Ammonia is a common impurity that can be found in many gas turbine-type fuels derived from coal or biomass and can also be used directly as a fuel in internal combustion engines. Past research showed that ammonia can be the source of “fuel NOx” during its combustion but can also be used in NOx reduction strategies in industrial processes. It is therefore important to understand the details of the high-temperature oxidation of ammonia. Unfortunately, a strong disagreement was observed amongst detailed kinetics mechanisms from the literature for predictions under conditions of practical interest. Ignition delay time measurements for ammonia have been performed several decades ago and conditions are not well reported into the literature. To have well characterized data and to assess the validity of the models, new measurements have been performed in diluted conditions (98 and 99% Ar) and for large pressure (around 1.4, 11.0, and 30 atm), temperature (1560-2490 K), and equivalence ratio ranges (0.5, 1.0, and 2.0). Only one mechanism from the literature was capable of modeling these data with good accuracy. On the other hand, comparison with H2/O2/NOx literature data shows that this model requires improvements.

1. Introduction

Ammonia (NH3) is an impurity commonly found in gaseous fuels derived from gasification processes of biomass or coal (Xu et al. (2011)) and is one of the largest source of nitrogen leading to NO formation during coal combustion (Mendiara and Glarborg (2009)). Depending on the conditions under which fuels are burned, the ammonia can either be converted to NO (fuel-NOx formation mechanism) or N2 (Kohse-Höinhaust et al. (1989), Mendiara and Glarborg (2009)). Ammonia also has a key role in de-NOx processes (Salimian et al. (1984), Kohse-Höinhaust et al. (1989)) and can be used directly as a fuel in internal combustion engines (Pratt and Starkman (1969), Duynslaegher et al. (2012)) or as a hydrogen vector (Duynslaegher et al. (2012)). To control these NOx formation/removal mechanisms or to use NH3 as a fuel efficiently, it is therefore mandatory to understand the details of the combustion of ammonia in a wide range of conditions.

A large number of detailed combustion mechanisms containing ammonia sub-mechanisms are currently available in the literature (Duynslaegher et al. (2012), Mével et al. (2009), Dagaut et al. (2008), Dagaut and Nicolle (2005), Hughes et al. (2001), Mueller et al. (2000), Smith et al. (1999), and Miller and Bowman (1989)). Unfortunately, large discrepancies can be seen amongst predictions from these mechanisms, making difficult the choice of a reliable mechanism for the industry. Ignition delay time (τign) is a convenient measurement to assess the overall validity of the combustion chemistry of a fuel at given conditions. Although many studies focused on the ignition delay time measurement of ammonia mixtures two or three decades ago (Takeyama and Miyama (1965 (a, b), 1966 (a, b)), Miyama and Endoh (1967 (a, b)), Bull (1968), Miyama (1968 (a, b)), Bradley et al. (1968), Drummond, (1972), Fujii et al. (1981)), these studies did not report the pressure and temperature conditions accurately. Also, except for the study of Drummond (1972), there is no study available for pressures above 10 atm.

The aim of this study was therefore to measure ignition delay times for NH3 mixtures highly diluted (98-99% Ar dilution) in a shock tube. Experiments were performed behind reflected shock waves for pressures around 1.4, 11, and 30 atm and for equivalence ratios set to 0.5, 1.0, and 2.0. Details on the experimental procedure are covered first, followed by the results. In this later section, effects of equivalence ratio, pressure, and mixture dilution on the ignition delay time are presented. Detailed kinetics mechanisms from the literature were then tested against these data to assess
their validity. A discussion on the possible improvements of the best literature mechanism is provided in the latter portion of the paper.

2. Methods

The single-diaphragm, stainless steel, shock tube has a driven section of 15.24-cm i.d., 4.72-m long, and a driver section of 7.62-cm i.d., 2.46-m long. A schematic of the shock-tube setup can be found in Mathieu et al. (2012). Five PCB P113A piezoelectric pressure transducers, equally spaced alongside the driven section and mounted flush with the inner surface were used along with four Fluke PM-6666 timer/counter boxes to measure the incident-wave velocities. A curve fit of these four velocities was then used to determine the incident wave speed at the end wall location. Post reflected-shock conditions were obtained using this extrapolated wave speed in conjunction with one-dimensional shock relations and the initial conditions at the test region. This method was proven to maintain the uncertainty in the temperature determination behind reflected shock waves ($T_3$) below 10 K (Petersen et al. (2005)). Test pressure was monitored by one PCB 134A located at the end wall and one Kisler 603 B1 located at the sidewall, in the same plane as the observation window (Sapphire, located 16 mm from the end wall). Non-ideal boundary layer effects measured by the change in pressure (dP/dt) behind the reflected shock wave were determined to be less than 2% per ms for all experiments. The corresponding increase in temperature for these dP/dt levels would be less than 10 K for the longest ignition delay times reported in this study and therefore does not have a noticeable impact on the results herein.

Experiments were performed at three different pressure conditions (around 1.4, 11, and 30 atm), and three equivalence ratios ($\phi$), 0.5, 1.0, and 2.0. Polycarbonate diaphragms were used for test pressures of 1.4 and 11 atm (0.25-mm and 2 × 1.02-mm thickness, respectively), while pre-scored aluminum diaphragms (2.29-mm thickness) were used for the 30-atm experiments. When polycarbonate diaphragms were used, a cross-shaped cutter was employed to facilitate breakage of the diaphragm and prevent diaphragm fragments from tearing off. Helium was used as the driver gas during this study. The driven section was vacuumed down to 2×10^{-5} Torr or better using a roughing pump and a Varian 551 Turbomolecular pump prior to every run. The pumping time between experiments was minimized using a pneumatically driven poppet valve matching the inside diameter of the driven section and allowing for a passage of 7.62-cm diameter between the vacuum section and the driven tube. The pressure in the mixing tanks was measured using two MKS Baratron model 626A capacitance manometers (0-10 Torr and 0-1000 Torr) and an ion gauge for high vacuums. Test mixtures were prepared manometrically in a mixing tank of 3.05-m length made from stainless steel tubing with a 15.24-cm ID. The pressure in the mixing tanks was measured using a Setra GCT-225 pressure transducer (0-17 atm). The mixing tank is connected to the vacuum system and can be pumped down to pressures below 1×10^{-6} Torr. The gases (Ammonia (Praxair, 99.9% purity diluted in 94.92 % Ar (99.999 %)), O$_2$ (Praxair, 99.999 %), and Ar (Acetylene Oxygen Company, 99.999 %)) were passed through a perforated stinger traversing the center of the mixing tank to allow for rapid, turbulent mixing. To further ensure homogeneity through diffusion processes, mixtures were allowed to rest for at least 1 hour prior to making the first run. No difference in the results was observed for longer mixing times. Since NH$_3$ adsorbs on stainless steel (Roose et al. (1981), Kohse-Höinghaus et al. (1988)), the mixing tank and shock-tube surfaces were passivated with NH$_3$ before the mixture preparation and before each experiment (introduction of around 100 torr of NH$_3$ for at least 5 minutes and then vacuumed for 5 minutes with the rough pump, until around 40 mtorr, typically). Conditions investigated during this study are provided in Table 1.
Table 1: Experimental conditions investigated behind reflected shock waves.

<table>
<thead>
<tr>
<th>Mixture composition (mole fraction)</th>
<th>Equivalence ratio (ϕ)</th>
<th>T₅ (K)</th>
<th>P₅ (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.004 NH₃ / 0.006 O₂ / 0.99 Ar</td>
<td>0.5</td>
<td>1925-2480</td>
<td>1.4 ± 0.1 atm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1625-2015</td>
<td>10.9 ± 0.5 atm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1560-1895</td>
<td>28.7 ± 1.0 atm</td>
</tr>
<tr>
<td>0.005715 NH₃ / 0.004285 O₂ / 0.99 Ar</td>
<td>1.0</td>
<td>1985-2490</td>
<td>1.4 ± 0.1 atm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1660-2080</td>
<td>10.8 ± 0.4 atm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1565-1930</td>
<td>28.7 ± 1.0 atm</td>
</tr>
<tr>
<td>0.01143 NH₃ / 0.00857 O₂ / 0.98 Ar</td>
<td>1.0</td>
<td>1825-2455</td>
<td>1.4 ± 0.1 atm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1615-2085</td>
<td>10.5 ± 0.4 atm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1565-1870</td>
<td>28.6 ± 0.6 atm</td>
</tr>
<tr>
<td>0.007373 NH₃ / 0.002727 O₂ / 0.99 Ar</td>
<td>2.0</td>
<td>1990-2360</td>
<td>1.4 ± 0.1 atm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1650-2040</td>
<td>10.6 ± 0.6 atm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1580-1910</td>
<td>28.9 ± 1.5 atm</td>
</tr>
</tbody>
</table>

The ignition delay time was measured using the chemiluminescence emission from the A²Σ⁺ → X²Π transition of the excited-state hydroxyl radical (OH*) using an interference filter centered at 307 ± 10 nm with a Hamamatsu 1P21 photomultiplier tube. The ignition delay time is defined herein as the time between the passage of the reflected shock wave, indicated by a pressure jump in the signal delivered by the sidewall pressure transducer, and the intersection of lines drawn along the steepest rate-of-change of OH* de-excitation and a horizontal line which defines the zero-concentration level, as can be seen in Fig. 1. Time zero is defined as the time of arrival of the reflected shock wave at the sidewall measurement location. Note the typical OH* profiles for NH₃, where the OH* signal does not come back to zero and stays flat for a few hundreds of microseconds after the ignition. All of the data signals were recorded through a 14-bit GageScope digital oscilloscope with sampling rates of 1 MHz or greater per channel.

![Figure 1: Typical pressure and OH* profiles and method of determination of the ignition delay time.](image-url)

There are essentially two sources of uncertainties in the ignition delay time: the uncertainty in the determination of the temperature behind the reflected shock wave (T₅) and the uncertainty associated with the determination of the steepest rate of change from the OH* profile. The temperature determination is the most important uncertainty and, as mentioned earlier, the experimental setup and method used allow for a determination of T₅ within less than 10 K. The second source of uncertainty is typically smaller than the uncertainty in the temperature, and is neglected. Overall, the total uncertainty
in \( \tau_{\text{ign}} \) reported in this study is estimated to be 10\% (which also includes the minimal temperature variation with facility dP/dt).

3. Results and Discussion

Equivalence ratio effect

The equivalence ratio effects on ammonia ignition delay times are visible in Fig. 2 at pressures around 1.4 atm (a), 11 atm (b), and 30 atm (c). As can be seen, at pressures of 11 atm and above, the ignition delay time obtained at \( \phi = 1.0 \) and 2.0 are very similar, while \( \tau_{\text{ign}} \) obtained at \( \phi = 0.5 \) are shorter (by a factor around 1.5). At the lowest pressure investigated, around 1.4 atm (a), the equivalence ratio seems to have only a moderate effect on \( \tau_{\text{ign}} \). At the stoichiometry and at this low-pressure condition, ignition delay times seem to be longer than for the other conditions but \( \tau_{\text{ign}} \) at \( \phi = 0.5 \) are similar at high temperatures while \( \tau_{\text{ign}} \) compare with those obtained at \( \phi = 1 \) on the low-temperature side. The activation energies (Ea) extracted from Fig. 2 show that Ea does not vary much with the equivalence ratio at 11 atm and above (Ea = 39.5, 40.1 and 40.1 kCal/mol at 11 atm for \( \phi = 0.5, 1.0 \) and 2.0, respectively and Ea = 42.5, 42.0 and 44.1 kCal/mol at 30 atm for \( \phi = 0.5, 1.0 \) and 2.0, respectively). However, it seems that Ea increases slightly with the equivalence ratio for the lowest pressure investigated: Ea = 44.6, 51.7 and 56.3 kCal/mol for \( \phi = 0.5, 1.0 \) and 2.0, respectively, at 1.4 atm. Note that this result could partly come from the small amount of curvature observed on the low temperature side of the curve.

Pressure effect

As can be seen in Fig. 3 (a-d), there is an important effect of pressure on the ignition delay time, for all the equivalence ratios and Ar dilution studied. Indeed, it is visible that the ignition delay time decreases with the increase in the pressure. A factor around 7 is found between \( \tau_{\text{ign}} \) obtained at 1.4 and 11 atm at 2000 K for all conditions investigated, while factors of 1.8, 1.9, and 2.2 were found at 1700 K between \( \tau_{\text{ign}} \) obtained at 11 and 30 atm for \( \phi = 0.5, 1.0 \) (at both dilution level), and 2.0, respectively.
Figure 3: Effects of the pressure on the ignition delay time of NH\textsubscript{3} mixtures diluted in 99% Ar at around 1.4 atm (a), 11 atm (b) and 30 atm (c).

Fuel concentration effect
By comparing the data obtained at $\phi = 1.0$ for the 98% and 99%dilutions in Ar, Fig. 4, one can see the effect of the dilution level on the ignition delay time. As can be seen in this figure, at around 1.4 atm (a), the ignition delay time is typically shorter for the 98% dilution case. However, the ignition delay times tend to converge toward a similar value as the temperature increases, and it can be seen that $\tau_{\text{ign}}$ are similar above 2270 K. For higher pressure, 11 atm (b) and 30 atm (c), the ignition delay times are also shorter for the lowest dilution ratio and also tend to converge toward a similar value at a given temperature. However, at these high pressures, one can see that ignition delay times converge toward the same value for the lowest temperatures investigated. Activation energies for the mixtures with 98% Ar dilution are 42.0, 43.0, and 46.7 kCal/mol at 1.4, 11, and 30 atm, respectively. These values compare with the value obtained for the 99% Ar dilution, except for the low-pressure case where $E_a$ is higher for the highest dilution level (51.7 kCal/mol).
Using the shock-tube data presented herein, it was possible to derive the following correlation ($r^2 = 0.955$):

$$\tau_{ign}(\mu s) = 16.81 \times 10^{-3} \Phi^{0.18} p^{-0.89} \exp(44.11 (kCal)/RT)$$

**Models comparison**

To assess the validity of the aforementioned detailed kinetics models, data from this study were modeled with mechanisms available in the literature. To do so, whenever necessary, the OH* model from Hall and Petersen (2006) was merged to these detailed kinetics mechanisms. Due to the large differences in the ignition delay time and shape of the computed OH* profiles with the profiles obtained experimentally, it was found necessary to add the reaction $N_2O + H = OH^* + N_2$ from Hidaka et al. (1985) to the OH* mechanism from Hall and Petersen (2006). Some representative experimental profiles obtained at various conditions have been modeled using the mechanism from Dagaut et al. (2008) along with the OH* chemistry from Hall and Petersen (2006) with and without the reaction from Hidaka et al. (1985).

These profiles are visible in Fig. 5 and, as can be seen, this combination of reactions allow for a good modeling of both the experimental profiles and ignition delay times, whereas a strong disagreement in the shape ((a) and (c)) and in the ignition delay time was observed without the OH* formation from $N_2O$ and H. Note that the normalized OH* profile does not reach 1 in Fig. 5(c) because the computed OH* profile is increasing after the visible peak and reach its maximum value after the time frame of Fig. 5(c).

Using this complete OH* sub-mechanism, the comparison between some selected and representative data from this study and the models is visible in Fig. 6. Note that the results from the mechanism of Smith et al. (1999), (GRI 3.0 mechanism)
are not included in this figure. Indeed, this mechanism does not contain the dissociation reaction \( \text{NH}_3 + \text{M} = \text{NH}_2 + \text{H} + \text{M} \). This reaction is very important to initiate the combustion of \( \text{NH}_3 \). As a result, this mechanism is significantly too slow, from at least one order of magnitude, compared to the experimental data. As can be seen in Fig. 6, the mechanism of Dagaut et al. (2008) is predicting the experimental data with high accuracy. The predicted ignition delay times are well captured for pressures higher than 1.4 atm, whatever the ammonia concentration and the equivalence ratio. At around 1.4 atm, however, the model tends to be slightly under-reactive but is still the closest of the mechanisms. The model of Dagaut and Nicolle (2005), although too reactive, also provides relatively acceptable results. Then the model of Miller and Bowman (1998) generally presents a too-high activation energy and mediocre prediction of \( \tau_{\text{ign}} \). The other mechanisms are somewhat close to each other in terms of predictions and are significantly too reactive. However, note that the mechanism of Duynslaegher et al. (2012) was developed for low-pressure conditions only, and that the model of Mével et al. (2009) is essentially a model describing the combustion of \( \text{H}_2/\text{N}_2\text{O} \) mixtures but with an ammonia sub-mechanism. The results in Fig. 6 are representative of the results obtained for the other conditions investigated.

Figure 6: Comparison between models from the literature and selected, representative data from this study. (a): 1.4 atm, \( \Phi = 0.5 \); (b): 11.0 atm, \( \Phi = 1.0 \); (c): 30 atm, \( \Phi = 2.0 \); (d): 11.0 atm, \( \Phi = 1.0, 98\% \text{ Ar} \).

As seen previously, the \( \text{N}_2\text{O} \) chemistry seems to be of great importance for the \( \text{NH}_3 \) combustion as the reaction \( \text{N}_2\text{O} + \text{H} = \text{N}_2 + \text{OH}^* \) is critical for the determination of the ignition delay time. To assess the validity of the \( \text{N}_2\text{O} \) sub-mechanism in the mechanism of Dagaut et al. (2008), \( \text{H}_2\text{O}_2/\text{N}_2\text{O} \) results from Mathieu et al. (2012) were modeled. As can be seen in Fig. 7, the model of Dagaut et al. (2008) does not predict very well these data and is significantly under-reactive. To
better estimate whether this discrepancy was due to the H$_2$/O$_2$ sub-mechanism or to the N$_2$O sub-mechanism, the hydrogen mechanism from Kéromnès et al. (2013) was merged to the model of Dagaut et al. (2008). The same H$_2$ mechanism is used in the work of Mathieu et al. (2012). As can be seen, results are significantly improved using this H$_2$ mechanism. However, the predicted ignition delay times are now slightly too short. Although acceptable, the predictions could probably be improved. Note that this replacement of H$_2$/O$_2$ chemistry has nearly no effect on the predictions for NH$_3$ ignition. A future work will then be needed to improve the model of Dagaut et al. (2008) merged with the H$_2$/O$_2$ mechanism from Kéromnès et al. (2013). The aim of this model will be then to model NH$_3$ data from this study and the literature as well as the H$_2$/NO$_2$ (Mathieu et al. (2013)) and H$_2$/N$_2$O (Mathieu et al. (2012)) data to propose a consistent base model. This base model for mixtures involving H$_2$ and NH$_3$/NOx species will then later be extended to hydrocarbons/NH$_3$/NOx interactions.

Figure 7: Comparison between the 0.01 H$_2$/0.01O$_2$/3200 ppm N$_2$O / 0.9768 Ar data at around 13 atm from Mathieu et al. (2012) with the models of Dagaut et al. (2008), the model of Dagaut et al. (2008) merged with the H$_2$ mechanism from Kéromnès et al. (2013) and the model from Mathieu et al. (2012).

4. Conclusions

It is important to understand the details of NH$_3$ combustion chemistry for practical reasons such as the control of NOx formation or NOx removal processes. To date, several shock-tube studies have been performed several decades ago, and several detailed kinetics mechanisms are available from the literature. Unfortunately, the experimental conditions are not accurately reported in the experimental studies and a large discrepancy is observed amongst models, making the selection of a good model to predict NH$_3$ combustion difficult. Thus, new ignition delay time measurements have been performed over a wide range of conditions (around 1.4, 11.0, and 30 atm, between 1560 and 2490 K, and for equivalence ratios 0.5, 1.0, and 2.0). Results showed that both the equivalence ratio and the pressure had an important effect on the ignition delay time. To model the data, it was found necessary to add the reaction N$_2$O + H = N$_2$ + OH* from Hidaka et al. (1985) to the OH* mechanism from Hall and Petersen (2006). Modeling results showed that only the mechanism from Dagaut et al. (2008) was capable of reproducing satisfactorily the experimental results. However, further analysis showed that this mechanism needs to be improved at the H$_2$/O$_2$ and NOx sub-mechanisms levels.

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References


