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A Shock-tube Study of the H₂-N₂O System Using H₂O Absorption and Ignition Delay Times

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Abstract: The hydrogen-nitrous oxide (H₂-N₂O) system is of paramount importance in safety considerations for nuclear waste management and semiconductor manufacturing. For less-dilute H₂-N₂O mixtures, a reaction of key importance in determining ignition delay times is the direct reaction between H₂ and N₂O to give H₂O and N₂, although this reaction has received only one direct investigation in the work of Kosarev et al. (2007). To examine the importance of the title reaction, new H₂O time histories were obtained using a laser absorption technique at 1.39 μm in a mixture of 0.222% N₂O/1.778% H₂/Ar between 1414 and 1811 K near 1.2 atm. Additionally, the ignition delay time measurements of Kosarev et al. (2007) were repeated using endwall emission and pressure diagnostics. The new datasets show excellent agreement with the predictions of a recent mechanism when the title reaction is completely removed. Furthermore, the accurate mechanism predictions of H₂-N₂O ignition delay time data available in the literature (other than those of Kosarev et al.) were not degraded when the title reaction was removed. It is thus recommended that the title reaction be removed from all future modeling of the H₂-N₂O system. It is also recommended that the data of Kosarev et al. (2007) be neglected in future mechanism validations as these data appear to be strongly influenced by non-ideal pressure rise effects.

Keywords: H₂-N₂O, laser absorption, hydrogen, nitrous oxide

1. Introduction

The hydrogen-nitrous oxide (H₂-N₂O) system is critical in nuclear waste processing/storage and in semiconductor manufacturing, where potential safety hazards require accurate predictions of H₂-N₂O chemistry [1]. Many of the elementary reactions involved in H₂-N₂O chemistry are also key in the modeling of NO_x formation, a topic of paramount interest to combustion modelers. A number of studies have accordingly proposed models for H₂-N₂O and/or NO_x chemistry [2-9].

In the most recent NO_x mechanism, Zhang et al. [9] chose to include the direct reaction between H₂ and N₂O,



To the best of the authors' knowledge, there are only two values for the R1 rate constant (k_1) given in the literature. In 1978, Roose et al. [3] performed IR emission measurements of NH₃, NO, and N₂O in shock-heated mixtures of 2% NH₃/2% NO/Ar and suggested a rate of $k_1 =$

$2 \times 10^{11} T^{0.5}$ (with T in Kelvin and k_1 in $\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$). However, “interferences [due to other emitting species] encountered were significant” [3] and required corrections as large as 41%. Furthermore, the NH_3 , NO , and N_2O profiles are almost completely insensitive to R1 for the mixture used by Roose et al., as confirmed via a sensitivity analysis using the mechanism of Zhang et al. [9]. In fact, no discussion as to the reasoning behind the value of k_1 chosen is given by Roose et al. Consequently, the Roose et al. rate should be treated as an estimate only, and it is described as such (see Table 1 of [3]).

In 2007, Kosarev et al. [4] measured ignition delay times in shock-heated mixtures of 10% H_2 /10% N_2O /Ar and 3.2% O_2 /32.3% H_2 /10.8% N_2O /Ar. It was demonstrated that the ignition delay times of the 10% H_2 /10% N_2O /Ar mixture were highly sensitive to R1, and Kosarev et al. thus proposed $k_1 = 2.1 \times 10^{14} \exp(-16,356/T)$ by fitting the model to their data for this mixture. The Kosarev et al. rate is 2 and 5 orders of magnitude smaller than the rate proposed by Roose et al. [3] at 2000 and 1000 K, respectively. Zhang et al. [9] used the Kosarev et al. value for k_1 .

Interestingly, the only H_2 - N_2O mechanisms to include R1 are those of Roose et al. [3], Kosarev et al. [4], and Zhang et al. [9]. Since less-dilute H_2 / N_2O mixtures are important from a process safety perspective and are highly sensitive to this reaction, it seems prudent to further investigate the value of k_1 to ascertain the importance or unimportance of R1. To this end, a new set of H_2O laser absorption measurements and OH^* ignition delay time measurements were obtained. The laser measurements were carried out in a highly diluted mixture that was chiefly sensitive to R1, while the same mixture used by Kosarev et al. was utilized for the ignition delay time experiments. These new data demonstrate that R1 is completely unimportant at all conditions tested and that the measurements of Kosarev et al. seem to be in error. Presented herein is a description of the experimental apparatus, followed by a presentation of the experimental results. A discussion of these results is then given, including modeling comparisons to literature data.

2. Experiment

2.1. Shock Tube

Experiments were conducted in a pressure-driven, high-purity, stainless steel shock tube. The driver section had a length of 3.0 m and an inner diameter of 7.62 cm, while the driven section had a length of 6.78 m and an inner diameter of 16.2 cm. The driven section was vacuumed down to $\sim 10^{-5}$ Torr prior to each experiment using an Agilent turbomolecular pump. Helium was used as the driver gas to burst polycarbonate diaphragms of thickness 0.127 or 0.254 mm. Sidewall and endwall pressure time histories were recorded using PCB P113A transducers. The sidewall measurements were taken using a port located 1.6 cm from the endwall. Four additional PCB P113A transducers were used to measure the velocity of the incident shock wave. The slight attenuation of the incident shock wave was extrapolated to the endwall and used to calculate the temperature (T_5) and pressure (P_5) behind the reflected shock wave.

Mixtures were prepared manometrically in a 40-L mixing tank using a series of capacitance manometers (0-10 Torr, 0-1000 Torr, 0-13000 Torr). The mixing tank was vacuumed overnight to an ultimate pressure of $\sim 10^{-6}$ Torr. Mixture components were filled through a perforated stinger to encourage turbulent mixing. Final mixtures were allowed to mix for at least one hour before experiments were performed. Gases were supplied by Praxair and had purity levels of 99.999% for Ar and H_2 and 99.5% for N_2O .

For the laser absorption experiments, a fuel-rich ($\phi = 8$) $\text{H}_2\text{-N}_2\text{O}$ mixture diluted in 98% Ar was chosen because the production of H_2O is primarily sensitive to R1 in this mixture, as shown in Fig. 1, assuming that R1 has the rate given by Kosarev et al. [4]. For the ignition delay time experiments, the 10% H_2 /10% N_2O /Ar mixture used by Kosarev et al. was used. Kosarev et al. showed that, assuming their value for k_1 , OH^* ignition delay times in this mixture are primarily sensitive to R1 (see Fig. 8a in [4]).

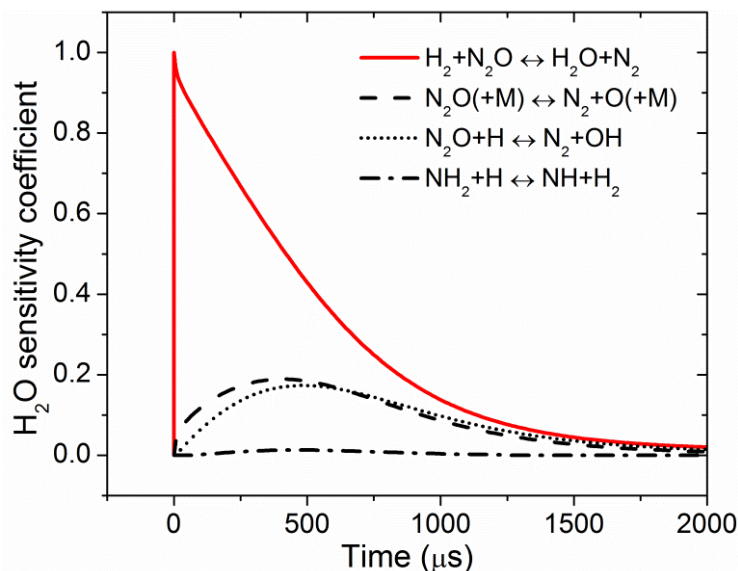


Figure 1: Normalized H_2O sensitivity coefficients for the four most important reactions in a mixture of 0.222% N_2O /1.778% H_2 /Ar. Conditions are 1586 K, 1.17 atm. Analysis was performed using the mechanism of Zhang et al. [9].

All modeling was performed in CHEMKIN. Shock-tube data were modeled using the Closed Homogenous Batch Reactor with the constant volume/internal energy assumption. Flame speeds were modeled using the Premixed Laminar Flame Speed Calculation.

2.2. H_2O Diagnostic

The $5_{5,1} \leftarrow 5_{5,0}$ transition of H_2O in the fundamental $\nu_1 + \nu_3$ band at 7203.890 cm^{-1} (1388.139 nm) was accessed with a tunable diode laser (Toptica Photonics DL 100) with a linewidth of $\sim 1 \text{ MHz}$. The laser wavelength and power were controlled with temperature and current controllers. A Burleigh WA-1000 wavemeter was used to monitor the laser wavelength. A beamsplitter divided the beam into incident (I_0) and transmitted (I_t) legs, which were monitored by two InGaAs photodetectors (New Focus NF2317) with bandwidths of 150 kHz. The I_t portion passed through the shock tube via two sapphire window ports, located in the same plane as the sidewall pressure transducer, before being focused onto the I_t detector. Both detectors were fitted with bandpass filters with center 1384 nm and full width 10 nm. Detector signals were sampled at 1 MHz via a DAQ using common mode rejection. In accordance with the detector bandwidths, detector signals were post-processed using a first-order Butterworth filter with a cutoff frequency of 150 kHz. Sample sidewall pressure and laser transmission time histories are shown in Fig. 2.

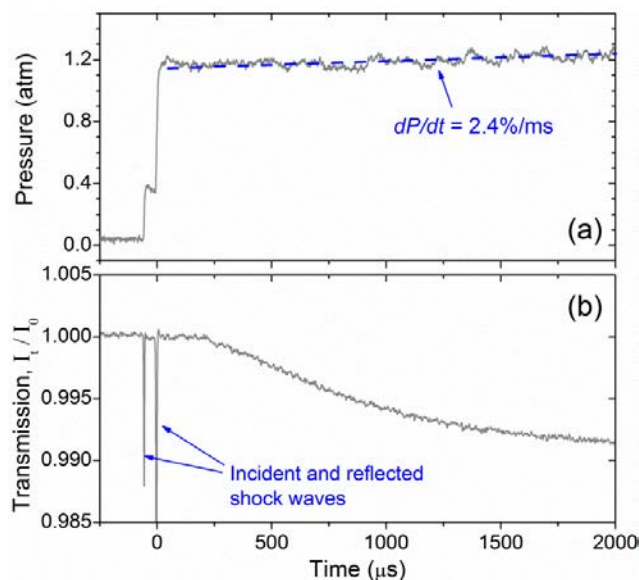


Figure 2: Representative (a) sidewall pressure and (b) laser transmission time histories in a mixture of 0.222% N₂O/1.778% H₂/Ar. Conditions are 1586 K, 1.17 atm.

If the transmission I_t/I_0 has been measured (e.g., Fig. 2b), the Beer-Lambert relation $I_t/I_0 = \exp(-k_v P X_{abs} L)$ can be used to calculate the mole fraction X_{abs} of an absorbing species given that the absorption coefficient k_v , the pressure P , and the path length L are known. Here, L is the shock-tube inner diameter, and P is the measured sidewall pressure (including the slight non-ideal pressure rise dP/dt ; typically between 1.7 and 3.1 %/ms); while k_v can be calculated as the product of the linestrength and the lineshape. Linestrengths for the selected transition were calculated from HITRAN 2004 [10] using the partition function from Laraia et al. [11]. A Voigt lineshape was assumed, and the H₂O-Ar broadening parameters were estimated according to Nagali et al. [12]. A separate set of fixed-wavelength tests with a known amount of H₂O diluted in Ar revealed a slight collisional lineshift for the selected transition that was in excellent agreement with the predictions from Li et al. [13]. Therefore, the Li et al. expression was used to simulate the collisional lineshift for the calculations of k_v herein, and the laser wavelength was fixed at 1388.140 nm for all experiments to attain maximum absorption.

During the typical ~2 ms of test time, the exothermicity of the mixture caused a slight temperature rise: 15 and 45 K for the coldest and hottest experiments, respectively. Since k_v is a strong function of temperature, the simulated temperature rise using the mechanism of Zhang et al. [9] with R1 removed was used to correct k_v . A similar procedure has been used previously by the authors and others [14, 15]. Calculated decreases in k_v (relative to the initial k_v at T_5 and P_5) by the end of the test time were 3 and 8% for the coldest and hottest tests, respectively. The choice of mechanism used for the temperature correction was found to have little effect on the final shape of the H₂O profiles and had no impact on the conclusions drawn from these results.

2.3. OH* Diagnostic

Emission from the $A^2\Sigma^+ \rightarrow X^2\Pi$ transition of OH was captured using a Hamamatsu 1P21 photomultiplier tube (PMT). The PMT was fitted with a bandpass filter with center 307 nm and full width 10 nm. The light exited the tube through a sapphire window port situated in the center

of the endwall. Ignition delay time (τ_{ign}) was defined as the interval between the arrival of the shock wave at the endwall and the onset of ignition. The latter was determined by extrapolating the steepest slope of the pressure or emission trace back to the baseline. Sample endwall pressure and emission traces are shown in Fig. 3, with the two definitions of τ_{ign} illustrated. Evident in Fig. 3 are signs of pre-ignition energy release, which has also been observed in H_2 - O_2 mixtures of similar Ar-dilution levels by Pang et al. [16].

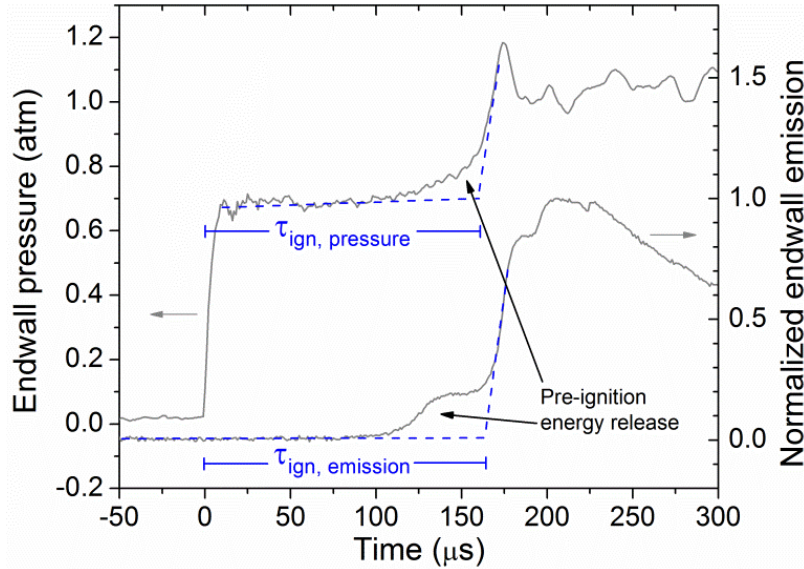


Figure 3: Representative endwall pressure and endwall emission time histories in a mixture of 10% H_2 /10% N_2O /Ar. Conditions are 1491 K, 0.68 atm.

3. Results

A sample H_2O time history is shown in Fig. 4, along with several model predictions using varying values of k_1 . It is observed that the best fit to the data is achieved by completely removing R1 from the mechanism. A factor of 20 reduction in k_1 produced nearly identical results to completely removing R1.

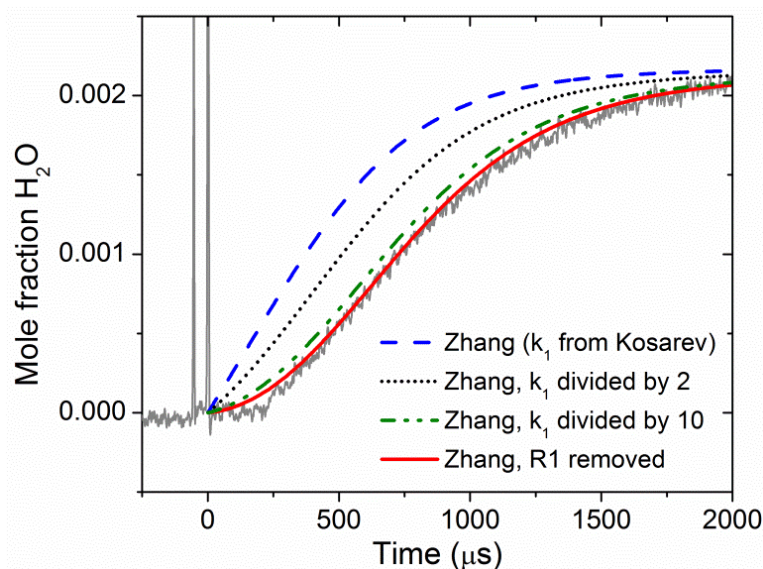


Figure 4: H_2O time history at the conditions of Fig. 2. Dashed line: unmodified mechanism of Zhang et al. [9] with k_1 from Kosarev et al. [4], dotted line: Zhang et al. with $k_1/2$, dash-dot-dot line: Zhang et al. with $k_1/10$, solid line: Zhang et al. with R1 removed.

Figures 5a-5d show four H_2O time histories compared to model predictions; additional H_2O time histories are included in the Supplemental Material. Across the range of temperatures tested, it is evident that the Zhang et al. mechanism [9] leads to incorrect predictions. Upon the removal of R1, however, the predictions of the Zhang et al. mechanism become rather good. Conversely, the Mével et al. mechanism [5], although it does not include R1, incorrectly reproduces the experimental data. The addition of R1 into the Mével et al. mechanism would speed up the formation of H_2O and make the Mével et al. mechanism even more inaccurate. Further consideration of the differences between the two models is given in the Discussion.

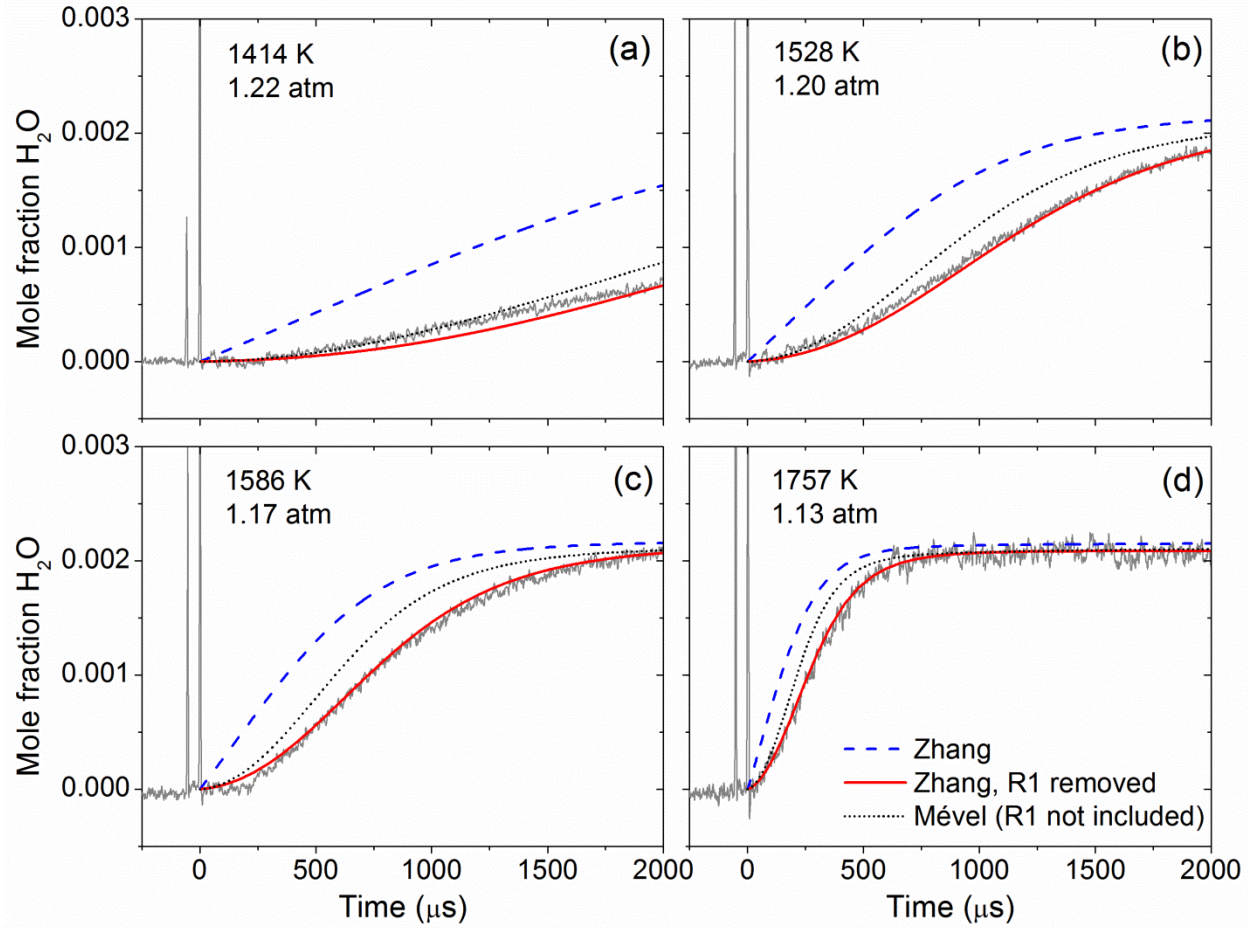


Figure 5: Sample H_2O time histories in a mixture of 0.222% N_2O /1.778% H_2 /Ar. Dashed lines: unmodified mechanism of Zhang et al. [9], solid lines: Zhang et al. with R1 removed, dotted lines: mechanism of Mével et al. [5].

Ignition delay times using both endwall pressure and endwall emission diagnostics are shown in Fig. 6a alongside model predictions. The two diagnostic techniques show excellent agreement, which is to be expected for highly energetic mixtures such as the 10% H_2 /10% N_2O /Ar mixture used in the present study [17]. The ignition delay times of Kosarev et al. [4], which they obtained using the same mixture, are shown in Fig. 6b for comparison, as are model predictions. The two datasets differ enough in average pressure to prevent displaying them on the same plot; therefore, in lieu of pressure correcting one dataset, two panels are shown.

Two observations can be drawn from Fig. 6. First, the mechanism of Zhang et al. [9] vastly underpredicts the ignition delay times of the present study. However, the removal of R1 yields model predictions that are in excellent agreement with the new data. Second, the data of Kosarev et al. [4] are somewhat well predicted by the Zhang et al. mechanism when R1 is included, but the removal of R1 leads to a large overprediction of τ_{ign} . These observations are explored in detail below.

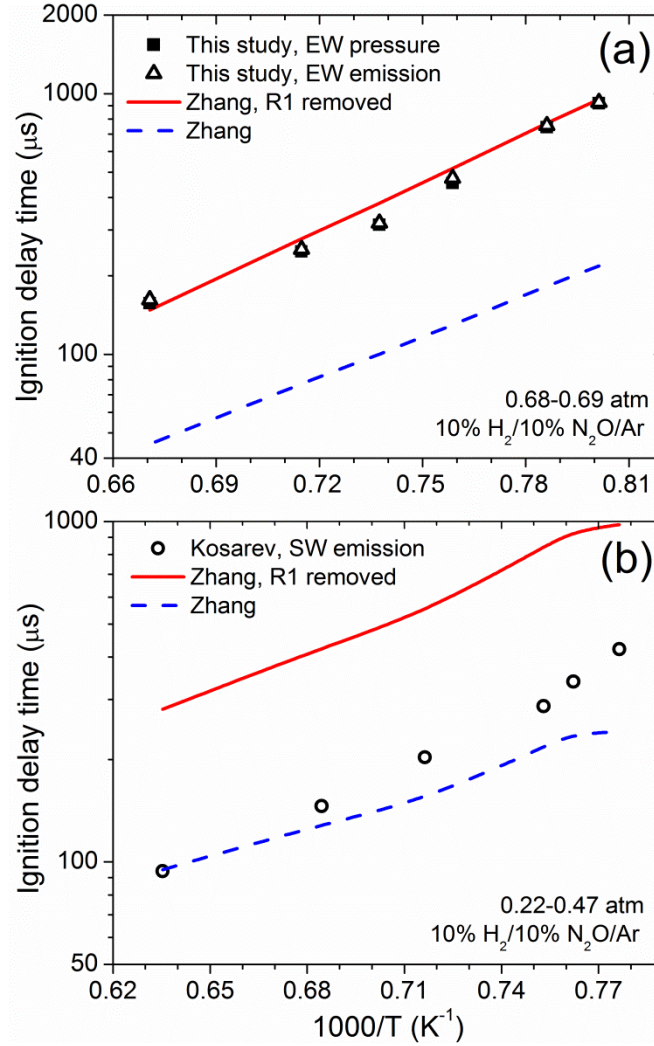


Figure 6: Measurements of τ_{ign} from (a) this study and (b) Kosarev et al. [4] in identical mixtures of 10% H_2 /10% N_2O /Ar. Dashed lines: unmodified mechanism of Zhang et al. [9], solid lines: Zhang et al. with R1 removed. Individual P_5 values were used to evaluate the models. Definitions of τ_{ign} : (a) see Fig. 3, (b) time to point of maximum OH^* slope. EW = endwall, SW = sidewall.

It has been previously noted that trace hydrocarbon impurities, which are difficult to fully remove from shock-tube experiments, can noticeably accelerate the ignition of highly dilute H_2/O_2 mixtures by decomposing into radicals such as H atoms and accelerating the growth of the radical pool [18]. To test the impurities sensitivity of the $\phi = 8$, 98% Ar mixture, simulations were performed at 1500 K and 1.2 atm using the model of Zhang et al. [9] with R1 removed, with and without 0.5 ppm H atoms. The value of 0.5 ppm H atoms is the suggested value at 1500 K according to Urzay et al. [18]. Even with these H atoms included, the model predictions were completely identical. This impurities insensitivity is not surprising since N_2O decomposition provides a supply of O atoms to the radical pool, thereby reducing the importance of trace H atoms in inflating the radical pool. Not unexpectedly, the 10% H_2 /10% N_2O /Ar mixture was also found to be insensitive to H atoms.

4. Discussion

4.1. H_2O Time Histories

Figures 4 and 5 demonstrate that the Zhang et al. mechanism [9] only provides accurate time-history predictions when R1 is removed, indicating that R1 is completely unimportant at these conditions. It is also worth noting that although the Mével et al. mechanism [5] does not include R1, it still predicts accelerated H_2O profiles (Fig. 5); the addition of R1 into the Mével et al. mechanism would accelerate H_2O formation and draw the Mével et al. predictions even farther from the data.

To elucidate the differences between the mechanisms of Mével et al. [5] and Zhang et al. [9] (with R1 removed), a sensitivity analysis was conducted using the Mével et al. mechanism. The results were very similar to those in Fig. 1 calculated using the Zhang et al. mechanism, save that R1 is not present in the Mével et al. mechanism. The H_2O time histories at the conditions studied herein are most sensitive to



and



For k_2 , the Zhang et al. and Mével et al. mechanisms both used the low-pressure limit from Javoy et al. [19], the high-pressure limit from Zuev and Starikovskii [20], and the third-body efficiencies given by Konnov [6]. The differences between the two mechanisms are therefore primarily due to R3. For k_3 , Mével et al. used the fit of Marshall et al. to their experimental data [21], while Zhang et al. used the recent computational results of Klippenstein et al. [22]. The two expressions differ by 35-45% in the temperature range of the present results (1414-1811 K), with the rate used by Mével et al. being faster and thus responsible for the faster formation of H_2O .

The final source of the difference between the Zhang et al. [9] and Mével et al. [5] mechanisms is that Mével et al. included the reaction



Mével et al. used the value of k_4 given in the review by Hanson and Salimian [23], which was based on the work of Dove and Nip [24]; this is the only value of k_4 available in the literature. Dove and Nip fitted four average time histories of NH_3 , N_2 , NH_2 , and NH between 2511 and 2873 K using a multi-parameter optimization. They state that their optimization was subject to many unknown rate constants and much uncertainty in thermochemical data on several species. The two most recent NO_x mechanisms excluded R4 entirely [8, 9].

H_2O time histories showed slight sensitivity to the reaction



Zhang et al. [9] and Mével et al. [5] both used k_5 from Linder et al. [25], but Zhang et al. did so indirectly by copying the work of Skreiberg et al. [26]. Skreiberg et al. made a transcription error and took the activation energy from Linder et al. in the incorrect units ($\text{cal}\cdot\text{mol}^{-1}$ instead of K).

The correct activation energy is 799 K, or 1587 cal-mol⁻¹. Rectifying this minor mistake in the Zhang et al. mechanism had no effect on any of the modeling results herein.

As a final note, mechanism predictions from Mathieu et al. [7] (not shown in Fig. 5) were found to be slightly more accelerated than those from Mével et al. [5]. Mathieu et al. used k_2 and k_3 from the review by Baulch et al. [27]. The Baulch et al. value of k_2 is ~8% lower than the value used by Zhang et al. [9] and Mével et al., while the Baulch et al. value of k_3 is ~60% larger than the value of k_3 used by Zhang et al., making R3 responsible for the accelerated H₂O formation of the Mathieu et al. mechanism. The Mathieu et al. mechanism does not include R1 and, as noted for the Mével et al. mechanism, adding R1 would move the predictions of the Mathieu et al. mechanism even farther from the experimental data.

4.2. Ignition Delay Times and Non-ideal dP/dt Effects

Figure 6 indicates that there is some discrepancy between the data of the present study and that of Kosarev et al. [4] as the two datasets show significantly different levels of agreement with the model of Zhang et al. [9]. Mével et al. [5], whose mechanism did not include R1, had similar difficulties reproducing the data of Kosarev et al. Mével et al. chose to discount the Kosarev et al. data on the basis that Kosarev et al. used a sidewall emission diagnostic to measure τ_{ign} in a highly energetic mixture. Indeed, Petersen has demonstrated that such a misapplication of diagnostics can lead to artificially accelerated ignition delay times [17]. However, the maximum difference between sidewall and endwall diagnostics presented by Petersen was 30-40 μ s, and this was with a sidewall port located 1.6 cm from the endwall. The Kosarev et al. shock tube had sidewall ports that were 0.5 cm from the endwall, meaning that the sidewall acceleration effect was likely even smaller than 30-40 μ s. This fact notwithstanding, even a 30-40 μ s difference cannot account for the discrepancy between the model and data observed in Fig. 6b.

Instead, it is likely that significant dP/dt effects accelerated the Kosarev et al. data. Kosarev et al. [4] did not provide the inner diameter of their shock tube, but subsequent papers from the same group (e.g., [28]) describe a very similar shock tube as described by Kosarev et al. [4], and this shock tube had a cross-section of 25x25 mm. This cross-section is smaller than the shock tube used herein (162-mm diameter) and thus, given that dP/dt effects are exaggerated in smaller shock tubes [29], the Kosarev et al. data are almost certainly dP/dt -affected. Kosarev et al. do not quantify dP/dt for their shock tube, nor could any sample pressure time histories be found in papers from this group. However, using the calculations of ΔT_5 from Fig. 7 of Petersen and Hanson [30], one can estimate, based on the shock-tube inner diameter, that the Kosarev et al. shock tube would have a ΔT_5 that is 7-9 times greater than that for the shock tube used herein. It can also be mentioned that the Kosarev et al. [4] data were obtained at a lower pressure than the new data herein and that turbulent boundary layer growth is exacerbated at lower pressures [29]. Typical dP/dt values in the authors' laboratory are 1.5-3.0%/ms, which is within the accepted range for measurements of ignition delay times near or below 1 ms [16].

4.3. Other Evidence Against the Inclusion of R1

Mével et al. [5] cited reduced activation energy as an argument for omitting R1 from their mechanism. The reduced activation energy, θ , is a method of quantifying the instability of the detonation of a mixture; more-unstable mixtures have a higher value of θ , while more-stable mixtures have a lower value. Mével et al. pointed out that adding R1 into their mechanism

reduced θ from 11 (highly unstable) to around 8 (moderately unstable), even though $\text{H}_2\text{-N}_2\text{O}$ detonations are well known to be highly unstable [1].

One can also consider the issue of R1 from a theoretical standpoint, albeit a rudimentary one. Recent $\text{H}_2\text{-O}_2$ mechanisms (e.g., [31-33]) contain only one pathway for H_2O formation from H_2 , namely



However, the H_2O formation in R6 takes place due to H-abstraction by OH rather than insertion of an O atom into the H_2 molecule [34]. Such insertion of an O atom into H_2 would require multiple bond reconfigurations and thus seems highly unlikely, which is the reason that no recent $\text{H}_2\text{-O}_2$ mechanisms include such a process. By analogy, the H_2O formation of R1 is also highly unlikely.

A final piece of evidence against the inclusion of R1 is its unimportance in modeling any of the shock-tube data in the literature. For example, consider the data of Mathieu et al. [7] shown in Fig. 7. Mathieu et al. measured OH^* ignition delay times of $\text{H}_2\text{-O}_2$ mixtures with varying levels of N_2O (100, 400, 1600, and 3200 ppm); the results with 3200 ppm N_2O are shown in Fig. 7, along with model predictions from Zhang et al. [9] with and without R1. The model predictions with and without R1 are identical near 2 and 13 atm, and are nearly identical near 35 atm. In all cases, the model predicts the data rather well, demonstrating the unimportance of R1 in modeling these data.

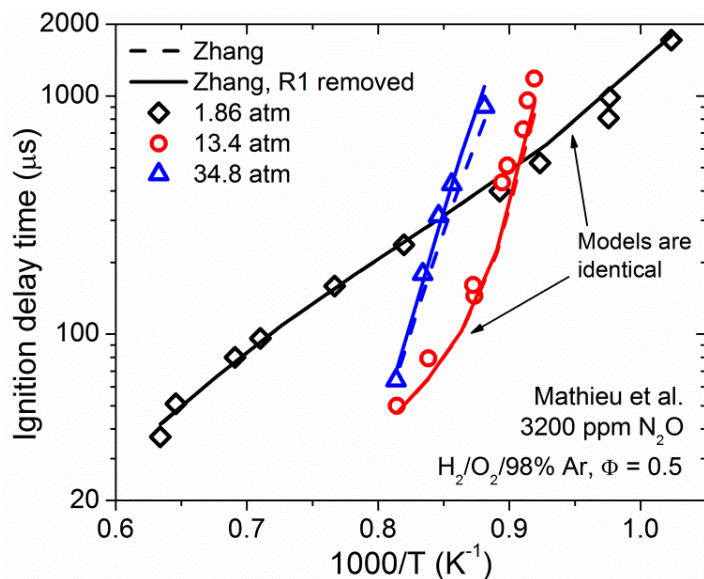


Figure 7: Ignition delay time data of Mathieu et al. [7] alongside model predictions. Dashed lines: unmodified mechanism of Zhang et al. [9], solid lines: Zhang et al. with R1 removed. Definition of τ_{ign} : same as this study.

Similarly, Fig. 8 illustrates the insensitivity of the Kopp et al. data [35] to the inclusion of R1. Kopp et al. measured OH^* ignition delay times in a mixture of 0.05% H_2 /1% N_2O /3% CO/Ar near 1.4 and 10.4 atm. The predictions of the Zhang et al. mechanism [9] with and without R1 are nearly identical, and both sets of predictions closely model the data of Kopp et al.

The results of Figs. 7 and 8 demonstrate that R1 is unimportant for dilute ignition delay time measurements. In further support of the unimportance of R1 for such conditions, Kosarev et al. [4] have demonstrated that the shock-tube data of Soloukhin and Van Tiggelen [36] and Hidaka et al. [37] are also insensitive to the presence of R1 (see Figs. 4 and 5 in [4]).

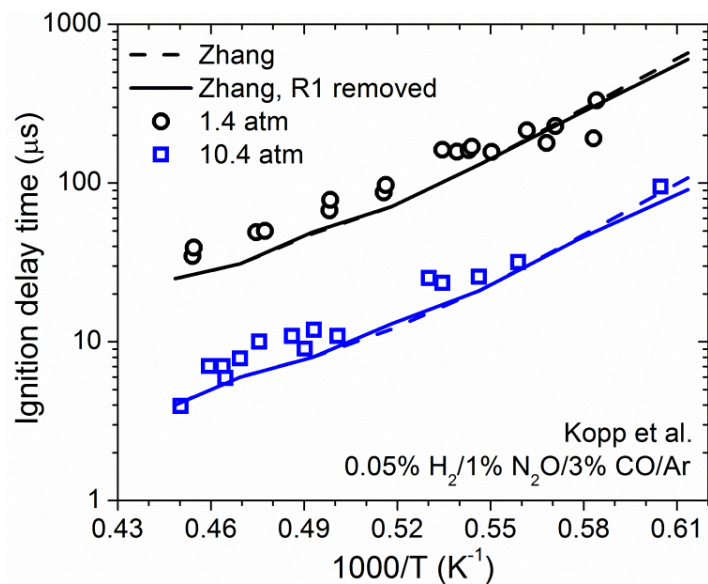


Figure 8: Ignition delay time data of Kopp et al. [35] alongside model predictions. Dashed lines: unmodified mechanism of Zhang et al. [9], solid lines: Zhang et al. with R1 removed. Definition of τ_{ign} : same as this study.

It is perhaps not surprising that the dilute τ_{ign} data are insensitive to R1 given that Kosarev et al. [4] have pointed out that R1 becomes increasingly more important in H_2 - N_2O mixtures with lower dilution levels. Since the only H_2 - N_2O τ_{ign} data at low dilution are those of Kosarev et al. and these have already been discussed, the authors chose to model some of the available flame speed data, which are typically taken at lower dilution levels. Shown in Fig. 9 are the laminar flame speed data of Mével et al. [38] compared with model predictions from Mével et al. [5] and Zhang et al. [9] with and without R1. For this less-dilute case (60% Ar), R1 has a significant impact, particularly for fuel-rich flame speeds, and removing R1 from the Zhang et al. mechanism moves the model predictions farther from the data. Note that the Mével et al. mechanism [5], which does not include R1, struggles to accurately predict the data, and that adding R1 to the Mével et al. mechanism [5] would move the predictions even farther from the data. As pointed out by Mével et al. [38], the sensitive reactions at these conditions are primarily R3 and the reaction



The differences between the two models primarily stem from the different rates used for R3 and R7. For certain, more investigation is needed on the flame speed modeling of H_2 - N_2O mixtures, but this is beyond the scope of the present work. The difficulty in modeling the flame speed data

is related to factors other than R1, and the evidence presented in this work calls strongly for the removal of R1 from future consideration in $\text{H}_2\text{-N}_2\text{O}$ chemistry.

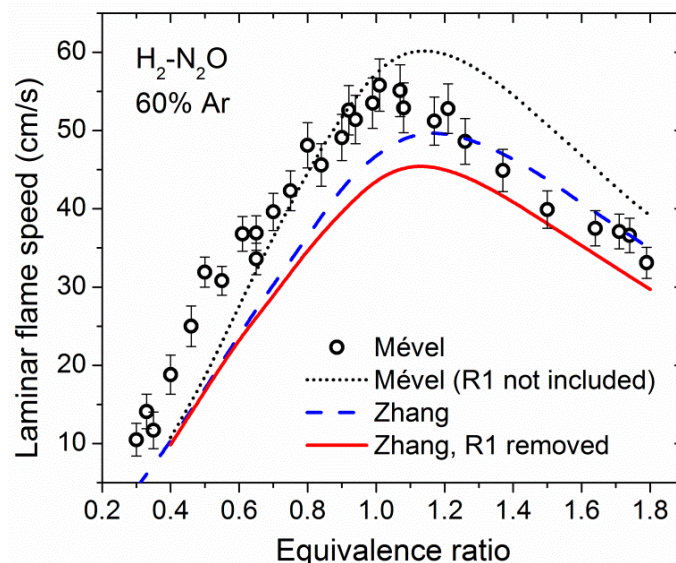


Figure 9: Laminar flame speed data of Mével et al. [38] alongside model predictions. Conditions are 300 K, 1 atm. Dotted line: mechanism of Mével et al. [5] (taken from Fig. 7 of [38]), dashed line: unmodified mechanism of Zhang et al. [9], solid line: Zhang et al. with R1 removed.

5. Conclusions

New laser absorption H_2O time histories were measured in a dilute (98% Ar) $\text{H}_2\text{-N}_2\text{O}$ mixture. Analysis of the time-histories revealed that the reaction $\text{H}_2 + \text{N}_2\text{O} \rightleftharpoons \text{H}_2\text{O} + \text{N}_2$ (R1) needed to be removed from a recent NO_x mechanism (Zhang et al. [9]) to accurately predict the H_2O profiles. Furthermore, new ignition delay time data were obtained by repeating the experiments of Kosarev et al. [4], whose measurements provided the sole basis for the rate of R1. The new data showed excellent agreement with the mechanism of Zhang et al. when R1 was removed. The Kosarev et al. [4] data, including both mixtures used therein, are believed to be significantly accelerated by dP/dt effects and thus should not be used in future mechanism validations. This sample case highlights the need for careful observance of dP/dt and other facility-related effects and also demonstrates the advantage of using shock tubes with larger inner diameters. Finally, comparisons with previous shock-tube ignition delay time measurements showed that the removal of R1 does not degrade the accuracy of mechanism predictions for these data. For all these reasons, we recommend that R1 should not be included in future mechanism developments concerning N_2O chemistry.

6. Acknowledgments

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