH₃-concentration measurements are critical in developing and optimizing the NH₃ mechanisms because NO_x or unburned NH₃ in the burnout state will pollute the environment. Fig. 1 shows a comparison between the measured and simulated NH₃-concentration profiles for the mixtures 4 and 6 used in this study. The simulated data were based on the GRI-Mech 3.0 [25], the Konnov et al. [26] mechanism, the Klippenstein et al. [27] mechanism, the Mathieu & Petersen [8] mechanism, the Glarborg et al. [28] mechanism, the Wang et al. [29] mechanism, and the Shrestha et al. [30] mechanism. There are significant differences among the measured and simulated data, especially in the burnout state of the fuel-rich mixture, emphasizing the importance of quantitative NH3-concentration measurements in improving the mechanism performances. Previous researchers developed the LAS techniques for NH₃ monitoring in the atmosphere by selecting transition lines in the v_2 fundamental vibrational band [31]. Owen [32] measured the linestrengths and collisional broadening coefficients of NH₃ transition lines near 1103.46 cm⁻¹. Alturaifi and Petersen [33] measured the temperature dependence of collisional broadening coefficients of NH₃ lines near 10.4 µm under high-temperature conditions behind reflected shock waves. Alturaifi et al. [34] measured the NH₃-concentration time histories during the pyrolysis processes of the shock-heated NH₃/Ar and NH₃/H₂/Ar mixtures over a temperature range of 2100-3000 K. However, the data for time-dependent NH₃-concentration measurements during NH₃ oxidation processes behind reflected shock waves are lacking. In addition, NH₃ has a strong adsorption tendency in stainless steel. Thus, quantifying the NH₃ concentration in the driven section of the shock tube is difficult. Mathieu and Petersen [8] used the passivation method to compensate for the NH₃ adsorption in the driven section and mixing vessel during the mixture preparation. Shu et al. [4] and He et al. [5] used a similar method during the ignition-delay-time measurements of NH₃ mixtures. However, the passivation method cannot guarantee the accuracy of NH₃ concentration in the test section, which increases the uncertainties in the measured data. As reported by Alturaifi et al. [34], when compared to the passivation method, the LAS technique is capable of accurately measuring the NH₃ concentration in the test section for each experiment.



Fig. 1. Comparisons between the measured and simulated NH₃-concentration profiles.

In this work, the LAS technique will be developed for simultaneous temperature and NH₃-concentration time-history measurements during the combustion processes of NH₃/H₂ mixtures behind reflected shock waves. CO was used as a target species for temperature measurements. Two transition lines ($\nu' = 1 \leftarrow \nu'' = 0$, P8, 4.73 µm and $v' = 2 \leftarrow v'' = 1$, R21, 4.56 µm) in the CO fundamental vibrational band were selected. One transition line (v' = 1 \leftarrow v" = 0, R88, 4.18 µm) in the CO₂ v₃ fundamental vibrational band was selected to measure the time-resolved CO₂ concentration and subtract the interferences of CO₂ absorbances at the centers of CO P8 and R21 lines. Details of this procedure can be found in the previous study [21]. The current study selected nine transition lines in the v₂ fundamental vibrational band of NH₃ near 8.91 µm for NH₃-concentration time-history measurements. Firstly, a glass-made single-pass cell is designed for NH₃ absorbance measurements at room temperature. The glass-made optical cell helps to reduce the NH₃ adsorption, and the flowing-gas method ensures that the NH₃ achieves a saturation state in the optical cell during the measurements. The NH₃ absorbance was then measured over a wide range of temperatures and pressures, and the absorption cross-section was fitted as a function of temperature and pressure. The time-resolved temperature and NH₃ concentration during the combustion processes of NH3/H2 mixtures with various NH3:H2 ratios (approximately 1.0:1.0 and 1.5:1.0) and equivalence ratios (approximately 1.0 and 2.0) were also measured. The measured data were compared to the predictions based on different kinetics mechanisms. Comprehensive kinetics analyses were performed to illustrate the underlying reasons for different NH₃-concentration time histories predicted by the selected mechanisms. Sensitivity analyses were proceeded to update the rate coefficients of key elementary reaction to improve the mechanism performances.

2. Experiments

2.1. Shock tube

As described in the previous studies [35,36], all the shocks were performed in a shock tube with a 2.5-m driver section and a 5.5m driven section divided by aluminum diaphragms. The inner diameter of the shock tube is 6.9 cm. Helium was used as driver gas. Five pressure transducers (four PCB 113B26 and one Kistler 603CBA, with acceleration compensation) fixed on the sidewall of the driven section were used to measure the incident shock wave velocity. The velocity at the endwall was determined through extrapolation. The temperature (T_5) and pressure (p_5) behind reflected shock waves were calculated based on the one-dimensional shock wave equation and initial temperature (p_1) and pressure (T_1) in the driven section. The uncertainties in the T_5 and p_5 are around 1.0% and 1.5%, respectively. The typical attenuation rate of the incident shock wave is around 6.5 %/m. This study used the measured pressure profiles as inputs during kinetics simulation to diminish the influences caused by gaps between experiments and simulation. Details were shown in Section 3. The pressure transducers have the same response frequency and surface area, guaranteeing the accuracy on determination of the shock wave velocity and therefore the accuracy on the temperature. All the pressure transducers were coated with a thin layer of silicon components (Momentive RTV 106) to reduce the influences of gas ionization and heat transfer. The Kistler pressure transducer fixed at 20 mm from the endwall was used to measure the time-resolved pressure profiles. The measured pressure profiles were used as inputs for LAS measurements. The time point corresponding to the passage of the reflected shock wave was selected as time zero to initiate the combustion processes of NH₃/H₂ mixtures. Two opposed optical windows (CaF₂) fixed at 20 mm from the endwall (the same crosssection as the Kistler pressure transducer installed) were used for the LAS measurements. The windows were wedged at 3° to avoid the unwanted interferences caused by back reflection.

The driven section was pumped to below 5×10^{-3} Pa by a turbo pump before each shock. The typical leakage rate of the driven section is around 5×10^{-3} Pa/min. We opened the end-wall of the driven section after each shock, and cleaned the broken diaphragms inside the shock tube by the high-pressure gas flows.

2.2. Mixture compositions and experimental conditions

Table 1 shows the details of mixture compositions and experimental conditions used in this study. Mixture 1 was used for the low-pressure NH3-absorbance measurements under roomtemperature condition. The flowing-gas method was employed to ensure that the glass cell reached a saturated state during the measurements. Mixture 2 was used to measure the absorption cross-section of argon-diluted NH3 at elevated temperatures. Mixtures 3-6 were used for the time-resolved temperature and NH₃-concentration measurements during the combustion processes of NH₃/H₂ mixtures with various NH₃:H₂ ratios (approximately 1.0:1.0 and 1.5:1.0) and equivalence ratios (approximately 1.0 and 2.0). A total of 0.50% CO was seeded as the target species for the time-resolved temperature measurements. The oxidation of NH₃ and H₂ were considered while the oxidation of CO was not considered for calculating the equivalence ratio. Kinetics simulation demonstrated that the seeded CO showed almost negligible influences on the mixture reactivities. Details can be found in supplemental material S1. The accurate NH₃ concentration for mixtures 2-6 used in the driven section was measured by the LAS technique before the incident shock waves. To reduce the disparity between experiment and simulation, the measured NH₃ concentration in the driven section of each shock was used for the kinetics simulation. Mixture 1 is the standard gas (1005 ppm NH₃ highly diluted in argon). Mixtures 2-6 were prepared in a 20.13 L mixing vessel based on Dalton's law of partial pressure and allowed to settle for at least 12 h before use to ensure homogeneity. The passivation method was employed during the preparation procedures of mixtures 2-6 (the mixing vessel was fed with pure NH₃ for 5 minutes and pumped for 5 minutes before mixture preparation) to diminish the adsorption of NH₃ inside the mixing vessel. The addition of H₂ in mixtures 3-6 was used to study the NH₃ combustion behaviors at different NH3:H2 ratios. The H2 addition helps to accelerate the combustion processes of NH₃ mixtures and to ensure the temperature range within 1000-2200 K (the temperature range for NH₃-absorption cross-section measurements, as shown in Fig.4). In addition, H₂ helps to accelerate the vibrational relaxation processes of CO. According to the Millikan and White relationship [37], the relaxation time of CO in mixture 3 is around 50 μ s at 1200 K and 3.6 bar with 1.00% H₂ addition. Therefore, accurate thermal equilibrium temperature can be provided to convert NH₃ absorbance profiles into NH₃ concentration profiles during the oxidation processes of mixtures 3-6.

2.3. Laser absorption spectroscopy

2.3.1. Basic theory

When a narrow-bandwidth laser beam transmits through a uniform gas medium, the incident beam intensity (I_0) and the transmitted beam intensity (I_t) follow the Beer-Lambert law according to Eq. (1).

$$-\ln\left(l_t/l_0\right) = pS(T)x_i L\varphi(v) = \alpha(v) = \sigma(T, p)n_i L$$
(1)

where *p* is the pressure, *S*(*T*) is the linestrength at a specific temperature, x_i is the mole fraction of the target species, *L* is the optical path, $\varphi(v)$ is the line-shape function (this study used the

Table 1

Mixture compositions and experimental conditions.

Mixture	NH ₃ (mol %)	H ₂	02	СО	Ar	p / bar	Т / К	φ *
1	0.1005	-	-	-	99.8995	0.09	293	-
2	~1.00-1.50	-	-	-	Balance	0.8-3.9	1000-2200	-
3	~1.00	1.00	1.25	0.50	96.25	3.0-3.6	1200-1560	$\sim \! 1.0$
4	~ 1.50	1.00	1.63	0.50	95.37	3.0-3.4	1240-1500	$\sim \! 1.0$
5	~1.00	1.00	0.63	0.50	96.87	2.6-3.3	1290-1840	~ 2.0
6	~ 1.50	1.00	0.81	0.50	96.19	2.6-3.2	1310-1880	~ 2.0

 * The oxidation of NH_{3} and H_{2} were considered. The oxidation of CO was not considered.



Fig. 2. Schematic of the laser-absorption setup for simultaneous temperature and NH₃-concentration time-history measurements. (PM: plane mirror; BS: beam splitter; OAPM: off-axis parabolic mirror; CM: concave mirror; RC: reflective collimator; WTW: wedged transport window, CaF₂; NBF: narrow bandpass filter; D: detector).



Fig. 3. The measured NH_3 absorbance near 8.91 μm over a wide range of temperatures and pressures.

Voigt line-shape function, which is a convolution of the Gauss and Lorentz line-shape functions), $\alpha(v)$ is the absorbance, $\sigma(T, p)$ is the temperature- and pressure-dependent absorption cross-section, and n_i is the mole concentration of the target species.



Fig. 4. The measured temperature- and pressure-dependent absorption cross-section of NH_3 near 8.91 μm .

2.3.2. LAS system for simultaneous temperature and NH₃-concentration time-history measurements

This section describes the LAS system for simultaneous temperature and NH_3 -concentration time-history measurements. Before each shock, we measured the NH_3 absorbance of mixtures 2–6 in the driven section and converted the absorbance profiles into NH_3 concentration profiles based on the measured and integrated absorbance area of mixture 1 in a glass-made optical cell using flowing-gas method. Details for the room-temperature NH_3 -absorbance measurements of mixture 1 can be found in supplemental material S2.

Fig. 2 shows the schematic of the laser absorption setup. Two transition lines in CO fundamental vibrational band ($v' = 1 \leftarrow$ v'' = 0, P8, 4.73 µm and $v' = 2 \leftarrow v'' = 1$, R21, 4.56 µm) were selected for temperature measurements. One transition line in CO₂ v_3 fundamental vibrational band ($v' = 1 \leftarrow v'' = 0$, R88, 4.18 µm) was selected to subtract the CO₂ absorbance interferences at the centers of CO P8 and R21 lines for accurate temperature measurements. Nine transition lines in the NH₃ v_2 fundamental band near 8.91 µm were selected for NH₃-concentration time-history measurements (as shown in Fig.S3 in supplemental material S2). The line strengths of CO P8 and R21 lines were taken from the HITEMP 2010 database [38]. The collisional broadening coefficient and corresponding temperature exponent of P8 in argon were taken from He et al. [10], while those of R21 in argon were obtained from Ren et al. [9]. The temperatureand pressure-dependent absorption cross-section of the CO₂ R88 line was obtained from Zheng et al. [21]. Details and results of the temperature- and pressure-dependent absorption cross-section measurements of the NH₃ transition lines near 8.91 were shown in supplemental material S5 and Section 4.1, respectively. We did not find any absorption interferences of CO₂ and H₂O at the centers of



Fig. 5. Temperature time-history profiles of mixture 3.

the selected CO, CO_2 , and NH_3 lines near 4.56, 4.73, 4.18, and 8.91 µm under room-temperature and atmospheric conditions based on the HITRAN 2020 database [39]. Previous studies [10,20] reported the broadband CO_2 absorption interferences at the centers of CO P8 and R21 lines at elevated temperatures. The detailed data processing procedure about the subtraction of CO_2 absorption is presented in supplemental material S6. The simulated spectra based on the HITEMP 2010 database [38] indicated the presence of H_2O interferences in the spectra range near 8.91 µm at elevated temperatures, and the H_2O absorbance is around 1/40 of NH_3 absorbance under the same experimental conditions (e.g., species concentration, temperature, pressure, and optical path).

The laser-absorption setup for simultaneous temperature and NH₃-concentration time-history measurements can be divided into three parts as shown in Fig. 2. Two quantum cascade lasers (AdTech Optics), placed in the laser part, were used to probe the transition lines of CO near 4.73 and 4.56 µm. One interband cascade laser (Nanoplus) was utilized to probe the transition line of CO2 near 4.18 µm. The beams of two AdTech lasers were focused into a single-mode fiber (Thorlabs) by an off-axis parabolic mirror. The beams were then collimated again by a reflecting collimator. Two beam splitters were used to access the collinear beams (near 4.73, 4.56, 4.18, and 8.91 µm) from the single-mode fiber, the Nanoplus laser, and the Hamamatsu laser. The collinear beams were then focused into the shock tube by a concave mirror. The collinear beams in the detection part were afterwards separated by three wedged transport windows and collected by four mid-IR detectors (Vigo PVI-4TE-5 and PVI-4TE-10.6). Four (narrow) bandpass filters (Spectrogon NB-4560-135 nm, NB-4720-100 nm, NB-8834-210 nm, and Andover 4200.0/130-66139-B) were fixed in front to ensure that each detector probes only the beam from the respective laser. The fixed-wavelength direct-absorption method was used for P8-, R21-, and R88-absorbance measurements. Therefore, in the calibration part, a 14-cm single-pass cell filled with lowpressure highly-diluted CO was utilized to adjust the absorption peak of CO P8 line. And a 9.1-m Herriot cell filled with lowpressure pure CO and CO₂ was used to adjust the absorption peak of CO R21 and CO₂ R88 lines considering the weak absorption of the two lines at room temperature. Details regarding the experimental setup of two-line thermometry and simultaneous temperature, CO-, and CO₂-concentration time-history measurements can be found in the previous studies [10,17,19,21,24]. Temperature measurements have a time resolution of less than 1 μ s when using the fixed-wavelength method, and NH₃-concentration measurements have a time resolution of 50 μ s when using laser scanning with a 20 kHz sinusoidal signal.

Notably, the nine NH₃ transition lines (shown in Fig.S3 in supplemental material S2) in the selected spectral range help to increase the absorbance feature of NH₃ and the signal-to-noise ratios of the measured data at elevated temperatures behind reflected shock waves. The scanned-wavelength method was used to measure the absorbance of NH₃ and to obtain the NH₃ concentration based on the peak absorbance of NH₃. However, when compared to the fixed-wavelength method, the scanned-wavelength method sacrifices the time resolution of NH₃-concentration measurements. Furthermore, the current study provided a methodology of absorption cross-section measurements at elevated temperatures for developing the LAS technique for species-concentration measurements of complicated molecules, especially those having dense spectra lines or continuous spectra feature.

3. Data processing

Supplemental material S6 shows the detailed data processing procedure to automatically calculate the temperature and NH₃-concentration time histories behind the reflected shock waves. The iteration method used here ensures that the final values at a certain point in time are not influenced by the initial assumed values.

The closed homogeneous model in Chemkin-Pro software was used to perform kinetics simulation. The temperature and NH_3 concentration time histories were simulated using the Mathieu & Petersen [8] mechanism, the Glarborg et al. [28] mechanism, the Wang et al. [29] mechanism, and the Shrestha et al. [30] mechanism during the oxidation processes of mixtures 3–6 behind reflected shock waves. The Mathieu & Petersen [8] mechanism contains 56 species and 278 reactions, using the updated sub-



Fig. 6. NH₃-concentration time-history profiles of mixture 3.



Fig. 7. NH₃-concentration time-history profiles of mixture 4.

mechanisms of $H_2/O_2/CO$, N_2O , NO_2 , and NNH available in the literature. The Glarborg et al. [28] mechanism was developed with 151 species and 1397 reactions, including the oxidation processes of C_1 - C_2 hydrocarbons and NH₃. The Wang et al. [29] mechanism was developed for the syngas/NO_x combustion reaction system. The model contains 44 species and 253 reactions, including the formation of NO_x during syngas combustion and ignition of NH₃, H_2/N_2O , and H_2/NO_2 mixtures. The Shrestha et al. [30] mechanism

contains 125 species and 1099 reactions. All the above-mentioned models include the species listed in Table 1.

The non-ideal effects inside the shock tube, such as incident shock wave attenuation and boundary layer growth, cause unstable pressure behaviors behind reflected shock waves. In addition, the heat release/sink during the fuel reaction processes results in poor system behavior. The aforementioned factors cause deviations between the real thermodynamic states inside the shock tube and



Fig. 8. Temperature time-history profiles of mixture 5.



Fig. 9. NH₃-concentration time-history profiles of mixture 5.

the predictions based on the constant-pressure, constant-enthalpy or the constant-volume, constant-internal-energy assumptions. He et al. [17] proposed to use the ConstrainP method (using measured and smoothed pressure profiles as inputs for kinetics simulation) to compensate for the influences of non-ideal effects and the heat release/sink during kinetics simulation. By using this method, the mixture is isentropically compressed (or expanded) based on the pressure measured during the calculation of each timestep. The ConstrainP method was used in this study to simulate the temperature and NH₃-concentration time histories during the oxidation processes of mixtures 3–6.

4. Results and discussion

4.1. Temperature- and pressure-dependent absorption cross-section measurements of NH_3 near 8.91 μ m

This section presents the measured NH_3 absorbance and absorption cross-section in the temperature range of 1000–2200 K and pressure range of 0.8–3.9 bar, which covers the experimental conditions of mixtures 3–6. The measured NH_3 absorbance data were categorized into three pressure ranges, as shown in Fig. 3. The measured data illustrate an indirect pressure- and



Fig. 10. NH₃-concentration time-history profiles of mixture 6.



Fig. 11. Simulated profiles of multi-species (H₂, CO, H radical, and OH radical) during the oxidation processes of H₂/CO/O₂/Ar mixtures.



1.00% NH₃, 1.00% H₂, 0.50% CO, 1.25% O₂, 96.25% Ar T = 1300 K, p = 3.0 bar, $\phi = 1.0$

1.00% NH₃, 1.00% H₂, 0.50% CO, 0.63% O₂, 96.87% Ar T = 1400 K p = 3.0 bar $\phi = 2.0$

Fig. 12. Simulated profiles of multi-species (NH₃, H₂, CO, H radical, and OH radical) during the oxidation processes of NH₃/H₂/CO/O₂/Ar mixtures.

temperature-dependent relationship under the above-mentioned conditions. Moreover, the NH₃ concentration in mixture 2 varies in each shock due to approximately 1.00%-1.50% NH₃ used in the mixture preparation procedure and the NH₃ adsorption inside the mixing vessel and shock tube. Therefore, Eq. (1) is used to calculate the absorption cross-section of NH₃ to reduce the influences of varying NH₃ concentrations in each shock by normalizing the NH₃ concentration. As shown in Fig. 4, the absorption cross-section was normalized by the pressure with a factor of -0.46 to obtain an explicit function of temperature. The $\sigma \times p^{-0.46}$ was fitted as a cubic function of temperature in the temperature range of 1000-2200 K, and the expression of absorption cross-section is shown in Eq. (2). The maximum deviation between the measured and fitted data is less than 3.0%. Therefore, the fitted temperature- and pressuredependent absorption cross-section is suitable for converting NH₃absorbance profiles into NH3-concentration profiles for the mixtures in this study.

$$\sigma\left(cm^{2}mol^{-1}\right) = \begin{bmatrix} -31817.08 \times (T/1000)^{3} + 203531.10 \times (T/1000)^{2} \\ -452753.69 \times (T/1000) + 355914.37 \end{bmatrix} \times p^{-0.46}$$
(2)

4.2. Temperature and NH₃-concentration time-history measurements for mixtures 3–6

This section presents the measured temperature and NH₃concentration time histories during the oxidation processes of mixtures 3–6. The simulated data based on the Mathieu & Petersen [8] mechanism, the Glarborg et al. [28] mechanism, the Wang et al. [29] mechanism, and the Shrestha et al. [30] mechanism were also presented for comparison to illustrate the performances (predictions on the reactivity and NH₃ concentration in the burnout state) of the four mechanisms in predicting NH₃-concentration time histories under the experimental conditions in this study. The mechanism showing the best performance will be selected to perform the kinetics analyses in Section 4.3.2. The ConstrainP method was used during kinetics simulation. All the species in Table 1 were considered during the kinetics simulation. The measured temperature, NH₃-concentration, and CO-concentration time histories are provided in supplemental material S8. The measured pressure profiles were also included considering the influences of the non-ideal effects inside the shock tube and the heat released during the oxidation processes of mixtures 3–6.

4.2.1. Mixtures 3 and 4 (x_{NH3} : $x_{H2} \approx$ 1.0:1.0 and 1.5:1.0, respectively)

This section presents the comparison among measured and simulated data for the mixtures under near-stoichiometric conditions. The main gaps between experiments and predictions based on specific mechanism will be highlighted. Figures 5 and 6 show the temperature and NH₃-concentration time-history profiles of mixture 3 during the near stoichiometric oxidation processes in the temperature range of 1200–1560 K and pressure range of 3.0–3.6 bar. The measured temperature reached a thermal-equilibrium state in the time scale of around 20 μ s after the passage of the reflected shock waves for all the cases shown in Fig. 5. Moreover, the measured thermal-equilibrium temperature fits well with the simulated temperature before the start of the oxidation processes. The four mechanisms were considerably slow in predicting the temperature and NH₃-concentration time histories, especially for the low-temperature cases in Fig. 5 and Fig. 6. The pre-



Fig. 13. NH_3 sensitivity analyses based on the Glarborg et al. [28] mechanism

dicted NH₃-concentration time histories based on the Glarborg et al. [28] mechanism and the Shrestha et al. [30] mechanism were similar to the measured data.

Fig. 7 shows the measured and simulated NH₃-concentration time histories during the near-stoichiometric oxidation processes of mixture 4. The corresponding temperature profiles are shown in supplemental material S9. The four mechanisms predicted excessively slow NH₃ consumption processes compared with the measured data, in which the Glarborg et al. [28] mechanism showed the best performances while the Wang et al. [29] mechanism showed the most nonreactive predictions. At the early stage, the predictions based on the Mathieu & Petersen [8] mechanism fitted well with the measured data. However, the mechanism predicted overall slower NH₃ consumption processes than the measured data, especially during rapidly decreasing stage. The Shrestha et al. [30] mechanism was less reactive in predicting the NH₃-concentration time histories for mixture 4 than it did for mixture 3, as shown in Figs. 6 and 7.

Supplemental material S10 shows an example of the CO-, CO₂-, and NH₃-concentration time-history profiles during the oxidation processes of mixture 4 at 1318 K and 3.3 bar. The oxidation process of CO was substantially slower than that of NH₃.

4.2.2. Mixtures 5 and 6 ($x_{NH3}{:}x_{H2}\approx$ 1.0:1.0 and 1.5:1.0, respectively)

Figures 8 and 9 shows the measured and simulated temperature and NH₃-concentration time histories during the partial oxidation processes of mixture 5. The four mechanisms showed similar temperature-rising behaviors. The predicted data for the hightemperature cases fit well with the measured data. As the temperature decreases, there are noticeable discrepancies between the measured and simulated data. The NH₃ was entirely consumed in the observation time scale for the high-temperature cases (e.g., 1834 and 1666 K). But at low temperatures, small amount of NH₃ still existed in the burnout state within the observation time scale.



Fig. 14. Rate coefficients of $NH_3 + OH = NH_2 + H_2O$ (R636)

The Shrestha et al. [30] mechanism showed the best performances in predicting the NH₃-concentration time histories for mixture 5, followed by the Glarborg et al. [28] mechanism. The Mathieu & Petersen [8] mechanism overpredicted the NH₃ concentration in the burnout state, especially for the low-temperature cases (e.g., 1443 K).

Fig. 10 shows the measured and simulated NH₃-concentration time histories during the partial oxidation processes of mixture 6. The corresponding temperature profiles are shown in supplemental material S9. The Glarborg et al. [28] mechanism and the Shrestha et al. [30] mechanism showed good performances in predicting



Fig. 15. NH₃-concentration profiles of mixtures 3–6. Point: measured data. Dash line: predictions based on the Glarborg et al. [28] mechanism. Dot line: predictions based on the updated Glarborg et al. [28,41] mechanism.

the NH_3 -concentration time histories for high-temperature cases. The four mechanisms demonstrated slower NH_3 -consumption processes than the measured data with the decrease of temperature. The predicted NH_3 concentration based on the Glarborg et al. [28] mechanism and the Shrestha et al. [30] mechanism fitted well with the measured data in the burnout state, whereas the Mathieu & Petersen [8] mechanism overpredicted the NH_3 concentration. The Wang et al. mechanism [29] predicted too slow NH_3 -consumption processes for mixtures 5 and 6, as shown in Figs. 9 and 10.

4.3. Kinetics analyses

This section will perform kinetics analyses to illustrate the differences among the four mechanisms and to highlight the key reactions influencing the mixture reactivity under the experimental conditions in this study. Specific reactions will be updated to improve the mechanism performances.

4.3.1. Effects of NH₃ addition

As discussed in Section 4.2, the four mechanisms were excessively slow in predicting the NH₃ consumption processes during the oxidation of stoichiometric NH₃/H₂ mixtures (mixtures 3 and 4). And the four mechanisms predicted different NH₃ concentrations in the burnout state of fuel-rich NH₃/H₂ mixtures (mixtures 5 and 6). Therefore, this section aims to proceed comprehensive kinetics analyses to illustrate the differences among the H₂/CO subset of the selected mechanisms and effects of NH₃ addition on species time-history profiles. The effects of NH₃ addition on the formation of main products were shown in supplemental material S11.

Fig. 11 shows a comparison among the predicted profiles of H_2 , CO, H radical, and OH radical during the oxidation processes of the $H_2/CO/O_2/Ar$ mixtures based on the four mechanisms. The four mechanisms showed nearly identical H_2 - and CO-concentration profiles, indicating that the above-mentioned differences in predicting NH₃-concentration profiles were not caused by the potential inaccuracy of the H_2/CO subset in the selected mechanisms. Furthermore, the Mathieu & Petersen [8] mechanism, the Glarborg et al. [28] mechanism, and the Wang et al. [29] mechanism showed nearly identical time-history profiles of H radical and OH radical. Therefore, the following analyses will focus on the effects of NH₃ addition on species-concentration time histories and mixture reactivity.

Fig. 12 shows a comparison among the predicted profiles of NH₃, H₂, CO, H radical, and OH radical during the oxidation processes of the NH₃/H₂/CO/O₂/Ar mixtures based on the four mechanisms. The NH₃ addition significantly inhibits the mixture reactivity. For stoichiometric and fuel-rich NH₃/H₂ mixtures, the four mechanisms predicted different H and OH radical time-history profiles and peak values. Therefore, it is expected that the four mechanisms contain different reaction channels for NH₃ oxidation and the NH₃ addition evidently influences the product formation in the burnout state of the fuel-rich mixtures.

4.3.2. Sensitivity analyses

This section selected the Glarborg et al. [28] mechanism to perform the sensitivity analyses of NH₃ considering its overall good performances in Section 4.2. Key elementary reactions will be highlighted and updated to improve the mechanism. The analyses results were shown in Fig. 13. The reactions, $H + O_2 = O + OH (R1), NH_2 + H (+ M) = NH_3 (+ M) (R633),$ and $NH_3 + OH = NH_2 + H_2O$ (R636), are the key reactions influencing the reactivity of stoichiometric mixture. However, R1 and R633 are the main reactions influencing the reactivity of fuel-rich mixture. We assumed that the rate coefficients of R1 and R633 are well updated considering the good performances of Glarborg et al. [28] mechanism in predicting the NH₃ time histories of fuel-rich mixtures in Section 4.2.2. Therefore, R636 was selected as the target to improve the mechanism performance. Fig. 14 shows a comparison between the rate constants of R636 measured by Salimian et al. [40] (used in the Glarborg et al. [28] mechanism) and Samu et al. [41]. The data summarized by Samu et al. [41] are substantially lower than the data summarized by Salimian et al. [40]. This study updated the Glarborg et al. [28] mechanism by using the rate coefficients of R636 from Samu et al. [41]. The updated mechanism presented improved performances in predicting the NH₃concentration time histories of the mixtures in this study, especially for the stoichiometric NH_3/H_2 mixtures, as shown in Fig. 15. The updated mechanism was too reactive in predicting NH₃ concentration of stoichiometric NH₃/H₂ mixtures when the temperature is lower than 1250 K. Using the rate constant between the values from Salimian et al. [40] and Samu et al. [41] is expected to improve the mechanism for low temperature cases. Therefore, further studies were suggested to improve the rate constant of R636 in the temperature region below 1250 K.

Conclusion

This study reported the simultaneous temperature and NH₃concentration time-history measurements during the oxidation processes of the shock-heated reacting NH₃/H₂ mixtures by combining LAS techniques. The CO was used as a target species, and two transition lines in the fundamental vibrational band of CO $(v'' = 0, P8, 4.73 \ \mu m \text{ and } v'' = 1, R21, 4.56 \ \mu m)$ were selected for temperature measurements. One transition line in the v_3 fundamental vibrational band of CO₂ (ν " = 0, R88, 4.18 µm) was selected to subtract the CO₂-absorbance interferences at the centers of CO P8 and R21 lines. Meanwhile, nine transition lines in the v_2 fundamental vibrational band of NH3 near 8.91 µm were selected for NH₃-concentration measurements. The flowing-gas method was used to accurately measure the absorbance of the selected transition lines of NH₃ near 8.91 µm in a glass-made optical cell. The collected data helps to accurately measure the NH₃ concentration in the driven section during the shock-tube experiments. The following are the main research findings and conclusions:

- 1. The absorption cross-section of NH_3 near 8.91 μ m was measured in the temperature range of 1000–2200 K and pressure range of 0.8–3.9 bar. The measured data were fitted as a function of temperature and pressure.
- 2. The temperature and NH₃-concentration time histories were measured during the oxidation processes of the shock-heated reacting NH₃/H₂ mixtures. The predictions based on the Mathieu & Petersen [8] mechanism, the Glarborg et al. [28] mechanism, the Wang et al. [29] mechanism, and the Shrestha et al. [30] mechanism were selected for comparison. The four mechanisms were too slow in predicting the NH₃-concentration profiles for the stoichiometric NH₃/H₂ mixtures. The Glarborg et al. [28] mechanism showed very good agreements with the experiments for the fuel-rich NH₃/H₂ mixtures.
- 3. The comprehensive kinetics analyses illustrated that the differences in predicting NH₃-concentration profiles were not caused by the potential inaccuracy of the H₂/CO subset in the selected mechanisms. NH₃ addition evidently influences the mixture reactivity and formation and consumption processes of H and OH radicals.
- 4. The sensitivity analyses based on Glarborg et al. [28] mechanism illustrated that the reaction, $NH_3 + OH = NH_2 + H_2O$, is one of the key reactions influencing NH_3 consumption for the stoichiometric NH_3/H_2 mixtures. This study updated the rate coefficient of the above-mentioned reaction. The modified Glarborg et al. mechanism demonstrated improved performances in predicting NH_3 -concentration profiles, especially for the stoichiometric NH_3/H_2 mixtures.

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.

Acknowledgments

This study was supported by the National Natural Science Foundation of China (grant number 11972213), the Provincial Natural Science Foundation of Anhui (grant number 2208085QE162), the China Postdoctoral Science Foundation (grant number 2021M703084), and the Fundamental Research Funds for the Central Universities (WK209000043).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.combustflame.2022. 112349.

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