is varied and so contribute to α . The role of α via eqs 3.1 and 3.4 is to correct the rate constant to the value k_s it would have at $E = E^{\circ}_{N}$ (eq 3.5). The value of k_{0} , obtained via eq 3.8, is then to be compared with the theoretical k_0 obtained from eqs 2.2 and 5.1. Alternatively, should one wish to test eq 2.11, the experimental k_0 can be corrected for the work terms by using eq 5.1, and then compared with k_1^{el} and k_2^{el} , as in eq 2.11, each having also been corrected for the work terms.

In the case of the work terms mentioned there may be an advantage to minimizing the electrostatic contribution to them, by (1) using large supporting electrolyte concentrations and (2) using reactants and products with small or zero charge. The increased supporting electrolyte reorganizational contribution to λ will be larger, at larger electrolyte concentrations, but may approximately cancel in a ratio such as $k_0/[k_1^{\rm el}k_2^{\rm el}]^{1/2}$ in eq 2.11. Should it be necessary in other cases to calculate the work terms there is an option of doing so with numerical, e.g., Monte Carlo, or continuum-like (e.g., modified Gouy-Chapman), or still other methods.¹² Which method would be employed, or whether one would be employed at all, would depend both on the experimental conditions and on experimental results on the effect of supporting electrolytes on the rate constants. Some discussion of electrolyte effects on equilibrium properties of interfaces is given in ref 12. The use of a large supporting electrolyte concentration also serves to uncouple the electron transfer across the interface from any ion transfer, which might otherwise have been required to maintain local electrical neutrality.

The various approximations made in obtaining the principal equations, eq 2.11, have been mentioned. It is possible, as has happened in earlier work,⁶ that ratios of rate constants such as 2.11 involve somewhat milder assumptions than those used to derive individual expressions for each rate constant. Nevertheless, some of the assumptions made in deriving, say, 2.2 may be summarized: They include an "ideal" (sharp boundary) interface, a local and linear dielectric continuum theory, spherical reactants, and no specific reactant-solvent or reactant-reactant effects. Use of more refined treatments of these aspects can be expected to lead to more accurate though also to more complicated expressions with more detailed information or parametrization being needed for interpretation of experiments. Such detailed approaches can be considered as complementary to the present first-order type theory, as recent statistical mechanical results for an electron transfer in homogeneous solution have already shown.¹³

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Laser Induced Fluorescence Studies of the Reactions of NH($a^{1}\Delta$) with NO and HCN

W. Hack* and K. Rathmann

Max-Planck-Institut für Strömungsforschung, Bunsenstrasse 10, D-3400 Göttingen, West Germany (Received: October 12, 1989)

The reactions of electronically excited imidogen NH($a^{1}\Delta$) with NO and HCN have been studied at room temperature and low total pressures (20 mbar): $NH(a) + NO \rightarrow$ products (1); $NH(a) + HCN \rightarrow$ products (2). NH(a), produced by laser photolysis of HN₃ at λ_L = 308 nm, was detected directly by laser-induced fluorescence (LIF). Measurements of the rate constants were performed under pseudo-first-order conditions, i.e., $[R] \gg [NH(a)]$, whereby the time resolution resulted from the delay between the photolysis and the probe lasers. The following rate constants were measured at T = 298 K: $k_1 = 1.7 \times 10^{13} \text{ cm}^3/(\text{mol s}); k_2 = 2.1 \times 10^{13} \text{ cm}^3/(\text{mol s}).$ Direct detection of the primary products NH(X), OH(X), NH₂(\tilde{X}), $CH_2(\tilde{a}^{1}A_1)$, and CN(X) was performed by LIF. The contribution of physical quenching of NH(a) to form NH(X) for reactants NO and HCN was found to be 40% and 4%, respectively. In reaction 1 OH and in reaction 2 CN were detected as chemical products.

Introduction

The electronic structure determines the reactivity of any chemical species. An intriguing radical with which to study experimentally the influence of electronic structure on reactivity is the imidogen radical in its five lowest electronic states [NH- $(X^{3}\Sigma^{-}, a^{1}\Delta, b^{1}\Sigma^{+}, c^{1}\Pi, and A^{3}\Pi)$]. The reactions of NH(a) have attracted the experimental and theoretical interest, mainly since it is isoelectronic to $CH_2(\tilde{a})$ and $O({}^1D)$. The excitation energy of NH(a), $\Delta E_{el} = 151$ kJ/mol, lies between the excitation energies of $O(^{1}D)$ (190 kJ/mol) and $CH_{2}(\tilde{a}^{1}A_{1})$ (39 kJ/mol).

HN3 or HNCO laser photolysis provides a suitable NH(a) source.¹ Three different methods to detect NH(a) directly are described in the literature, namely, absorption,² laser-induced fluorescence (LIF),³ and phosphorescence from the forbidden transition NH(a-X),⁴ besides the somewhat more indirect method using the chemiluminescence of $NH_2(A^2A_1)$ formed in the reaction $NH(a) + HN_3 \rightarrow NH_2(\tilde{A}) + N_3$. In this work LIF, by means of the (c-a) transition, was used to detect NH(a) since it is a very sensitive method and simultaneously enables direct detection of NH(X) by the A-X transition formed by physical quenching.

Several reactions of NH(a) have been studied. The quenching by inert gases^{4,5} was found to be significantly slower than quenching of $CH_2(\tilde{a})^6$ due to the small energy gaps between

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 $CH_2(\tilde{a}^1A_1)$ and (\tilde{X}^3B_1) and the resulting singlet-triplet interaction.⁷⁻⁹ Reactions of NH(a) with diatomic molecules H_2 , O_2 , N₂, HCl, CO, and NO have been studied by several authors with different methods.^{5,10-13} For several reactants good agreement is obtained in the recent measurements.^{10,14} Besides O_2 with its triplet ground state all these molecules are singlet states except NO($X^2\Pi$). The unpaired electron in the ² Π state should lead to a higher reactivity of NO compared to the other species, which makes it worthwhile to study its reaction. Moreover, the NH(a) + NO reaction might represent a new access to the interesting $H + N_2O$ system. Therefore, it is of importance to study the primary products of this reaction. The rate of this reaction has been measured previously by following the NH(a) depletion in the presence of NO. The final products in the HN_3/NO photolysis system have been studied by Fueno et al.¹⁵

For some triatomic molecules like H₂O, striking evidence between $CH_2(\tilde{a})$, NH(a), and $O(^1D)$ is found in the reaction mechanism.^{14,16,17} For other tri- and polyatomic molecules N_2O , NO₂, CO₂, NH₃, N₂H₄, HNCO, and HN₃ the rate constants for the NH(a) depletion were measured, whereas only a few of these reactions were studied with respect to the reaction products.

For the reactions of saturated hydrocarbons with NH(a) the rate constants were obtained directly with different methods^{10,11} and indirectly (relative to $NH(a) + HN_3$)^{18,19} and were found to be in good agreement. The reactions proceed as abstraction reactions with significant activation energies (e.g., for $CH_4 E_A$ = 7.8 kJ/mol^{11}). It was predicted²⁰ and confirmed experimentally that NH(a) cycloadds to C-C double bonds in unsaturated hydrocarbons. No activation energy was found for the reaction with C_2H_4 and *cis*-2-butene.¹¹ For the substrate with a triple bond (methylacetylene), also no activation energy was observed.¹¹ Bifunctional molecules with double or triple bonds, such as HCN, have not yet been studied theoretically or experimentally.

The aim of this study was to determine in the reactions

$$NH(a^{1}\Delta) + NO(X^{2}\Pi) \rightarrow NH(X^{3}\Sigma^{-}) + NO$$
 (1a)

$$\rightarrow$$
 products (1b)

the relative contributions of the two channels, the physical quenching and the chemical reaction pathway, and to observe the primary products of reaction 1b. For the substrate HCN, the rate constant of the NH(a) depletion in the reactions

$$NH(a^{1}\Delta) + HCN(\tilde{X}^{1}\Sigma) \rightarrow NH(X^{3}\Sigma^{-}) + HCN$$
 (2a)

as well as the contribution of reactions 2a and 2b and the chemical products of the chemical pathway (2b) were to be determined.

Experimental Section

The experiments were carried out in a quasistatic flash pho-

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tolysis system. The apparatus and procedure for measuring time-resolved laser-induced fluorescence (LIF) have been described previously.16,21

Briefly, NH(a) was generated in the fluorescence cell by photolysis of HN₃ with a XeCl exciplex laser (EMG 101 E, Lambda Physik) at $\lambda = 308$ nm. The flow rate of HN₃ and the other gases was controlled by flow controllers (MKS 256, Tylan FC 280) to provide $\phi = 500-2000 \text{ cm}^3/\text{min}$, a rate fast enough to replenish the gas in the cell between the laser shots. The main product of the HN₃ photolysis is singlet NH in the vibrational ground state.

$$HN_3 + h\nu \rightarrow NH(a,\nu=0) + N_2(X)$$

Excess translational and rotational energy was reduced by collision-deactivation with the inert gas He. The contribution of other primary products like NH(X), NH(c), and NH(A) is below 1%.2.21-23

The probe laser was an exciplex pumped dye laser (EMG 200; Fl 3002, Lambda Physik) which was triggered with a time delay (Δt) after the photolysis laser. A homemade multichannel pulse generator controlled the triggering. The pulse rate was 5 Hz. The signals were detected by a photomultiplier (R 995, Hamamatsu) and stored in a transient digitizer (R 7912 AD, Tektronix). Interpretation of the signals was performed by minicomputer (PDP 11/04, DEC).

Detection of NH(a) was performed by the P₂ line of the NH- $(c^1\pi, v = 0 - a^1\Delta, v = 0)$ transition at $\lambda = 325.8$ nm.²⁴ The primary products NH(X) and OH(X) were excited at $\lambda = 336.1$ nm [Q₁ branch of NH($A^{3}\Pi - X^{3}\Sigma^{-}$)]²⁵ and at $\lambda = 308.16$ nm [P₁(1) line of OH($A^{2}\Sigma^{+}$, $v = 0-X^{2}\Pi$, v = 0)]²⁶ respectively. Reference spectra were consulted for the identification of $CN(X^2\Sigma^+)$, $NH_2(\tilde{X}^2B_1)$, and $CH_2(\tilde{a}^1A_1)$. CN(X) was formed in the reaction F + HCN, F being generated from F_2 in the microwave discharge. The excitation spectrum in the range $\lambda = 386-388$ nm was compared to that of the reaction NH(a) + HCN. The R₄ line at $\lambda = 387.2$ nm of the transition CN(B² Σ^+ , $v = 0-X^2\Sigma^+$, v =0) was taken as the excitation line.²⁷ The reaction $F + NH_3$ was used as the $NH_2(X)$ source. A spectrum was taken in the range $\lambda = 596-598$ nm and employed as a comparative spectrum. The excitation was performed via $\lambda = 597.7$ nm at the P_Q branch of the NH₂[$\bar{A}^2A_1(0,9,0)-\bar{X}^2B_1(0,0,0)$] transition.^{28,29}

A $CH_2(\tilde{a})$ reference spectrum was taken by photolysis of ketene in the presence of He at 248 nm. The excitation at $\lambda = 590.7$ nm [${}^{P}Q_{1,4}$ line of CH₂($\bar{b}{}^{1}B_{1}(0,14,0)$ K = 0-CH₂($\tilde{a}{}^{1}A_{1}$)(0,0,0) K = 1] was used to detect $CH_2(\tilde{a})$.

The pressure in the cell was adjusted by a valve and was measured with pressure heads (MKS 220). The pressure of He was 20 mbar. The HN₃ and reactant flows were adjusted so that the pressures were in the range $p(HN_3) \approx 10^{-3}$ mbar and p(M) $\approx 0.01-0.1$ mbar.

The following substances at the stated purity were used: He, 99.9996%; Xe, 99.99%; NO, 99.85% (all Messer Griesheim). NO was cleaned by freezing out the impurities at T = -56 °C. HN₃ was generated by melting stearic acid [CH₃(CH₂)₁₆COOH] and NaN_3 at T = 140 °C in a vacuum. Impurities were examined by mass spectroscopy and IR absorption and were found to be less than 0.3 mol %. HCN was produced by addition of concentrated H₃PO₄ to KCN at room temperature. The gaseous HCN was trapped in a glass tube at T = -20 °C and dried over phosphorus pentoxide.

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TABLE I: Experimental Conditions for the Determination of the Removal Rate Constants $k_1(R)$ in the Reactions NH(a) + HCN \rightarrow Products

R	p(R), mbar (10 ⁻¹)	no. of runs	p(He), mbar	$p(HN_3),$ mbar (10 ⁻³)	$k(NH_3)[HN_3],$ s ⁻¹ (10 ⁴)	$\Delta t, \mu s$	k(R), cm ³ /(mol s) (10 ¹³)
HCN	0.4-1.8	10	20	4.7	1.4	10-40	2.1

The results are presented in two sections: (i) measurement of the reaction rates and (ii) the reaction mechanisms.

Reaction Rates. The depletion of NH(a) is due to the reaction

$$NH(a) + R \rightarrow products \qquad (i)$$

and collisions with the other gases He and HN, being present in the fluorescence cell. The inert gas He was added in excess, both to effect thermalization of NH(a,J) and to restrict diffusion in the gas cell¹⁶ (diffusion did not influence the measured concentration profiles in the period of time $\Delta t = 5-80 \ \mu s$). NH(a) depletion was not influenced by He, since the rate constant of the reaction

$$NH(a) + He \rightarrow products$$
 (3)

with $k_3 < 6 \times 10^8$ cm³/(mol s)^{12,21} is too small, even at a He pressure of [He] $\leq 10^{-7}$ mol/cm³. The collision-free decay of NH(a) via the forbidden radiative transition

$$NH(a) \xrightarrow{1/\tau_0} NH(X)$$

is with $1/\tau_0 = 0.59 \text{ s}^{-1.30,31}$ too slow to have any effect on the depletion of NH(a). The reaction

$$NH(a) + HN_3 \rightarrow products \tag{4}$$

with $k_4 = 7.3 \times 10^{13} \text{ cm}^3 / (\text{mol s})^{3,11,21,32}$ contributes to the NH(a) depletion and has to be taken into account.

The rate constants of the reactions of NH(a) with the reactants R = NO and HCN

$$NH(a) + R \rightarrow products$$
 (i)

were obtained by taking the NH(a) concentration profiles. The fluorescence intensity was detected as a function of the time delay Δt between the photolysis and probe laser. The excess of R and HN_3 over NH(a) enabled a straightforward interpretation of the experimental data to obtain rate constants at pseudo first order. The NH(a) concentration is given by

$$d[NH(a)]/dt = k_i[R][NH(a)] + k_4[HN_3][NH(a)]$$

= $k_{ex}[NH(a)]$

with

$$k_{\text{ex}} = k_i[\text{R}] + k_4[\text{HN}_3] = \text{constant}$$

The LIF intensities of NH(a), I[NH(a)], were proportional to the concentrations of NH(a). The concentration profiles in semilogarithmic plots $\ln I[NH(a)]$ vs Δt resulted in straight lines with constant HN_3 concentrations. The first-order rate constant k_{ex} was determined from the slope. The experimental conditions for reaction 2 are listed in Table I. The rate constant k_i was determined by the plot of k_{ex} vs [R]. The plot for the reactant HCN is shown in Figure 1. The small intercept of the plot corresponds to the collision-induced removal of NH(a) by HN_3 .

For the reaction

$$NH(a) + HCN \rightarrow products$$
 (2)

the rate constant for the overall NH(a) depletion was determined to be

$$k_2 = (2.1 \pm 0.6) \times 10^{13} \,\mathrm{cm^3/(mol s)}$$

from the slope of the straight line determined from the 11 mea-



Figure 1 Reaction rates for the reaction NH(a) + HCN.

sured points plotted in Figure 1. The error of k_2 was calculated by the maximal difference of the least-squares fit.

The rate constant for the reaction

$$NH(a) + NO \rightarrow products$$
 (1)

was determined from the NH(X) profiles at short reaction times. The rate constant obtained

$$k_1 = (1.7 \pm 0.6) \times 10^{13} \text{ cm}^3/(\text{mol s})$$

is in good agreement with the value obtained directly from the NH(a) depletion $k_1 = 1.9 \times 10^{13} \text{ cm}^3/(\text{mol s})$,¹⁶ indicating that NH(X) is formed in the reaction NH(a) + NO (see Discussion).

Reaction Mechanisms. The rate constant $k_i(\mathbf{R})$ in general consists of the physical quenching k_a and the chemical reaction pathway k_{chem} :

$$NH(a) + R \xrightarrow{\kappa_a} NH(X) + products$$
 (ii)

$$\xrightarrow{\text{reherm}}$$
 products [\neq NH(X)] (iii)

The first step is to determine the branching ratio between these two channels, and the second step is to determine the primary products of the chemical reaction pathway.

Branching Ratio. The primary quenching product NH(X) of the reaction of NH(a) with HCN and NO was followed by LIF, to obtain the branching ratio k_a/k_i . Calibration of [NH(X)] relative to [NH(a)] was performed with the reference system

$$NH(a) + N_2 \rightarrow NH(X) + N_2$$
 (5)

N₂ is a slow quencher with $k_5 = 5.0 \times 10^{10} \text{ cm}^3/(\text{mol s})^{12,21}$ and does not react chemically with NH(a); i.e., $k_{5a}/k_5 = 1.0$. To determine k_{ia} , the LIF intensities of NH(X), obtained in the reaction NH(a) with N₂, were compared with the intensities of NH(X) observed in the reaction of NH(a) with R. The fluorescence intensity of $[NH(X)](\Delta t)$ from the reaction NH(a)

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TABLE II: Experimental Conditions for the Determination of the Branching Ratios of Physical Quenching $k_{1a}(R)/k_1(R)$.

R	p(R), mbar (10 ⁻¹)	[R], mol/cm ³ (10 ⁻⁸)	p(He), mbar	p(HN ₃), mbar (10 ⁻³)	$\Delta t, \mu s$	$ au_0({ m NH}({ m A}))/ au_R({ m NH}({ m A}))^a~(10^{-2})$
N ₂	200	80.0	0.1	4.5-6.4	30	<1.07 ^b
HCN	0.82	0.33				с
NO	0.5	0.2	20	6.4	30	7.34 ^b

 $a \tau_0(NH(A)) =$ collision-free lifetime of NH(A); $\tau_R(NH(A)) =$ lifetime of NH(A) due to quenching by the reactant R. ^bReference 44; given as an upper limit for the quenching rate. Cuenching rate not known.

and

TABLE III: Data for Simulations for the NO/NH(a,X) Reaction System^a

Reactions $k_1 = 1.9 \times 10^{13} \text{ cm}^3/(\text{mol s}) \text{ (ref 21)}$ $NH(a) + NO \rightarrow products$ $k_{1a} = 8.6 \times 10^{12} \text{ cm}^3/(\text{mol s})$ $NH(a) + NO \rightarrow NH(X) + NO$ (this work)b $NH(a) + He \rightarrow NH(X) + He$ $k_3 = 6.0 \times 10^8 \text{ cm}^3/(\text{mol s})$ (refs 12, 21) $k_4 = 7.3 \times 10^{13} \text{ cm}^3/(\text{mol s})$ (refs 3, $NH(a) + N_3 \rightarrow products$ 11, 21, 32) $NH(X) + NO \rightarrow products$ $k_6 = 2.3 \times 10^{13} \text{ cm}^3/(\text{mol s}) \text{ (ref 34)}$ $NH(X) + HN_3 \rightarrow NH_2 + N_3$ $k_7 = 2.1 \times 10^{10} \text{ cm}^3/(\text{mol s})$ (ref $NH_2 + NO \rightarrow H_2O + N_2$ $k_8 = 1.26 \times 10^{13} \text{ cm}^3/(\text{mol s}) \text{ (ref 45)}$ $[\text{He}] = 8.1 \times 10^{-7} \text{ mol/cm}^3, x_{\text{He}} = 9.97 \times 10^{-1}$ $\begin{bmatrix} \text{IPe} \end{bmatrix} = 0.1 \times 10^{-10} \text{ mol/cm}^3, \quad x_{\text{NO}} = 2.6 \times 10^{-3} \\ \begin{bmatrix} \text{IN}_3 \end{bmatrix} = 2.6 \times 10^{-10} \text{ mol/cm}^3, \quad x_{\text{NN}_3} = 3.2 \times 10^{-4} \\ \begin{bmatrix} \text{NH}(a) \end{bmatrix} = 2.3 \times 10^{-14} \text{ mol/cm}^3, \quad x_{\text{NH}(a)} = 2.9 \times 10^{-8}$

^a At p = 20 mbar; T = 298 K. ^b The measured branching ratio k_{1a} - $(NO)/k_1(NO)$ determined in this work.

+ N₂ increased rapidly to its flat maximum at about 20 μ s and then decreased slowly to longer times. For the calibration, the maximum LIF intensities of NH(X) resulting from the reactions $NH(a) + N_2$ and NH(a) + R were determined under identical experimental conditions with respect to gas flows, total pressure, laser intensities, and the delay time as given in Table II. The branching ratio k_{ia}/k_i is obtained directly by the ratio of both signals, if NH(X) does not react with the R and if the fluorescence quantum yield is unaffected by R (see Discussion).

The System NO + NH(a). For the reaction NH(a) + NO abranching ratio k_{1a}/k_1 of 13% would be obtained directly from the measured NH(X) concentration profiles. The fast decrease of the plot I[NH(X)] vs Δt at longer reaction times showed that the consecutive reaction

$$NH(X) + NO \rightarrow products$$
 (6)

could not be neglected. This reaction, with $k_6 = (2.3-2.9) \times 10^{13}$ $cm^3/(mol s)^{11,33,34}$ is faster than the overall reaction NH(a) with NO $(k_1 = 1.7 \times 10^{13} \text{ cm}^3/(\text{mol s}))$. Therefore the branching ratio of 13% as given above has to be corrected due to this fast consecutive reaction. In order to determine the true branching ratio, a simulation program was used³⁵ with all reactions in the system NO/HN₃/He given in Table III. The rate constants and the initial concentrations used are also given in Table III. With these data, calculated concentration profiles [NH(X)] vs Δt were obtained, one of which is shown in Figure 2. The contribution of the formation of NH(X) in the reaction NH(a) + NO could be determined by comparison with the measured profiles. The best fit is given, if the fraction of NH(X) formed in the reaction NH(a)+ NO is chosen to be 40% of the overall reaction. This leads to a physical quenching rate constant of

$$k_{1a} = 7.5 \times 10^{12} \text{ cm}^3/(\text{mol s})$$

OH radicals were detected with LIF when HN_3 ([HN₃]₀ = 5.8 $\times 10^{-10}$ mol/cm³) was photolyzed in the presence of NO ([NO]₀



Figure 2. Calculated and measured NH(X) profiles in the reaction $NH(a) + NO \rightarrow$ products. The sensitivity analysis is given as a separate diagram relative contributions of the following reactions: S, NH(a) + $NO \rightarrow products; \blacksquare, NH(a) + NO \rightarrow NH(X)$ (the other reactions are related to this reaction); \Box , NH(X) + NO \rightarrow products; \Box , NH(a) + He \rightarrow NH(X) + He; \boxtimes , NH(a) + HN₃ \rightarrow NH₂ + N₃ \bullet , measurements with relative errors; -, calculation (see text).

= 9.9 × 10⁻⁹ mol/cm³) at a total pressure of p = 20.7 mbar (p(He) = 20 mbar). No OH was observed in the absence of NO and in the absence of HN₃, respectively.

The amount of OH did not change when N_2 (4 \leq [N₂] \times 10⁻⁷ $mol/cm^3 \le 8$) was added to quench NH(a) to NH(X) in the NO experiment. The measured LIF signal of OH was corrected for the quenching effects of OH (A) by N₂. When Xe was added in the range $0.64 \le [Xe] \times 10^{-8} \text{ mol/cm}^3 \le 2$, no effect was observed except for the quenching of OH(A). The simplest interpretation of these observations is that both reactions

 $NH(a) + NO \rightarrow products$

 \rightarrow OH + N₂

$$NH(X) + NO \rightarrow products$$

 $\rightarrow OH + N_2$

produce nearly the same amount of OH. These experimental results are analyzed in detail in the Discussion section.

The calibration of OH was performed via the reaction NH(a) + $H_2O \rightarrow NH_2$ + OH when the same amount of HN_3 was photolyzed in the presence of H_2O ([H_2O]₀ = 1.8 × 10⁻⁸ mol/cm³) with NO absent. The ratio of the fluorescence signals in the presence of NO $[I_F^{OH}(NO)]$ and the absence of H₂O and vice versa $[I_F^{OH}(H_2O)]$ was found to be $I_F^{OH}(NO)/I_F^{OH}(H_2O) = 0.42 \pm 0.06$. The System HCN + NH(a). For the reactant HCN the

branching ratio k_{2a}/k_2 amounted to $(4 \pm 1)\%$; i.e., the chemical reaction of NH(a) with HCN is the major channel. In the reaction of NH(a) with HCN, CN radicals were observed by LIF as a product, indicating that the reaction pathway

$$NH(a) + HCN \rightarrow CN(X) + NH_2(\tilde{X})$$
 (2b)

is a chemical channel. The proportion of CN was not determined. The other product $NH_2(\tilde{X})$, postulated in reaction 2b, could not, however, be observed directly by LIF.

Since the explanation for the failure to observe $NH_2(\bar{X})$ was assumed to be due to a significant decrease of the LIF detection sensitivity of $NH_2(\tilde{X})$ in the presence of HCN (see Discussion),

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Figure 3. $NH_2(\tilde{A})-(\tilde{X})$ fluorescence intensity as a function of time for two different HCN concentrations. O, [HCN] = 0 mol/cm³; \bullet , [HCN] = 2.7 × 10⁻¹⁰ mol/cm³.



Figure 4. Correlation diagram for NH(a), NH(X) with NO(X).

the detection sensitivity was measured in an independent experiment. $NH_2(\tilde{X})$ was produced in the reaction $F + NH_3 \rightarrow NH_2$ + HF in the presence of HCN. The quenching rate constant of $NH_2(\tilde{A})$ by HCN was measured by taking the time-dependentfluorescence signals of $NH_2(\tilde{A})$. The fluorescence intensity was plotted vs Δt in a semilogarithmic plot, to determine the half-life τ of $NH_2(\tilde{A})$ at various HCN concentrations (see Figure 3). The rate constant is given by

$$k_{\rm a} > 4 \times 10^{14} \, {\rm cm}^3 / ({\rm mol \ s})$$

This result can be compared with the quenching of $NH_2(\bar{A})$ by HCl, which was found to be very rapid, with $k = 2.5 \times 10^{14}$ cm³/(mol s).³² Due to this large quenching rate of $NH_2(\bar{A})$ by HCN, the detection limit of $NH_2(\bar{X})$ in the presence of HCN is reduced ($[NH_2] \gtrsim 10^{-12}$ mol/cm³ at [HCN] = 10⁻⁹ mol/cm³) so that the $NH_2(\bar{X})$ concentration present from the NH(a) + HCN reaction is not large enough to be detected.

 $CH_2(\tilde{a})$ could not be detected by LIF. In view of the experimental conditions the reaction pathway to $CH_2(\tilde{a})$ was less than 5%.

The total removal rate of NH(a) by HCN k_1 (HCN) = 2.1 × 10¹³ cm³/(mol s) includes a quenching rate of k_{1a} (HCN) = 8.4 × 10¹¹ cm³/(mol s); i.e., the main reaction pathway turns out to be a chemical reaction with $k_{chem} = 2.0 \times 10^{13}$ cm³/mol.

Discussion

The Reaction NH(a) + NO. The rate constant of this reaction was found to be $k_1 = 1.7 \times 10^{13} \text{ cm}^3/(\text{mol s})$, which is in

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agreement with earlier determinations.^{5,21} An indirect value for k_1 relative to NH(a) + HN₃ \rightarrow NH₂ + N₃ (4) was determined from the reaction products to be $k_1/k_4 = 0.79 \pm 0.06$ leading to $k_1 = 4.4 \times 10^{13} \text{ cm}^3/(\text{mol s})$, if $k_4 = 5.6 \times 10^{13} \text{ cm}^3/(\text{mol s})^2$ is inserted. This value is higher by a factor of 2.6 than the value determined here directly. The problems due to the reaction mechanism leading to that value are discussed in detail later.

For the mechanism of the reaction, there are, besides the quenching channel

$$NH(a) + NO(X) \rightarrow NH(X) + NO$$
 $\Delta H = -151.0 \text{ kJ/mol}$

the following exothermic chemical product pathways

 $NH(a) + NO(X) \rightarrow N_2 + OH(X)$ $\Delta H = -540.8 \text{ kJ/mol}$ (a)

$$\rightarrow$$
 N₂O + H $\Delta H = -280.1 \text{ kJ/mol}$ (b)

$$\rightarrow$$
 N₂ + OH(A) $\Delta H = -153.2 \text{ kJ/mol}$ (a')

$$\rightarrow$$
 N₂ + H + O $\Delta H = -112.9 \text{ kJ/mol}$ (c)

$$\rightarrow$$
 N₂H + O $\Delta H = -112.9 \text{ kJ/mol}$

$$\rightarrow$$
 HNO + N $\Delta H = -7.3 \text{ kJ/mol}$ (d)

as shown in Figure 4. For the physical quenching pathway the final estimation that 40% of the NH(a) removal is due to quenching cannot be obtained in a straightforward way, since direct measurements of the contribution of the quenching channel via the NH(X) profiles are hindered by the consecutive reaction NH(X) + NO. This reaction is so fast ($k_6 = 2.8 \times 10^{13} \text{ cm}^3/(\text{mol s})$) that the quenching channel cannot be obtained directly from the experimental [NH(X)](Δt) profile but has to be calculated in a computer simulation. A sensitivity analysis is shown in Figure 2.

The chemical pathways contribute 60% of the overall NH(a) depletion. The possible chemical products are listed above. In this study OH(X) radicals were examined directly as a chemical product. From the thermodynamic data OH could also appear in its OH(A) state but no OH emission following the photolysis pulse was observed. The OH was calibrated via the reaction

$$NH(a) + H_2O \rightarrow OH + NH_2$$
(9)

For this reaction it was found that NH(a) is mainly (> 50%) converted into OH.¹⁴

In other experiments the NH(a) was converted to NH(X) by N_2 or Xe. In these experiments the same amount of OH was observed by LIF, if the quenching of the laser-excited OH(A) is taken into account; i.e., using the quenching rate constants for OH(A) + N_2 as given in ref 36, the OH concentration seems to be nearly unaffected by N_2 addition.

OH is not formed if HN_3 or NO is absent; thus direct photolysis products or photolysis of impurities can be excluded. A singlephoton photolysis of NO at $\lambda = 308$ nm via an allowed transition is not possible. The reaction

$$HN_3 + NO \rightarrow OH + 2N_2 \tag{10}$$

with all molecules in the ground state is exothermic, but in the dark no OH was observed. However, it cannot be excluded that reaction 10 is photoinitiated in a complicated way. Experiments to quench NH(a) and react NH(X) in competition with the reactions $\{NH(a), NH(X)\} + NO$ are in progress. The obvious explanation of the observation that the concentration of OH does not change with addition of N₂ or Xe is that NH(a) and NH(X) lead in the reactions have nearly the same amount of OH. Since both reactions have nearly the same rate, there is no way to discriminate from the OH profile between these two OH sources.

The mechanism of the reaction NH(a) + NO in the gas phase was recently studied by Fueno et al.,¹⁵ who photolyzed HN_3 at

 $\lambda = 254$ nm for 0.5-4 h at room temperature, in the presence of a controlled amount of NO. Mass spectrometric analyses of the final products of mixtures of 1.3-9.3 mbar of HN₃, 4-53 mbar of NO, and 0-266 mbar of SF₆ show that N_2O and H_2O have been formed. The yield of N_2O , $\phi(N_2O)$, defined as the amount of N₂O formed per number of absorbed photons was found to be $0.2 \le \phi(N_2O) \le 0.67$ depending on the amount of NO present. In the absence of NO neither N₂O nor H₂O was observed. The reaction

$$NH(a) + NO \rightarrow N_2O + H$$
 (b)

is determined to be the major pathway $k_b/(k_a + k_b + k_c) = 0.70$. In the mechanism discussed in ref 15 the only NH(a)-consuming reactions are NH(a) + NO and NH(a) + HN₃ \rightarrow NH₂ + N₃ (4). The only N_2O -producing reaction is assumed to be NH(a)+ NO. From the reaction of NH(a) with ethane and propane the authors conclude that the physical quenching of NH(a) to NH(X) is negligible.

In the system used by those authors there are, however, further reactions that produce N₂O. The reaction

$$N_3 + NO \rightarrow N_2O + N_2 \tag{11}$$

which leads to N₂O as reaction product, is fast, k(295 K) = 7.2 \times 10¹¹ cm³/(mol s),³⁷ and can compete with the other main N_3 -depletion reaction, $N_3 + HN_3$ (12). Since the quenching channel is not negligible, reactions of NH(X) as

$$NH(X) + HN_3 \rightarrow NH_2 + N_3 \tag{13}$$

have to be taken into consideration, because the formation of N_3 radicals¹⁹ with an estimated rate constant of $k_{13}(300 \text{ K}) = 2.1$ $\times 10^{10}$ cm³/(mol s)¹⁸ further lead to the production of N₂O. On the other hand, N₂O might be produced directly in the fast reaction $[k(300 \text{ K}) = 3.5 \times 10^{13} \text{ cm}^3/(\text{mol s})]^{33}$

$$NH(X) + NO \rightarrow N_2O + H$$
 (6)

as studied theoretically by Melius and Binkley.³⁸

Clearly these problems make it complicated to determine the channel distribution from the analysis of the final product N_2O .

Theoretical investigations for the reaction $\{NH(a), NH(X)\}$ + NO were made by Melius and Binkley³⁸ and by Fueno et al.¹⁵ The results are summarized in the correlation diagram given in Figure 4. The deactivation channel via the lower lying ${}^{2}A'$ state of HNNO is possible only if the planar symmetry is broken; otherwise the NH(X) + NO correlates only with the higher lying ²A" state. The activation barrier along the reaction coordinate via a cis-configurated [HNNO] adduct to form N_2 + OH is not significantly higher ($\Delta E = 13 \text{ kJ/mol}$) than the barrier for the $N_2O + H$ products.

It can be concluded that the reaction

$$NH(a) + NO \rightarrow products$$
 (1)

is fast $(k_1 = 1.7 \times 10^{13} \text{ cm}^3/(\text{mol s}))$. The physical quenching contributes 40% $(k_q = 6.8 \times 10^{12} \text{ cm}^3/(\text{mol s}))$. The chemical reaction is the main pathway whereby OH is a significant primary product. The formation of N₂O can occur as a reaction product.

The reactions of the isoelectronic species $O(^1D)$ and $CH_2(\tilde{a})$ with NO have not yet been studied very extensively. NO is known to be an efficient quencher of $O(^{1}D)$ atoms with a rate of k(298)K) = $2.4 \times 10^{13} \text{ cm}^3/(\text{mol s})$.³⁹ The energy-transfer quenching channel

$$O(^{1}D) + NO \rightarrow NO^{*} + O(^{3}P)$$

dominates the reactive channel

$$O(^{1}D) + NO \rightarrow N + O_{2}$$

by a factor of $10^3-10^{4.40}$ This is understandable since the O(¹D) + NO(X) correlates with N(2 D) + O₂(X) as the lowest product states, which, however, are endothermic.⁴¹ For $N(^{4}S) + O_{2}(X)$ and NO(X) + O(³P), in both cases a nonadiabatic A'-A'' transition is required.

The removal of CH₂(\tilde{a}) by NO is with $k(295 \text{ K}) = 9.6 \times 10^{13}$ also extremely rapid.⁶

The Reaction NH(a) + HCN. The reaction of NH(a) with HCN is a fast process $(k_2 = 2.1 \times 10^{13} \text{ cm}^3/(\text{mol s}))$ but is considerably slower than the addition of NH(a) to the triple bond in $CH_3 - C \equiv C - H$, for which a room temperature rate constant of $k(NH(a) + methylacetylene) = 8.4 \times 10^{13} \text{ cm}^3/(\text{mol s})$ is observed.¹¹ For this reaction an activation energy $E_A \simeq 0$ is observed. Taking the same A factor as for the reaction NH(a)+ C_3H_4 , an activation energy of $E_A = 4 \text{ kJ/mol}$ results for reaction

The reaction of imidogen radicals with HCN leads mainly $(\geq 96\%)$ to different chemical products. The following reaction channels are available from the energetic point of view:

$$\begin{split} \mathrm{NH}(\mathrm{a}) &+ \mathrm{HCN}(\mathrm{X}^{1}\Sigma^{+}) \rightarrow (\mathrm{NH}_{2}\mathrm{CN})^{*} \\ &\rightarrow \mathrm{CH}_{2}(\tilde{\mathrm{a}}^{1}\mathrm{A}_{1}) + \mathrm{N}_{2}(\tilde{\mathrm{X}}^{1}\Sigma_{\mathrm{g}}^{+}) \qquad \Delta H_{\mathrm{R}} = -235.4 \text{ kJ/mol} \\ &\rightarrow \mathrm{NH}(\mathrm{X}) + \mathrm{HCN}(\tilde{\mathrm{X}}) \qquad \Delta H_{\mathrm{R}} = -151.0 \text{ kJ/mol} \\ &\rightarrow \mathrm{NH}_{2}(\tilde{\mathrm{X}}^{2}\mathrm{B}_{1}) + \mathrm{CN}(\mathrm{X}^{2}\Sigma^{+}) \qquad \Delta H_{\mathrm{R}} = -57.1 \text{ kJ/mol} \end{split}$$

The chemical product that was detected directly by LIF was $CN(X^2\Sigma^+)$. The corresponding product $NH_2(\bar{X})$ was not detected by LIF due to the fast quenching of $NH_2(\overline{A})$ by HCN. The reaction channel to $CH_2(\tilde{a})$ can be neglected. The exothermic reaction to the triplet carbone $CH_2(\bar{X}^3B_1)$ and $N_2(X^1\Sigma_g^+)$, is spin-forbidden, and therefore an electronic-adiabatic reaction pathway is not available. Also the formation of NCN in its $X^3\Sigma_g$ electronic ground state and $H_2(X^1\Sigma_g^+)$ ($\Delta H_R = -232.4 \text{ kJ/mol}$) requires a nonadiabatic transition to the triplet surfaces, whereas for the NCN($\tilde{a}^1 \Delta$) the reaction enthalpy cannot be given since the energy separation between the ${}^{1}\Delta$ and ${}^{3}\Sigma$ state of NCN is unknown.

For the reaction of HCN with the species $O(^1D)$ and $CH_2(\tilde{a}^1A_1)$ isoelectronic to NH(a), the available experimental information might be used to elucidate the reaction NH(a) + HCN. In the reaction $O(^{1}D)$ + HCN the electronic adiabatic pathway

$$O(^{1}D) + HCN(\tilde{X}^{1}\Sigma^{+}) \rightarrow NH(a) + CO(X^{1}\Sigma^{+})$$

proceeding on the ${}^{1}A'$ ground-state surface with a nonadiabatic transition to the low-lying ¹A" surface prior to hydrogen migration is found to be the dominant chemical channel; the quenching channel leading to O(³P) and HCN is not known.⁴² The production of $OH(X^2\Pi)$, which is also available via an electronically adiabatic pathway, contributes less than 0.1 to the main channel. Products from nonadiabatic pathways including deactivation are of minor importance. The rate of the reaction $O(^{1}D) + HCN$ is not known.

The reaction of CH₂(\tilde{a}) with HCN is very fast; $k(298 \text{ K}) = 1.8 \times 10^{14} \text{ cm}^3/(\text{mol s}).^{43}$ Since little CN(X) is found as a primary product, a mechanism via a cyclic intermediate:

$$CH_2(\tilde{a}) + HCN \longrightarrow HC \longrightarrow N \longrightarrow products$$

in analogy to $O(^{1}D)$ + HCN may be assumed. Comparison with

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these two reactions suggests that the products $CH_2(\tilde{a}) + N_2(X)$ should be favored in the reaction of NH(a) with HCN, which, however, were not observed.

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Kinetic Study of the Reaction $K + O_2 + M$ (M = N₂, He) from 250 to 1103 K

John M. C. Plane,* B. Rajasekhar,

Rosenstiel School of Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Causeway, Miami, Florida 33149

and Libero Bartolotti

Department of Chemistry, University of Miami, Coral Gables, Florida 33124 (Received: October 9, 1989; In Final Form: December 1, 1989)

The recombination reaction $K + O_2 + M$ was studied by the technique of pulsed photolysis of a K atom precursor followed by time-resolved laser induced fluorescence spectroscopy of K atoms at $\lambda = 404$ or 760 nm. Termolecular behavior was demonstrated and absolute third-order rate constants obtained over the temperature range 250-1103 K. A fit of this data to the form AT^{-n} yields $k(T, M = N_2) = [(8.00 \pm 1.74) \times 10^{-30}](T/300)^{-(1.32\pm0.04)}$ cm⁶ molecule⁻² s⁻¹ and $k(T, M = He) = [(4.51 \pm 0.46) \times 10^{-30}](T/300)^{-(1.22\pm0.07)}$ cm⁶ molecule⁻² s⁻¹. These results are compared to two previous studies of these reactions by different experimental methods, which were in marked disagreement below 600 K. A lower limit of $D_0(K-O_2)$ > 203 kJ mol⁻¹ is derived. The rate coefficients are then extrapolated from the experimental temperature range to ambient mesopheric temperatures (140 K < T < 240 K) and to flame temperatures (1500 K < T < 2200 K), by means of the Troe formalism. Finally, the rates of formation and bond energies of LiO₂, NaO₂, and KO₂ are compared.

Introduction

The recombination reaction between potassium atoms and oxygen to form the superoxide

$$K + O_2 + M \rightarrow KO_2 + M (M = third body)$$
 (1)

is of both theoretical and practical interest. The reaction involves the association of two neutral fragments to form KO₂, which is known from matrix isolation studies¹ to exist predominantly as an ion pair, $K^+(O_2)^-$. Reaction 1 thus involves a crossing from a long-range covalent attractive surface onto a close-range ionic potential surface at a $K-O_2$ separation of 3.7 Å.² This type of covalent/ionic curve crossing, together with the relatively high densities of vibrational states characterizing ionic molecules, has the effect of dramatically enhancing the rates of recombination reactions between alkali-metal atoms and species such as OH,³ I,4 and O₂.5-8

A primary motivation for the present work is to gain an understanding of the chemistry of the alkali metals in the mesosphere, as in the case of our recent studies of the reactions $Li + O_2 +$ M^7 and $Na + O_2 + N_2$.⁸ These metals are believed to ablate from meteorites on the edge of the Earth's atmosphere,9 where a layer of the free metal atoms has been observed a few kilometers wide at an altitude of about 90 km.¹⁰ A number of recent atmospheric models^{11,12} have indicated that the principal sinks for the metals immediately beneath these layers are their superoxides, formed by recombination reactions with O_2 . Of particular interest is to understand the different seasonal behavior of the three metals, particularly striking at high latitudes where the mesosphere undergoes a substantial cooling in summer to about 140 K, compared to 230 K in winter.¹³ The column density of atomic Li shows about a 10-fold wintertime enhancement, compared to a 3-fold enhancement for Na and essentially no change for $K.^{14}$ $\,$ Termolecular reactions such as reaction 1 will be sensitive not only to temperature changes but also to the changes in atmospheric pressure that accompany these large seasonal temperature differences.¹² Thus, the measurement of k_1 below 300 K, and a comparison with the temperature dependences for the analogous reactions of Na and Li,^{7,8} is of primary importance for understanding the seasonal variations in the mesospheric chemistry of these metals.

In addition, the accurate measurement of k_1 above 1000 K is required to model the combustion of K in oxygen-rich flames.¹⁵ Recent measurements^{6,16,17} of k_1 have indicated that reaction 1 is sufficiently rapid at high temperatures that large fluxes of the superoxide will occur in oxygen-rich flames.

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