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### The multichannel reaction $NH_2 + NH_2$ at ambient temperature and low pressures

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#### Abstract

NH<sub>2</sub> profiles were measured in a discharge flow reactor at ambient temperature by monitoring reactants and products with an electron impact mass spectrometer. At the low pressures used (0.7 and 1.0 mbar) the gas-phase self-reaction is dominated by a 'bimolecular' H<sub>2</sub>-eliminating exit channel with a rate coefficient of  $k_{3b}(300 \text{ K}) = (1.3 \pm 0.5) \times 10^{-12} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> and leading to N<sub>2</sub>H<sub>2</sub> + H<sub>2</sub> or NNH<sub>2</sub> + H<sub>2</sub>. Although the wall loss for NH<sub>2</sub> radicals is relatively small ( $k_w \approx 6-14 \text{ s}^{-1}$ ), the contribution to the overall NH<sub>2</sub> decay is important due to the relatively slow gas-phase reaction. The heterogeneous reaction yields N<sub>2</sub>H<sub>4</sub> molecules.

#### 1. Introduction

Of the reactions of the isoelectronic radicals OH, NH<sub>2</sub> and CH<sub>3</sub>, the mutual and cross reactions of CH<sub>3</sub> and OH have attracted wide attention due to their importance in virtually all hydrocarbon combustion processes (see Ref. [1] for references). An extension of these investigations to include the reactions of NH<sub>2</sub> radicals is of practical interest because these radicals play a role in the conversion of fuelbound nitrogen to NO or N<sub>2</sub> [2]. For instance, NH<sub>1</sub> recombination provides a direct route to N<sub>2</sub> via N<sub>2</sub>H<sub>j</sub> [3]. This role of NH<sub>2</sub> radicals provided the motivation for two recent papers on NH<sub>2</sub> + NH<sub>2</sub> and NH<sub>2</sub> + OH [4] and on NH<sub>2</sub> + CH<sub>3</sub> [5].

A common feature of all these reactions is that they occur via bound intermediates which means that several exit channels are possible even at room temperature. Studies of this multichannel behavior are, however, scarce. For  $CH_3 + OH$ , a systematic study of the product channels has been performed in our laboratory [6–9].

For  $NH_2$  recombination, the possible reaction channels of the excited  $N_2H_4$  adduct are shown in the energy diagram, Fig. 1. The heats of formation are taken from either the Sandia compilation [10] or from Melius [11].

The termolecular stabilization channel has been the subject of a recent study by Fagerström et al. [4] as well as earlier ones which are referenced by Lesclaux [12]. In the work of Fagerström et al. [4] (200 and 1000 mbar), this termolecular stabilization channel is certainly the most dominant process. However, under the low-pressure conditions of the present work using He as a bath gas, it plays only a minor role. Indeed, Lesclaux gives  $k(NH_2 + NH_2 +$  $Ar) = 7 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 300 K and 1.0 mbar.

Of the exothermic 'bimolecular' channels and hence those accessible at room temperature, the path-



Fig. 1. Energy diagram for the reaction:  $NH_2 + NH_2$ . Units are kJ/mol.

way into  ${}^{3}NH + NH_{3}$  requires a crossing from the singlet to the triplet surface. This route can be ruled out because its rate coefficient has been found to be negligible [13–15]. This leaves the channels into  $N_{2}H_{3} + H$  and  $N_{2}H_{2} + H_{2}$ , which in some earlier studies [14,16] have been considered as likely candidates, although they have never been measured directly. (For the NNH<sub>2</sub> + H<sub>2</sub> channel, dashed line in Fig. 1, see Section 5.)

In the present study the products of these bimolecular channels are analyzed and rate coefficients are deduced at pressures which are complementary to the work of Fagerström et al. [4].

#### 2. Experimental

The fast-flow reactor technique and its application to the study of radical + atom reactions have been

described in an earlier paper [17], as has its use over an extended pressure range [18]. Thus only a brief outline will be given here. The reactor was a teflon tube of length 50 cm and internal diameter 38 mm. The flow velocities were of the order of 20 m/s (see Table 1) and helium was used as the carrier gas. Corrections for axial diffusion and for deviation from plug flow were made in the usual way [18] and were found to be negligible for the work described here. Species detection was accomplished by a quadrupole mass spectrometer, which was coupled to the flow reactor by the usual nozzle-skimmer arrangement. Low ionization energies were used to reduce fragmentation in the ion source.

 $NH_2$  radicals were produced by the reaction F +  $NH_3 \rightarrow NH_2 + HF$  which is described by Walther and Wagner [19]. F atoms were generated in a side-arm of the movable injector by means of a microwave discharge of  $F_2$  which was diluted in He.

Table 1				
Summary of	experimental	conditions	and	results

<i>p</i> (mbar)	<i>v</i> (m s <sup>-1</sup> )	t (ms)	$[NH_3]$ (molecule cm <sup>-3</sup> )	$10^{-12}$ [F] (molecule cm <sup>-3</sup> )	$10^{12} k_3$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	k <sub>4</sub> (s <sup>-1</sup> )
0.7	18.6	19.4	$2.8 \times 10^{14}$	6.5-18.3	$1.2 \pm 0.5$	10-14
1.0	21.3	16.1	$3.6  imes 10^{14}$	5.0-15.0	$1.4 \pm 0.5$	6-8

 $k_{3b}(\text{NH}_2 + \text{NH}_2 \rightarrow \text{N}_2\text{H}_2 + \text{H}_2) = (1.3 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} k_4(\text{NH}_2 \rightarrow \text{wall}) = 6-14 \text{ s}^{-1}$ 

The nearly complete dissociation of  $F_2$  was monitored with the mass spectrometer.  $NH_3$ , also diluted in He, was fed into the reactor along with He for the main flow. Consequently, the complete reactor surface was always exposed to  $NH_3$  so that adsorption effects upon displacement of the injector were minimized. This reactor configuration allows the residence time to be varied by the stepwise displacement of the F-source. For concentrations of the reactants and other conditions see Table 1. All gases were admitted into the reactor using mass flow controllers (Tylan) which were periodically calibrated. The gas purity grades were as follows: helium 99.999%,  $NH_3$ 98% (5.36% mixture in helium 99.996%),  $F_2$  99.99% (3.0% mixture in helium 99.996%).

If the excess of  $NH_3$  over F is sufficiently large (about 20-fold in our case) then the initial F atom concentration can be used to calibrate the  $NH_2$  concentration [14]. Under these conditions the subsequent reaction  $NH_2 + F$  can be neglected and the  $NH_3$  consumption is equal to the initial F concentration. This can be easily checked since no  $NH_3$  is reformed via  $NH_2$  self-reaction (see below). Indeed, within the experimental error the change in the mass spectrometric  $NH_3$  signals corresponded to  $[F]_0$ . Additional attempts to calibrate  $NH_2$  radicals by scavenging them in an excess of  $NO_2$  (as used for  $CH_3$ calibration in Ref. [6]) led to ambiguous results possibly due to surface effects in combination with  $NH_3$ .

A problem for the interpretation of the  $NH_2$  profiles is the wall loss (reaction (4)) which occurs in addition to the gas phase reactions (3a)–(3d) (see Table 2). The strong influence of the reactor walls on  $NH_2$  has also been observed by other workers [12,14,16,21,22]. We tried several wall treatments: the usual HF wash of quartz reactors yielded unsatisfactory results. A coating with silicon oil (using an approach of Seetula and Gutman [23]) did eliminate any wall problems and even changed the product distribution; it was not used for extended kinetic measurements since it spoiled the vacuum system. The use of pure teflon reactors or teflon coated quartz reactors was quite satisfactory, although these surfaces had a tendency to deteriorate during extended operation.

Another problem associated with the generation of  $NH_2$  from the reaction of  $NH_3$  with F atoms is the build-up of  $NH_4$ F deposits [19]. These deposits may change the reactor wall characteristics, and may also have a detrimental effect on the mass spectrometer by causing a sluggish response along with decreased sensitivity. Simply washing the mass spectrometer with distilled water was usually sufficient to restore performance. In order to minimize such effects we tried to avoid large concentrations of  $NH_3$ and  $F_2$ . Another reason for avoiding large  $NH_3$ concentrations is its undesired fragmentation at the mass of  $NH_2$ . The usable concentration range of  $NH_3$  and hence  $NH_2$  is therefore rather limited.

# 3. Evaluation and simulation of the measured profiles

Under our conditions the NH<sub>2</sub> profiles were mostly governed by the homogeneous recombination  $(k_3 = k_{3a} + k_{3b} + k_{3c} + k_{3d})$  and the heterogeneous

Table 2

Reaction scheme and rate coefficients. Units:  $k_4$  and  $k_5$  are in s<sup>-1</sup>, all other rate coefficients in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>

	•	
$(1) \operatorname{NH}_3 + F \to \operatorname{NH}_2 + \operatorname{HF}$	$1.2 \times 10^{-10}$ [4]	
(2) $NH_2 + F \rightarrow NH + HF$	$1.2 \times 10^{-10}$ [4]	
$(3a) \overline{NH}_2 + \overline{NH}_2 + \overline{M} \rightarrow N_2H_4 + M$	$7.0 \times 10^{-14}$ M = He, 1 mbar, see text	
$(3b) \operatorname{NH}_2 + \operatorname{NH}_2 \rightarrow \operatorname{N}_2 \operatorname{H}_2 + \operatorname{H}_2$	$(1.3 \pm 0.5) \times 10^{-12}$ this work	
$(3c) \operatorname{NH}_2 + \operatorname{NH}_2 \to \operatorname{NH}_3 + \operatorname{NH}$	$3.0 \times 10^{-15}$ [14]	
$(3d) \operatorname{NH}_2 + \operatorname{NH}_2 \to \operatorname{N}_2\operatorname{H}_3 + \operatorname{H}_3$	$< 1 \times 10^{-13}$ estimated	
(4) $NH_2$ (wall) $\rightarrow N_2H_4$	6-14 this work	
(5) NH (wall) $\rightarrow$ products	5 assumed	
(6) $\mathbf{NH} + \mathbf{NH}_2 \rightarrow \mathbf{N}_2\mathbf{H}_2 + \mathbf{H}$	$1.4  imes 10^{-10}$ [14,20]	
(7) $NH_2 + N_2H_2 \rightarrow NNH + NH_3$	$3 \times 10^{-12}$ [2]	
$(8) \text{ NNH} + \text{NH}_2 \rightarrow \text{N}_2 + \text{NH}_3$	$8.3  imes 10^{-11}$ [2]	

loss  $(k_4)$  of NH<sub>2</sub>. If other NH<sub>2</sub> reactions can be ignored these contributions can be separated as follows, using the rate equation for a mixed first and second order decay,

$$-d[NH_2]/dt = 2k_3[NH_2]^2 + k_4[NH_2],$$

which may be written as

$$-d \ln[\mathrm{NH}_2]/dt = 2k_3[\mathrm{NH}_2] + k_4.$$

Thus if the tangents to  $\ln[NH_2]$  versus time curves are plotted against the respective instantaneous  $NH_2(t)$  concentrations a straight line should be obtained with a gradient of  $2k_3$  and intercept of  $k_4$ . However, due to interference by other reactions, the above assumptions were not strictly obeyed and the  $k_3$  and  $k_4$  values obtained through the outlined procedure could only be used as starting data for computer simulations which then yielded refined values.

The mechanism shown in Table 2 was used for the modelling work. Following the procedure of Fagerström and co-workers [4] we adopted the high rate coefficient obtained by Setser and co-workers [24,25] for the source reaction. For the subsequent reaction  $NH_2 + F$ , no direct measurements exist in the literature. The rate coefficient used here was deduced by Fagerström et al. [4] to give agreement with their experimental  $NH_2$  profiles. (The sensitivity of the mechanism to these reactions is discussed later.) For the disproportionation of  $NH_2$  radicals into  $NH + NH_3$ , we used the low rate coefficient given in the literature [14,15] although this reaction could have been omitted as shown by the sensitivity analysis. The reaction sequence (7) + (8) forms an additional loss mechanism, particularly at the higher  $[NH_2]_0$ . Rate coefficients are available in the literature [2] for this sequence which involves the formation and subsequent reaction of NNH, although the validity of this sequence may be doubted on the basis of lifetime calculations for NNH [26].

 $NH_2$ -decay profiles were simulated for each set of experimental conditions at 0.7 and 1.0 mbar and the experimental decays were then normalised to the respective curves. Using the rate coefficients given in Table 2,  $k_{3b}$  and  $k_4$  were optimised so that the simulated curves correctly predicted each profile, as well as the change in curvature with increasing  $[NH_2]_0$  (given by  $[F]_0$ ). A comparison of several experimental and simulated decays at 0.7 mbar is shown in Fig. 2.

The  $NH_2$  consumption is governed to a large extent by the wall loss (4). Modelling has shown that





for p = 0.7,  $[F]_0 = 1.3 \times 10^{13}$  molecule cm<sup>-3</sup>  $\approx 30\%$ of the NH<sub>2</sub> removed is lost through heterogeneous processes at the wall on the timescale shown in Fig. 2, rising to  $\approx 45\%$  for p = 0.7,  $[F]_0 = 6.5 \times 10^{12}$ molecule cm<sup>-3</sup>. The amount of NH<sub>2</sub> consumed through reaction (3b) increases only marginally (from  $\approx 41\%$  to 48%) with  $[F]_0$  despite the quadratic dependence of the concentration term. This is due to subsequent reactions of N<sub>2</sub>H<sub>2</sub> which lead to an additional sink for NH<sub>2</sub> via (7) and (8). These account for  $\approx 7\%$  and 15% removal at  $[F]_0 = 6.5 \times 10^{12}$  and  $1.8 \times 10^{13}$  respectively. The pressuredependent NH<sub>2</sub> recombination reaction (3a) plays a negligible role at these pressures, contributing to about 2% of NH<sub>2</sub> consumed.

#### 4. Analysis of reaction products

Channel (3a), product  $N_2H_4$ . Signals were observed, but were assigned to the wall reaction. See also Section 5.

Channel (3b), products  $N_2H_2 + H_2$ . Distinct signals corresponding to  $N_2H_2$  were seen, which showed the convex shape typical for a direct product profile. For reasons given below, this is the main product.

Channel 3c, products  $NH_3 + {}^3NH$ . The product  $NH_3$  is hardly measurable since  $NH_3$  is already present in excess. Detection of  ${}^3NH$  is difficult due to its expected high reactivity. The reaction should be unimportant [13–15].

Channel (3d), products  $N_2H_3 + H$ . H is difficult to measure quantitatively due to its low mass spectrometric sensitivity. The sensitivity for  $N_2H_3$  is also low since fragmentation of  $N_2H_4$  must be avoided. No signals were observed (even in a silicon oil coated reactor, see below). The upper limit  $k_{3d} < 1$  $\times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> is an estimate related to the detection sensitivity of  $N_2H_4$ .

Reaction (4), wall reaction. The observed  $N_2H_4$  signals were too strong to be assigned to channel (3a). These signals disappear completely when a silicon oil wall coating is used (the  $N_2H_2$  signals remain unchanged under these conditions). This indicates that when using teflon reactors,  $N_2H_4$  is formed through heterogeneous NH<sub>2</sub> loss.

#### 5. Discussion

#### 5.1. Role of the termolecular stabilization channel

Fagerström and co-workers [4] recently presented new measurements for this channel along with a review of earlier results. By means of a Troe calculation, these workers were able to essentially reproduce current experimental data. For Ar as a bath gas they obtained

$$k_0[M]^{-1} = 6.9 \times 10^{-30} \text{ cm}^6/\text{molecule}^2 \text{ s}$$

yielding  $k_{3a} = 1.5 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 1 mbar, which is approximately twice as large as the result of Khe et al. [27] In our case using He as the bath gas the value of  $k_{3a}$  should be smaller. Consequently, the termolecular reaction amounts only to approximately 5% of the total rate coefficient  $k_3$  at our pressures. Consequently, no attempt was undertaken to determine  $k_{3a}$  from our measurements. For the simulations, the lower value of Khe et al. [27] was used to allow for the smaller collisional efficiency of He.

## 5.2. Rate coefficients of the bimolecular channels and sensitivity analysis

According to the NIST data base [28] and to the best of our knowledge there are no studies in the literature other than that of Khe et al. [27] providing data on the rate coefficient for the bimolecular channel(s). Their value of  $(1.4 \pm 0.7) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> is in favorable agreement with our result. Other references [2,29], to a value of  $8 \times 10^{-13}$  for a bimolecular channel seem to be the result of a misprint in a paper by Miller et al. [30] which refers to the original paper of Khe et al. [27]. For no obvious reasons, Miller et al. [30] quote N<sub>2</sub>H<sub>2</sub> + H<sub>2</sub> as the reaction products.

As a derived quantity, our rate coefficient  $k_{3b}$  is subject to uncertainties in the model. The sensitivity analysis (Fig. 3) shows that the rate coefficient for the initiation reaction NH<sub>3</sub> + F ( $k_1$ ) is the most critical. Essentially two values for  $k_1$  are currently in use. Walther and Wagner [19] obtained  $3.3 \times 10^{-11}$ cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> whereas Setser and co-workers [24,25] report  $1.2 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Fortunately, in our system the effect of  $k_1$  is partly



Fig. 3. Sensitivity analysis of the simulated NH<sub>2</sub> profiles to a 30% increase in specific rate coefficient  $([F]_0 = 1.3 \times 10^{13} \text{ molecule cm}^{-3}, P = 0.7 \text{ mbar})$ . Those reactions not shown have less than 3% sensitivity. (**■**)  $k_1$ , (**●**)  $k_7$ , (**▲**)  $k_4$ , (**♦**)  $k_{3b}$ .

counterbalanced by the subsequent reaction, NH<sub>2</sub> + F  $(k_2)$ . Walther and Wagner give  $k_2 = 3.8 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, whereas Fagerström et al. [4] determined an optimized value of  $1.2 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> in combination with  $k_1$  from Setser et al. Our  $k_{3b} = 1.3 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> is deduced by using  $k_1$  and  $k_2$  from Fagerström and shifts to  $1.5 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> if the data of Walther and Wagner are used.

Apart from  $k_1$  the most important rate coefficients affecting our profiles are  $k_4$  and  $k_{3b}$  which are the adjustable parameters in our model.

Allowing for an estimated uncertainty in the modelling of 30% and an experimental error of 25% we arrive at

$$k_{3b}(300 \text{ K})$$
  
= (1.3 ± 0.5) × 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

#### 5.3. Reaction products of the bimolecular channels

In the early paper of Khe et al. [27] as well as in the review of Lesclaux [12] the channel into NH + NH<sub>3</sub><sup>1</sup> is assumed to be the most likely one, although the channels into  $N_2H_2 + H_2$  and/or  $N_2 +$   $H_2 + H_2$  were not excluded. The latter route has already been suggested by Dove and Nip [31]. It is not considered here since it requires a complex molecular rearrangement which is highly improbable at our low temperature. For the potential channel to NH + NH<sub>3</sub>, Zetsch and Stuhl [15] derived an upper limit of  $8 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> based on resonance fluorescence measurements of <sup>3</sup>NH. Correspondingly, Dransfeld and co-workers [14] did not find measurable NH yields with their sensitive LMR method. They concluded that N<sub>2</sub>H<sub>2</sub> + H<sub>2</sub> and N<sub>2</sub>H<sub>3</sub> + H are the 'most likely candidates'.

In the current work the reaction products  $N_2H_2 + H_2$  have been identified. This channel is by far the most dominant under our conditions. However, the structure of the reaction product  $N_2H_2$  remains unclear. Melius [11] provides the following heats of formation (at 298 K, kJ/mol) obtained by BAC-MP4 calculations: HNNH trans 196.4, HNNH cis 218.7, NNH<sub>2</sub> 288.4. A channel yielding this latter species (dashed level <sup>2</sup> in Fig. 1) would also be exothermic and hence accessible at ambient temperature.

It is noteworthy that the multichannel reaction of the isoelectronic radicals  $CH_3$  and OH also shows pathways involving  $H_2$  elimination [8,9]. In this case the production of the less stable biradical HCOH is favored over  $H_2CO$  formation. By analogy, it is conceivable that in the present case the product of reaction (3b) could be NNH<sub>2</sub>.

#### 5.4. Other channels open at higher temperatures

From their shock tube measurements of NH<sub>3</sub> pyrolysis, Davidson and co-workers [20] derived a rate coefficient of  $8 \times 10^{-11} e^{-10000/RT}$  for the channel to NH + NH<sub>3</sub> (probably <sup>1</sup>NH).

Finally, in a study dealing with fuel-rich ammonia flames, Dean and co-workers [32] obtained data concerning the  $N_2H_3 + H$  channel. Their modelling

<sup>&</sup>lt;sup>1</sup> In the earlier papers no distinction is made between singlet-NH and triplet-NH although it is clear from energy considerations that at room temperature only the triplet-NH channel may be open.

<sup>&</sup>lt;sup>2</sup> For the cis-, trans-isomers of  $N_2H_2$  the heats of formation of Melius [11] are, on average, 13.8 kJ/mol below the Sandia data [10]. Somewhat arbitrarily, the Melius value for NNH<sub>2</sub> has been shifted upwards by this amount to 302.2 kJ/mol so as to be comparable to the Sandia data used in Fig. 1. The other heats of formation are: NH<sub>2</sub> 190.4, <sup>3</sup>NH 356.5, <sup>1</sup>NH 509.6, H 218.0, NH<sub>3</sub> 46.0, N<sub>2</sub>H<sub>4</sub> 95.4, N<sub>2</sub>H<sub>3</sub> 153.9, and N<sub>2</sub>H<sub>2</sub> trans 213.0 (all data in kJ/mol and referring to 298 K).

study yields an expression for the rate coefficient of  $1.2 \times 10^{-12} e^{-2500/T}$  which was in agreement with a QRRK calculation. Since the reaction is slightly exothermic (see Fig. 1) this activation energy indicates a barrier. Consequently, the reaction is unlikely to play a role at ambient temperature, in accordance with our mass spectrometric observations.

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