A shock tube study on ammonia decomposition and its reaction products

C. Naumann, M. Braun-Unkhoff, and P. Frank

DLR, Institute for Physical Chemistry of Combustion, 70569 Stuttgart, Germany

Abstract: The decomposition of NH₃ 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, NH₃-consumption was detected by non-resonant absorption at D_{α} . On the product side, D- and Hradical absorption profiles were taken by ARAS, NH₂profiles 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 NH₂-decay and of the reaction $\rm NH_2$ + $\rm NH$ \rightarrow $\rm N_2H_2$ + H should be decreased.

Key words: Chemical Kinetics, NH₃, 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 NH₂ which may influence the NH₃-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 NH₃ was investigated behind reflected shock waves by measuring resonance absorption of H atoms using low initial concentrations of NH₃. Furthermore – in order to gain more information about the role of subsequent reactions – absorption profiles of NH₂ were measured using laser absorption spectroscopy; absorption profiles at D_{α} were observed simultaneously.

2. Experimental

In the present work, measurements of H-, NH₂- and NH₃/D-absorption profiles in the NH₃-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 MgF₂ - windows located at a distance of 5mm from the end flange. Mixtures of NH_3/Ar were stored in two spherical stainlesssteel vessels at 1 bar. Both shock tube and mixing tanks were heated to 80°C and 130°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_{α}/L_{α} .

The initial ammonia concentration varies between 1.1% and $12\text{ppm NH}_3/\text{Ar}$, depending on the detection wavelength and -limit of the investigated species as listed in table (<u>1</u>). The determination of the initial concentration of NH₃ has been exercised intensively. These measurements were performed using a standard procedure to determine the initial NH₃-concentration photometrically at 672nm at a detection limit of 1ppm. Furthermore the

absorption cross section of NH₃ at D_{α} and L_{α} at room temperature was measured in order to determine the initial NH₃-concentration *in situ*:

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

The temperature dependence of the NH₃ - absorption cross section at D_{α} and L_{α} was evaluated from incident and reflected shock wave absorption data up to 2600K as shown in figure (<u>1</u>):

$$\sigma_{NH_3}(T)/10^{-17}cm^2 = (3.3 \pm 0.3) \cdot 10^{-4} \cdot T/K + (0.65 \pm 0.06).$$

Atomic resonance absorption spectroscopy (ARAS) has been used to monitor H-absorption profiles. Spectral separation was enabled by means of an L_{α} -inteference filter with 10nm FWHM and molecular oxgygen as an absorber. Calibration and spectral purity tests of the microwave driven gas discharge emission (1%H₂/He) were provided by the H₂/N₂O - kinetic system, which revealed an H-detection limit of 5 \cdot 10¹¹ 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_{α} has been detected with the same experimental setup as the H-ARAS measurements. Due to the *natural* abundance **p** of partially deuterated ammonia NDH₂ ($\mathbf{p}=4.4987 \cdot 10^{-4}$), resonant absorption of D radicals was measured simultaneously with the non-resonant absorption of NH_3 at D_{α} . This provides an indirect control on the predicted H radical concentration for those experiments performed with high initial concentrations of NH₃ assuming that the kinetic behavior of H and D radicals is practically nondistinguishable at high temperatures. The residual L_{α} intensity has been periodically determined to be $(5\pm1)\%$ of the total intensity due to unavoidable H₂-impurities of the $1\%D_2$ /He lamp gas using H-atoms produced by the H_2+O - reaction as a spectral filter. Because this residual L_{α} -emission is expected to be highly resonant and to have a non-inverted line profile (Michael et al. (1985)). resonant absorption of H-atoms in the NH₃-pyrolysis system removes the L_{α} -intensity instantly. Therefore the absorption at the isotope line D_{α} is measurable and provides kinetic information on the NH₃-pyrolysis system.

It should be stressed that the reaction system used for modelling calculations does not contain any reactions involving deuterated species. The amount of D radicals in the ammonia pyrolysis system has always been derived from the calculated H-concentration multiplied with the *natural* abundance \mathbf{p} of partially deuterated ammonia NDH₂.

It should be remarked that background absorption of reaction products like N_2 and H_2 at L_{α} or D_{α} is not

Figure 2. Absorption cross section of H_2 at D_{α}/L_{α} .

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

 $\sigma_{N_2}(D_\alpha; 1850K < T < 2600K) < 2 \cdot 10^{-19} cm^2,$

calculated for S/N = 1, and

$$\sigma_{H_2}(D_{\alpha}; 1800K < T < 2650K) = 4.25 \cdot 10^{-18} e^{-8980/T} cm^2$$

as shown in figure (2). The second absorption cross section for H₂ at D_{α} is considerably lower than the value for σ_{H_2} at L_{α} given by Natarajan et al. (1994).

Detection of the NH₂-species was enabled by means of resonant narrow-band laser absorption at the isolated ${}^{P}Q_{1,N}(7)$ -doublet transition in the $\tilde{A}^{2}A_{1} \leftarrow \tilde{X}^{2}B_{1}(090 \leftarrow 000)\Sigma$ sub-band at 597.375nm which overlap in the pressure range of the present work. The calculation of the absorption cross section of NH₂ is based on the calibration experiments of Kohse-Höinghaus et al. (1989), who claimed $\pm 30\%$ accuracy in σ_{NH_2} . Davidson et al. (1990) found that the values for the absorption cross section are consistent with the upper error limits of σ_{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-Unkhoff et al. (1993)). The output wavelength was controlled by a Burleigh WA-20 wavemeter and cross checked by NH₂-cw-LIF in a 2%NH₃/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 $4\mu s$ (FWHM of the laser Schlieren peak), a minimum detection limit of $\approx 1.6 \cdot 10^{14} \, cm^{-3}$ could be achieved.

 Table 1. Experimental Conditions

H-detection at L_{α}					
12ppm 1930K 2.2bar	< < <	$[\mathrm{NH}_3]_0 \\ \mathrm{T}_5 \\ \mathrm{p}_5$	< < <	210ppm 2500K 8.6bar	
NH ₃ - and D-detection at D_{α}					
1402ppm 1930K 2.4bar	< < <	$[\mathrm{NH}_3]_0 \\ \mathrm{T}_5 \\ \mathrm{p}_5$	< < <	4100ppm 2570K 3.0bar	
NH ₂ -detection at λ =597.375nm					
3160ppm 1880K 2.4bar	< < <	$[\mathrm{NH}_3]_0\\\mathrm{T}_5\\\mathrm{p}_5$	< < <	1.13% 2570K 3.1bar	

3. Results and Discussion

The measured H, NH_2 and D_{α} -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 NH_3 (see table (1)) used especially for the experiments at L_{α} , only four reactions were found to be of significant influence on the measured absorption profiles: for T < 2150K, the decay of NH₃ and the reaction of NH₃ + H are important. As the temperature increases, the decay of NH_2 and the bimolecular reaction of H atoms with NH₂ have to be taken into account as well, especially for T > 2150 K (reactions R_1 , R_2 , and R_8 , R_{11} , see table (2)). From modelling those absorption profiles at very low initial concentrations of NH₃ (12ppm – 58ppm) which were measured at L_{α} , an Arrhenius expression for the decay of NH_3 was derived. By modelling the L_{α} absorption profiles as well as the measured NH₂ absorption profiles, it was concluded that secondary reactions of the NH_2 radical formed in the initiation reaction R_1 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_{α} -absorption profiles it was possible to determine the initial amount of ammonia in situ from absorption observed at T_1 and p_1 (for $[NH_3]_0 > 1000 ppm$). Furthermore, these experimental profiles were used for validation of the reaction model.



Figure 3. L_{α} -absorption profile and model predictions: (a) best fit by adjusting k_1 , (b) Davidson et al. (1990), (c) best fit by variation of $k_2 \cdot 0.5$ and (d) by $k_2 \cdot 2.0$.

3.1. Absorption profiles measured at L_{α}

H atoms are produced directly via reaction R_1 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 Trange 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 > $200\mu s$ (fig. (3), curves (c) and (d)). For a pressure range of 2.2bar bar, the following rateexpression for the reaction R_1 : $NH_3 + M \rightarrow NH_2 + H$ + M was found:

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

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 K < T < 2800 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-



Figure 4. L_{α} -absorption profile at high pressure and model predictions: (a) Davidson et al. (1990), (b) $k_1 \cdot 0.5$ and (c) $k_1 \cdot 2$.

out any modification of the rate coefficients given by Davidson et al. (1990) as shown in figure ($\underline{4}$), curve (**a**). Due to the very low initial concentrations of NH₃ (12ppm), the observed absorption profile is very sensitive to variations of the rate coefficients for the decay of ammonia (see fig. ($\underline{4}$), curve (**b**): k₁ · 0.5; curve (**c**): k₁ · 2).



Figure 5. L_{α} -absorption profile at higher NH₃-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} : $NH_2 + NH \rightarrow N_2H_2$ + 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. NH₂- and D_{α} -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 NH₃ 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_{α} 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.)). Again, sensitivity analysis was calculated in order to determine the dominant reactions; the same reactions as in the case of L_{α} -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						
*	\mathbf{R}_{1}	$NH_3 + M$	\rightarrow	$NH_2 + H + M$			
*	\mathbf{R}_2	$NH_3 + H$	\rightarrow	$\mathrm{NH}_2 + \mathrm{H}_2$			
	R_3	$H_2 + M$	\rightarrow	H + H + M			
	\mathbf{R}_4	NH + M	\rightarrow	N + H + M			
	R_5	NH + H	\rightarrow	$N + H_2$			
	R_6	NH + N	\rightarrow	$N_2 + H$			
	\mathbf{R}_{7}	$\rm NH + NH$	\rightarrow	$N_2 + H + H$			
*	R_8	$NH_2 + M$	\rightarrow	NH + H + M			
	R_9	$NH_2 + H$	\rightarrow	$\mathrm{NH} + \mathrm{H}_2 + \mathrm{M}$			
	R_{10}	$NH_2 + N$	\rightarrow	$N_2 + H + H$			
*	R_{11}	$NH_2 + NH$	\rightarrow	$N_2H_2 + H$			
	R_{12}	$NH_2 + NH_2$	\rightarrow	$NH_3 + NH$			
	R_{13}	$\mathrm{NH}_2 + \mathrm{NH}_2$	\rightarrow	$\mathrm{N_2H_2} + \mathrm{H_2}$			
	R_{14}	$N_2H + M$	\rightarrow	$N_2 + H + M$			
	R_{15}	$N_2H + H$	\rightarrow	$N_2 + H_2$			
	R_{16}	$N_2H + NH$	\rightarrow	$N_2 + NH_2$			
	R_{17}	$N_2H + NH_2$	\rightarrow	$N_2 + NH_3$			
	R_{18}	$N_2H_2 + M$	\rightarrow	$N_2H + H + M$			
	R_{19}	$N_2H_2 + H$	\rightarrow	$N_2H + H_2$			
	R_{20}	$N_2H_2 + NH$	\rightarrow	$N_2H + NH_2$			
	R_{21}	$N_2H_2 + NH_2$	\rightarrow	$N_2H + NH_3$			

 \star important reactions in present work

is lowered according to the results of the modelled L_{α} absorption profiles, good agreement is achieved between calculated and experimental profiles with respect to the maximum observed absorption $A_{max}(NH_2;t)$, which is shifted by about $60\mu s$ towards longer reaction times (see fig. (7), curve (b)). In order to reproduce the experimental profile for reaction times > $300\mu s$, reaction R_{11} : $NH_2 + NH \rightarrow N_2H_2 + H$ 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 (§) shows a typical absorption profile taken at D_{α} for the same experiment as in figure (7). This profile also provides kinetic information (see section (2.)). Again, applying the Davidson-model, the calculated D_{α} 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 H₂ and N₂ to the total absorption at D_{α} is very small (see section (2.)).



Figure 7. NH₂-absorption profile at 597.375nm and model predictions: (a) Davidson et al. (1990), (b) k_1 adjusted to $[NH_2]_{max}(t)$, (c) same as (b), but with $k_{11} \cdot 0.4$.



Figure 8. D_{α} -absorption profile under same conditions as in fig. (7) and model predictions: (a) Davidson et al. (1990) resulting from (a₁) non-resonant NH₃-, (a₂) resonant D-absorption and small contribution from N₂- and H₂absorption (not separately shown), (b) k₁ adjusted to $A_{max}(NH_2;t)$ and (c) same as (b), but with k₁₁· 0.4.

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

$$R_8: NH_2 + M \rightarrow NH + H + M$$

by a factor of ${\approx}0.5~$ and for reaction

$$R_{11}$$
: $NH_2 + NH \rightarrow N_2H_2 + H$

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by a factor of ≈ 0.4 .

It should be mentioned that – in principle – the measured NH₂ absorption profiles could also be reproduced by modifying the rate coefficient of the reaction R₂: NH₃ + H \rightarrow NH₂ + H₂. However, in the case of modelling NH₂ absorption profiles, this value should be decreased (to about 0.2 \cdot k₂ [Davidson et al. (1990)]), whereas in the case of modelling L_{α} absorption profiles, this value should be increased (up to about 2 \cdot k₂ [Davidson et al. (1990)]). For these reasons, the rate coefficient for R₂ 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

- Braun-Unkhoff M, Naumann C, Frank P. A Shock Tube Study of the Reaction $CH_3 + O_2$. In: 19th ISSW@Marseille, Springer (1993), 203–208.
- Davidson DF, Kohse-Höinghaus K, Chang AY, Hanson RK. A Pyrolysis Mechanism for Ammonia. IntJChemKin 22 (1990) 513–535.
- Frank P, Just T. High Temperature Reaction Rate for $H + O_2 = OH + O$ and $OH + H_2 = H_2O + H$. Ber.Bunsenges.Phys.Chem. 89 (1985) 181–187.
- Kohse-Höinghaus K, Davidson DF, Chang AY, Hanson RK. Quantitative NH₂ Concentration Determination in Shock Tube Laser-Absorption Experiments. JQSRT 42 (1989) 1–17.
- Mertens JD, Chang, AY, Hanson RK, Bowman CT. A Shock Tube Study of the Reactions of NH with NO, O₂, and O. IntJChemKin 23 (1991) 173–196.
- Michael JV, Sutherland JW, Klemm RB. The Flash Photolysis – Shock Tube Technique using Atomic Resonance Absorption for Kinetic Studies at High Temperatures. IntJChemKin 17 (1985) 315–326.
- Natarajan K, Mick HJ, Woiki D, Roth P. A Shock Tube Study of the Reaction $H_2 + NO \rightarrow HNO + H$. Combustion and Flame 99 (1994) 610–616.