Kinetics of the Reactions of NH_2 Radicals with O_3 and O_2

Roger Patrick and David M. Golden*

SRI International, Menlo Park, California 94025 (Received: July 7, 1983)

NH₂ radicals were generated by the photolysis of O₂ in the presence of NH₃ and their subsequent kinetics were directly monitored by laser resonance absorption spectroscopy. Under our experimental conditions, NH₂ + O₃ and NH₂ + NH₂ were competitive reactions. The rate constant for NH₂ + O₃ was found to be $(1.57 \pm 0.51) \times 10^{-11} \exp(-(1151 \pm 123)/T)$ cm³ molecule⁻¹ s⁻¹ in the temperature range 272-348 K while the rate constant for NH₂ + NH₂ was found to be $(1.29 \pm 0.30) \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹ at 298 K and essentially independent of temperature at a pressure of ~200 torr. O₂ was added to the system in an attempt to observe a postulated third-order reaction leading to the formation of NH₂OO. An upper limit of 1.5×10^{-36} cm⁶ molecule⁻² s⁻¹ was set for this process indicating that bonding between NH₂ and O₂ is negligible.

Introduction

 NH_2 radicals are formed in the troposphere by the homogeneous reaction of ammonia and OH radicals and may also be produced in the stratosphere via the direct photolysis of ammonia by solar radiation at wavelengths shorter than 220 nm.

Subsequent reactions of NH_2 in the lower atmosphere include reaction with nitrogen oxides or ozone and might also be expected, by analogy with CH_3 radical reactions, to include a reaction with molecular oxygen

$$NH_2 + O_2 \rightarrow products$$
 (1)

Early indirect studies^{1,2} of reaction 1 suggested that it is very slow. In addition, Lesclaux and Demissy,³ who flash photolyzed ammonia in the presence of 500 torr of O_2 and monitored NH_2 radicals directly by laser absorption spectroscopy, set an upper limit on the rate constant of $(1-3) \times 10^{-18}$ cm³ molecule⁻¹ s⁻¹. However, more recently Hack et al.⁴ have made a systematic study of reaction 1 at low pressures using discharge-flow techniques. They generated NH₂ by the reaction of F atoms produced in a discharge with ammonia and monitored its concentration in the presence of O_2 by laser-induced fluorescence. They found the reaction rate to be slow, but appreciable, with bimolecular rate constants for reaction with O₂ varying linearly with total pressure from 4×10^{-16} cm³ molecule⁻¹ s⁻¹ at 1.5 torr to 2×10^{-15} cm³ molecule⁻¹ s⁻¹ at 16 torr. The rate constants were also found to decrease with increasing temperature. These results were interpreted as indicating the formation of a peroxy radical adduct, NH_2OO , by a reaction whose rate constant was at its third-order limit at the low pressures used in their study. The third-order rate constant at 295 K was reported as 3.5×10^{-33} cm⁶ molecule⁻² s⁻¹.

The slowness of this reaction rate suggests that the NH_2-O_2 bond is quite weak (50–60 kJ mol⁻¹), and thus redissociation of the adduct would be fast. Thus, under conditions of high total pressure and high O_2 concentrations such as those used by Lesclaux and Demissy, an equilibrium would be set up rapidly, and there would be no apparent reaction with O_2 on a millisecond timescale.

In this study NH_2 radicals were generated in the presence of a relatively high pressure (~160 torr) of an inert nitrogen diluent and low pressures (5–15 torr) of oxygen in an attempt to observe this postulated equilibrium directly.

In addition rate constants were determined for the reactions

$$NH_2 + O_3 \rightarrow products$$
 (2)

$$NH_2 + NH_2 \rightarrow N_2H_4 \tag{3}$$

Experimental Section

A block diagram of the apparatus is given as Figure 1. NH₂ radicals were generated by the photolysis of ozone in the presence of ammonia with KrF excimer laser radiation (Lambda-Physik EMG 500) at 248 nm. Ozone concentrations, which were determined in the reference absorption cell ($\sigma(O_3)$ at 2537 Å = 1.15 $\times 10^{-17}$ cm² molecule⁻¹),⁵ were typically in the range 5 $\times 10^{13}$ -5 $\times 10^{14}$ molecule cm⁻³ and ammonia concentrations were $\sim 10^{18}$ molecule cm⁻³. The reactants were mixed in a flow system along with ~ 120 torr of N₂ diluent immediately prior to entry into the photolysis cell in order to minimize any dark reaction between NH₃ and O₃⁶ Ozone was prepared in a low-frequency electric discharge from O₂ with a commercial ozonizer (Wellsbach Corp.) and stored on silica gel cooled to 195 K. It was pumped for several hours before use in order to remove residual O2. Commercial N2 (Matheson 99.998%), NH₃ (Matheson 99.99%, anhydrous), and O_2 (Matheson 99.993%) were used without further purification. Flow rates, which were determined with calibrated rotameters (Matheson), were in the range \sim 2.6 sLm of N₂ and \sim 650 sccm of NH₃. Total pressures in the system was monitored by a capacitance manometer (MKS Baratron, 0-1000 torr).

Under these conditions, the following sequence of reactions is anticipated:

$$O_3 \xrightarrow{h\nu} O_2 + O(^1D)$$
 (4)

 $\Phi = 0.85$ (ref 7)

$$O(^{1}D) + NH_{3} \rightarrow NH_{2} + OH$$
 (5)

 $k = (2.5 \pm 0.5) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 5)}$

$$OH + NH_3 \rightarrow NH_2 + H_2O \tag{6}$$

 $k = (1.64 \pm 0.16) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (\text{ref } 9)$

Thus, each ozone molecule photolyzed leads to the production of two NH_2 radicals and no other radical products are formed. This method has the advantage over direct NH_3 photolysis in that no H atoms are produced. In the presence of O_2 , H atoms would be converted to HO_2 radicals which are believed to react rapidly with NH_2 radicals¹ and would therefore complicate subsequent chemistry.

It was necessary to keep O_3 concentrations quite low in this system to ensure that absorption of KrF radiation in the photolysis cell was sufficiently uniform. In addition, a telescope arrangement of lenses was used to expand the beam of the excimer laser such that only the central, homogeneous portion was used.

Detection of NH_2 radicals was achieved via resonant absorption of CW-laser radiation. An Ar⁺ ion laser (Lexel Corp. 95-4) was used to pump a CW-dye laser (Coherent Inc., CR 599-21) which

S. G. Cheskis and O. M. Sarkisov, *Chem. Phys. Lett.*, **62**, 72 (1979).
 P. B. Pagsberg, J. Eriksen, and H. C. Christensen, *J. Phys. Chem.*, **83**, 433 (1976).

⁽³⁾ R. Lesclaux and M. Demissy, Nouv. J. Chim., 1, 443 (1977).
(4) W. Hack, O. Horie, and H. G. Wagner, J. Phys. Chem., 86, 765 (1982).

⁽⁵⁾ A. G. Hearn, Proc. Phys. Soc., 78, 932 (1961).

⁽⁶⁾ K. J. Olszyna and J. Heicklen, Adv. Chem. Ser., No. 113, 191 (1972).



Figure 1. Block diagram of laser flash photolysis/laser resonance absorption apparatus.

was operated in the single-frequency mode. This laser was tuned to the strong absorption in the NH₂ spectrum corresponding to the 3_{03} - 3_{13} rotational transition in the (0,9,0) band at 5978.895 Å.¹⁰ The mode structure of the laser output was monitored with a 5-GHz spectrum analyzer (Tropel), and the wavelength determined with a wavemeter reference to a He–Ne laser.¹¹ The width of the dye-laser output was nominally 1 MHz which is substantially narrower than the NH₂ absorption line (Doppler broadening ~ 0.024 Å).

The length of the photolysis cell was 49.7 cm and this was effectively increased to enhance the sensitivity of the system by using a pair of confocal mirrors (CVI Laser Corp.) with 0.5-m radius of curvature to produce a resonant multipass cell.¹² The mirrors were coated to reflect radiation around 600 nm but still transmit KrF radiation at 248 nm (transmittance = 0.71). For the experiments reported here, the number of passes used varied from 2 to 24 giving an effective pathlength of 0.99 to 11.9 m.

Temperature control in the reaction vessel was achieved by passing heated or cooled ethylene glycol from a constant temperature bath (Neslab LT-50, Haake) through an external tubing jacket surrounding each of the cells. Temperatures, in the jacket, were monitored with conventional thermometers once the system was equilibrated.

The emergent probe beam from the photolysis cell was detected by a photodiode (EG&G SGD-040-L) which had a rise time of 3 ns and a bandwith of 26 MHz. The signal was amplified (Tektronix AM 502) and recorded with a transient recorder (Biomation 805) operated in pretrigger mode. Both the transient recorder and the excimer laser were triggered simultaneously by a pulse generator (Hewlett Packard 3311A). From the transient recorder, the digitized signal was passed to a signal averager (Princeton Applied Research, 4202) where up to 2500 traces were

- (8) J. A. Davidson, H. I. Schiff, G. E. Streit, J. R. McAfee, A. L. Schneltekopf, and C. J. Howard, J. Chem. Phys., 67, 5021 (1977).
 (9) R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., J. Chem. Phys., 64, 3237
- (9) R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., J. Chem. Phys., 64, 5257 (1976).
 (10) K. Dressler and D. A. Ramsay, *Phil. Trans. R. Soc. London, Ser. A*,
- (11) J. Altmann, R. Baumgart, and C. Weitkamp, *Appl. Opt.*, **20**, 995
- (1981). (1981). (1981).
- (12) F. V. Kowalski, R. T. Hawkins, and A. L. Shalow, J. Opt. Soc. Am., 66, 9 (1976).



Figure 2. Typical NH₂ absorption profile from photolysis of NH₃/O₃ mixtures at 248 nm.



Figure 3. First-order rate constant as a function of O₃ concentration.

accumulated in order to obtain adequate signal-to-noise ratios. Data analysis and final storage was carried out with an on-line minicomputer (Digital Equipment LSI 11/02) with floppy disk storage.

Data Analysis

A typical NH₂ absorption trace, recorded in the absence of O₂, is given in Figure 2. In these experiments, initial NH₂ absorptions varied from 0.5 to 5.0% which, when combined with the extinction coefficient derived in the following section, corresponded to radical densities of 3×10^{12} - 3×10^{13} molecule cm⁻³.

Under these conditions, the disappearance of NH_2 was found to be mixed order and the following processes were assumed to be occurring:

$$NH_2 + O_3 \rightarrow products$$
 (2)

$$NH_2 + NH_2 \rightarrow N_2H_4 \tag{3}$$

The rate of loss of NH_2 is then given by

$$-d[NH_2]/dt = k_1[O_3][NH_2] + 2k_3[NH_2]^2$$
(7)

Since $[O_3] \ge 10[NH_2]$, the first term corresponds to a pseudofirst-order loss process for NH₂.

If we assume that Beer's law holds, the time dependence of the absorption signal may be shown to be given by^{13} .

$$\Delta I(t)/I_0 = 1 - \exp\{[-(1/A + B/C) \exp(Ct) + B/C]^{-1}\}$$
(8)

where $\Delta I(t)$ is the change in the transmitted light intensity at time t, I_0 is the initial light intensity, A is the absorption at t = 0, $B = 2k_3/\sigma l$ where σ is the extinction coefficient and l the effective pathlength, and C is $k_2[O_3]$.

⁽⁷⁾ S. T. Aminoto, A. P. Force, R. G. Gulotty, and J. R. Wiesenfeld, J. Chem. Phys., 71, 3640 (1979).

⁽¹³⁾ J. M. Tulloch, M. T. MacPherson, C. A. Morgan, and M. J. Pilling, J. Phys. Chem., 86, 3812 (1982).

TABLE I: Rate Constants, k_2 , as a Function of Temperature



Figure 4. Arrhenius plot of rate constant k_2 : (---) data of Hack et al.¹⁷; (---) data of Kurasawa and Lesclaux.¹⁶

The experimental absorption profiles were fitted to eq 8 by using nonlinear regression as described by Bevington¹⁴ with A, B, and C treated as adjustable parameters. Trial runs using simulated mixed-order data with added noise indicated that this procedure was capable of extracting all three parameters very reliably. Upon analysis of the experimental data, it was found the procedure converged on a particular parameter set when more than 400-600 points were included in the fit.

Results

Determination of k_2 . Experiments were conducted at 298 K in the absence of O_2 with O_3 concentrations varying from 5.5 \times 10^{13} to 5.5 × 10^{14} molecule cm⁻³. The absorption profiles were fitted to eq 8 as described in the previous section, and the firstorder rate constant was found to be linearly dependent on [O₃] as shown in Figure 3. This finding indicates that the first-order component of the NH₂ loss can indeed be accounted for by reaction 2 occurring under pseudo-first-order conditions. The slope of the line in Figure 3 thus gives the second-order rate constant for reaction 2 at 298 K. Similar experiments were conducted at 272, 320, and 348 K, and these results are also included in Figure 3. The rate constants, obtained as a function of temperature, are given in Table I and illustrated in an Arrhenius plot in Figure 4. All uncertainties in this work correspond to $\pm 1 \sigma$.

The best fit to the Arrhenius form of the temperature dependence is given by $k_2 = (1.57 \pm 0.51) \times 10^{-11} \exp\{-(1151 \pm 0.51)\}$ 123)/T. This corresponds to a positive activation energy of 9.6 \pm 1.0 kJ mol⁻¹ for reaction 2.

Extinction Coefficient Determination. Assuming that eq 4–6 correctly describe the mechanism, the rate of production of \mathbf{NH}_2 can be simply related to the rate of photolysis of ozone:

$$\frac{d[NH_2]}{dt} = -2\Phi \frac{d[O_3]}{dt} = 2\Phi \frac{f}{V}([O_3]_i - [O_3]_{ss})$$
(9)

where f is the total flow rate, V is the volume of the cell, Φ is the quantum yield for $O(^{1}D)$ production from O_{3} photolysis and $[O_{3}]_{i}$ and $[O_3)_{ss}$ are the initial and steady-state concentrations of O_3 , respectively. The rate of production of NH₂ is also related to the maximum absorption, A, obtained from the decay traces and the laser repetition rate, R:

Sciences", McGraw-Hill, New York, 1969.

$$\frac{\mathrm{d}[\mathrm{NH}_2]}{\mathrm{d}t} = \frac{AR}{\sigma_{\mathrm{NH}_2}l} \tag{10}$$

TABLE II: NH, Extinction Coefficients and Rate Constants for NH, Recombination

T/K	$\frac{10^{-5}(k_3/\sigma)}{\text{cm s}^{-1}}$	$10^{17}\sigma/cm^2$ molecule ⁻¹	$10^{11}k_{3}/\text{cm}^{3}$ molecule ⁻¹ s ⁻¹	<i>p</i> /torr
272	7.89 ± 1.27	1.34 ± 0.27	1.06 ± 0.27	213.5
298	7.68 ± 1.07	1.68 ± 0.31	1.29 ± 0.30	169.0
320	8.45 ± 1.37	1.77 ± 0.36	1.50 ± 0.39	220.0
348	7.81 ± 1.06	1.60 ± 0.41	1.25 ± 0.36	219.0

where $\sigma_{\rm NH_2}$ is the extinction coefficient and l is the effective pathlength. Hence

$$\sigma_{\rm NH_2} = \frac{RVA}{2\Phi fl} ([O_3]_i - [O_3]_{\rm ss})^{-1}$$
(11)

Both the steady-state and initial ozone concentrations were monitored for each of the experiments and A was obtained from the fits to eq 7. $\sigma_{\rm NH_2}$ was obtained from slope of the line obtained by plotting A vs. $([O_3]_i - [O_3]_{ss})$ and the corresponding values are given in Table II. The quoted errors in σ_{NH_2} correspond to $\pm 1\sigma$ in the slopes of the plots. It can be seen that there was no appreciable variation in $\sigma_{\rm NH_2}$ over the temperature range used in this study. However, it should be stressed that the uncertainties in $\sigma_{\rm NH_2}$ are comparatively large, and the experimental temperature range was not great so that a small temperature dependence might not be apparent.

Determination of k_3 . A detailed investigation of the pressure and temperature dependence of the rate constant for NH₂ recombination was not carried out in this study. However, it is useful to consider the values given by fits to the experimental data in order to verify that eq 8 is a reasonable description of the NH₂ chemistry occurring in this system in the absence of O_2 .

The parameter B obtained from fits to eq 8 is equal to $2k_3/\sigma l$ and so, since the extinction coefficients are known, absolute rate constants may be obtained at each of the four temperatures used in this study. Values of k_3/σ and k_3 are given in Table II.

The value of k_3 at 298 K and 169 torr agrees well with that reported by Van Khe et al.¹⁵ Based on their data the rate constant is in the falloff region under these conditions with $k/k_{\infty} \simeq 0.5$.

Effect of Added O_2 . A series of experiments was conducted at a total pressure of 228.6-243.2 torr $([N_2]/[NH_3] = 4.0, [O_3]$ = 3.5×10^{14} molecule cm⁻³) with O₂ pressures ranging from 0 to 14.6 torr. Under such conditions any reaction between NH₂ and O₂ would be manifest as an increase in the first-order component of the absorption profile as the O_2 pressure increased. In fact no appreciable change was observed ($\pm 6\%$) in k_2 , k_3 , or A_{max} and this leads to an upper limit on the termolecular rate constant of $\leq 1.5 \times 10^{-36} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$.

It was not practical to add large pressures of O₂ to this system in order to confirm or reduce the upper limit reported by Lesclaux and Demissy for the rate constant for the bimolecular reaction between NH_2 and O_2 . Under such conditions the $O(^1D)$ produced by ozone photolysis would be scavenged by O2 to re-form O3 rather than generating NH₂ by reaction with NH₃ unless large pressures of NH₃ were added also. The apparatus was not designed to handle pressures much in excess of 1 atm.

Discussion

 $NH_2 + O_3$. The temperature dependence of reaction 2 has been reported in two previous works. Kurasawa and Lesclaux¹⁶ photolyzed ammonia in the presence of ozone and followed the subsequent disappearance of NH2, in real time, using laser-induced fluorescence (LIF) detection. They reported $k_2 = 6.3 \times 10^{-14} \text{ cm}^3$ molecule⁻¹ s⁻¹ at 298 K and $k_2 = 4.2 \times 10^{-12} \exp(-1258/T) \text{ cm}^3$ molecule⁻¹ s⁻¹ over the range 298-380 K. Hack et al.¹⁷ produced NH₂ by the reaction of F atoms with ammonia in a low-pressure discharge flow system and also followed NH₂ disappearance using

⁽¹⁵⁾ P. V. Khe, J. C. Soulignac, and R. Lesclaux, J. Phys. Chem., 81, 210 (1977).

⁽¹⁶⁾ H. Kurasawa and R. Lesclaux, Chem. Phys. Lett., 72, 437 (1980). (17) W. Hack, O. Horie, and H. G. Wagner, Ber. Bunsenges. Phys. Chem., 85, 72 (1981).

TABLE III: Atom and Radical Reactions with Ozone

reaction ^a	A factor/cm ³ molecule ⁻¹ s ⁻¹
$\begin{array}{c} X + O_3 \rightarrow XO + O_2 \\ XY + O_3 \rightarrow XYO + O_2 \\ NO_2 + O_3 \rightarrow NO + 2O_2 \\ NH_2 + O_3 \rightarrow NH_2O + O_2 \\ CH_3 + O_3 \rightarrow CH_3O + O_2 \end{array}$	$\begin{array}{c} (2.2 \pm 0.8) \times 10^{-11} \\ (2.2 \pm 0.3) \times 10^{-12} \\ 1.2 \times 10^{-13} \\ 1.6 \times 10^{-11} \\ 3.4 \times 10^{-12} \end{array}$

^{*a*} $X = O(^{3}P)$, F, Cl, Br; XY = OH, NO, SO.

LIF. They reported $k_2 = 1.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and $k_2 = (2.0 \pm 0.1) \times 10^{-12} \exp(-710 \pm 48/T)$ over the range 250–358 K. These data are included in Figure 4. In addition, Bulatov et al.¹⁸ reported a value of $1.2 \times 10^{-13} \text{ cm}^3$ molecule⁻¹ s⁻¹ at 298 K.

The rate constant reported by Kurasawa and Lesclaux is almost a factor of 5 smaller at room temperature than ours and the discrepancy increases as the temperature is raised. At least part of this difference may be accounted for by their method of generating NH₂ by direct photolysis of NH₃. The photolytic step also produces H atoms which would be rapidly converted, on a microsecond timescale, to OH radicals by reaction with ozone. Since the NH₃ pressures were quite low, in the range 0.02–0.7 torr, OH radicals would react relatively slowly ($\tau = 0.2-9.4$ ms) (ref 9) to generate more NH₂ radicals on the same timescale as the reaction of NH₂ with O₃. This would in itself reduce the apparent rate constant for reaction 2. In addition, ozone concentrations were determined by increasing pressure changes rather than spectrophotometrically which might lead to an overestimate if any decomposition occurred.

The rate constant reported by Hack et al. is a factor of 1.6 smaller than that reported here for room temperature. This difference may be significant but its origin is not clear since in their experimental system NH_2 radicals were produced cleanly by the reaction $F + NH_3$ and ozone concentrations were monitored spectrophotometrically.

The products of reaction 2 have not, as yet, been identified and no attempt was made to characterize them in this study. The most likely process, by analogy with the reaction of other atoms and radicals with O_3 , seems to be the abstraction of an oxygen atom by NH₂ to form the NH₂O radical.

$$\mathrm{NH}_2 + \mathrm{O}_3 \rightarrow \mathrm{NH}_2\mathrm{O} + \mathrm{O}_2 \qquad \Delta H = -157 \text{ kJ mol}^{-1} \qquad (12)$$

The existence of the NH₂O has not been demonstrated experimentally but its heat of formation may be estimated as follows. Given $\Delta H_{\rm f}(\rm NH_2OH) = -37.6 \text{ kJ mol}^{-1}$, and assuming $D(\rm NH_2O-H) \sim D(\rm CH_3O-H) = 433.5 \text{ kJ mol}^{-1}$, one can predict the heat of formation of NH₂O to be 177.8 kJ mol⁻¹. Thus reaction 12 as written would be quite exothermic.

It is of interest to compare the A factors obtained for reaction 12 with those for the reactions of other species with ozone^{19,20} (Table III).

For atom + ozone reactions, with the exception of $H + O_3$, the A factors are all very close to 2.2×10^{-11} cm³ molecule⁻¹ s⁻¹. This implies that the transition-state structures are insensitive to the nature of X and that they are all quite "tight"; i.e., the bond lengths and frequencies resemble those which would be expected for stable molecules. Similarly, for diatomic + ozone reactions there is little variation in the A factor with all values close to 2.2×10^{-12} cm³ molecule⁻¹ s⁻¹. This is again indicative of a "tight" transition state, with the relative difference in A factors from atomic to diatomic reactants reflecting the additional loss of rotational entropy upon reaction of the latter.

In the case of polyatomic radical + ozone reactions the data are more sparse but there appears to be a wider variation in the

TABLE IV: Molecular Parameters for NH₂OO

ν/cm^{-1}	type	I/amu A²
3200 (2)	N-H stretch	51.5
1100	O-O stretch	10.0
1700	H-N-H bend	41.5
500 (2)	H-N-O bend	
700	N-O-O bend	
free rotation	torsion	

TABLE V: Calculated Rate Parameters for $NH_2 + O_2 \cong NH_2OO$

$\frac{D(\mathrm{NH_2-O_2})}{\mathrm{kJ} \mathrm{mol}^{-1}}$	k_a/cm^6 molecule ⁻² s ⁻¹	$k_{\rm d}/{\rm cm^3}$ molecule ⁻¹ s ⁻¹
50 60	$\frac{3.0 \times 10^{-32}}{6.9 \times 10^{-32}}$	$\begin{array}{c} 4.3 \times 10^{-16} \\ 1.7 \times 10^{-17} \end{array}$

A factors and hence in the corresponding transition-state structures. $HO_2 + O_3$ requires a substantially tighter transition state than the atom or diatomic reactions while the remaining three reactions, especially $NH_2 + O_3$, require quite "loose" transition states. This may indicate that there really is a substantial variation in the transition-state structure for different polyatomic radical and ozone reaction, with loose structures predominating, or that some of the values may be incorrect. In the case of our data for $NH_2 + O_3$, the A factor appears somewhat larger than the mean value. However, it would not be possible to reduce it by more than a factor of 2 and still obtain a reasonable fit to the experimental data.

It has been suggested^{17,18} that NH_2O may itself react with ozone, perhaps regenerating NH_2 via reaction 13a.

$$NH_2O + O_3 \rightarrow NH_2 + 2O_2 \qquad \Delta H = -128.0 \text{ kJ mol}^{-1}$$
(13a)

$$\rightarrow HNO + OH + O_2$$

$$\Delta H = -182.0 \text{ kJ mol}^{-1} (13b)$$

If k_{13a} were fast, then significant deviations from eq 8 should have been observed in our experiments with NH₂ concentrations being higher at long times than expected, especially in the presence of the higher O₃ concentrations. Similarly, if (13b) predominated, the OH radicals produced by this reaction would react rapidly with ammonia, again regenerating NH₂ at long times. Since no significant deviations were apparent this suggests, based on numerical simulations, either that reaction 13 preferentially goes via (13a) with a rate constant of $<5 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ or alternatively that NH₂O is lost by some other process than reaction with O₃.

 $NH_2 + O_2$. In contrast to the results of Hack et al.⁴ no evidence was found for the formation of a NH₂OO peroxy radical.

Troe's²¹ method for calculating low-pressure limiting association and dissociation rate constants may be used to assess the plausibility of the rate constants suggested in ref 4. By analogy with other species, especially CH₃OO, the molecular properties given in Table IV are proposed for a hypothetical NH₂OO species.

The dissociation energy was treated as an adjustable parameter in order to obtain a third-order association rate constant of the required order of magnitude to give agreement with the measurements reported in ref 4. $D(NH_2-O_2)$ was required to be in the range 50-60 kJ mol⁻¹ but with a bond this weak redissociation would be quite rapid (Table V), even at low pressures.

Thus distinct curvature should be apparent in the concentration vs. time plots on the timescale used in ref 4 as equilibrium is approached. This is illustrated by the simulation given in Figure 5. In order to linearize these concentration vs. time plots, some other process is needed that will remove NH₂OO from the system faster than its redissociation to NH₂ and O₂. The dissociation rate constant at 8 torr total pressure is calculated to be $\sim 100 \text{ s}^{-1}$ for a 50 kJ mol⁻¹ bond, and this sets a lower limit on the rate constant for this hypothetical removal process. A homogeneous removal process is ruled out by our experimental finding that there was no reaction between NH₂ and O₂ at high pressures, and the

(21) J. Troe, J. Chem. Phys., 66, 4758 (1977).

⁽¹⁸⁾ V. P. Bulatov, A. A. Buloyan, S. E. Cheskis, M. Z. Kozlines, O. M. Saskisov, and A. I. Trostin, *Chem. Phys. Lett.*, 74, 288 (1980).
(19) W. B. DeMore, R. T. Watson, D. M. Golden, R. F. Hampson, M.

⁽¹⁹⁾ W. B. DeMore, R. T. Watson, D. M. Golden, R. F. Hampson, M. Kuryl, C. J. Howard, M. J. Molina, and A. R. Ravishankara, "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling", JPL Publication No. 82-57, 1982.

⁽²⁰⁾ R. Simonaitis and J. Heicklen, J. Phys. Chem., 79, 298 (1975).



Figure 5. Comparison of calculated data for $NH_2 + O_2 \rightleftharpoons NH_2OO$ with that of Hack et al.⁴

required rate constant would be unusually fast for a heterogeneous wall loss.

It is possible to estimate the heat of formation of NH₂OO and hence $D(NH_2-O_2)$ if it is assumed that $D(NH_2O-O) \sim D(C-H_3O-O) = 236.0 \text{ kJ mol}^{-1}$. $\Delta H_f(NH_2OO)$ is then given by $\Delta H_f(NH_2O) + \Delta H_f(O) - 236.0 = 191.2 \text{ kJ mol}^{-1}$ and $D(NH_2-O_2) = -1.26 \text{ kJ mol}^{-1}$. The uncertainties in this estimate are undoubtedly large ($\pm 20 \text{ kJ mol}^{-1}$) but it does seem to support the contention that the bonding between NH₂ and O₂ is negligible.

This conclusion is supported qualitatively by the calculations of Pouchan and Chaillett²² who found the formation of NH_2O_2 from NH_2 and O_2 to be endothermic by 61 kJ mol⁻¹. However, it is in contrast with the observations of Giguere and Herman²³ who ascribed a long-lived transient absorption formed during the photolysis of KO₃ in liquid ammonia to NH_2O_2 .

It is difficult to account for the difference in the experimental findings in this study and those of ref 4. They generated NH_2 radicals in a way which would be expected to avoid complications due to the presence of other radicals. Indeed, care was taken to look for H and O atoms, which were not observed. The rate constants they measure are, however, very slow as far as flow tube measurements are concerned, as was pointed out by Hack et al.,⁴ and complications due to heterogeneous wall reactions are always a problem under such conditions. In their study, only a halocarbon reactor coating gave reproducible results and in a reactor treated with NaOH/HNO₃ there was no change in the apparent rate of NH₂ loss with added O₂. Fortunately, under the high-pressure conditions of the experiments reported here the possibility of heterogeneous reactions is avoided.

(22) C. Pouchan and M. Chaillet, Chem. Phys. Lett., 90, 310 (1982).
(23) P. A. Giguere and K. Herman, Chem. Phys. Lett., 44, 273 (1976).

The Journal of Physical Chemistry, Vol. 88, No. 3, 1984 495

TABLE VI: Tropospheric Lifetimes for NH₂ Radicals

reactant	concn/molecule cm ³	$\tau(\mathrm{NH_2})/\mathrm{s}$	ref
NO_x (clean air)	2.5 × 10°	20	24
NO_x (polluted air)	$2.5 \times 10^{11} - 2.5 \times 10^{12}$	0.02-0.2	24
0,	$2.9 \times 10^{11} - 2.5 \times 10^{12}$	1.27-11.0	24
O_2	5×10^{18}	< 0.08	

Atmospheric Implications

The major loss processes for NH_2 in the troposphere are expected to be reaction with NO_2 , $NO(NO_x)$, O_3 , and possibly O_2 . The chemical lifetimes with respect to each of these processes are given in Table VI.

Although we can rule out a three-body reaction between NH₂ and O₂, it is difficult to assess the importance of any possible bimolecular reaction since even with the limit of $(2-3) \times 10^{-18}$ cm³ molecule⁻¹ s⁻¹³ it could be important in the nonpolluted atmosphere. Consideration of possible products from this reaction gives some indication of the likely reaction pathway at 300 K:

$$NH_2 + O_2 \rightarrow NH + HO_2$$
 $\Delta H = 194.6 \text{ kJ mol}^{-1}$ (14a)

 \rightarrow NH₂O + O $\Delta H = 234.7 \text{ kJ mol}^{-1}$ (14b)

$$\rightarrow$$
 OH + HNO $\Delta H = -53.6 \text{ kJ mol}^{-1}$ (14c)

The direct abstraction reactions are very endothermic and the corresponding rate constants would be much too slow to be of atmospheric importance. Reaction 14c involves a four-center transition state but the A factor for such a process could be as high as 10^{-12} cm³ molecule⁻¹ s⁻¹ and so a rate constant of 10^{-18} cm³ molecule⁻¹ s⁻¹ would be possible if the activation energy is ≤ 36 kJ mol⁻¹. Experiments which observed NH₂ disappearance in the presence of several atmospheres of O₂ are obviously desirable in order to try to reduce the upper limit rate constant.

From Table VI it can be seen that the reaction of NH_2 with O_3 could be important in the clean troposphere if the reaction with O_2 is unimportant. If NH_2O is the product of this reaction and if NH_2O reacts further with O_3 then the possibility of a catalytic cycle destroying ozone arises:

$$NH_2 + O_3 \rightarrow NH_2O + O_2$$
$$NH_2O + O_3 \rightarrow NH_2 + 2O_2$$
$$2O_3 \rightarrow 3O_2$$

This might be relevant to stratospheric chemistry although the current literature indicates that stratospheric NH_3 concentrations are not known.²⁵

Acknowledgment. The authors are grateful for helpful discussions with many colleagues in the Chemical Kinetics and Molecular Physics departments at SRI International, especially Drs. J. R. Barker, G. P. Smith, and C. Becker and Dr. S. Bittensen of the San Francisco Laser Center. This work was supported by the Department of Energy under Contract No. DE-AC03-78-EV10121 and also in part by the San Francisco Laser Center, an NSF Regional Instrumentation Facility, under NSF Grant No. CHE79-16250 awarded to the University of California at Berkeley in collaboration with Stanford University.

Registry No. NH₂, 13770-40-6; O₂, 7782-44-7; O₃, 10028-15-6.

^{(24) &}quot;Troposphere Passive Remote Sensing", NASA Conference Publication 2237, 1982.

⁽²⁵⁾ D. G. Murcray, J. W. Williams, D. B. Barker, A. Goldman, C. Bradford, and G. Cook, "Proceedings of the WMO Symposium on Geophysical Aspects and Consequences of Changes in the Composition of the Stratosphere", Toronto, 1978, Vol. 61, p 522.