## The Reaction of NH<sub>2</sub> with O

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The reaction between atomic oxygen and the amidogen radical, NH<sub>2</sub>, has been studied at 295 K by infrared kinetic spectroscopy. The NH<sub>2</sub> radical was produced by excimer laser photolysis of NH<sub>3</sub> at 193 nm and reacted with O atoms produced by a microwave discharge of dilute  $O_2/He$  mixtures. IR transient absorptions of NH<sub>2</sub>, and of NH and OH radicals formed as reaction intermediates, were monitored using a tunable infrared color-center laser. The room-temperature rate constant for the overall reaction was measured as  $(6.5 \pm 1.3) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The minor channel leading to NH + OH was observed but accounted for at most about 8% of the NH<sub>2</sub> reacting. The rate constant for the reaction NH + O was determined from fitting the NH time profile to be  $(6.6 \pm 1.5) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

## Introduction

The reaction between  $NH_2$  and atomic oxygen is of importance in the oxidation of ammonia and hydrazine<sup>1-4</sup> and in the combustion of N-containing fuels.<sup>4.5</sup> In such systems, competitive reactions of  $NH_2$  determine the relative yields of the final nitrogencontaining products  $N_2$  and NO.

At room temperature, the following reaction channels for the titled reaction

$$NH_2 + O \rightarrow products$$
 (1)

are energetically possible:6

 $NH_2 + O \rightarrow HNO + H; \quad \Delta H = -124 \text{ kJ/mol}$  (2)

$$\rightarrow$$
 NH + OH;  $\Delta H = -43 \text{ kJ/mol}$  (3)

 $\rightarrow$  H<sub>2</sub>O + N;  $\Delta H = -211 \text{ kJ/mol}$  (4)

$$\rightarrow$$
 NO + H<sub>2</sub>;  $\Delta H = -351 \text{ kJ/mol}$  (5)

Channels 4 and 5 can be excluded on the basis of previous mass spectroscopic investigations which have shown that no  $H_2O$  is formed, and that NO and  $H_2$  are not formed simultaneously.<sup>6,7</sup>

Two previous studies of the kinetics of the reaction have been reported. In the first of these,<sup>8</sup> NH<sub>2</sub> was created in the presence of excess atomic oxygen by flash photolysis of ammonia. Oxygen atoms were generated continuously by microwave discharge and were injected into a fast flow reactor that formed an integral part of the flash photolysis apparatus. Kinetic absorption spectroscopy was used to monitor NH<sub>2</sub>. At 298 K, the rate constant for overall removal of NH<sub>2</sub> was measured as  $3.5 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The products of the reaction were not identified.

The second study<sup>6</sup> was performed using a fast discharge flow system that employed several detection techniques. The  $NH_2$  radical was produced by the fast reaction<sup>9</sup>

$$F + NH_3 \rightarrow HF + NH_2 \tag{6}$$

and was monitored by laser magnetic resonance (LMR). This technique also served for detection of OH and NH radicals. Atomic oxygen, which was always present in excess, was followed

by ESR, and laser-induced fluorescence (LIF) was used to monitor HNO produced by the reaction of NH<sub>2</sub> with O. In this second study, the overall rate constant for removal of NH<sub>2</sub> was determined to be  $(8.8 \pm 2.5) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, a value 25 times greater than that measured in the earlier study. Reaction channels 2 and 3 were determined separately in this study by Dransfeld *et al.*<sup>6</sup> with the rate constant for the most important channel, channel 2, measured as  $(7.6 \pm 1.9) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> while reaction 3 was determined to be 7 times slower, with a rate coefficient of  $(1.2 \pm 0.4) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

In the present investigation, the reaction was studied by infrared kinetic spectroscopy in a fast flow system. The  $NH_2$  radical was produced by 193-nm excimer laser photolysis of  $NH_3$ , and atomic oxygen was formed by microwave discharge. All observations were made near the center of the reactor at times too short to allow reactants formed by the laser photolysis to diffuse to and react with the walls.

## **Experimental Section**

The infrared kinetic spectrometer which has been described previously<sup>10</sup> was modified so as to incorporate the absorption cell into a fast discharge flow system. The experimental arrangement is shown schematically in Figure 1. Oxygen atoms were generated by microwave discharge of dilute mixtures (~1%) of  $O_2$  in He and injected into the main flow stream at a point approximately halfway along the multipass infrared absorption cell (54-mm i.d.). The flow system was operated at pressures of 2.2-3.4 Torr and at linear flow speeds of about 600 cm/s. In order to reduce atom recombination, the walls of the flow tube were poisoned with a coating of phosphoric acid. Absolute concentrations of atomic oxygen were determined by using the well-known NO<sub>2</sub> titration,<sup>11</sup> and relative concentrations along the flow tube were estimated by observing the afterglow produced when a small amount of NO<sub>2</sub> was added to the tube. A correction of 20% was made to the measured atomic oxygen concentrations to account for the decay that occurred between the titration point and the center of the reaction zone.

A standard multipass ("White") infrared absorption cell with a mirror spacing of 2 m was used in this study. The UV photolysis beam entered the cell through a window just below the "D" mirrors and rose as it traversed the cell until it struck a beam block just above the row of infrared spots on the notched mirror. The ArF excimer photolysis beam and the color-center infrared probe beams

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Figure 1. Experimental apparatus.

overlapped over the approximately 30-cm section of the cell that is shaded in Figure 1.

The  $NH_2$  radical was produced by 193-nm photolysis of ammonia, which was introduced into the flow cell immediately upstream from the overlap region. The photolysis laser was operated with a pulse energy of approximately 50 mJ, and at a repetition rate of 10 Hz. With linear flow rates of 600 cm/s, the volume in the overlap region was completely replaced between excimer laser pulses.

The concentration of NH<sub>2</sub> was monitored by measuring the absorption of the  $6_{4,2} \leftarrow 5_{3,3}$  line of  $\nu_1 \operatorname{at}^{12} 3428.8077 \operatorname{cm}^{-1}$ . The OH radical was detected by using the P(4.5)1+ line at <sup>13</sup> 3407.989 cm<sup>-1</sup>, and the NH radical was observed by using the J = 4,  $N = 3 \leftarrow J = 3$ , N = 2 line at <sup>14</sup> 3215.614 cm<sup>-1</sup>. To observe the time behavior of the various radicals, the laser was locked to the peak of an absorption line, and the transient signal was averaged over 200–800 excimer flashes. The response time of the detectoramplifier-data acquisition system has been determined to be somewhat less than 1  $\mu$ s by observation of the red F<sub>2</sub> excimer laser line.

Reaction mixtures typically contained 3-38 mTorr of NH<sub>3</sub>, 15-32 mTorr of O<sub>2</sub>, 0.4 Torr of CH<sub>4</sub>, and 2.3-3.5 Torr of He. The presence of helium ensured the rapid attainment of thermal equilibrium, and also moderated the temperature rise that occurred following photolysis and reaction. Methane was added in order to achieve rapid relaxation of the vibrationally excited NH<sub>2</sub> formed in the reaction photolysis. All gases were obtained commercially and, with the exception of NO<sub>2</sub>, were used without further purification. The specified purities of these commercial gases were as follows: He (99.995%), O<sub>2</sub> (99.9995%), and NH<sub>3</sub> (99.99%). The NO<sub>2</sub>, of stated purity 99\%, was passed through a drying tower containing anhydrous calcium sulfate. The most likely impurities other than water, namely  $N_2$  and NO (or  $N_2O_3$ ), do not interfere with the O-atom titration. Flow rates of He,  $O_2$ , and NO<sub>2</sub> were measured using calibrated MKS flow meters. Other flow rates were determined using rotameters. Partial pressures for individual components were calculated from the relative flow rate and the measured total pressure.

#### Results

The title reaction was investigated under pseudo-first-order conditions with atomic oxygen present in excess relative to  $NH_2$ . In the absence of O atoms and methane, absorption-time traces for  $NH_2$  exhibited a slow rise time which could be characterized



Figure 2. Experimental NH<sub>2</sub>, NH, and OH time profiles expressed as absolute column densities. Total pressure = 2.7 Torr; [O] =  $7.5 \times 10^{14}$  atoms/cc.

by a growth constant that varied between 20 and 50  $\mu$ s, depending upon the concentration of NH<sub>3</sub> in the photolysis mixture. It was discovered that the rise time could be significantly reduced by adding methane which, on the time scale of these experiments, is unreactive toward H, O, and OH.<sup>15</sup> It was found that addition of 400 mTorr of methane resulted in an NH<sub>2</sub> signal that reached 90% of its maximum value in 12  $\mu$ s. Thereafter all experiments were performed in the presence of 400 mTorr of methane. When atomic oxygen was added to the reaction mixture, NH<sub>2</sub> absorptiontime traces similar to that shown in Figure 2 were obtained. These traces were found to exhibit single exponential decays. Exponential decay first-order rate constants,  $k_{eff}$ , were estimated by fitting all points between 80% and 20% of the maximum signal size, weighting each point according to its magnitude.

Typically, NH<sub>2</sub> observations were made over time intervals ranging between 100 and 250  $\mu$ s, and effective first-order rate constants that varied between 10 000 and 50 000 s<sup>-1</sup> were measured. For each NH<sub>2</sub> time profile, an adjusted rate constant,  $k_{adj}$ , was calculated by subtracting from  $k_{eff}$  the value of the NH<sub>2</sub> decay constant measured in a similar experiment but performed in the absence of atomic oxygen. Normally, this adjustment produced little change because, in the absence of O, the major loss mechanism for NH<sub>2</sub> was diffusion out of the probe beam with  $k_{eff}$  approximately equal to 500 s<sup>-1</sup>.

Figure 3 shows a plot of  $k_{adj}$  vs [O]. Most of the experiments included in this plot were performed using a constant partial pressure of NH<sub>3</sub>, although two or three experiments, which produced similar rate constants, were performed with [NH<sub>3</sub>] reduced by a factor of 4. The initial concentration of NH<sub>2</sub> in the majority of the experiments could be estimated from the measured absorption coefficient, the published peak absorption cross



Figure 3. Adjusted decay constants for  $NH_2$  time profiles plotted against [O] to yield  $NH_2 + O$  overall rate constant. The data represented by open circles were obtained at a total pressure of 3.3 Torr, and the others were obtained at 2.26 Torr.

section<sup>16</sup> for NH<sub>2</sub>, and a knowledge of the cell geometry as approximately  $1 \times 10^{14}$  radicals cm<sup>-3</sup>. Unfortunately, the complex nature of the overlap between the UV beam and the multipassed infrared beam precluded this value from being estimated with an uncertainty better than a factor of 2. Thus the excess of O over NH<sub>2</sub> ranged from about a factor of 3 in the worst case to about a factor of 8 in the best case. The two high, discordant points were obtained with a higher total pressure of 3.3 vs 2.3 Torr, but also on a different occasion. The second-order rate constant,  $k_{ov}$ , for the overall reaction of NH<sub>2</sub> with O was determined from the slope of Figure 3 by using a linear least-squares fit as  $(6.5 \pm 1.3)$  $\times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The principal source of the scatter in the points which gives the ±20% error estimate above most likely arises from the measurement of [O].

The  $NH_2 + O$  rate constant obtained by this pseudo-firstorder method cannot be affected by hot spots across the excimer beam or longitudinal variations in excimer intensity caused by absorption of the excimer down the tube because the decay rate depends only on the O atom concentration not the local  $NH_2$ concentration.

A typical OH absorption-time profile is also shown in Figure 2. As can be seen, OH reaches its maximum concentration well after  $NH_2$  has significantly decayed, thereby suggesting that OH is formed primarily as a product of a secondary reaction, not as a primary product of the reaction between  $NH_2$  and O. No signals at the known transition frequencies of OH in its first excited vibrational state could be observed, thus ruling out the possibility that OH is being produced as a primary product in a vibrationally excited state that then relaxes. The OH concentration always peaked at a reaction time that was at least 4 times longer than that of the  $NH_2$  exponential decay time constant, i.e. after  $NH_2$  had decayed to less than 1% of its initial value. After reaching this peak value, the OH curve decayed approximately exponentially with a decay time considerably longer than that exhibited by the  $NH_2$  radical.

In these experiments with excess atomic oxygen, the maximum OH concentration was little affected by  $[O]_0$ , the initial concentration of atomic oxygen, but was roughly linearly dependent on  $[NH_3]_0$ . In a separate series of experiments, the absolute value of the peak OH concentration was determined to be approximately 10% of that of the initial NH<sub>2</sub> concentration using published values for their infrared absorption cross sections.<sup>16,17</sup>

As a result of multiphoton photolysis of  $NH_3$ , transient infrared absorption by NH in its electronic ground state was observed even in the absence of O atoms, but the NH signal became significantly stronger in the presence of O atoms. In order to isolate the NH produced by reaction, the NH signal arising from multiphoton photolysis was reduced to 15% of the overall NH signal by decreasing the photolysis energy. The resulting absorption-time profile for NH in the presence of oxygen is shown in Figure 2.

In order to convert the measured transient infrared absorption into column density as shown in Figure 2, the absorption cross

TABLE 1: Kinetic Scheme Used To Model NH Signal

Mod	Modeling Limits				
		$k (10^{-11} \text{ cm}^3 \text{ s}^{-1})$			
reaction rates	ref	fit 1	fit 2		
2. $NH_2 + O \rightarrow HNO + H$	this work	6.0	5.9		
3. $NH_2 + O \rightarrow NH + OH$	this work	0.5	0.6		
7. NH + O $\rightarrow$ products	this work	6.0	7.2		
8. $NH_2 + NH \rightarrow products$	6	13	13		
9. HNO + O $\rightarrow$ OH + NO	6	0.5	1.5		
10. OH + O $\rightarrow$ H + O <sub>2</sub>	24	3.8	3.8		
11. HNO + H $\rightarrow$ H <sub>2</sub> + NO		13	13		
Initial C	Concentrations				

	C (10+	<sup>14</sup> cm <sup>-3</sup> )
substance	fit 1	fit 2
0	7.5	7.5
NH <sub>2</sub>	0.5	1.0
н	0.5	1.0
NH	0	0

section for NH was calculated for a Doppler broadened line from the transition dipole moment<sup>18</sup> to be  $3.79 \times 10^{-17}$  cm<sup>2</sup>. At the relatively low pressures of this experiment, pressure broadening is insignificant compared with the measurement uncertainty. No correction for <sup>14</sup>N and <sup>1</sup>H hyperfine structure is required, as the six strong components of the NH hyperfine structure have a total range of only 8 MHz and therefore have an insignificant effect on the peak absorption cross section.

As can be seen, NH reaches its maximum concentration early in the reaction before  $NH_2$  had decayed to 50% of its initial concentration, indicating that NH is a primary reaction product. It should be noted, however, that when additional CH<sub>4</sub> relaxant was added to the system, the intensity of the NH signal decreased. We hypothesize that some NH might be produced from the reaction of O with the excited species  $NH_2^*$  intercepted before relaxation by CH<sub>4</sub>.

In order to estimate the rate of the reaction NH + O and the branching of NH<sub>2</sub> + O into the NH + OH channel, we have modeled the NH and NH<sub>2</sub> profiles simultaneously using the computer programs CHEMKIN<sup>19</sup> and SENKIN<sup>20</sup> and the reaction scheme given in Table 1. Assumptions of the modeling are that the CH<sub>4</sub> relaxant is effective enough to eliminate additional NH from the possible NH<sub>2</sub>\* channel just discussed and that the two-photon produced NH contribution is negligible.

If the O atom concentration were truly in very large excess (>100:1), the NH + O rate and the NH<sub>2</sub> + O branching would depend only upon this assumption and the effects of experimental errors. For the data of Figure 2, we estimate that the NH<sub>2</sub> concentration is between 0.5 and  $1.0 \times 10^{14}$  molecules/cm<sup>3</sup> compared with a corrected measured [O] of  $7.5 \times 10^{14}$  molecules/cm<sup>3</sup>. Thus, the results are somewhat affected by depletion of O by the NH<sub>2</sub> + O reaction and by the depletion of O by the HNO product of the NH<sub>2</sub> + O reaction with O via eq 9.

$$HNO + O \rightarrow OH + NO$$
 (9)

Therefore we believe the principal uncertainties in this modeling are the initial concentration of  $NH_2$  and uncertainty in the rate of the reaction HNO + O, which was estimated previously<sup>6</sup> from a similar modeling.

Two modeling fits are presented in Table 1 representing the extremes of behavior caused by these uncertainties. Similar values of the rate constant for NH + O and the branching of the NH<sub>2</sub> + O reaction into the channel NH + O were obtained from these two fits of the NH<sub>2</sub> and NH profiles. When the lower value ( $5 \times 10^{13}$  cm<sup>-3</sup>) of the NH<sub>2</sub> concentration and the lower value of the O + HNO rate constant ( $5 \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup>) are used, the NH + O rate obtained is  $6.0 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and the branching into NH + OH (reaction 3) is 7%. At the upper value



Figure 4. Comparison of the experimental data of Figure 2 with an extreme modeling calculation. Comparison of (a) experiment with (b) fit 1 of Table 1. In order to convert the column densities of Figure 2 to concentrations, a path length of 1000 cm was used. A similar comparison of fit 2 looks identical.

of the NH<sub>2</sub> concentration  $(1 \times 10^{14} \text{ cm}^{-3})$  and the largest estimate for the O + HNO rate  $(1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ , the NH + O rate is  $7.2 \times 10^{-11} \text{ cm}^3$  molecule $^{-1} \text{ s}^{-1}$  and the branching into NH + OH is 9%. Thus our best estimate for the NH + O rate is  $6.6 \times 10^{-11} \text{ cm}^3$  molecule $^{-1} \text{ s}^{-1}$ , and the branching ratio estimate for NH + OH from this approach is 8%. Fit 1 is compared with the experimental data in Figure 4. In this figure, the vertical scale (i.e. infrared pathlength) has been adjusted to match the NH<sub>2</sub> signal and this fixes the NH scale. Fit 2 matched the data similarly.

There are no direct measurements of the NH + O rate constant. Dransfeld *et al.* reported a value of  $8.3 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> in modeling their NH<sub>2</sub> + O reaction system at room temperature.<sup>6</sup> Collision frequency calculations, assuming the only barrier to reaction pathways is the centrifugal barrier as determined by Melius and Binkley,<sup>21</sup> led to a rate constant of  $5.5 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>,<sup>22</sup> From thermochemical data the recommended rate constant is  $1.2 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>,<sup>22</sup> Considering the uncertainties of each method, the rate constant from the present work is in good agreement with both Dransfeld *et al.*<sup>6</sup> and Melius and Binkley. The previous estimate<sup>6</sup> of the branching ratio was about 14%, somewhat higher than the value obtained here by fitting the NH signal.

A maximum value for the contribution to  $k_{ov}$  from channel 3 can also be estimated by determining the amount of OH formed from NH<sub>2</sub> at early reaction times, before significant OH production from secondary sources can occur.

In the presence of excess atomic oxygen, OH is removed almost entirely by the fast reaction:

$$OH + O \rightarrow H + O_2$$
 (10)

If reaction 3 is the *sole* source of OH in this system, and if O is present in sufficient excess (to make reactions 2, 3, and 10 pseudofirst-order), the OH concentration as a function of reaction time is given by eq 11, which can be derived by a simple modification

$$\frac{[OH]}{[NH_2]_0} = [k_3/(k_{ov} - k_{10})] [\exp(-k_{10}[O]t) - \exp(-k_{ov}[O]t)]$$
(11)

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to the standard expression<sup>23</sup> for consecutive first-order processes.



Figure 5. Comparison of OH curve assuming that the NH<sub>2</sub> + O reaction produced 100% OH + NH with experimental OH and NH<sub>2</sub> time profiles. Experimental curves are those from Figure 2. Clearly the experimental OH column density is far lower and peaks at a much later time than would be the case if the NH<sub>2</sub> + O reaction produced only OH and NH. Dividing the calculated OH column density at its maximum value (21 × 10<sup>15</sup> cm<sup>-2</sup> @ 27 µs) by the observed OH column density at the same time (1.5 × 10<sup>15</sup> cm<sup>-2</sup>) gives an upper bound for the contribution of this channel.

Figure 5 shows the OH time profile predicted by eq 11, assuming  $k_3 = k_{ov}$  for the data of Figure 2 and using the reported<sup>24</sup> value of  $k_{10}$  of  $3.8 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. In the calculation of this profile, [NH<sub>2</sub>]<sub>0</sub> was obtained by extrapolating the exponential fit of the NH<sub>2</sub> profile of Figure 4 back to t = 0. As can be seen, the observed OH column density is far lower than the predicted value and peaks at a much later time; this means that  $k_3 \ll k_{ov}$  and that most of the observed OH is not produced by reaction 3.

Whatever contribution reaction 3 makes to the OH signal, it will follow the time profile of eq 11. Note that in eq 11 the time of the maximum OH signal from reaction 3 will depend only upon the rate constants in the exponentials, i.e.  $k_{10}$  and  $k_{ov}$ , and not specifically upon  $k_3$ . Thus an upper limit to the ratio  $k_3/k_{ov}$  can be estimated by dividing the calculated OH column density of Figure 5 at its maximum ( $t = 27 \ \mu$ s) into the observed OH column density at the same time. The result is 0.07. When this was done with three data sets, this ratio ranged from 0.06 to 0.08, averaging to 0.07. Thus we have an independent estimate of the branching into reaction 3 which is in good agreement with that obtained from the NH signal.

### **OH Signal Modeling Efforts**

Given that the reaction  $NH_2 + O$  occurs primarily via reaction 2, the simplest mechanism for the overall reaction that accounts for the observed formation and decay of OH is as follows:

$$NH_2 + O \rightarrow HNO + H$$
 (2)

$$HNO + O \rightarrow OH + NO$$
 (9)

$$OH + O \rightarrow H + O, \tag{10}$$

Since  $k_2$  and  $k_{10}$  are known, we attempted to determine  $k_9$  by modeling the OH concentration time profile using the computer programs CHEMKIN<sup>19</sup> and SENKIN.<sup>20</sup> Unfortunately, it proved impossible to reproduce the experimental profile shape and absolute magnitude using this simple mechanism. Inclusion of the reaction HNO + H allowed us to successfully model the experimental profile for a given experimental stoichiometry. However, no unique set of rate constants for HNO + H and HNO + O could be found that modeled the experimental [OH] profiles obtained when  $[O]_0$  and  $[NH_2]_0$  were varied. Perhaps this result should have been expected: OH is the product of a second reaction, and we are observing it decaying by a third reaction.

We might have had more success modeling the HNO signal instead of the OH signal. However, we would still have complications because HNO is reacting with both H and O as it is being produced. Unfortunately we are not able to monitor HNO transient infrared absorption because no strong IR absorption occurs in the color-center laser region. A more direct approach following the disappearance of HNO in the absence of H atoms will be required to determine  $k_9$ .

## Summary

In this work, the overall rate constant for the reaction of NH<sub>2</sub> with O was measured and found to be  $(6.5 \pm 1.3) \times 10^{-11} \text{ cm}^3$ molecule<sup>-1</sup> s<sup>-1</sup>, which is in fair agreement with the most recent previous study<sup>6</sup> where a value of  $(8.8 \pm 2) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> was obtained. The branching into the channel producing NH + OH was measured and found to be 5-8% as compared with the value of about 14% into this channel reported previously.6 The rate constant for NH + O has been determined by modeling to be  $(6.9 \pm 2) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, which is somewhat less than that from another modeling of experimental data<sup>6</sup> of  $8.3 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and somewhat more than a centrifugal barrier calculation estimate<sup>21</sup> of  $5.5 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

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