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–NH₃ mixtures to initiate the reaction F + NH₃ → HF + NH₂. Decay rates of NH₂ were studied by monitoring the transient absorption signals of NH₂ at 597.6 nm in the presence of varying amounts of NO and NO₂. Values of $k(NH_2 + NO) = (1.3 \pm 0.2) \times 10^{10}$ M⁻¹ s⁻¹ and $k(NH_2 + NO_2) = (1.1 \pm 0.3) \times 10^{10}$ M⁻¹ s⁻¹ were obtained at 298 K. By montitoring the transient absorption of OH radicals at 309 nm we have determined a very low branching for the reaction channel NH₂ + NO → N₂H + 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.[1,2] In particular the reaction with NO has been extensively studied because of its importance as a natural atmospheric sink for NOₓ. 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.[3] In experimental studies NH₂ has been produced by photolysis or radiolysis of ammonia or by abstraction reactions, X + NH₃ → HX + NH₂, which require highly reactive species such as X = F,O(¹D) or OH to overcome the high bond energy of D(H–NH₂) = 44 ± 4 kJ mol⁻¹.[4]

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[5,6] 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[7] in 1939. Experimental results obtained by photolysis of ammonia in the presence of NO[8-10] 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.[11-15]

$$NH_2 + NO \rightarrow \begin{cases} N_2 + H_2O & \text{(1a)} \\ N_2H + OH & \text{(1b)} \\ N_2 + H + OH & \text{(1c)} \end{cases}$$
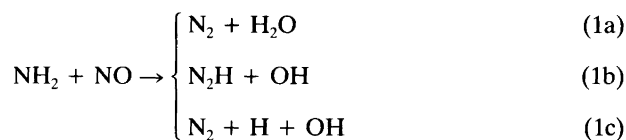
The direct observation of OH radicals may be taken as evidence for the occurrence of reactions (1b) and/or (1c). Several groups[5,12,16] have considered reaction (1c) as the most probable reaction producing OH radicals. On the

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

$10^{-10} k/M^{-1} s^{-1}$	T/K	$P/mbar$	Method[a]	Ref.
1.2	298	400	PR-AS	19,20
0.5±1.0	298	1.3–13.3	DF-MS	21
0.001	2010		Flame	22
1.3±0.1	298	1.33	FP-LIF	23
1.1±0.2	300–500	2.7–9.33	FP-AS	24
1.0±0.2	296	0.1–1.3	FP-LA	25
0.7	210–500	1.3	DF-LIF	26
1.1	298	3.9–13.3	FP-LIF	27
0.55±0.09	294–1215	1.3–3.7	DF-LIF	12,13
1.23±0.02	216–480	3.3–26.7	FP-LIF	17
1.09±0.07	298	1.3–2.7	LP-LIF	28
0.54	298	1.7	DF-LIF	29
1.00±0.03	295		LP-IR	16
1.0	298	10.6–26.7	FP-IR	18
1.0	300	13.3	DF-MS	14

[a]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,[12,16] indicating that reaction (1b) is the more 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.[12-18]
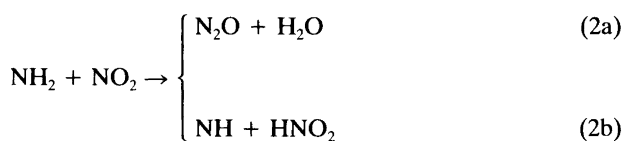
The overall rate constant for the reaction $NH_2 + NO \rightarrow$ products has been measured by different techniques, including pulse radiolysis, flash photolysis and discharge flow reactors, combined with various detection systems such as UV and IR spectroscopy and mass spectrometry. The reported rate 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} s^{-} and 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.[12,17,24,26] Recently Lesclaux[2] has recommended the expression $k_1 = 1.1 \times 10^{10} \times (T/298)^{-1.5}$ M^{-1} s^{-1}, which appears to account reasonably well for most of the reported experimental results.

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[30-36] considering various isomers of the adduct, N-nitrosamide, which is unstable, and apart from a single report on NH_2NO^{21} this molecule has never been well characterized experimentally.

A review of the available experimental data on reaction (1) shows that ambiguities remain regarding the identity of the products[37] 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.[38]

The reaction of NH_2 with NO_2 proceeds via a similar mechanism, reaction (2). Observation of N_2O and H_2O as

$$NH_2 + NO_2 \rightarrow \begin{cases} N_2O + H_2O & (2a) \\ \\ NH + HNO_2 & (2b) \end{cases}$$

the only reaction products was taken as evidence for reaction (2a) as the most important channel,[26] while other experimental work indicates that reaction (2b) is the main channel.[39] The reported values of the overall rate constant for reaction (2) vary from 0.7×10^{10} M^{-1} s^{-1}, determined by discharge flow,[26] to $(1.3 \pm 0.2) \times 10^{10}$ M^{-1} s^{-1}, determined by laser photolysis and flash photolysis experiments.[27,28]

The rate and products of the reactions of NH_2 with NO_x and other atmospheric constituents are of general interest in order to identify the most important source and sink reactions for NO_x. In a clean atmosphere, where the concentrations of nitrogen oxides are low, the reaction rates of NH_2 with NO and 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 $DeNO_x$ process and other methods by which NO is converted into molecular nitrogen via reaction (1a). In the present investigation we have studied the yields and kinetics of NH_2 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.[40] 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. 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 Å 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 CHEM-SIMUL[41] 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^{-5} 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, SF_6, NH_3, NO and NO_2) were supplied by Hoechst, and H_2O was triply distilled.

Results and discussion

Source reactions for NH$_2$ and OH. High yields of F atoms were obtained by pulse radiolysis of gas mixtures containing 50 mbar SF$_6$ 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 CH$_3$ produced in the titration reaction (T). Using the well established value of

$$F + CH_4 \rightarrow HF + CH_3 \qquad \text{(T)}$$

1.07×10^4 M^{-1} cm^{-1} [42] for the extinction coefficient of CH$_3$ at 216.4 nm we obtain from the observed transient absorption maximum, measured with an optical path length of L = 40 cm, $[F]_0 = (1.40 \pm 0.10) \times 10^{-6}$ M. Based on studies of the yield of CH$_3$ at varying partial pressures of CH$_4$ we find that less than 1 % of the F atoms are lost in competing reactions when $p(CH_4) > 5$ mbar. The yield of F atoms was kept constant in the subsequent kinetic studies by employing a fixed value of $p(SF_6)$ = 50 mbar, and with $p(Ar) + p(\text{additive})$ = 950 mbar to maintain a constant stopping power for the electron beam.

Direct conversion of F atoms into NH$_2$ or OH radicals via the source reactions (S1) and (S2) was accomplished using 1–5 mbar of ammonia or water vapour as additives.

$$F + NH_3 \rightarrow HF + NH_2 \qquad \text{(S1)}$$

$$F + H_2O \rightarrow HF + OH \qquad \text{(S2)}$$

The transient absorption signals due to NH$_2$ 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 NH$_2$ and OH, respectively.

Reactions of NH$_2$ with NO and NO$_2$. These reactions [(1) and (2)] were initiated by pulse radiolysis of gas mixtures containing 50 mbar SF$_6$, 5 mbar NH$_3$ and 0–1 mbar NO or NO$_2$. The overall decay rate of NH$_2$ 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 $[NO]_0 \gg [NH_2]_0$, the NH$_2$ decay was simple exponential with an initial decay rate which can be expressed by eqn. (E1). The first term on the

$$-(\text{d ln } [NH_2]/\text{d}t)_0 = 2k_4[NH_2]_0 + (k_{1a} + k_{1b})[NO]_0 \qquad \text{(E1)}$$

right-hand side accounts for the self-reaction of NH$_2$, 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 $k_1/\ln 2$. Fig. 1 shows the results of our studies of the overall decay rate. The value of $k_1 = k_{1a} + k_{1b} = (1.3 \pm 0.2) \times 10^{10}$ M^{-1} 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 NO$_2$ we have studied the overall decay rate of NH$_2$ consumed in reactions (2a) and (2b). The decay rate was studied at partial pressures of NO$_2$ 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 $k_2 = k_{2a} + k_{2b} = (1.1 \pm 0.3) \times 10^{10}$ M^{-1} s^{-1}. The estimated error limit is relatively large in this case, mainly because of noticable effects of NO$_2$ adsorption on the surface of the reaction cell. The value of k_2 derived in this study is close to that of $(1.3 \pm 0.2) \times 10^{10}$ M^{-1} s^{-1} obtained by the other pulsed methods.[27,28]
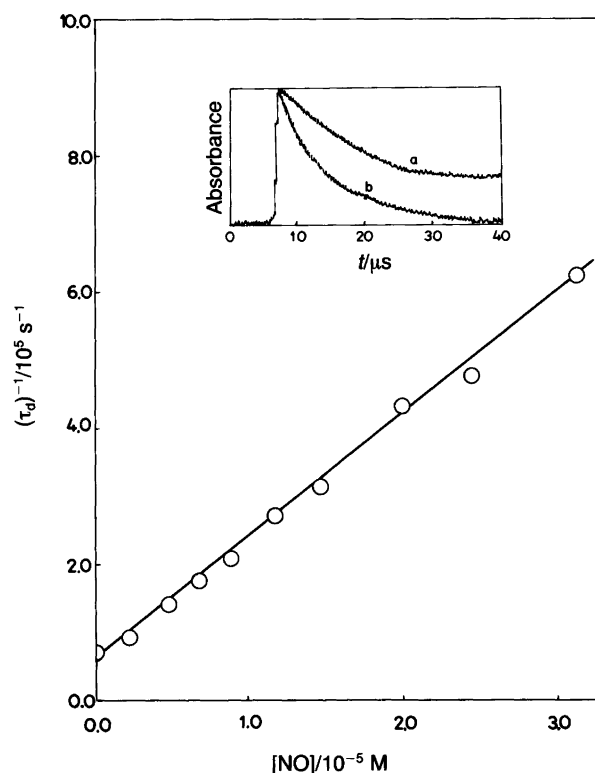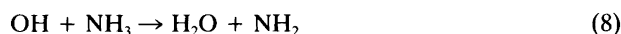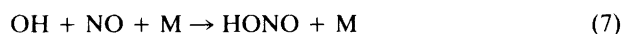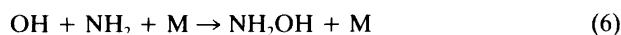

Fig. 1. NH$_2$ reciprocal decay half-life vs. NO concentration at 298 K and total pressure of 1 bar. NH$_2$ kinetics monitored at 597.6 nm in pulse radiolysis of 8 mbar NH$_3$, 50 mbar SF$_6$ and Ar to 1 bar without (a) and with (b) NO (0.15 mbar) is shown in the insert. The corresponding half-lives are 15.4 and 4.5 μs, respectively.

Branching ratio for the reaction NH_2 + NO. To determine the branching ratio of reaction (1) we have studied the kinetics of OH produced via reaction (1b), which was initiated by pulse radiolysis of gas mixtures containing 50 mbar SF_6, 5 mbar NH_3 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:

$$F + NH_3 \rightarrow HF + NH_2 \qquad (S1)$$

$$F + NO + M \rightarrow FNO + M \qquad (3)$$

$$2\,NH_2 + M \rightarrow N_2H_4 + M \qquad (4)$$

$$NH_2 + NO \rightarrow N_2 + H_2O \qquad (1a)$$

$$NH_2 + NO \rightarrow N_2H + OH \qquad (1b)$$

$$OH + OH + M \rightarrow H_2O_2 + M \qquad (5)$$

$$OH + NH_2 + M \rightarrow NH_2OH + M \qquad (6)$$

$$OH + NO + M \rightarrow HONO + M \qquad (7)$$

$$OH + NH_3 \rightarrow H_2O + NH_2 \qquad (8)$$

Based on sensitivity analysis we find that the observable yield of OH is controlled mainly by reactions (1b) and (3) under the chosen experimental conditions. A value of $p(NH_3)$ = 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 + NH_2 $\rightarrow$ HF + NH. This was confirmed experimentally by studying the yield of NH_2 as a function of $p(NH_3)$.

Special attention was given to the competition between reactions (S1) and (3). The relative yields of NH_2 and FNO depend on the NH_3/NO ratio. Previously the rate of F + NO + M has been studied with SF_6 as a third body at total pressures < 0.5 mbar.[43] 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 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 ± 1.8)× $10^9\,M^{-1}\,s^{-1}$ at 1 atm and k_3 = (5.9 ± 1.2)× $10^9\,M^{-1}\,s^{-1}$ at 0.5 atm. This pressure dependence indicates a limiting high-pressure value which is significantly higher than $10^{10}\,M^{-1}\,s^{-1}$. Knowing the rate constants of reactions (S1) and (3) we can define a range of NO/NH_3 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 NH_2 kinetics in the presence of NO. At low NO/NH_3 ratios we observed only a variation in the decay
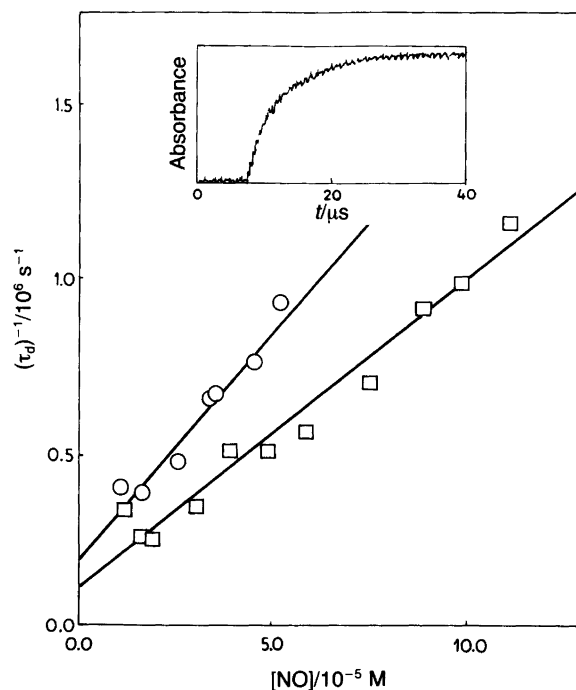

Fig. 2. The reciprocal FNO formation half-life vs. NO concentration for experiments performed at 298 K and SF_6 total pressures of 0.5 bar (□) and 1.0 bar (○). The FNO kinetics was monitored at 317 nm. The FNO formation half-life for the experiment [p(NO) = 0.31 mbar and $p(SF_6)$ = 0.5 bar] shown in the insert is 3.0 μs.

half-lives, while the maximum of the transient absorption remained constant wihtin a few percent.

To provide an internal standard for measurements of the absolute yields of hydroxyl radicals we have studied the kinetics of OH produced by pulse radiolysis of Ar–SF_6–H_2O, $p(SF_6)$ = 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 ± 0.010 corresponds to [OH] = [F]$_0$ = 1.40 ± 0.10 μM using the F atom yield determined by the titration reaction (T).

In addition, we have studied the decay rate of 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 ± 0.5)× $10^9\,M^{-1}\,s^{-1}$, in good agreement with the value of 4.1× $10^9\,M^{-1}\,s^{-1}$ recommended by Atkinson and Lloyd[44] for this pressure-dependent reaction at 298 K and 1 atm. In a previous investigation[40] we have determined a value of k_8 = k(OH + NH_3) = (1.6 ± 0.2)× $10^8\,M^{-1}\,s^{-1}$ 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 OH time profiles are realistic in predicting the observable yields under varying experimental conditions.
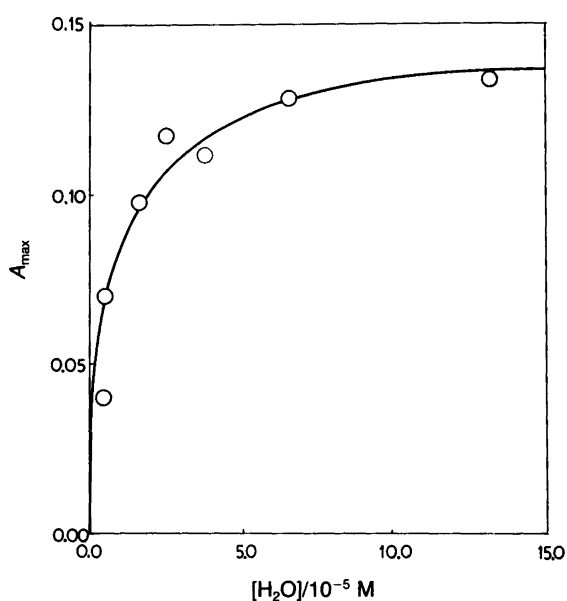
Fig. 3. OH yield in the pulse radiolysis of 50 mbar SF_6, Ar to 1 bar and various concentrations of added H_2O.

the dominant formation and decay rates are equal, i.e. when $d[OH]/dt = k_{1b} [NH_2][NO] - k_7 [OH][NO] = 0$. The additional effect of reaction (8) is shown by curve (c), which corresponds to $p(NH_3) = 5$ mbar combined with the experimental value of k_8. 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 $p(NO) = 0.5–0.7$ mbar, which corresponds to about 7 % of the maximum yield, i.e. $[OH]_{max} = 0.07 [F]_0$. 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.

Fig. 4 shows a series of model curves based on an assumed branching ratio of 1/13, i.e. with $k_{1a} = 1.2 \times 10^{10}$ M^{-1} s^{-1} = $12 \times k_{1b}$. 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 [NO]/[NH₃] 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_7, while k_6 was still kept equal to zero. Now OH passes through a maximum, while the concentration of NH₂ is still a factor of $k_7/k_{1b} = 4$ higher than $[OH]_{max}$. The maximum concentration of OH occurs when
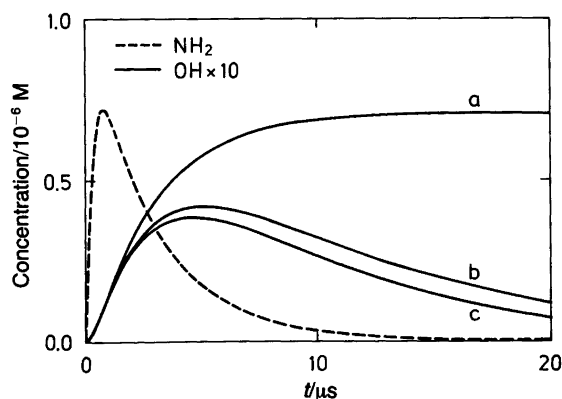
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Fig. 4. OH and NH₂ radical concentration profiles simulated for the NO–NH₃–SF₆–Ar system.

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