Spectrokinetic Studies of the Gas Phase Reactions NH₂ + NOₓ
Initiated by Pulse Radiolysis

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NH₂ radicals were produced by pulse radiolysis of Ar-SF₆-NH₂ mixtures to initiate the reaction F + NH₂ → HF + NH₂. Decay rates of NH₂ were studied by monitoring the transient absorption signals of NH₃ at 597.6 nm in the presence of varying amounts of NO and NO₂. Values of k(NH₂ + NO) = (1.3 ± 0.2) × 10¹⁰ M⁻¹ s⁻¹ and k(NH₂ + NO₂) = (1.1 ± 0.3) × 10¹⁰ M⁻¹ s⁻¹ were obtained at 298 K. By monitoring the transient absorption of OH radicals at 309 nm we have determined a very low branching for the reaction channel NH₂ + NO → NH₃ + H + OH, suggesting that NH₂ + NO → N₂ + H₂O is the most important product channel at room temperature. The analysis of the experimental results was based on computer modelling of the observed radical yields and kinetics, taking into account various competing reactions which were shown to be important by the evaluation of branching ratios.

The NH₂ radical is an important intermediate in the atmospheric chemistry of ammonia, and the chemical reactivity of NH₂ has been the subject of a large number of experimental studies. In particular the reaction with NO has been extensively studied because of its importance as a natural atmospheric sink for NO. NH₂ is formed in many reactions involving ammonia, hydrazine and amines. In the troposphere the reaction of hydroxyl radicals with ammonia is the main source of NH₂. In experimental studies NH₂ has been produced by photolysis or radiolysis of ammonia or by abstraction reactions, X + NH₂ → HX + NH₂, which require highly reactive species such as X = F₂O(OD) or OH to overcome the high bond energy of D(H-NH₂) = 44 ± 4 kJ mol⁻¹.

Emissions of SO₂ and NOₓ produced by combustion of fossil fuels give rise to severe air pollution, e.g. smog and acid rain, and several techniques have been developed to remove these compounds from flue gases. The thermal DeNOₓ process is based on addition of ammonia to the flue gas in order to initiate the reaction NH₂ + NO → N₂ + H₂O. This reaction was originally suggested by Bamford in 1939. Experimental results obtained by photolysis of ammonia in the presence of NOx have indicated that the quantum yield for N₂ formation is near unity at 300 K, implying that nitrogen and water are the only products. However, other product channels shown in reaction (1) have been proposed.

\[ \begin{align*}
\text{NH}_2 + \text{NO} &\rightarrow \text{N}_2 + \text{H}_2\text{O} \\
\text{NH}_2 + \text{NO} &\rightarrow \text{N}_2\text{H} + \text{OH} \\
\text{NH}_2 + \text{H} &\rightarrow \text{N}_2 + \text{H} \text{O}
\end{align*} \]

The direct observation of OH radicals may be taken as evidence for the occurrence of reactions (1b) and (1c). Several groups have considered reaction (1c) as the most probable reaction producing OH radicals. On the other hand, reaction (1b) has been suggested as the main channel for NO removal in the absence of water vapor.

Table 1. Comparison of experimental rate constant determinations for the reaction NH₂ + NO → products.

<table>
<thead>
<tr>
<th>10⁻¹⁰ k M⁻¹ s⁻¹</th>
<th>T/K</th>
<th>P/bar</th>
<th>Method*</th>
<th>Ref.</th>
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<tr>
<td>1.2</td>
<td>298</td>
<td>400</td>
<td>PR-AS</td>
<td>19,20</td>
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<tr>
<td>0.5±1.0</td>
<td>298</td>
<td>1.3–13.3</td>
<td>DF-MS</td>
<td>21</td>
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<td>0.001</td>
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<td>1.3</td>
<td>Flame</td>
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<td>1.33</td>
<td>FP-LIF</td>
<td>23</td>
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<tr>
<td>1.1±0.2</td>
<td>300–500</td>
<td>2.7–9.33</td>
<td>FP-AS</td>
<td>24</td>
</tr>
<tr>
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<td>0.1–1.3</td>
<td>FP-LA</td>
<td>25</td>
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<tr>
<td>0.7</td>
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<td>1.3</td>
<td>DF-LIF</td>
<td>26</td>
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<tr>
<td>1.1</td>
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<td>3.9–13.3</td>
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<td>27</td>
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<td>0.55±0.09</td>
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<td>3.3–26.7</td>
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<td>10.6–26.7</td>
<td>FP-IR</td>
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<tr>
<td>1.0</td>
<td>300</td>
<td>13.3</td>
<td>DF-MS</td>
<td>14</td>
</tr>
</tbody>
</table>

*PR, pulse radiolysis; FP, flash photolysis; LP, laser photolysis; DF, discharge flow; AS, absorption spectrometry; LA, laser absorption; LIF, laser-induced fluorescence; MS, mass spectrometry; IR, infrared spectrometry.

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other hand, H atoms have never been detected as a reaction product, indicating that reaction (1b) is the most important reaction. The yields of OH have been determined in several investigations employing different experimental techniques. Reported branching ratios for the OH product channel cover a wide range of values from near zero to more than 65% at room temperature.

The overall rate constant for the reaction \( \text{NH}_3 + \text{NO} \rightarrow \text{products} \) has been measured by different techniques, including pulse radiolysis, flash photolysis and discharge flow reactors, combined with various detection systems such as UV and IR spectroscopy and mass spectrometry. The reported rate constants are summarized in Table 1. At room temperature the reported rate constants are in the range \((0.5-1.3) \times 10^{10} \ M^{-1} \cdot s^{-1}\). It appears that the values obtained by pulsed techniques are generally a factor of two higher than those obtained by the discharge flow method. The temperature dependence of the overall rate constant has been studied by several groups. Recently Lesclaux has recommended the expression \( k_1 = 1.1 \times 10^{10} \times (T/298)^{1/2} \ M^{-1} \cdot s^{-1} \), which appears to account reasonably well for most of the reported experimental results.

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The products of reaction (1) imply a complex addition reaction proceeding via a hot adduct which undergoes isomerization before dissociation into different product channels.

The dynamics of reaction (1) has been the subject of several theoretical studies considering various isomers of the adduct, N-nitrosamide, which is unstable, and apart from a single report on \( \text{NH}_3 \cdot \text{NO} \) this molecule has never well characterized experimentally.

A review of the available experimental data on reaction (1) shows that ambiguities remain regarding the identity of the products and the true value of the branching ratio. At room temperature it appears that reaction (1a) is by far the most important channel. However, at 1400 K the relative yield of OH was reported to be 80% or higher.

The reaction of \( \text{NH}_3 \) with \( \text{NO} \) proceeds via a similar mechanism, reaction (2). Observation of \( \text{N}_2 \text{O} \) and \( \text{H}_2 \text{O} \) as the only reaction products was taken as evidence for reaction (2a) as the most important channel, while other experimental work indicates that reaction (2b) is the main channel. The reported values of the overall rate constant for reaction (2) vary from \( 0.7 \times 10^{10} \ M^{-1} \cdot s^{-1} \), determined by discharge flow, to \( (1.3 \pm 0.2) \times 10^{10} \ M^{-1} \cdot s^{-1} \), determined by laser photolysis and flash photolysis experiments.

The rate and products of the reactions of \( \text{NH}_3 \) with \( \text{NO} \) and other atmospheric constituents are of general interest in order to identify the most important source and sink reactions for \( \text{NO}_x \). In a clean atmosphere, where the concentrations of nitrogen oxides are low, the reaction rates of \( \text{NH} \) with \( \text{NO} \) and \( \text{NO}_2 \) are low and relatively unimportant. However, in a polluted atmosphere these reactions become increasingly important. The greatest interest in the reactions stems from its utilization in the treatment of flue gases, e.g. the thermal \( \text{DeNO}_x \) process and other methods by which \( \text{NO} \) is converted into molecular nitrogen via reaction (1a). In the present investigation we have studied the yields and kinetics of \( \text{NH}_3 \) and OH radicals which occur as intermediates in reactions (1) and (2). Based on computer modelling we have identified important competing reactions which must be taken into account in the evaluation of branching ratios from measurements of radical time profiles under different experimental conditions.

**Experimental**

The experimental technique was based on pulse radiolysis combined with transient UV/VIS absorption spectrophotometry. A detailed description of the experimental set-up has been reported previously. Free radicals were produced by irradiating a gas mixture with a 50 ns pulse of 2 MeV electrons from a field emission accelerator. Formation and decay rates of the radicals were studied by monitoring the transient absorption signals corresponding to electronic transitions which are characteristic of the individual radicals, e.g. \( \text{NH}_2 \) radicals were monitored at 597.6 nm and OH at 309 nm. The optical detection system is composed of a pulsed xenon lamp combined with Suprasil quartz lenses to provide a high-intensity analyzing light beam; this passed through the sample cell, which is equipped with internal spherical mirrors, in order to obtain optical path lengths of 40–120 cm by multiple reflections. A 1 m grating monochromator with a reciprocal dispersion of 8 A⁻¹ mm⁻¹ was used to select wavelength and spectral band pass of the analyzing light, and the intensity was recorded with a fast photomultiplier coupled with a transient recorder. A PDP-11 minicomputer was used for collection and on-line analysis of spectral and kinetic data, which were supplied with comments and specifications of experimental conditions before transfer to a main-frame computer where the final analysis took place.

Computer modelling employing the program CHEMSIMUL was used in the analysis of the experimental kinetic features in non-trivial cases for which several reactive species were present simultaneously. Gas mixtures were prepared by admitting one component at a time and reading the corresponding partial pressure with an absolute membrane manometer having a resolution of 10⁻³ bar. A platinum resistance thermometer was used to measure the temperature of the gas mixture in the sample cell. All experiments were carried out at 298 K. High purity gases (Ar, SF₆, NH₃, NO and NO₂) were supplied by Hoechst, and \( \text{H}_2 \text{O} \) was triply distilled.
Results and discussion

Source reactions for NH₃ and OH. High yields of F atoms were obtained by pulse radiolysis of gas mixtures containing 50 mbar SF₆ and 0–5 mbar of additives backed up with Ar to a total pressure of 1 atm.

The initial yield of F atoms was determined by monitoring the transient absorption of CH₃ produced in the titration reaction (T). Using the well established value of

\[ F + CH₄ \rightarrow HF + CH₃ \]  

(T)

1.07 × 10⁴ M⁻¹ cm⁻¹ for the extinction coefficient of CH₃ at 216.4 nm we obtain from the observed transient absorption maximum, measured with an optical path length of \( L = 40 \text{ cm} \), \([F]_b = (1.40 \pm 0.10) \times 10^{-8} \text{ M} \). Based on studies of the yield of CH₃ at varying partial pressures of CH₄ we find that less than 1% of the F atoms are lost in competing reactions when \( p(CH₄) > 5 \text{ mbar} \). The yield of F atoms was kept constant in the subsequent kinetic studies by employing a fixed value of \( p(SF₆) = 50 \text{ mbar} \), and with \( p(Ar) + p(\text{additive}) = 950 \text{ mbar} \) to maintain a constant stopping power for the electron beam.

Direct conversion of F atoms into NH₃ or OH radicals via the source reactions (S1) and (S2) was accomplished using 1–5 mbar of ammonia or water vapour as additives.

\[ F + NH₃ \rightarrow HF + NH₂ \]  

(S1)

\[ F + H₂O \rightarrow HF + OH \]  

(S2)

The transient absorption signals due to NH₃ and OH were monitored at 597.6 nm and 309 nm, respectively. From studies of the radical yields as a function of the concentration of additives we found that losses of F atoms in competing reactions were less than 1% when the partial pressures of the parent molecules were kept at 3 mbar or above. In the absence of other additives the observed second-order decay kinetics is accounted for in terms of the self-reactions of the radicals, i.e. combination and disproportionation of NH₃ and OH, respectively.

Reactions of NH₃ with NO and NO₂. These reactions [(1) and (2)] were initiated by pulse radiolysis of gas mixtures containing 50 mbar SF₆, 5 mbar NH₃ and 0–1 mbar NO or NO₂. The overall decay rate of NH₃ in the presence of NO was monitored at 597.6 nm using an optical path length of 120 cm and a spectral band pass of 0.1 nm. Under pseudo-first order conditions, i.e. when \([NO]₀ \gg [NH₃]₀\), the NH₃ decay was simple exponential with an initial decay rate which can be expressed by eqn. (E1). The first term on the right-hand side accounts for the self-reaction of NH₃, which controls the decay rate in the absence of NO. At very high NO concentrations, for which the last term becomes dominant, the decay half-life becomes very nearly equal to \( t(1/2) = \ln 2/(k_{1a} + k_{1b})[NO]₀ \). In the general case the reciprocal half-life is a linear function of the NO concentration, i.e. the overall rate constant can be obtained from a plot of \([t(1/2)]^{-1} \) versus \([NO]₀\) which should be linear with a slope of \( k_f/\ln 2 \). Fig. 1 shows the results of our studies of the overall decay rate. The value of \( k_f = k_{1a} + k_{1b} = (1.3 \pm 0.2) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \) obtained from the plot is in fair agreement with the results of previous investigations which are summarized in Table 1.

Replacing NO by NO₂ we have studied the overall decay rate of NH₃ consumed in reactions (2a) and (2b). The decay rate was studied at partial pressures of NO₂ varying from 0 to 0.70 mbar, which caused a decrease in the observed half-lives from 15.4 to 1.9 µs. From a series of nine experiments we obtained a value of \( k_f = k_{2a} + k_{2b} = (1.1 \pm 0.3) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \). The estimated error limit is relatively large in this case, mainly because of noticable effects of NO₂ adsorption on the surface of the reaction cell. The value of \( k_f \) derived in this study is close to that of \((1.3 \pm 0.2) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \) obtained by the other pulsed methods.²⁷,²⁸

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Fig. 1. NH₃ reciprocal decay half-life vs. NO concentration at 298 K and total pressure of 1 bar. NH₃ kinetics monitored at 597.6 nm in pulse radiolysis of 8 mbar NH₃, 50 mbar SF₆ and Ar to 1 bar without (a) and with (b) NO (0.15 mbar) is shown in the insert. The corresponding half-lives are 15.4 and 4.5 µs, respectively.
Branching ratio for the reaction \( \text{NH}_2 + \text{NO} \). To determine the branching ratio of reaction (1) we have studied the kinetics of \( \text{OH} \) produced via reaction (1b), which was initiated by pulse radiolysis of gas mixtures containing 50 mbar \( \text{SF}_6 \), 5 mbar \( \text{NH}_2 \), and 0.2–1 mbar NO backed up with Ar to 1 atm. Analysis of the experimental results was based on computer modelling taking into account the following reactions:

\[
F + \text{NH}_2 \rightarrow \text{HF} + \text{NH}_3 \\
\text{F} + \text{NO} + M \rightarrow \text{FNO} + M \\
2 \text{NH}_2 + M \rightarrow \text{N}_2\text{H}_4 + M \\
\text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O} \\
\text{NH}_2 + \text{NO} \rightarrow \text{N}_2\text{H} + \text{OH} \\
\text{OH} + \text{OH} + M \rightarrow \text{H}_2\text{O}_2 + M \\
\text{OH} + \text{NH}_2 + M \rightarrow \text{NH}_2\text{OH} + M \\
\text{OH} + \text{NO} + M \rightarrow \text{HONO} + M \\
\text{OH} + \text{NH}_2 \rightarrow \text{H}_2\text{O} + \text{NH}_3
\]

(S1)  
(S2)  
(S3)  
(S4)  
(S5)  
(S6)  
(S7)  
(S8)

Based on sensitivity analysis we find that the observable yield of \( \text{OH} \) is controlled mainly by reactions (1b) and (3) under the chosen experimental conditions. A value of \( \rho(\text{NH}_2) = 5 \) mbar was chosen to ensure that, in the absence of NO, all F atoms are consumed in reaction (S1) without losses in competing reactions such as \( F + F \rightarrow F_2 \) and \( F + \text{NH}_2 \rightarrow \text{HF} + \text{NH}_3 \). This was confirmed experimentally by studying the yield of \( \text{NH}_3 \) as a function of \( \rho(\text{NH}_2) \).

Special attention was given to the competition between reactions (S1) and (3). The relative yields of \( \text{NH}_2 \) and FNO depend on the \( \text{NH}_2/\text{NO} \) ratio. Previously the rate of \( F + \text{NO} + M \) has been studied with \( \text{SF}_6 \) as a third body at total pressures \(< 0.5 \) mbar.\( ^{49} \) To obtain reliable values of the rate constant at higher pressures we have studied the rate of formation of FNO initiated by pulse radiolysis of \( \text{SF}_6 \)-NO mixtures employing total pressures of 0.5 and 1.0 atm. As shown in Fig. 2, the kinetics of FNO formation was studied by monitoring the transient absorption at 317 nm.

Analysis of the experimental results gives values of the apparent bimolecular rate constants of \( k_3 = (9.3 \pm 1.8) \times 10^9 \text{ M}^{-1} \text{s}^{-1} \) at 1 atm and \( k_3 = (5.9 \pm 1.2) \times 10^9 \text{ M}^{-1} \text{s}^{-1} \) at 0.5 atm. This pressure dependence indicates a limiting high-pressure value which is significantly higher than \( 10^{10} \text{ M}^{-1} \text{s}^{-1} \). Knowing the rate constants of reactions (S1) and (3) we can define a range of \( \text{NO}/\text{NH}_2 \) ratios where losses of \( F \) atoms via reaction (3) are unimportant, e.g. 10 \% or less. Again, this has been confirmed experimentally during our studies of \( \text{NH}_2 \) kinetics in the presence of NO. At low \( \text{NO}/\text{NH}_2 \) ratios we observed only a variation in the decay half-lives, while the maximum of the transient absorption remained constant within a few percent.

To provide an internal standard for measurements of the absolute yields of hydroxyl radicals we have studied the kinetics of \( \text{OH} \) produced by pulse radiolysis of Ar–\( \text{SF}_6 \)-\( \text{H}_2\text{O} \) mixture with \( \rho(\text{SF}_6) = 50 \) mbar and the same initial yield of F atoms. Fig. 3 shows a plot of the transient absorption maxima monitored at 309 nm. The yield approaches a maximum value at higher water concentrations, where practically all F atoms are consumed in reaction (S2). Thus, a transient absorption signal of 0.135 \pm 0.010 corresponds to \( [\text{OH}] = [\text{F}]_0 = 1.40 \pm 0.10 \) \( \mu \text{M} \) using the F atom yield determined by the titration reaction (T).

In addition, we have studied the decay rate of \( \text{OH} \) in the presence of NO. From a series of exponential decay curves obtained with varying amounts of NO we find \( k_7 = (4.6 \pm 0.5) \times 10^9 \text{ M}^{-1} \text{s}^{-1} \), in good agreement with the value of \( 4.1 \times 10^9 \text{ M}^{-1} \text{s}^{-1} \) recommended by Atkinson and Lloyd\( ^{48} \) for this pressure-dependent reaction at 298 K and 1 atm. In a previous investigation\( ^{49} \) we have determined a value of \( k_8 = k(\text{OH} + \text{NH}_2) = (1.6 \pm 0.2) \times 10^8 \text{ M}^{-1} \text{s}^{-1} \) at 300 K. Using reliable values of the rate constants for the important reactions (7) and (8) in the computer model we may expect that calculated \( \text{OH} \) time profiles are realistic in predicting the observable yields under varying experimental conditions.
Fig. 3. OH yield in the pulse radiolysis of 50 mbar SF₆, Ar to 1 bar and various concentrations of added H₂O.

Fig. 4 shows a series of model curves based on an assumed branching ratio of 1/13, i.e. with \( k_{\text{in}} = 1.2 \times 10^{16} \text{ M}^{-1} \text{s}^{-1} = 12 \times k_{\text{in}} \). The gas mixture contained 5 mbar NH₃ and 0.7 mbar NO, which control the yield of NH₂ and the time profile of OH. Curve (a) was obtained by setting the rate constants for the main loss reactions (7) and (8) equal to zero. In this case OH builds up to a value which is controlled mainly by the branching ratio of reaction (1). However, with the chosen \([\text{NO}] / [\text{NH}_3]\) ratio about 7% of the F atoms are consumed in the reaction producing FNO, while 93% yield NH₂. Curve (b) was obtained using the experimental value of \( k_{\text{r}} \), while \( k_{\text{f}} \) was still kept equal to zero. Now OH passes through a maximum, while the concentration of NH₂ is still a factor of \( k_{\text{f}} / k_{\text{r}} = 4 \) higher than \([\text{OH}]_{\text{max}}\). The maximum concentration of OH occurs when

the dominant formation and decay rates are equal, i.e. when \( [\text{OH}] / [\text{NO}] = k_{\text{f}} [\text{NH}_3][\text{NO}] - k_{\text{r}} [\text{OH}][\text{NO}] = 0 \). The additional effect of reaction (8) is shown by curve (c), which corresponds to \( p(\text{NH}_3) = 5 \text{ mbar} \) combined with the experimental value of \( k_{\text{f}} \). Sensitivity analysis has shown that radical–radical reactions such as reaction (5) play a minor role for the observable yield of OH under the chosen experimental conditions. The OH time profile shown in Fig. 4(c) represents a best fit to our experimental results, where the observed OH absorption signal reached a maximum of 0.010 ± 0.003 at \( p(\text{NO}) = 0.5–0.7 \text{ mbar} \), which corresponds to about 7% of the maximum yield, i.e. \([\text{OH}]_{\text{max}} = 0.07 \text{ [FL]}\). Thus in the present study we have derived a very low branching ratio for the reaction channel (1b), suggesting that reaction (1a) is the most important product channel at room temperature.

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References


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