A shock tube study on ammonia decomposition and its reaction products

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Abstract: The decomposition of NH$_3$ with argon as collisional partner has been studied behind reflected shock waves in the temperature range from 1850K to 2500K and at total pressures between 2.2 and 8.6bar. The reaction progress was observed by measuring absorption profiles of educt and product species. On the educt side, NH$_3$-consumption was detected by non-resonant absorption at D$_\alpha$. On the product side, D- and H-radical absorption profiles were taken by ARAS, NH$_2$-profiles by laser absorption measurements. The profiles were modelled using the reaction mechanism given by Davidson et al. (1990). We found that the NH$_3$-decomposition should proceed slower at pressures in the range of 2 to 3bar. The rate coefficients of the NH$_2$-decay and of the reaction NH$_2$ + NH $\rightarrow$ N$_2$H$_2$ + H should be decreased.

Key words: Chemical Kinetics, NH$_3$, Absorption Spectroscopy, Modelling

1. Introduction

Nitrogen chemistry has become an important part of flame modelling due to the increasing importance of reduction in emissions of nitrogen oxides NO$_x$ from combustion applications. Ammonia is important not only for its role in NO$_x$ reduction, but also for the role of NH$_i$ fragments in the process of fuel NO$_x$ formation. Consequently, a number of studies on the decomposition of ammonia has been carried out (see for example Davidson et al. (1990)). Special care was employed in the determination of the decay rate of ammonia and of the rate coefficient for the reaction of NH$_3$ + H. Their evaluation may easily become too complicated due to secondary reactions of NH$_2$ which may influence the NH$_3$-pyrolysis system considerably, particularly for experiments carried out at higher temperatures and relatively high initial concentrations of ammonia.

Therefore, in the present work, the thermal decomposition of NH$_3$ was investigated behind reflected shock waves by measuring resonance absorption of H atoms using low initial concentrations of NH$_3$. Furthermore – in order to gain more information about the role of subsequent reactions – absorption profiles of NH$_2$ were measured using laser absorption spectroscopy; absorption profiles at D$_\alpha$ were observed simultaneously.

2. Experimental

In the present work, measurements of H-, NH$_2$- and NH$_3$/D-absorption profiles in the NH$_3$-pyrolysis system have been performed behind the reflected shock front in a stainless-steel, high-purity, heatable UHV-shock tube. Driver (5.2m) and driven (11.1m) section of the shock tube have a inner diameter of 9.8cm. Molecular hydrogen was used as driver gas, argon as bath gas. Solving the appropriate conservation equations, temperatures and pressures behind the reflected shock wave were calculated from initial pressures and temperatures and from the velocity of the incident shock front, measured with four thin-film platinium gauges. Further details can be found in the paper by Frank and Just. (1985). Optical access is provided by Suprasil- and MgF$_2$- windows located at a distance of 5mm from the end flange. Mixtures of NH$_3$/Ar were stored in two spherical stainless-steel vessels at 1 bar. Both shock tube and mixing tanks were heated to 80$^\circ$C and 130$^\circ$C, resp., and evacuated to $1 \cdot 10^{-7}$mbar before each series of experiments in order to reduce the amount of water.

Figure 1. Absorption cross section of NH$_3$ at D$_\alpha$/L$_\alpha$.

The initial ammonia concentration varies between 1.1% and 12ppm NH$_3$/Ar, depending on the detection wavelength and -limit of the investigated species as listed in table (1). The determination of the initial concentration of NH$_3$ has been exercised intensively. These measurements were performed using a standard procedure to determine the initial NH$_3$-concentration photometrically at 672nm at a detection limit of 1ppm. Furthermore the
absorption cross section of NH$_3$ at D$_{\alpha}$ and L$_{\alpha}$ at room 
temperature was measured in order to determine the initial 
NH$_3$-concentration in situ:

$$\sigma_{NH_3}(296K) = (7.76 \pm 0.31) \cdot 10^{-18} \text{cm}^2.$$  

The temperature dependence of the NH$_3$-absorption cross section at D$_{\alpha}$ and L$_{\alpha}$ was evaluated from incident 
and reflected shock wave absorption data up to 2600K as shown in figure (1):

$$\sigma_{NH_3}(T)/10^{-17}\text{cm}^2 =$$

$$(3.3 \pm 0.3) \cdot 10^{-4} \cdot T/K + (0.65 \pm 0.06).$$

Atomic resonance absorption spectroscopy (ARAS) has been used to monitor H-absorption profiles. Spectral 
separation was enabled by means of an L$_{\alpha}$-interference filter with 10nm FWHM and molecular oxygen as an 
asorber. Calibration and spectral purity tests of the microwave driven gas discharge emission (1%H$_2$/He) 
were provided by the H$_2$/N$_2$O - kinetic system, which 
revealed an H-detection limit of $5 \cdot 10^{13}$cm$^{-3}$ and a 
resonant absorption limit of (96±2)%. A time resolution of less than 3µs has been achieved by the use of 1mm 
slits in front of emission and detection windows.

Non-resonant absorption of NH$_3$ at D$_{\alpha}$ has been detected with the same experimental setup as the H-ARAS 
measurements. Due to the natural abundance $p$ of partially deuterated ammonia ND$_2$H$_2$ ($p=4.4987 \cdot 10^{-4}$), resonant 
absorption of D radicals was measured simultaneously 
with the non-resonant absorption of NH$_3$ at D$_{\alpha}$. 
This provides an indirect control on the predicted H-radical 
absorption of D radicals was measured simultane-
ously with the non-resonant absorption of NH$_3$

Figure 2. Absorption cross section of H$_2$ at D$_{\alpha}$/L$_{\alpha}$.

significant because of their low absorption cross sections 
which have been experimentally determined in separate 
experiments to be

$$\sigma_{N_2}(D_{\alpha};1850K<T<2600K) < 2 \cdot 10^{-19} \text{cm}^2,$$
calculated for S/N = 1, and

$$\sigma_{H_2}(D_{\alpha};1800K<T<2650K) =$$

$$4.25 \cdot 10^{-18} \, e^{-8980/T} \text{cm}^2$$
as shown in figure (2). The second absorption cross section 
for H$_2$ at D$_{\alpha}$ is considerably lower than the value 
for $\sigma_{H_2}$ at L$_{\alpha}$ given by Natarajan et al. (1994).

Detection of the NH$_2$-species was enabled by means of resonant narrow-band laser absorption at the isolated 
$^3Q_{1,1}(7)$-doublet transition in the $A^2A_1 \leftrightarrow$ 
$X^2B_1(090 \leftarrow 000)\Sigma$ sub-band at 597.375nm which 
overlap in the pressure range of the present work. 
The calculation of the absorption cross section of 
NH$_2$ is based on the calibration experiments of 
Kohse-Höinghaus et al. (1989), who claimed ±30% accuracy 
in $\sigma_{NH_2}$. Davidson et al. (1990) found that 
the values for the absorption cross section are consistent 
with the upper error limits of $\sigma_{NH_2}$ given by 
Kohse-Höinghaus et al. (1989).

A Spectra-Physics 380D ring dye laser was used with 
rhodamine 6G dye pumped with 3W all lines from a Spectra-Physics 2020 Ar$^+$ laser (see also 
Braun-Unkoff et al. (1993)). The output wavelength 
was controlled by a Burleigh WA-20 wavemeter and 
cross checked by NH$_2$-cw-LIF in a 2%NH$_3$/He plasma 
at 2 to 5mbar with emission detection by lock-in 
amplification. Single mode quality was verified with a 
Spectra-Physics model 450 2GHz spectrum analyser. 
The laser output beam was guided to the shock tube 
through a fiber. A multiple reflection setup has been 
used to increase the absorption path length up to 4
shock tube diameters. With a time resolution of at least 4μs (FWHM of the laser Schlieren peak), a minimum detection limit of ≈ 1.6 · 10^{14} cm^{-3} could be achieved.

<table>
<thead>
<tr>
<th>Table 1. Experimental Conditions</th>
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<tr>
<td>H-detection at ( L_\alpha )</td>
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<tr>
<td>12ppm &lt; [NH₃]₀ &lt; 210ppm</td>
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<tr>
<td>1930K &lt; ( T_\alpha ) &lt; 2500K</td>
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<tr>
<td>2.2bar &lt; ( p_5 ) &lt; 8.6bar</td>
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<tr>
<td>NH₃- and D-detection at ( D_\alpha )</td>
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<tr>
<td>1402ppm &lt; [NH₃]₀ &lt; 4100ppm</td>
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<tr>
<td>1930K &lt; ( T_\alpha ) &lt; 2570K</td>
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<tr>
<td>2.4bar &lt; ( p_5 ) &lt; 3.0bar</td>
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<tr>
<td>NH₂-detection at ( \lambda = 597.375 \text{nm} )</td>
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<tr>
<td>3160ppm &lt; [NH₂]₀ &lt; 1.13%</td>
</tr>
<tr>
<td>1880K &lt; ( T_\alpha ) &lt; 2570K</td>
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<tr>
<td>2.4bar &lt; ( p_5 ) &lt; 3.1bar</td>
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3. Results and Discussion

The measured H, NH₂ and \( D_\alpha \)-absorption profiles were modelled by applying the reaction scheme of 21 reactions and 10 species given by Davidson et al. (1990) as listed in table (2). Sensitivity analysis was carried out for each individual experiment in order to determine the dominant reactions. Due to the low initial concentration of NH₃ (see table (1)) used especially for the experiments at \( L_\alpha \), only four reactions were found to be of significant influence on the measured absorption profiles: for \( T < 2150 \text{K} \), the decay of NH₃ and the reaction of NH₃ + H are important. As the temperature increases, the decay of NH₂ and the bimolecular reaction of H atoms with NH₂ have to be taken into account as well, especially for \( T > 2150 \text{K} \) (reactions R1, R2, and R8, R11, see table (2)). From modelling those absorption profiles at very low initial concentrations of NH₃ (12ppm – 58ppm) which were measured at \( L_\alpha \), an Arrhenius expression for the decay of NH₃ was derived. By modelling the \( L_\alpha \) absorption profiles as well as the measured NH₂ absorption profiles, it was concluded that secondary reactions of the NH₂ radical formed in the initiation reaction R₁ should be decreased in order to reproduce the experimental absorption profiles for temperatures greater than 2150 K at the end of the observation period. Using the measured \( D_\alpha \)-absorption profiles it was possible to determine the initial amount of ammonia in situ from absorption observed at \( T_1 \) and \( p_1 \) (for [NH₃]₀ > 1000ppm). Furthermore, these experimental profiles were used for validation of the reaction model.

3.1. Absorption profiles measured at \( L_\alpha \)

H atoms are produced directly via reaction R₁ during the decay of ammonia leading also to the formation of NH₂. In order to derive an Arrhenius expression for the decay of NH₃, only absorption profiles at very low initial concentrations of NH₃ (27ppm – 58ppm) were modelled. As may be seen in figure (3), the absorption profile, which was observed at the lower end of the investigated \( T \)-range at a total pressure of about 3bar, is very sensitive towards variations of \( k_1 \). Using the rate coefficient for \( k_1 \) given by Davidson et al. (1990), the calculated profile is much too high (fig. (3), curve (b)). Excellent agreement between experimental and calculated absorption profiles can be achieved if the k-value for the NH₃-decay is lowered by a factor of two (solid curve (a)). The evaluation of \( k_1 \) could be performed without appreciable influence of subsequent reactions as the secondary reaction of NH₃+H becomes important only for reaction times > 200μs (fig. (3), curves (c) and (d)). For a pressure range of 2.2bar < \( p < 3.2 \text{bar} \), the following rate expression for the reaction R₁: \( \text{NH₃} + \text{M} \rightarrow \text{NH₂} + \text{H} + \text{M} \) was found:

\[ k_1 = 1.5 \cdot 10^{16} \exp(-46860K/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}. \]

As may be seen in figure (6), the Arrhenius expression derived in the present work is lower by about a factor of 0.7 than the one given by Davidson et al. (1990) for \( 2200 \text{K} < T < 2800 \text{K} \), the activation energy remains nearly the same.

It should be remarked that in the case of those experiments which have been carried out for total pressures around 8.5bar, excellent agreement between measured and calculated profiles is achieved with-
out any modification of the rate coefficients given by Davidson et al. (1990) as shown in figure (4), curve (a). Due to the very low initial concentrations of NH$_3$ (12ppm), the observed absorption profile is very sensitive to variations of the rate coefficients for the decay of ammonia (see fig. (4), curve (b): $k_1\cdot 0.5$; curve (c): $k_1\cdot 2$).

Figure 5. L$_{\alpha}$-absorption profile at higher NH$_3$-concentrations and model predictions: (a) Davidson et al. (1990), (b) $k_1\cdot 0.75$, (c) $k_8\cdot 0.6$ and $k_{11}\cdot 0.4$.

Modelling the experiments involving higher initial concentrations of NH$_3$ and performed at higher temperatures, subsequent reactions of the NH$_2$ radical have to be considered as well, as sensitivity analysis revealed. Again, applying the Davidson model, the calculated profile is much too high (see fig. 5, curve (a)). If the decay of ammonia is decreased, the steep rise of the absorption profile is reproduced much better (see fig. 5, curve (b)). By lowering the rate coefficients of R$_8$: NH$_2$ + M $\rightarrow$ NH + H + M and R$_{11}$: NH$_2$ + NH $\rightarrow$ N$_2$H$_2$ + H by a factor of 0.6 and 0.4, resp., excellent agreement between measured and calculated absorption profile is achieved (see fig. 5, curve (c)).

Figure 6. Arrhenius plot for the ammonia decomposition reaction R$_1$ as derived from the H-radical measurements in the pressure range of 2.2 to 3.3bar in comparison to Davidson et al. (1990).

3.2. NH$_2$- and D$_{\alpha}$-absorption profiles

The decomposition of NH$_3$ (R$_1$) and its reaction with H atoms (R$_2$) both lead to the formation of NH$_2$-radicals. Hence, by measuring the time history of the amidogen species using laser absorption spectroscopy further information may be derived about the influence of subsequent reactions in the NH$_3$ pyrolysis system on the evaluated kinetic reaction model. Due to the multiple reflection setup, it was possible to simultaneously observe the absorption of NH$_2$ and the absorption at D$_{\alpha}$ which - additionally - enables the determination of the initial concentration of ammonia by measuring the absorption at room temperature just before the shock is run (see section (2.1)). Again, sensitivity analysis was calculated in order to determine the dominant reactions; the same reactions as in the case of L$_{\alpha}$-absorption measurements were identified.

Figure (7) shows a typical absorption profile for NH$_2$ measured at 597.375 nm for initial concentration of NH$_3$ of 3160ppm at T = 2283K. As can be seen from the experimental curve, the absorption profile increases very fast without any noticable induction period. Applying the reaction model given by Davidson et al. (1990), the calculated absorption profile is increasing too fast at the onset of the reaction, and - furthermore - lies much too low for longer observation times (see fig. (7), curve (a)). If the value of the rate coefficient for the decay of NH$_3$
Table 2. Ammonia pyrolysis mechanism. For rate coefficients refer to Davidson et al. (1990)

| Reactions | rate expressions given by Davidson et al. (1990) should be adjusted to 0.4 \cdot k_{11} for reaction (a1) non-resonant NH$_3$, (a2) resonant D-absorption and small contribution from N$_2$- and H$_2$-absorption (not separately shown), (b) $k_1$ adjusted to $A_{\text{max}}(\text{NH}_2;t)$ and (c) same as (b), but with $k_{11} \approx 0.4$.

Figure 7. NH$_2$-absorption profile at 597.375nm and model predictions: (a) Davidson et al. (1990), (b) $k_1$ adjusted to $A_{\text{max}}(\text{NH}_2;t)$, (c) same as (b), but with $k_{11} \approx 0.4$.

| Reactions | rate expressions given by Davidson et al. (1990) should be adjusted to 0.4 \cdot k_{11} for reaction (a1) non-resonant NH$_3$, (a2) resonant D-absorption and small contribution from N$_2$- and H$_2$-absorption (not separately shown), (b) $k_1$ adjusted to $A_{\text{max}}(\text{NH}_2;t)$ and (c) same as (b), but with $k_{11} \approx 0.4$.

Figure 8. D$_\alpha$-absorption profile under same conditions as in fig. 7 and model predictions: (a) Davidson et al. (1990) resulting from (a1) non-resonant NH$_3$, (a2) resonant D-absorption and small contribution from N$_2$- and H$_2$-absorption (not separately shown), (b) $k_1$ adjusted to $A_{\text{max}}(\text{NH}_2;t)$ and (c) same as (b), but with $k_{11} \approx 0.4$.

| Reactions | rate expressions given by Davidson et al. (1990) should be adjusted to 0.4 \cdot k_{11} for reaction (a1) non-resonant NH$_3$, (a2) resonant D-absorption and small contribution from N$_2$- and H$_2$-absorption (not separately shown), (b) $k_1$ adjusted to $A_{\text{max}}(\text{NH}_2;t)$ and (c) same as (b), but with $k_{11} \approx 0.4$.

is lowered according to the results of the modelled L$_\alpha$-absorption profiles, good agreement is achieved between calculated and experimental profiles with respect to the maximum observed absorption $A_{\text{max}}(\text{NH}_2;t)$, which is shifted by about 60μs towards longer reaction times (see fig. 7, curve (b)). In order to reproduce the experimental profile for reaction times $> 300μs$, reaction R$_{11}$: NH$_2$ + NH $\rightarrow$ N$_2$H + H was lowered by a factor of 0.4 compared to the value given by Davidson et al. (1990), because reaction R$_{11}$ turns out to be the dominant reaction on the absorption profile at longer observation times as sensitivity analysis reveals.

Figure (8) shows a typical absorption profile taken at D$_\alpha$ for the same experiment as in figure (7). This profile also provides kinetic information (see section (2.1)). Again, applying the Davidson-model, the calculated D$_\alpha$ absorption profile decreases much too fast resulting in absorption levels which are much too low compared to the experimental ones (see fig. 8, curve (a)). The total absorption consists of the (decreasing) absorption due to the decay of ammonia (a) (see fig. (8), curve (a1)) and of the (increasing) absorption due to the production of D-atoms (see fig. 8, curve (a2)). The contribution from H$_2$ and N$_2$ to the total absorption at D$_\alpha$ is very small (see section (2.1)). Excellent agreement between measured and calculated profile is achieved by employing the same modifications (reactions and rate coefficients) as in Fig. 7 (see fig. 8, curve (c)).

These modelling studies suggest that the Arrhenius expressions given by Davidson et al. (1990) should be lowered for reaction

$$R_8: \text{NH}_2 + \text{M} \rightarrow \text{NH} + \text{H} + \text{M}$$

by a factor of ≈0.5 and for reaction

$$R_{11}: \text{NH}_2 + \text{NH} \rightarrow \text{N}_2\text{H}_2 + \text{H}$$
by a factor of $\approx 0.4$.

It should be mentioned that – in principle – the measured NH$_2$ absorption profiles could also be reproduced by modifying the rate coefficient of the reaction R$_2$: NH$_3$ + H $\rightarrow$ NH$_2$ + H$_2$. However, in the case of modelling NH$_2$ absorption profiles, this value should be decreased (to about 0.2 $\cdot$ k$_2$ [Davidson et al. (1990)]), whereas in the case of modelling L$_x$ absorption profiles, this value should be increased (up to about 2 $\cdot$ k$_2$ [Davidson et al. (1990)]). For these reasons, the rate coefficient for R$_2$ was not modified in the present work.

It should be remarked that – in addition to the reactions presented in the discussion of the absorption profiles up to now –, reaction R9: NH$_2$ + H $\rightarrow$ NH + H$_2$ reveals a slight influence on the NH$_2$ profiles at longer reaction times for high temperatures. Further information on the chemical kinetic system may be derived if the time history of the NH radical would be measured as well. Plans for future experiments include narrow line-width laser absorption spectroscopy of NH in conjunction with multiple reflection setup.

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**References**


