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Published in:

Journal of Physical Chemistry Part A: Molecules, Spectroscopy, Kinetics, Environment and General Theory

Link to article, DOI:

[10.1021/acs.jpca.0c11011](https://doi.org/10.1021/acs.jpca.0c11011)

Publication date:

2021

Document Version

Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):

Glarborg, P., Hashemi, H., Cheskis, S., & Jasper, A. W. (2021). On the Rate Constant for $\text{NH}_2 + \text{HO}_2$ and Third Body Collision Efficiencies for $\text{NH}_2 + \text{H}(+\text{M})$ and $\text{NH}_2 + \text{NH}_2(+\text{M})$. *Journal of Physical Chemistry Part A: Molecules, Spectroscopy, Kinetics, Environment and General Theory*, 125(7), 1505–1516.
<https://doi.org/10.1021/acs.jpca.0c11011>

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On the Rate Constant for $\text{NH}_2 + \text{HO}_2$ and Third Body Collision Efficiencies for $\text{NH}_2 + \text{H} (+\text{M})$ and $\text{NH}_2 + \text{NH}_2 (+\text{M})$

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Abstract

In low temperature flash photolysis of $\text{NH}_3/\text{O}_2/\text{N}_2$ mixtures, the NH_2 consumption rate and the product distribution is controlled by the reactions $\text{NH}_2 + \text{HO}_2 \rightarrow \text{products}$ (R1), $\text{NH}_2 + \text{H} (+\text{M}) \rightarrow \text{NH}_3 (+\text{M})$ (R2), and $\text{NH}_2 + \text{NH}_2 (+\text{M}) \rightarrow \text{N}_2\text{H}_4 (+\text{M})$ (R3). In the present work, published flash photolysis experiments by, among others, Cheskis and coworkers, are re-interpreted, using recent direct measurements of $\text{NH}_2 + \text{H} (+\text{N}_2)$ and $\text{NH}_2 + \text{NH}_2 (+\text{N}_2)$ from Altinay and Macdonald. To facilitate analysis of the FP data, relative third body collision efficiencies compared to N_2 for R2 and R3 were calculated for O_2 and NH_3 , as well as for other selected molecules. Results were in good agreement with the limited experimental data. Based on reported NH_2 decay rates in flash photolysis of $\text{NH}_3/\text{O}_2/\text{N}_2$, a rate constant for $\text{NH}_2 + \text{HO}_2 \rightarrow \text{NH}_3 + \text{O}_2$ (R1a) of $k_{1a} = 1.5(\pm 0.5) \cdot 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 295 K was derived. This value is higher than earlier determinations based on the FP results, but in good agreement with recent theoretical work. Kinetic modeling of reported

N_2O yields indicates that $\text{NH}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{NO} + \text{O}$ (R1c) is competing with R1a, but perturbation experiments with addition of CH_4 indicate that it is not a dominating channel. Measured HNO profiles indicate that this component is formed directly by $\text{NH}_2 + \text{HO}_2 \rightarrow \text{HNO} + \text{H}_2\text{O}$ (R1b), but theoretical work indicates that R1b is only a minor channel. Based on this analysis, we estimate $k_{1c} = 2.5 \cdot 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{1b} = 2.5 \cdot 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 295 K, with significant uncertainty margins.

Introduction

Ammonia has attracted interest as a potential carbon-free energy carrier,^{1,2} in particular for high pressure applications such as engines and gas turbines. Use of ammonia as a fuel is challenging, however, due to its comparatively low calorific value, a low laminar burning velocity, and narrow flammability limits.³ There has been a number of studies on the use of NH_3 as an engine fuel, but its poor combustion characteristics for conventional engine combustion techniques have been difficult to overcome.

To facilitate use of ammonia as an energy carrier, it is important to have access to reliable and versatile chemical kinetic models for ignition and oxidation of NH_3 . Despite the simplicity of the molecule and the extensive research conducted, its ignition and oxidation chemistry is still in discussion.⁴⁻¹³ The reactivity of ammonia is to a large extent governed by the reactions of the amino radical NH_2 . At the high pressure and intermediate temperatures typical of ignition in engines, HO_2 is the main chain carrier and its reaction with NH_2 ,

becomes a key step.^{5,12} The experimental results relevant for characterizing this step have been obtained from room temperature flash photolysis studies of NH_3/O_2 mixtures,¹⁴⁻²⁸ but also pulse radiolysis results have been reported.^{29,30} The main objective of most of these studies was to determine the rate constant for $\text{NH}_2 + \text{O}_2$. This reaction, however, is

extremely slow at room temperature, and the observed enhanced consumption rate for NH_2 in the presence of O_2 can be attributed to the $\text{NH}_2 + \text{HO}_2$ reaction. Kurasawa and Lesclaux (unpublished, cited in²²), derived an overall rate constant for $\text{NH}_2 + \text{HO}_2$ of $3.1 \cdot 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at room temperature. Cheskis and coworkers reported values of $1.5 \cdot 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$,¹⁸ $3.7 \cdot 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$,²⁰ and $4.5 \cdot 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.²³ The differences in rate constants were mainly caused by uncertainties in the starting concentration of NH_2 and in the rate constants for the side reactions,

The $\text{NH}_2 + \text{HO}_2$ reaction has several possible product channels,

Lesclaux²² concluded in his review of NH_2 reactions that reported low-temperature measurements were consistent with the major products being $\text{NH}_3 + \text{O}_2$ (R1a) and $\text{HNO} + \text{H}_2\text{O}$ (R1b). However, it has not been possible from the experimental work to determine unambiguously the product branching fraction. In the flash photolysis studies, either the product distribution^{14-16,27} or the NH_2 consumption rate^{18,22-24,26,28} were monitored. In flash photolysis experiments where NH_2 loss was detected, the occurrence of the H_2NO channel (R1c) would go undetected, due to rapid regeneration of NH_2 by $\text{NH}_3 + \text{OH}$.²⁷

The $\text{NH}_2 + \text{HO}_2$ reaction has been studied theoretically by several groups,^{13,31-36} but the

branching fraction of the reaction is still in discussion. Sumathi and Peyerimhoff³³ calculated rate constants for formation of the adduct H_2NOOH (R1d) and its isomers $\text{HN}(\text{OH})\text{OH}$ and $\text{H}_2\text{N}(\text{OH})\text{O}$, as well as the products $\text{NH}_3 + \text{O}_2$ (R1a), $\text{NH}_2\text{O} + \text{OH}$ (R1c), $\text{HNO} + \text{H}_2\text{O}$ (R1b), and $\text{HON} + \text{H}_2\text{O}$. The predominant contribution to the total rate constant was predicted to be dissociation of the energized H_2NOOH to $\text{NH}_2\text{O} + \text{OH}$. In a more recent study, Xian et al.³⁵ concluded that the reaction takes place on both the singlet surface, yielding $\text{H}_2\text{NO} + \text{OH}$, and on the triplet surface, forming $\text{NH}_3 + \text{O}_2$. On the singlet potential surface, HO_2 adds barrierless to NH_2 to form HOO-NH_2 , which dissociates without an exit barrier to OH and H_2NO . On the triplet surface, the reaction mechanism involves mainly a barrierless addition of HO_2 to NH_2 to form an intermediate OOH-NH_2 adduct, which goes through an H transfer forming the products NH_3 and O_2 . In a recent study, Stagni et al.¹³ calculated the rate constant for H-abstraction from NH_3 by O_2 . Their rate constant corresponds to a very fast rate of $1.5 \cdot 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at room temperature for the reverse step, $\text{NH}_2 + \text{HO}_2 \rightarrow \text{NH}_3 + \text{O}_2$, significantly faster than observed experimentally.^{18,20,22,23}

The purpose of the present work is to re-interpret the low temperature flash photolysis work on NH_3/O_2 mixtures in terms of the current understanding of amine reactions⁹ to obtain more accurate data for the rate constant and branching ratio for the $\text{NH}_2 + \text{HO}_2$ reaction. The analysis relies on the recent experimental characterization of the reactions $\text{NH}_2 + \text{H} (+\text{M}) \rightarrow \text{NH}_3 (+\text{M})$ (R2) and $\text{NH}_2 + \text{NH}_2 (+\text{M}) \rightarrow \text{N}_2\text{H}_4 (+\text{M})$ (R3) by Altinay and Macdonald.³⁷⁻³⁹ To interpret the FP data, also reliable values for the third body collision efficiencies of O_2 and NH_3 are required for R2 and R3; as part of the present work relative efficiencies compared to N_2 are calculated for these and other selected molecules.

Kinetics and theory

Recombination reactions of NH_2 with H and NH_2

The interpretation of the flash photolysis work on NH_3/O_2 mixtures rely on the rate constants of the competing reactions,

Very little work has been published on reaction R2. Its rate constant is difficult to measure by flash photolysis or radiolysis of NH_3 , because of interference by the NH_2 self-reaction (R3). Gordon et al.⁴⁰ conducted pulse radiolysis of NH_3 in the pressure range 250-1520 Torr. By analysing the NH_2 decay kinetics, they were able to discriminate between reactions (R2) and (R3) and derive rate constants as function of pressure with NH_3 as collision partner. Pagsberg et al.²⁹ conducted pulse radiolysis experiments of $\text{NH}_3/\text{O}_2/\text{Ar}$ mixtures and estimated a value of k_2 at 349 K and 760 Torr from kinetic modeling of the fairly complex system. In a more recent study, Arthur et al.⁴¹ combined flash photolysis with direct recording of hydrogen atoms to measure the rate constant for $\text{NH}_2 + \text{H} + \text{Ar}$. They found the reaction to be trimolecular at pressures ranging from 400 to 700 Torr and a temperature of 300 K, with a rate constant of $3(\pm 0.8) \cdot 10^{17} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$.

Rate constants at low temperature for the $\text{NH}_2 + \text{NH}_2$ reaction (R3) have been reported by several groups.^{20,23,24,37-40,42-48} The early work, much of which was reviewed by Lesclaux²², involved relative measurements of the amino radical and suffered from uncertainty in the determination of the starting concentration of NH_2 , and the data are scattered. Bair and coworkers^{42,43} studied R3 at very low pressure, where it is difficult to distinguish between recombination and disproportionation. Results obtained at higher pressures by Gordon et al.⁴⁰, Back and Yokota⁴⁴, Lozovskii et al.²⁰, and Fagerstrom et al.⁴⁶ are difficult to compare

directly, as they were obtained with different collision partners, but they all indicate a high pressure limit in the range $(4-7) \cdot 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at room temperature. Khe et al.⁴⁵, using flash photolysis of ammonia, conducted a comprehensive study of the reaction, covering the complete fall-off region (0.3-1000 Torr) in the presence of NH_3 , N_2 , and Ar, respectively. Khe et al. concluded that the $\text{NH}_2 + \text{H} (+\text{M})$ reaction was too slow to compete with R3 except at the higher pressures. However, their measured high pressure limit is significantly lower than that reported in other studies.^{20,40,44,46}

These studies of R2 and R3 suffered from the difficulty of measuring the rate constant of a second order radical-radical reaction from relative concentrations of one the reactants and in the presence of competing steps. In recent work, Macdonald and coworkers^{37-39,48} resolved this problem by measuring simultaneously and quantitatively the concentrations of NH_2 and NH_3 . Altinay and Macdonald³⁷⁻³⁹ reported flash photolysis results for NH_3 /inert mixtures as a function of bath gas, temperature (292-533 K) and pressure (from a few Torr up to 400 Torr). By quantitative monitoring of both NH_2 and NH_3 using high-resolution time-resolved laser absorption spectroscopy, they were able to determine simultaneously recombination rate constants for both $\text{NH}_2 + \text{H} (+\text{M})$ (R2) and $\text{NH}_2 + \text{NH}_2 (+\text{M})$ (R3). The experiments were difficult to conduct and there is some deviation between the results from the three studies.

Based on their measurements, Altinay and Macdonald derived rate parameters in the Troe format for $\text{NH}_2 + \text{H} (+\text{N}_2)$, while for $\text{NH}_2 + \text{NH}_2 (+\text{N}_2)$, they recommended the theoretical rate coefficients from Klippenstein et al.⁴⁹ In the present work, we have adopted these values and calculated the relative third body efficiencies of Ar, O_2 , NH_3 and selected other collision partners compared to N_2 for the two reactions (see below). Figure 1 shows a comparison between data from Altinay and Macdonald³⁹ and model predictions with the present rate constants for R2 and R3. The discrepancy seen at longer reaction times could indicate a slight overprediction of k_2 , but Altinay and Macdonald attribute the difference to experimental artifacts.

Figure 1: Comparison of the measurements of Altinay and Macdonald³⁹ for NH_2 and NH_3 with modeling predictions. The experiment was conducted at 292 K and a pressure of 0.45 atm (342 Torr) in N_2 . The initial concentrations of NH_3 and NH_2 were 50 ppm and 4.1 ppm, respectively.

Figure 2 compares the chosen rate constant for R2 with measurements for Ar,⁴¹ N_2 ,³⁹ and NH_3 ⁴⁰ as collision partners. The agreement is very good for Ar and N_2 over the range of pressures investigated. For NH_3 , the agreement is good at 200-500 Torr, while at 1000-1500 Torr the values reported by Gordon et al. are about a factor of two higher than those predicted. We attribute this difference mainly to experimental uncertainties in the work of Gordon et al.

Altinay and Macdonald obtained a rate constant for $\text{NH}_2 + \text{H} (+\text{N}_2)$ that is significantly faster at low pressure than previously assumed²² and their results indicate that early measurements^{20,45} of k_3 as a function of N_2 pressure near 300 K were actually a composite of both k_2 and k_3 . The larger value of k_2 implies that reaction R2 plays an important role for NH_2 consumption, contrary to assumptions in some of the early flash photolysis work. Figure 3 compares the measured rate constants of Khe et al.⁴⁵ and Lozovskii et al.²⁰ for Ar and N_2 as collision partners with the calculated sum $k_2 + k_3$. The calculated value of $k_2 + k_3$ is in good agreement with the results of Lozovskii et al., while the rate constants obtained by Khe et al. are significantly lower at pressures above 100 Torr. This discrepancy is consistent with their reported high pressure limit for k_3 being lower than those derived in

Figure 2: Comparison of experimental data for the $\text{NH}_2 + \text{H}(+\text{M})$ reaction with the rate constants used in the present work. Symbols denote the experimental data from Arthur et al.,⁴¹ Altinay and Macdonald,³⁹ and Gordon et al.,⁴⁰ while the lines are the predicted values based on the Troe expression of Altinay and Macdonald³⁹ and the collision efficiencies calculated in the present work.

other studies.^{20,40,44,46}

Figure 3: Comparison of experimental rate constants reported by Khe et al.⁴⁵ and Lozovskii et al.²⁰ for $\text{NH}_2 + \text{NH}_2 (+\text{M})$ (R3) with the calculated sum of the sum of the rate constants for $\text{NH}_2 + \text{H} (+\text{M})$ and $\text{NH}_2 + \text{NH}_2 (+\text{M})$, i.e., $k_2 + k_3$. Symbols denote experimental data, while the lines are the predicted values with the current model.

Theoretical third-body collision efficiencies for $\text{NH}_2+\text{H}(+\text{M})$ and $\text{NH}_2+\text{NH}_2(+\text{M})$

Measurements of the rate constants for $\text{NH}_2+\text{H}(+\text{M})$ (R2) and $\text{NH}_2+\text{NH}_2(+\text{M})$ (R3) were conducted with different inert gases and are not easily comparable. Furthermore, knowledge of third body collision efficiencies for NH_3 and O_2 for these two steps are required to interpret the FP work on NH_3/O_2 mixtures. Consequently, the relative third body collision efficiencies were calculated for R2 and R3 for selected molecules in the present work.

The relative third-body collision efficiency $\mathcal{M}_\text{M}$ for the reaction $\text{A}+\text{B}(+\text{M})$ is the ratio of its low-pressure-limit rate constant $k_0(\text{M})$ to that for a reference bath, often N_2 , i.e., $\mathcal{M}_\text{M} = k_0(\text{M})/k_0(\text{N}_2)$. Although k_0 depends on a variety of properties such as the density of states and the reaction energetics, these factors (largely) cancel out when evaluating $\mathcal{M}_\text{M}$, and $\mathcal{M}_\text{M}$ is more easily and accurately predicted than k_0 .

Here, $\mathcal{M}_\text{M}$ was calculated for R2 and R3 in several baths and at several temperatures using a combination of classical trajectories and newly parameterized potential energy surfaces. Briefly, if $\mathcal{M}_\text{M}$ is rewritten via the equilibrium constant to be a function of the reverse (unimolecular decomposition) reaction of R2 or R3 and if a weak collider approximation is made for the decomposition rate constants, we are left with $\mathcal{M}_\text{M} = Z_\text{M}\beta_\text{M}/Z_{\text{N}_2}\beta_{\text{N}_2}$, where Z_M is the total bimolecular collision rate constant for the unimolecular reactant (NH_3 or N_2H_4) and M , and β_M is a weak collider efficiency correction.^{50,51} A variety of expressions for β_M have been given, and here we used Troe's $\beta_\text{M} = (\alpha_\text{M}/(\alpha_\text{M} + F_\text{E}k_\text{BT}))^2$, where α_M is the average energy transferred in deactivating collisions $\langle \Delta E_\text{d} \rangle$ and may be called the collision efficiency range parameter when using this model, and F_E is related to the thermal fraction of the reactant's population above threshold.⁵⁰ All of these quantities are functions of temperature, and therefore so is $\mathcal{M}_\text{M}$.

F_E was evaluated using the rigid rotor/harmonic oscillator approximation and experimental values for the frequencies, geometries, and energetics.⁵² This quantity is typically

close to unity for small molecular systems at low and moderate temperatures, and indeed $F_{\text{E}k_{\text{B}}T} \sim 200 \text{ cm}^{-1}$ at 300 K for both NH_3 and N_2H_4 . $\mathcal{M}_{\text{M}}$ is likely more sensitive to the theoretical treatment of Z_{M} and α_{M} , and these were predicted as described next.

Full dimensional potential energy surfaces were constructed for each system by combining molecular mechanics descriptions of the colliding partners with newly fitted interaction potentials. The interaction potentials were trained against large data sets of ab initio (counterpoise corrected MP2 with cc-pVTZ and cc-pVQZ complete basis set extrapolations) energies. Several separable and nonseparable permutationally invariant polynomial⁵³ (PIP) descriptions of the intermolecular potential were generated for each system, and convergence with respect to both the completeness of the training data and the complexity of the fitting basis was quantified as described previously;⁵⁴ results reported here were obtained using nonseparable PIP44 expansions with out-of-sample fitting errors of less than 10%.

The fitted potential energy surfaces were used in classical trajectory calculations where the unimolecular reactant was initially prepared with an internal energy close to its dissociation threshold and with the other coordinates prepared at the temperature of interest, as is appropriate for calculating α_{M} .^{55,56} In a separate set of calculations, the fitted interaction surfaces were used to perform orientationally-averaged rigid body optimizations⁵³ to determine effective Lennard-Jones parameters⁵⁷ from which the total collision rate constant Z_{M} was obtained.

The approximations central to the *a priori* approach described here were recently tested against more detailed descriptions of collisional energy transfer and specifically against the results of so-called “two-dimensional” *a priori* master equation calculations⁵⁸ for a varied test set of small-molecule decomposition reactions.⁵⁹ There, this approach was shown to predict k_0 with a mean-unsigned deviation of just 28%, and, as noted above, one expects even smaller errors in $\mathcal{M}_{\text{M}}$ than in k_0 . In fact, in a similar study of $\text{CH}_4(+\text{M})$ in several baths, this approach was shown to quantitatively reproduce $\mathcal{M}_{\text{M}}$ when compared with more detailed calculations,⁶⁰ and, furthermore, good agreement with available experimental studies was

shown in a comprehensive but as yet unpublished analysis.⁶¹

The present results are summarized in Table 1 where they are compared with the experimental results of Altinay and MacDonald³⁷⁻³⁹ and Khe et al.⁴⁵ at 300 K. The N₂, Ar, O₂, and NH₃ baths are of direct interest to the present study, while the CO₂ and CH₄ baths were included to provide more extensive comparisons with experiment. The experimentally-determined values of k_0 were assigned by the original authors 2σ relative errors of 20-40% and 50%, respectively, and one could assign somewhat larger errors to the ratio $\mathcal{M}_M$ if uncorrelated experimental errors are assumed. The theoretical values are indeed within these error bounds, with an average relative deviation from experiment of just $\sim 25\%$. As mentioned above, based on previous examinations of errors in the theoretical approaches the deviations from experiment quantified here are likely representative of their general accuracy for these systems.

Table 1: Calculated third body efficiencies relative to $M = N_2$. These are compared with available experimental results given in parentheses taken from *a* Altinay and MacDonald³⁷⁻³⁹ or *b* Khe et al.⁴⁵

System	T (K)	M = N ₂	Ar	O ₂	NH ₃	CH ₄	CO ₂
NH ₃ (+M)	300	1.00	0.32	0.50	4.39	3.15 (2.60 ^a)	3.54 (2.83 ^a)
	1000	1.00	0.41	0.59	8.11	5.38	5.44
	2000	1.00	0.45	0.70	9.90	6.36	5.76
N ₂ H ₄ (+M)	300	1.00	0.50 (0.77 ^a , 0.4 ^b)	0.61	2.93 (4.0 ^b)		
	1000	1.00	0.59	0.69	4.87		
	2000	1.00	0.70	0.80	6.02		

Reaction mechanism

An amine reaction mechanism was established to model the flash photolysis experiments selected from literature. Table 2 shows a subset of the model. In addition to R1 to R3 discussed above, the mechanism includes reactions of NH₃ with O/H radicals (R10-R12), reactions of NH₂ with O₂ (R4), NO (R5), NO₂ (R6), and HNO (R7), as well as reactions

of HNO and H₂NO with radicals and with O₂. The full mechanism, which is available as Supplementary Information, is drawn from the review of Glarborg et al.,⁹ except for reactions R1-R3.

Table 2: Selected reactions in the NH₃ oxidation subset. Parameters for use in the modified Arrhenius expression $k=AT^\beta\exp(-E/[RT])$. Units are mol, cm, s, cal.

	A	β	E	Source
1a. $\text{NH}_2 + \text{HO}_2 \rightleftharpoons \text{NH}_3 + \text{O}_2$	1.5E14	0.000	0	pw, see text
1b. $\text{NH}_2 + \text{HO}_2 \rightleftharpoons \text{HNO} + \text{H}_2\text{O}$	2.5E12	0.000	0	est, see text
1c. $\text{NH}_2 + \text{HO}_2 \rightleftharpoons \text{H}_2\text{NO} + \text{OH}$	2.5E13	0.000	0	est, see text
2. $\text{NH}_2 + \text{H}(+\text{M}) \rightleftharpoons \text{NH}_3(+\text{M})$	1.6E14	0.000	0	³⁹
Low pressure limit:	3.6E22	-1.760	0	
Third body efficiencies (300 K): N ₂ =1.0, Ar=0.32, O ₂ =0.50, NH ₃ =4.39				
Troe parameters: 0.5 1.0E-30 1.0E30				
3. $\text{NH}_2 + \text{NH}_2(+\text{M}) \rightleftharpoons \text{N}_2\text{H}_4(+\text{M})$	5.6E14	-0.414	66	⁴⁹
Low pressure limit:	1.6E34	-5.49	1987	
Third body efficiencies (300 K): N ₂ =1.0, Ar=0.50, O ₂ =0.61, NH ₃ =2.93				
Troe parameters: 0.31 1.0E-30 1.0E30				
4a. $\text{NH}_2 + \text{O}_2 \rightleftharpoons \text{H}_2\text{NO} + \text{O}$	2.6E11	0.487	29050	⁶²
4b. $\text{NH}_2 + \text{O}_2 \rightleftharpoons \text{HNO} + \text{OH}$	2.9E-2	3.764	18185	⁶²
5a. $\text{NH}_2 + \text{NO} \rightleftharpoons \text{NNH} + \text{OH}$	4.3E10	0.294	-866	^{9,63}
5b. $\text{NH}_2 + \text{NO} \rightleftharpoons \text{N}_2 + \text{H}_2\text{O}$	2.6E19	-2.369	870	^{9,63}
6a. $\text{NH}_2 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O} + \text{H}_2\text{O}$	2.2E11	0.110	-1186	⁹
6b. $\text{NH}_2 + \text{NO}_2 \rightleftharpoons \text{H}_2\text{NO} + \text{NO}$	8.6E11	0.110	-1186	⁹
7. $\text{NH}_2 + \text{HNO} \rightleftharpoons \text{NH}_3 + \text{NO}$	5.9E02	2.950	-3469	⁶⁴
8. $\text{HNO} + \text{O}_2 \rightleftharpoons \text{NO} + \text{HO}_2$	2.0E13	0.000	16000	³⁴
9. $\text{H}_2\text{NO} + \text{O}_2 \rightleftharpoons \text{HNO} + \text{HO}_2$	2.3E02	2.994	16500	⁹
10. $\text{NH}_3 + \text{H} \rightleftharpoons \text{NH}_2 + \text{H}_2$	6.4E05	2.390	10171	⁶⁵
11. $\text{NH}_3 + \text{O} \rightleftharpoons \text{NH}_2 + \text{OH}$	9.4E06	1.940	6460	⁶⁶
12. $\text{NH}_3 + \text{OH} \rightleftharpoons \text{NH}_2 + \text{H}_2\text{O}$	2.0E06	2.040	566	⁶⁷

When simulating results obtained at low pressure, it is important to take into account loss of radicals on the reactor surface. Following Frank-Kamenetskii⁶⁸ and Lozovsky et al.,²⁸ we estimate the rate constant k_s for first order heterogeneous destruction as

$$\frac{1}{k_s} = \frac{1}{k_{\text{kin}}} + \frac{1}{k_{\text{diff}}}$$

where k_{kin} and k_{diff} are the rate constants for the two limiting modes of destruction, i.e., kinetic control and diffusion control. For a cylindrical static reactor,²⁸

$$k_{\text{kin}} = \frac{\gamma \bar{v}}{d}$$

$$k_{\text{diff}} = \frac{23.2}{d^2} D \frac{760}{P}$$

Here, γ is the radical sticking probability at the quartz wall, $\bar{v}$ is the mean thermal velocity of the radical, d is the reactor diameter, D is the diffusion coefficient of the radical, and P (Torr) is the reactor pressure. For the NH_3/N_2 and $\text{NH}_3/\text{O}_2/\text{N}_2$ experiments, the radicals in question are NH_2 , HO_2 , and H . The sticking coefficients and therefore rate of heterogeneous recombination strongly depend on the type and quality of the used surface. Lozovsky et al.²⁸ derived values of $\gamma_{\text{NH}_2} = 1.5 \cdot 10^{-3}$ and $\gamma_{\text{HO}_2} = 1.1 \cdot 10^{-3}$ from flash photolysis experiments using quartz cells. They considered the heterogeneous recombination of hydrogen atoms to be negligible under their conditions. This is in agreement with measurements of the heterogeneous recombination of H on quartz,⁶⁹ with a γ_{H} of around $2 \cdot 10^{-5}$ at room temperature.

Flash photolysis of $\text{NH}_3/\text{O}_2/\text{N}_2$: Implications for $\text{NH}_2 + \text{HO}_2$

In the present work, selected flash photolysis experiments from the literature are re-interpreted in terms of our present understanding of the key amine reactions. The low-temperature flash photolysis experiments were mainly designed to measure the rate constant for $\text{NH}_2 + \text{O}_2$ by following the NH_2 decay rate,

It was not possible in these studies to detect any reaction between NH_2 and O_2 ;^{17-19,25-28} only upper limits were reported. This is consistent with the present knowledge of the reaction. The entrance channel to form NH_2OO is barrierless, but the energy of this adduct is only about 5 kcal mol⁻¹ lower than that of the reactants.⁶² The upper limit for k_1 of $3.6 \cdot 10^3 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ²⁷ indicates that NH_2OO is not collisionally stabilized. Other product channels, i.e., $\text{H}_2\text{NO} + \text{O}$ (R4a) or $\text{HNO} + \text{OH}$ (R4b), have high barriers⁶² and are too slow to consume NH_2 at low temperature. Consequently, if the FP experiments are conducted at low levels of O_2 , NH_2 is mainly consumed by recombination reactions, $\text{NH}_2 + \text{H} (+\text{M})$ (R2) and $\text{NH}_2 + \text{NH}_2 (+\text{M})$ (R3). At sufficiently high oxygen concentrations, the NH_2 consumption is instead governed by the sequence,

The flash photolysis studies involved either measurement of the NH_2 decay or determination of the product composition. Below, selected experiments of both categories are analyzed in terms of the current reaction mechanism and the implications for our understanding of the $\text{NH}_2 + \text{HO}_2$ reaction is discussed.

NH_2 consumption measurements

The difficulties of obtaining rate coefficients for radical-radical reactions from decay measurements of one of the reactants, discussed above for R2 and R3, also apply to the FP studies of NH_3/O_2 mixtures. For example, Michael et al.²⁶ report first order decay rates for NH_2 in flash photolysis of $\text{NH}_3/\text{O}_2/\text{Ar}$ mixtures, obtained at 25 Torr and varying temperature (245-459 K), O_2 concentration, and flash energy. As for much of the other work, the purpose of their study was to determine an upper limit for $\text{NH}_2 + \text{O}_2$ (R4). From their data, which are quite scattered, it is only possible to derive values for $k_1[\text{NH}_2]_0$. Unfortunately, the starting concentration of NH_2 could not be estimated reliably, and for this reason no conclusions can

be made regarding k_1 . Other reported photolysis and radiolysis studies have similar issues. However, a few reported studies allow assessment of $[\text{NH}_2]_0$.

Cheskis and Sarsikov¹⁸ measured the loss of NH_2 in flash photolysis experiments of mixtures of NH_3 , O_2 , and N_2 . Table 4 provides an overview of those of their experiments that are considered in the present work.

Table 3: Selected flash photolysis experiments from Cheskis and Sarsikov.¹⁸ The table shows the initial partial pressures. All data were obtained with the same flash energy (300 J) and flash duration. The partial pressure of NH_2 after photolysis was estimated in the present work to be 1.7E-4 Torr (see text).

Case	NH_3 Torr	O_2 Torr	N_2 Torr
A	0.6	0	100
B	0.6	100	0
C	0.6	0	570
D	0.6	1	569
E	0.6	100	470
F	0.6	570	0

Since only relative measurements of NH_2 could be obtained, derivation of the second order rate constants depended on estimates of the initial NH_2 level. Cheskis and Sarsikov estimated $[\text{NH}_2]_0$ from data for photolysis of NH_3/N_2 mixtures at different pressures but constant flash energy and flash duration, relying on the measured rate constant for $\text{NH}_2 + \text{NH}_2 (+\text{M})$ (R3)⁴⁵. Referring to the work of Khe et al.,⁴⁵ Cheskis and Sarsikov assumed that the reaction $\text{NH}_2 + \text{H} (+\text{M}) \rightarrow \text{NH}_3 (+\text{M})$ (R2) could be ignored. As discussed above, the recent work of Altinay and Macdonald^{38,39} indicate that R2 is sufficiently fast to compete with R3 at a pressure of 560 Torr and should be taken into account.

Following the approach of Cheskis and Sarsikov, we have estimated the initial concentration of NH_2 after the lamp photolysis in the NH_3/N_2 mixtures at different pressures, using the present values of k_2 and k_3 . Based on their data for 0.6 Torr of NH_3 in N_2 at 100 Torr and 570 Torr, respectively, a partial pressure of NH_2 after photolysis was estimated to 1.7E-4 Torr, about a factor of three lower than the estimate of Cheskis and Sarsikov. As shown in Fig. 4, the combination of this value of $P_{\text{NH}_2,0}$ with the current rate constants for R2 and

R3 provides a good prediction of the NH_2 loss as a function of time at both pressures.

Figure 4: Comparison of experimental data¹⁸ and modeling predictions for flash photolysis of NH_3/N_2 at 295 K. Symbols denote experimental data, while lines denote modeling predictions. Starting conditions: $\text{NH}_3 = 0.6$ Torr, $\text{N}_2 = 100$ Torr (case A) or 570 Torr (case C). Based on the measured NH_2 loss (arbitrary scale) in cases A and C, together with the values of k_2 and k_3 , the partial pressure of NH_2 after photolysis was estimated to $1.7\text{E-}4$ Torr.

Figure 5 shows the first order sensitivity coefficients of NH_2 for the conditions of Fig. 4 (cases A and C). Among the gas-phase reactions, only R2 and R3 show up as sensitive. However, at the lower pressure of 100 Torr, also loss of NH_2 at the reactor surface contributes to the decay.

Figure 5: Sensitivity coefficients for prediction of NH_2 for the conditions of Fig. 4; cases A (100 Torr) and C(570Torr).

The chemical kinetic model was then used to interpret the data from Cheskis and Sarsikov

where O₂ was added. Little information on the product branching fraction can be obtained from these data. Among the three important channels,

only R1a and R1b are detectable by monitoring the NH₂ decay. The occurrence of the H₂NO channel (R1c) would go undetected, due to rapid regeneration of NH₂ by NH₃ + OH. Furthermore, the modeling predictions are not very sensitive to the assumed product ratio between channels R1a and R1b. The products of these two channels are largely inert towards NH₂, even though the HNO + NH₂ reaction (R7) may constitute a minor consumption channel if channel R1b is active.

While experimental results are inconclusive, the theoretical study of Xiang et al.³⁵ indicates that only R1a (triplet surface) and R1c (singlet surface) are major product channels for NH₂ + HO₂. The HNO + H₂O channel (R1b) is also accessible on the singlet surface, but believed to be a minor pathway at most. Based on these results, we assume in the present work that R1a dominates compared to R1b and tentatively set $k_{1b} = 0$. The rate constant k_{1a} was then varied to obtain the best agreement with experiment.

In the following figures, predictions are compared with experimental results assuming $k_{1a} = 1.5(\pm 0.5) \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. It is seen that at the lower pressure of 100 Torr (case B, Fig. 6), the model slightly overpredicts the NH₂ consumption rate. Under these conditions, a value of $k_{1a} = 1.0 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ provides the best fit.

Modeling predictions with a 50% branching fraction between channels R1a and R1b, i.e., $k_{1a} = k_{1b} = 7.5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, yielded the same result as that shown in Fig. 6. Even though the HNO + NH₂ reaction (R7) now consumes a minor fraction of the NH₂, it is not sufficient to impact the predictions.

Figure 6: Comparison of experimental data for case B¹⁸ and modeling predictions for flash photolysis of NH_3/O_2 at 295 K. Symbols denote experimental data, while lines denote modeling predictions. The solid lines show calculations with the model ($k_{1b} = k_{1c} = 0$), while dashed lines show the effect of varying $k_{1a} \pm 5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}$. Starting conditions: $\text{NH}_2 = 1.7 \times 10^{-4} \text{ Torr}$ (est), $\text{NH}_3 = 0.6 \text{ Torr}$, $\text{O}_2 = 100 \text{ Torr}$.

Figure 7 shows results obtained at 570 Torr. In these experiments, the O_2 partial pressure was varied from 1 to 570 Torr. In this range, the O_2 concentration has only little impact on the NH_2 consumption rate. The modeling predictions are in very good agreement with the measurements, supporting a value of $k_{1a} = 1.5(\pm 0.5) \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (with $k_{1b} = 0$).

Figure 8 shows a sensitivity analysis with respect to NH_2 for the conditions of Figs. 6 and 7. For the 100 Torr O_2 condition (case B), the predicted NH_2 consumption rate is sensitive mainly to $\text{NH}_2 + \text{HO}_2$ (R1) and $\text{NH}_2 + \text{NH}_2 (+\text{M})$ (R3), and to a smaller extent to $\text{HO}_2 + \text{HO}_2$. In addition, loss of NH_2 at the reactor wall plays a role at this pressure. At the higher pressure of 570 Torr (case D and F), diffusive loss of radicals is negligible. The corresponding sensitivity analysis shows that at 570 Torr pressure and 100-570 Torr of O_2 , predictions are not sensitive to reactions other than $\text{NH}_2 + \text{HO}_2$ (R1) and $\text{NH}_2 + \text{NH}_2 (+\text{M})$ (R3). For the 1 Torr O_2 condition (case D), the $\text{H} + \text{HO}_2$ reaction competes with $\text{H} + \text{O}_2 (+\text{M})$ and both steps show up with small sensitivity coefficients.

Based on our reinterpretation of the FP data from Cheskis and Sarsikov, we conclude that the $\text{NH}_2 + \text{HO}_2$ reaction is faster than previously acknowledged, with $k_{1a} (+k_{1b}) =$

Figure 7: Comparison of experimental data for cases D, E and F¹⁸ with modeling predictions for flash photolysis of $\text{NH}_3/\text{O}_2/\text{N}_2$ at 295 K. Symbols denote experimental data, while lines denote modeling predictions. The solid lines show calculations with the model ($k_{1b} = k_{1c} = 0$), while dashed lines show the effect of varying $k_{1a} \pm 5\text{E}13 \text{ cm}^3 \text{ mol}^{-1} \text{ s}$ for case F. Starting conditions: $\text{NH}_2 = 1.7\text{E}-4 \text{ Torr}$ (est), $\text{NH}_3 = 0.6 \text{ Torr}$, $\text{O}_2/\text{N}_2 = 1/569 \text{ Torr}$ (case D), $100/470 \text{ Torr}$ (case E) or $570/0 \text{ Torr}$ (case F).

Figure 8: Sensitivity coefficients for prediction of NH_2 for cases B (100 Torr O_2), D (1 Torr O_2 , 569 Torr N_2) and F (570 Torr O_2).

$(1.5 \pm 0.5) \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. To support this conclusion, modeling predictions were compared with the data from Lozovsky et al.,²⁸ who photolyzed 7.6 Torr NH_3 in O_2 at varying pressure. Figure 9 compares data obtained at 113, 216, 400 and 596 Torr with modeling predictions. The results reported for 400 Torr show that experiments were very repeatable. Lozovsky et al. reported most of the data in terms of pseudo-first order parameters, i.e., as $\text{NH}_2(\text{relative}) = -Y_0 \exp(-k_{\text{eff}}t)$, where Y_0 and k_{eff} were fitting parameters. This implies a smoothing of the data. However, for the 596 Torr case, the original data are shown.

For the present purposes, the reported NH_2 level was renormalized by an estimated

Figure 9: Comparison of experimental data for flash photolysis at 295 K of 7.6 Torr NH_3 in O_2 at varying pressure²⁸ with modeling predictions ($k_{1b} = k_{1c} = 0$). Symbols denote experimental data, while lines denote modeling predictions. Starting conditions: $\text{NH}_2 = 4\text{E-}7$ Torr (est), $\text{NH}_3 = 7.6$ Torr, $\text{O}_2 = 105\text{-}588$ Torr.

starting pressure $P_{\text{NH}_2,0}$, assumed to be the same for all experiments, since the flash energy (50 J) was constant for the selected data sets. The value of $P_{\text{NH}_2,0}$ that provided the best overall agreement was $4 \cdot 10^{-7}$ Torr, in reasonable agreement with the estimate of 1×10^{-6} Torr by Lozovsky et al. In accordance with the lower flash energy, this value is significantly smaller than that of the Cheskis and Sarsikov experiments. As discussed by Lozovsky et al., due to the lower starting concentrations of NH_2 and H , the second order reactions are inhibited and diffusive losses play a larger role.

The comparison in Fig. 9 shows a very good agreement between measured and calculated values of NH_2 at shorter reaction times, where the bimolecular steps R1 and R3 dominate. The consumption rate is underpredicted at reaction times beyond 0.2 s. The reason for this discrepancy is not clear. At longer times, when NH_2 reaches very low concentrations, the diffusive losses become a more competitive path for NH_2 at the lower pressures, but at pressures of 400 Torr and above the impact should be small.

Figure 10 shows a sensitivity analysis for the conditions of Fig. 9. The key reactions are the same as for the conditions of the Cheskis and Sarsikov experiments, but the relative importance of reactions is different due to the very low reactant concentrations. As expected, the heterogeneous losses of NH_2 and HO_2 are most important at the lower pressures, while the $\text{NH}_2 + \text{NH}_2 (+\text{M})$ reaction has the highest sensitivity coefficients at the high pressures. However, at all investigated pressures, the predictions are most sensitive to the $\text{NH}_2 + \text{HO}_2$ reaction.

Figure 10: Sensitivity coefficients for prediction of NH_2 for the conditions of the FP experiments of Lozovsky et al.²⁸ (Fig. 9), conducted at 295 K of 7.6 Torr NH_3 in varying pressures of O_2 (105-588 Torr.)

Table 4 compares the present value for k_{1a} ($+k_{1b}$) with data reported in literature. Our value for k_{1a} is in excellent agreement with the recent theoretical study by Stagni et al.,¹³ but it is a factor of 3-10 faster than earlier interpretations of the flash photolysis experiments.^{18,20,22,23} This difference is due to the more accurate values of k_2 and k_3 used in the present analysis.

The present value of k_{1a} is limited to room temperature. The theoretical work of Stagni et al.¹³ indicates that the reaction has a significant temperature dependence, with k_{1a} decreasing more than a factor of five as the temperature increases towards 2000 K. However, there are no experimental data available at elevated temperature and more work is desirable to confirm the results of Stagni et al.

Table 4: Room temperature rate constants for $\text{NH}_2 + \text{HO}_2$, obtained experimentally or theoretically.

Reaction	Temperature K	Rate constant $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	Technique	Reference
R1a + R1b	298	1.5×10^{13}	FP	Cheskis and Sarsikov ¹⁸
R1a + R1b	298	3.7×10^{13}	FP	Lozovskii et al. ²⁰
R1a + R1b	298	3.1×10^{13}	FP	Kurasawa and Lesclaux (see ²²)
R1a + R1b	300	4.5×10^{13}	FP	Sarsikov et al. ²³
R1a	298	1.5×10^{14}	Theory	Stagni et al. ¹³
R1a (+ R1b)	295	$1.5(\pm 0.5) \times 10^{14}$	FP	pw

Product measurements and perturbation studies

A number of flash photolysis studies were conducted to provide information on the product composition for $\text{NH}_2 + \text{HO}_2$, either by direct measurements of products or by perturbation by adding species to the starting mixture. These results are discussed below.

Addition of CH_4

Cheskis and Sarsikov¹⁸ conducted a few experiments at 570 Torr, where part of the O_2 was replaced with 15 Torr of CH_4 . The presence of CH_4 introduces an alternative consumption path for OH and thereby a measure of the importance of reaction R1c. They did not observe any impact experimentally on the NH_2 consumption rate of introducing CH_4 and took it as an indication that $\text{H}_2\text{NO} + \text{OH}$ (R1c) could at most be a minor product channel for $\text{NH}_2 + \text{HO}_2$.

In Fig. 11 the impact of the $\text{H}_2\text{NO} + \text{OH}$ product channel (R1c) is investigated computationally for the conditions of the Cheskis and Sarsikov experiment. Predictions are made for values of k_{1c} of 2.5×10^{13} and $5.0 \times 10^{13} \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1}$, with and without the presence of CH_4 . In the absence of CH_4 , addition of R1c does not affect the initial consumption rate of NH_2 , but NH_2 is seen to level out at a higher concentration than predicted when R1c is omitted.

The predictions in Fig. 11 confirm that addition of CH_4 cancels out the effect of R1c,

Figure 11: Comparison of modeling predictions for flash photolysis of NH_3/O_2 at 295 K: effect of including the $\text{H}_2\text{NO} + \text{OH}$ channel (R1c) and of adding 15 Torr of CH_4 to the mixture. Starting conditions: $\text{NH}_2 = 1.7\text{E-}4$ Torr (est), $\text{NH}_3 = 0.6$ Torr; $\text{O}_2/\text{CH}_4 = 570/0$ Torr 560/15 Torr.

because methane, present in much larger amount than NH_3 , scavenges the OH radicals and prevents reformation of NH_2 . Formation of methylamine from recombination of CH_3 with NH_2 is not significant, according to the model. Based on the calculations, we support the finding of Cheskis and Sarsikov that $\text{H}_2\text{NO} + \text{OH}$ is not the dominating channel, with a rate constant most likely less than $5.0 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Based on the data in Fig. 11, a reasonable estimate is $k_{1c} = 2.5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, in good agreement with the value of $k_{1c} = 1.6 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ chosen by Stagni et al.¹³ in their modeling study.

Detection of HNO

Dalby⁷⁰ observed formation of HNO in the flash photolysis of NH_3/NO mixtures, but report that HNO was not detected when NH_3/O_2 mixtures were photolyzed. Later, Nadtochenko et al.¹⁹ using a more sensitive technique (ICLAS - IntraCavity Laser Absorption Spectroscopy) detected HNO during pulse photolysis of an NH_3/O_2 mixture. The extinction coefficient for HNO turns out to be more than two orders of magnitude lower than that of NH_2 .⁷¹

Figure 12 compares the experimental decay profiles of NH_2 and HNO from Lozovsky et al.²¹ with modeling predictions. Under their conditions, the starting concentrations of NH_2

and H after photolysis were comparatively high, and NH_2 was consumed within 0.1 ms. An assumption of a starting pressure of NH_2 of 0.002 Torr leads to a reasonable prediction of the NH_2 decay profile.

Figure 12: Comparison of experimental data²¹ and modeling predictions for NH_2 and HNO in flash photolysis of NH_3/N_2 at 295 K. Symbols denote experimental data, while lines denote modeling predictions. Starting conditions: $\text{NH}_3 = 60$ Torr, $\text{O}_2 = 185$ Torr. Based on the measured NH_2 loss rate (arbitrary scale), the partial pressures of NH_2 and H after photolysis was estimated to 0.002 Torr.

The measured HNO profile shows a fast initial formation, followed by a largely constant level beyond 0.1 ms. If k_{1b} is assumed to be zero (solid curve in Fig. 12), HNO is formed

only by H-abstraction from H_2NO . This is a slow process and the predicted HNO level is two orders of magnitude below that of H_2NO . Furthermore, HNO is slowly increasing beyond 0.1 ms, in disagreement with observations. A small value of $k_{1b} = 2.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, an order of magnitude below the estimated value of k_{1c} , is sufficient to bring the predictions (dashed curve) in accordance with the experiments. Use of a faster rate constant for R1b provides an HNO profile (relative), which cannot be distinguished from the dashed curve in Fig. 12. Based on the results of Lozovsky et al.,²¹ we conclude that the R1b channel is active. However, theoretical work³⁵ indicates that it is only a minor channel.

Detection of NO and N_2O

Detection of nitrogen oxides (NO , NO_2 , and N_2O) has been reported for a number of photooxidation studies of NH_3 in the presence of O_2 . Husain and Norrish¹⁵ and Jayanty et al.¹⁶ detected NO as a major product, with minor amounts of N_2O , while Tyndall et al. observed N_2O as the major product, with NO and NO_2 below the detection limit.²⁷ Tyndall et al. were able to explain both their own data and the data of Jayanty et al. in terms of the same reaction mechanism and found the data sets to be compatible.

In the present work, we take a look at selected results from Tyndall et al.²⁷ Their results were obtained for slow photolysis of small amounts of NH_3 in O_2/N_2 mixtures at 296 K, a total pressure of 620 Torr, and reaction times of 75-150 min. The photolysis rate of NH_3 was estimated from experiments where NO was added.

Tyndall et al. rationalized the N_2O formation in terms of the following sequence:

Based on the detected N_2O yield, they concluded that $\text{NH}_3 + \text{O}_2$ (R1a) was the major product channel for $\text{NH}_2 + \text{HO}_2$, with either $\text{HNO} + \text{H}_2\text{O}$ (R1b) or $\text{H}_2\text{NO} + \text{OH}$ (R1c) contributing about 20%.

The interpretation by Tyndall et al. is flawed, because more recent work has shown that the N_2O yield from $\text{NH}_2 + \text{NO}_2$ (R6a) is only about 20%,⁹ rather than the 100% assumed in their analysis; the major products are now known to be $\text{H}_2\text{NO} + \text{OH}$ (R6b). We have re-interpreted their work in terms of the present mechanism, focusing on the experiment with NH_3 in 1 Torr of O_2 . Comparisons between the observed N_2O formation and calculated values are shown in Table 5.

Table 5: Comparison of modeling predictions with a selected flash photolysis experiment from Tyndall et al.²⁷ Starting conditions: $\text{NH}_3 = 0.095$ Torr, $\text{O}_2 = 1$ Torr, $\text{N}_2 = 619$ Torr; temperature 296 K, reaction time 120 min. Following Tyndall et al., the following photolysis rates were used in the model: $\text{NH}_3 \rightarrow \text{NH}_2 + \text{H}$ ($1.1\text{E-}6 \text{ s}^{-1}$), $\text{HNO} \rightarrow \text{H} + \text{NO}$ ($2\text{E-}3 \text{ s}^{-1}$), $\text{N}_2\text{H}_4 \rightarrow \text{N}_2\text{H}_3 + \text{H}$ ($1.0\text{E-}4 \text{ s}^{-1}$), $\text{NO}_2 \rightarrow \text{NO} + \text{O}$ ($2\text{E-}3 \text{ s}^{-1}$), and $\text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}$ ($1.0\text{E-}4 \text{ s}^{-1}$). In addition, the effect of H_2NO photolysis to $\text{HNO} + \text{H}$ was investigated, with a rate similar to that of HNO ($2\text{E-}3 \text{ s}^{-1}$).

	k_{1c} ($\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	H_2NO photolysis rate (s^{-1})	N_2O (ppm)
Experiment			0.35
Model	2.5E13	2E-3	0.28
Model	2.5E13	0	0.16
Model	0	2E-3	0.08
Model	0	0	0.03

Under the conditions of this experiment, very little reaction is predicted if the $\text{NH}_2 + \text{HO}_2$ reaction yields only $\text{NH}_3 + \text{O}_2$ (R1a). This is in line with the findings of Tyndall et al. and support the importance of either R1b or R1c. Formation of NO through H_2NO (R1c) or HNO (R1b) is required to form observable products. The system is quite complex kinetically, however, and it is not possible from the data to achieve accurate estimates of

the branching fractions for R1. Figure 14 shows a sensitivity analysis for the formation of N_2O . Once NO and NO_2 are formed, R1 is no longer the main consumption pathway for NH_2 , and in addition to $\text{NH}_2 + \text{HO}_2$, predictions are sensitive to a number of other NH_2 reactions. Furthermore, the photolysis rates for NH_3 , HNO , and NO_2 show up as sensitive. A particular concern here is the possible photolysis of H_2NO , which is formed through R1c and R6b in considerably larger amounts than predicted by Tyndall et al.

Figure 13: Sensitivity coefficients for prediction of N_2O for the conditions of Table tab:TC.

In conclusion, the experiments of Tyndall et al. support a product channel for $\text{NH}_2 + \text{HO}_2$ leading eventually to NO . Based on the theoretical work discussed above, the most likely candidate is R1c. However, it is not possible to quantify the rate constant for this channel due to the complexity of the system and uncertainty about photolysis rates of intermediate products.

Conclusions

Published flash photolysis experiments of $\text{NH}_3/\text{O}_2/\text{N}_2$ mixtures were re-interpreted using an updated detailed reaction mechanism. For the key reactions $\text{NH}_2 + \text{H} (+\text{M}) \rightarrow \text{NH}_3 (+\text{M})$ (R2), and $\text{NH}_2 + \text{NH}_2 (+\text{M}) \rightarrow \text{N}_2\text{H}_4 (+\text{M})$ (R3), we relied on the recent direct measurements of Altinay and Macdonald³⁹ for N_2 as collision partner. Relative third body collision efficiencies compared to N_2 were calculated for O_2 and NH_3 , as well as other selected

molecules, with results in good agreement with available literature values. Based on reported NH_2 decay rates in flash photolysis of $\text{NH}_3/\text{O}_2/\text{N}_2$ by Cheskis and Sarsikov,¹⁸ a rate constant for $\text{NH}_2 + \text{HO}_2 \rightarrow \text{NH}_3 + \text{O}_2$ (R1a) of $k_{1a} = 1.5(\pm 0.5) \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 295 K was derived. This value is higher than earlier experimental determinations from the flash photolysis experiments, but in good agreement with the recent theoretical work of Stagni et al.¹³ Analysis of the product measurements of N_2O by Tyndall et al.²⁷ support their finding that $\text{NH}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{NO} + \text{OH}$ (R1c) is competing with R1a, but the perturbation experiments by Cheskis and Sarisikov¹⁸ with addition of CH_4 indicate an upper limit for this channel of $5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The HNO profiles measured by Lozovsky et al.²¹ indicate that HNO is a direct product of the $\text{NH}_2 + \text{HO}_2$ reaction (R1b), but based on theoretical work R1b is expected to be a minor channel. Based on our analysis, we estimate $k_{1c} = 2.5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{1b} = 2.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 295 K, with significant uncertainty margins. High level theoretical work on the $\text{NH}_2 + \text{HO}_2$ reaction is desirable to predict the temperature dependence of the overall rate constant and the branching fraction between the product channels.

Acknowledgements

P.G. would like to acknowledge funding from Orient’s Fund and Innovation Fund Denmark. S.G. gratefully acknowledges the support of Israel Science Foundation, ISF (grant No. 2187/19). A.W.J. was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences through Argonne National Laboratory. Argonne is a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC, under Contract Number DE-AC02-06CH11357. We gratefully acknowledge computing resources provided by Bebop, a high-performance computing cluster operated by the Laboratory Computing Resource Center at Argonne National Laboratory.

Supporting Information

The Supporting Information includes the thermodynamic data file and the reaction mechanism used for the modeling.

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Figure 14: TOC graphic.