Collision-Induced Intersystem Crossing of NH($a^1\Delta$, v''=0,1) by N₂ and Xe: Temperature Dependence (N_2) and Product States (N_2, X_2)

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The elementary reactions of NH($a^{1}\Delta$, v''=0,1) with N₂ and Xe have been studied in the gas phase. NH(a, v'') was produced by laser photolysis of HN₃ at λ_L = 248 nm and λ_L = 308 nm and detected directly by laser-induced fluorescence (LIF) via the $(c^{1}\Pi - a^{1}\Delta)$ transition. Time resolution is based on the delay between the photolysis and the probe laser. The reaction rates were determined under pseudo-first-order conditions $([N_{2}] \gg [NH(a, v'')]_{0})$, at different temperatures in the range $290 \le T/K \le 515$. The temperature dependence of the reaction rates, described by an Arrhenius expression, are given by the following: NH(a, v''=0) + N₂ \rightarrow products (1), $k_1 = (3.9 \pm 1.2) \times 10^{11} \exp(-(5.4 \pm 1.2) \text{ kJ mol}^{-1}/RT) \text{ cm}^3/(\text{mol s})$; NH(a,v''=1) + N₂ \rightarrow products (2),k₂ = (8.6 ± 2.7) × 10¹¹ exp(-(4.4 ± 2.3) kJ mol⁻¹/RT) cm³/(mol s); ND(a,v''=0) + N₂ \rightarrow products (3),k₃ = (4.7 ± 1.7) × 10¹¹ exp(-(5.2 ± 1.1) kJ mol⁻¹/RT) cm³/(mol s). The NH(X,v), which appeared as the product of physical quenching, was detected by LIF with the transition $(A^3\Pi - X^3\Sigma^{-})$. In the reactions 1, 2, and 3 NH(X) and ND(X), respectively, were formed only in the vibrational ground state. The rate constant for the process NH(a, v''=1)+ Xe \rightarrow products (5) was determined to be $k_5 = (7.7 \pm 0.9) \times 10^{12} \text{ cm}^3/(\text{mol s})$. In the physical quenching of NH(a,v') (produced at $\lambda_L = 248$ nm) by Xe vibrationally excited NH in the electronic ground state NH(X, v=0,1,2) was detected. NH(a,v"=0) (produced at λ_L = 308 nm) was quenched to NH(X,v=0). The different quenching dynamics of NH(a,v') by N_2 and Xe are discussed.

Introduction

The quenching of NH($a^{1}\Delta$) by N₂ (see Figure 4 in the discussion section):

$$NH(a^{1}\Delta) + N_{2}(X^{1}\Sigma_{g}^{+}) \rightleftharpoons HN_{3}(\bar{X}^{1}A')^{*} \rightarrow NH(X^{3}\Sigma^{-}) + N_{2}(X^{1}\Sigma_{g}^{+})$$

which proceeds via a highly vibrationally excited hydrazoic acid molecule $(HN_3(\tilde{X}^1A)^*)$ has been studied by several authors.¹⁻⁶ The NH($a^{1}\Delta$) radicals abbreviated as NH(a) throughout this paper were generated by photolysis of HN3^{1-4,6} at different wavelengths ($\lambda = 193, 248, 266, and 308 \text{ nm}$) and of HNCO and N_2H_4 at $\lambda = 193$ nm.¹ The NH(a) concentration was followed by $LIF^{1-4,6}$ or by the phosphorescence from its forbidden transition to the $NH(X^3\Sigma^{-})$ ground state.² With the LIF technique the (c¹ Π -a¹ Δ) 0-0 transitions in NH were used,^{1,3-5} i.e., the concentration of NH(a,v''=0) was followed. Also with the emission technique^{2,7} the (v''=0) state was observed.

For the quenching of NH(a) in its first vibrationally excited state by N_2 , a rate constant was estimated by Rohrer,⁷ who followed the NH(a,v''=1) concentration via the transition (c, 0-a, 1) with LIF after KrF laser photolysis of HN_3 in the gas phase at room temperature. Direct measurements of this quenching rate constant at room temperature were done recently.^{6,8} The quenching process described above requires the spin-forbidden decomposition of HN₃ out of its singlet state. This decomposition of HN₃ and DN₃ respectively has been studied by overtone pumping,⁹ and by IRMPD with a CO₂ laser¹⁰ which leads to NH in both $X^3\Sigma^-$ and $a^1\Delta$ electronic states. From the Doppler profiles of the laser-induced transitions NH($^{1}\Pi, 0 \leftarrow ^{1}\Delta, 0$) a total kinetic

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energy of about 1500 cm⁻¹ was observed for the channel $N_2(X)$ + NH(a),¹⁰ which gives the barrier height for this dissociation channel. The excitation of the NH fragments was detected by the REMPI method.¹¹ The energy in the N_2 molecules after UV photolysis was obtained by 2 + 1 REMPI of the N₂ formed.¹² By means of ab initio calculations Alexander, Werner, and Dagdigian^{13,14} have determined the barrier height in the spin-allowed decomposition channel. They also investigated the origin of the barrier. The spin-orbit interaction matrix elements for the intersystem crossing were calculated by Jarkony¹⁵ for selected geometries of HN₃.

The quenching of NH(a,v') with N_2 is the full collision, with respect to the half-collision photodissociation of HN₃. If the HN₃ laser photolysis is used as the NH source, a variety of wellcharacterized initial states are available in the quenching experiments. The final states of NH(X) from the quenching of NH(a) by N_2 can be observed directly. A hint that a barrier might exist in the exit channel was obtained from quenching experiments, in which very small rate constants at room temperature were observed.2,3

The aim of this study was to measure the temperature dependence of the rate of the quenching process

$$NH(a,v''=0) + N_2 \rightarrow NH(X,v) + N_2$$
(1)

and of NH(a) in the first vibrationally excited state.

$$NH(a,v''=1) + N_2 \rightarrow products$$
 (2)

The quenching of the deuterated NH(a)

$$ND(a,v''=0) + N_2 \rightarrow products$$
 (3)

was observed in independent experiments. Moreover, we were interested in the vibrational states of NH(X) produced in reaction 1 to compare them with the vibrational states of NH(X) produced in the quenching reactions

$$NH(a, v''=0) + Xe \rightarrow NH(X) + Xe$$
(4)

$$NH(a,v''=1) + Xe \rightarrow NH(X) + Xe$$
 (5)

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which are known to be very fast.³ While this work was in progress, the temperature dependence of the quenching process of NH(a) in its vibrational ground state has been measured and reported by Nelson, McDonald, and Alexander,⁴ and this reaction was also studied during this time by Adams and Pasternack.⁶

Experimental Section

The experiments were carried out in a quasi-static laser pulsed photolysis system with the laser-induced fluorescence pump-probe technique; this system has been described in detail in refs 3 and 5 except for the heating system.

The gas was heated in a heated steel cylinder having an inner diameter of 5 cm and a wall thickness of 1.5 cm, which was plugged into the fluorescence cell. The temperature was controlled by a Pt-100 resistance thermometer, which was attached to the steel tube. The temperature of the gas in the observation volume was measured directly under experimental conditions with a second Pt-100 resistance thermometer in an independent experiment. It was found that the temperature in the gas phase and of the steel cylinder differed by less than 0.5 K under all experimental conditions used.

 HN_3 (DN₃) was photolysed in the fluorescence cell by an exciplex laser (LPX 205i, Lambda Physik) at $\lambda_L = 308$ nm (XeCl line) and $\lambda_L = 248$ nm (KrF line) to generate NH(a,v') (ND-(a,v'')). NH(a,v'') (ND(a,v'')) and the quenching products NH-(X,v) (ND(X,v)) were detected by laser-induced fluorescence (LIF). The photolysis and probe laser beams counterpropagate through the reaction cell. The probe laser was an exciplex-pumped dye laser (LPX 205iCC, FL 3002, Lambda Physik) which was triggered by a homemade multichannel pulse generator. The time resolution was determined by the delay between the photolysis and probe laser pulse ($\Delta t = 5-100 \ \mu s$). The fluorescence signals measured perpendicular to the laser beam with a photomultiplier (9817 QB, EMI), were stored in a transient digitizer (R 7912/AD, Tektronix) and the data analysis was performed by a minicomputer (PDP 11/04, DEC). For the detection of NH(a,v''=0) the P₂ line of the transition NH($c^{1}\Pi, v'=0-a^{1}\Delta, v''=0$) was excited at λ = 325.8 nm.¹⁶ NH(a,v''=1) was detected at λ = 337.6 nm (P₂ line of the NH(c,v'=1-a,v''=1) transition) and at $\lambda = 363.6$ nm (P₂ line of the NH(c,v'=0-a,v''=1) transition).¹⁷ The detection of ND(a,v''=0) was performed via the Q₄ line of the ND-(c,v'=0-a,v''=0) transition at $\lambda = 324.4$ nm.¹⁸ The spectra of NH(X,v=0,1,2) were observed in the range $\lambda = 334-339$ nm. The Q-branch of the transition NH($A^3\Pi, v=0-X^3\Sigma^-, v=0$) was excited in the range $335.7 \le \lambda/\text{nm} \le 336.3^{19}$ NH(X,v=1) and NH-(X,v=2) were detected in the range 336.7 $\leq \lambda/\text{nm} \leq 337.4$ (Qbranch of the NH(A,v=1-X,v=1) transition) and in the range $338.2 \le \lambda/\text{nm} \le 338.8$ (Q-branch of the NH(A,v=2-X, v=2) transition.²⁰

The flow rates of HN₃ and the other gases were regulated by flow controllers (MKS 256, Tylan FC 280) and were high enough to replace the gas in the observation volume between successive photolysis laser shots. The pressure in the cell was measured with pressure heads (MKS 220). The experiments were carried out at p = 20 mbar, while the pressure of HN₃ was $\approx 10^{-3}$ mbar. The chemicals were used at the stated purity: He 99.9996%, N₂ 99.999%, Xe 99.999%, as received. HN₃ (DN₃) was generated in a closed apparatus by melting stearic acid $(C_{17}H_{35}COOH)$ $(C_{17}H_{35}COOD)$ with NaN₃ at T = 140 °C. The gaseous HN₃ (DN_3) was dried over CaCl₂. The DN₃ produced this way contained about 10% HN₃.

Results

The photolysis of HN₃ at $\lambda_{\rm L}$ = 248 nm generated NH(a,v')

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$$HN_3 \xrightarrow{\lambda = 248 \text{ nm}} NH(a,v') + N_2$$

The populations of the states NH(X), NH(A), NH(c), and NH(b) were found to be below 1%.17 The relative populations of the vibrational states were obtained to be: 32.8% for NH(a,v"=0); 46.8% for NH(a,v''=1); 16.9% and 3.8% for NH(a,v''=2) and NH(a,v''=3), respectively.^{17,21} In the HN₃ photolysis at $\lambda_L =$ 308 nm.

$$HN_3 \xrightarrow{\lambda = 308 \text{ nm}} NH(a, v''=0) + N_2$$

NH(a) in the vibrational ground state v'' = 0 was the major product. The fraction [NH(a,v''=0)]/[NH(a,v'>0)] was observed to be >95%. Thus the photolysis at different wavelengths enabled studying of the quenching reactions of NH(a) with different initial vibrational state distributions, whereby the vibrational states in NH(X) are of special interest in these experiments. The excess of buffer gas He, which does not quench NH(a,v'') either electronically or vibrationally (see below), ensured the fast thermalization of NH(a) with respect to rotation and translation. Moreover, the buffer gas limited the diffusion out of the observation volume. The ND(a,v'') was produced in an analogous way from the photolysis of DN_3 .

Quenching Rates. The temperature dependence of the reaction rates of the reactions 1, 2, and 3 were examined and the product state distributions were analyzed. Concentration profiles [NH-(a,v')] = $f(\Delta t)$ were measured in the temperature range 290 \leq $T/K \le 515$ to determine the rate constants and their temperature dependences. In addition to reaction 1 or 2 the fast reaction

$$NH(a,v''=0) + HN_3 \rightarrow NH_2 + N_3$$
(6)

with a rate constant $k_6 = 7.3 \times 10^{13} \text{ cm}^3/(\text{mol s})^{5,22-24}$ and the reaction

$$NH(a,v''=1) + HN_3 \rightarrow NH_2 + N_3$$
(7)

with a rate constant $k_7 = 7.6 \times 10^{13} \text{ cm}^3/(\text{mol s})^{17}$ must be considered in the analysis of the reaction rates. The rate constant for reaction

$$ND(a,v''=0) + DN_3 \rightarrow ND_2 + N_3 \tag{8}$$

was found to be $k_8 = 7.7 \times 10^{13} \text{ cm}^3/(\text{mol s})$ from the [ND-(a,v''=0)] depletion.²⁵ The slow reaction of the buffer gas He with NH(a,v''); NH(a,v''=0) + He \rightarrow products (9) and NH- $(a,v''=1) + He \rightarrow \text{products}$ (10) with a rate constant $k_9 < 6 \times$ $10^8 \text{ cm}^3/(\text{mol s})$ and $k_{10} < 6 \times 10^8 \text{ cm}^3/(\text{mol s})$,^{1,5,17} and the collision-free decay of NH(a) via the forbidden singlet-triplet transition $(\tau_0 = 1.7 \text{ s})^{26.27}$ were too small to influence the NH(a,v") concentration profiles.

The concentrations of NH(a,v''=0,1) and of ND(a,v''=0) were measured as a function of the delay time between the photolysis $(\lambda_L = 248 \text{ nm})$ and analysis lasers. The experimental conditions are listed in Table I. For [NH(a,v''=0)](t) and [NH(a,v''=1)](t)a different behavior was observed. For [NH(a,v''=0)](t) an increase was observed in a ln [NH(a,v''=0)] versus Δt plot for short reaction times, whereas the ln [NH(a,v''=1)] versus Δt plots were linear as expected for a normal pseudo-first-order behavior. For long reaction times ($\Delta t > 20 \ \mu s$) the formation of NH(a,v''=0) by vibrational relaxation was over and the plot for NH(a,v''=0)also turned into a straight line. In an earlier determination³ it was shown by using two different photolysis wavelengths (λ_L = 308 and 248 nm) that the rate constant obtained at long reaction times is k_1 . The slope of the semilogarithmic plot of $\ln [NH(a,v'')]$

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TABLE I: Experimental Details and Results for the Measurements of the Temperature Dependence of the Rate Constants of Reactions 1, 2, and 3^a

			NH(a	<i>,v''=</i> 0)			
<i>T</i> , K	$p(N_2)$, mbar	p(He), mbar	$p(HN_3)$, mbar	no. of runs	$\Delta t, \ \mu s$	$k_{\rm ex}, 10^4 {\rm s}^{-1}$	k_1 , 10 ¹⁰ cm ³ /(mol s)
291	3-20	0-20	0.0030	7	10-70	0.9-4.0	4.0 ± 1.4
395	3-20	0-20	0.0033	7	10-70	1.0-5.0	6.6 ± 1.8
505	3-20	0-20	0.0030	7	10-70	0.7-6.1	10.9 ± 5.0
			NH(a	<i>v''</i> =1)			
<i>T</i> , K	$p(N_2)$, mbar	p(He), mbar	$p(NH_3)$, mbar	no. of runs	$\Delta t, \mu s$	$k_{\rm ex}, 10^4 {\rm s}^{-1}$	k_2 , 10 ¹⁰ cm ³ /(mol s)
290	3-20	0-20	0.0028	7	10-50	0.8-12	13 ± 3
395	4-20	0-20	0.0031	7	1050	0.7-17	27 ± 15
515	3-20	0-20	0.0030	7	10-50	1.0-15	29 ± 11
			ND(a	<i>,v″</i> =0)			
<i>T</i> , K	$p(N_2)$, mbar	p(He), mbar	$p(DN_3)$, mbar	no. of runs	$\Delta t, \ \mu s$	$k_{\rm ex}, 10^4 {\rm s}^{-1}$	k_3 , 10 ¹⁰ cm ³ /(mol s)
296	3-20	0-20	0.0037	6	10-60	1.9-5.7	5.7 ± 1.0
348	3-20	0-20	0.0039	6	10-60	1.5-6.2	7.9 ± 2.3
398	3-20	0-20	0.0038	6	10-60	1.2-6.7	10.1 ± 4.4
457	3-20	0-20	0.0039	6	10-60	1.3-6.7	12.5 🗨 5.1
508	3-20	0-20	0.0039	6	10-60	1.6-6.9	13.2 ± 2.2
527	3-20	0-20	0.0039	6	1060	1.4-7.0	14.5 ± 5.7

^a Photolysis wavelength $\lambda_L = 248$ nm.



Figure 1. Quenching of NH(a,v''=0) by N₂ at different temperatures: (**D**) T = 505 K, (**O**) T = 395 K, (**A**) T = 291 K.

versus Δt in the linear regime yielded the first-order rate constant k_{ex} . The rate constants k_1 , k_2 , and k_3 are obtained from the plot of k_{ex} versus N₂ concentrations as listed in Table I for different temperatures. The errors of k_1 , k_2 , and k_3 in Table I correspond to 2σ of the slope.

The plot of k_{ex}^{-1} versus $[N_2]$ for the reaction NH(a,v''=0) + N₂ at different temperatures is shown in Figure 1. The temperature dependences of $k_1(T)$, $k_2(T)$, and $k_3(T)$ follow Arrhenius expressions. The plots of ln k_1 , ln k_3 versus T^{-1} are given in Figure 2. The Arrhenius expression

$$k_1 = (3.9 \pm 1.2) \times 10^{11} \exp(-(5.4 \pm 1.2) \text{ kJ mol}^{-1}/RT) \text{ cm}^3/(\text{mol s})$$

was determined in the temperature range $291 \le T/K \le 504$ and $L = (0.4 \pm 2.7) \times 10^{-10}$

$$k_2 = (8.6 \pm 2.7) \times 10^{11} \exp(-(4.4 \pm 2.3) \text{ kJ mol}^{-1}/RT) \text{ cm}^3/(\text{mol s})$$



Figure 2. Arrhenius plot $\ln k$ versus T^{-1} of the reaction $NH(a,v''=0) + N_2(\blacksquare)$ and the reaction $ND(a,v''=0) + N_2(\blacksquare)$.

in the temperature range $290 \le T/K \le 515$. For the reaction ND(a,v''=0) + N₂ the Arrhenius expression

$$k_3 = (4.7 \pm 1.7) \times 10^{11} \exp(-(5.2 \pm 1.1) \text{ kJ mol}^{-1}/RT) \text{ cm}^3/(\text{mol s})$$

was determined in the temperature range $296 \le T/K \le 527$. The errors of the activation energies correspond to 2σ in the slope of the lines given in the plot of ln k versus T^{-1} .

States Produced by Quenching. The reaction channel of NH(a) + N₂ consisted only of physical quenching, i.e., NH(X) is formed. Excitation spectra of NH(A-X) were recorded for both HN₃ photolysis wavelengths $\lambda_L = 248$ nm and $\lambda_L = 308$ nm. In both cases NH(X) was detected in the vibrational ground state, i.e., [NH(X,v=1)]/[NH(X,v=0)] < 0.01.

The reaction NH(a,v'') + Xe was also examined for v'' = 0and 1. HN₃ was photolyzed at $\lambda_L = 248$ nm. The rate of the quenching of NH(a,v''=0) by Xe

$$NH(a,v''=0) + Xe \rightarrow NH(X) + Xe$$
(4)



Figure 3. Quenching of NH(a,v''=1) by Xe at T = 298 K ($p(HN_3) = 6.3 \times 10^{-3}$ mbar; k_6 '[HN₃] = 1.94×10^4 s⁻¹).

TABLE II: Experimental Conditions for the Determination of the Removal Rate Constant k_5 in the Reaction NH(a, r''=1) + Xe

					k		
<i>Т</i> , К	p(Xe), mbar	p(He), mbar	p(HN ₃), mbar	of runs	$\Delta t, \mu s$	$k_{ex},$ 10 ⁴ s ⁻¹	10 ¹² cm ³ / (mol s)
293	0-3.7	16.3-20.0	0.0063	6	10-70	2.0-13.8	7.7

was already measured in an earlier experiment to be $k_4 = 7.3 \times 10^{12} \text{ cm}^3/(\text{mol s})$.³ The [NH(a,v''=1)] was followed directly to determine the rate of the overall depletion of NH(a,v''=1) in the reaction

$$NH(a,v''=1) + Xe \rightarrow NH(final states) + Xe$$
 (5)

The plot of k_{ex} versus [Xe] is shown in Figure 3, and the experimental conditions are given in Table II. The reaction rate of NH(a,v''=1) + Xe was determined to be

$$k_5 = (7.7 \pm 0.9) \times 10^{12} \text{ cm}^3/(\text{mol s})$$

The error corresponds to 2σ of the slope determined from Figure 3. The ln [NH(a,v''=0)] versus t plots were straight lines under all experimental conditions; i.e., no formation of [NH(a,v''=0)] from higher vibrational states (initially produced in the photolysis) was observed. Thus no indication was found that in the process 5 vibrational quenching occurs. NH(X) was detected in the vibrational states v = 0, 1, 2; i.e., the quenching is described by

$$NH(a,v'') + Xe \rightarrow NH(X,v=0,1,2) + Xe$$

whereby NH(a,v') stands for the vibrational state distribution obtained from the HN₃ photolysis at $\lambda_L = 248$ nm. When NH(a) was produced in the photolysis at $\lambda_L = 308$ nm and quenched by Xe, no NH(X,v>0) was obtained; i.e., [NH(X,v>0] were below the detection limits. The quenching path

$$NH(a,v''=0) + Xe \rightarrow NH(X,v\geq 1) + Xe$$

can be excluded from experimental results using different photolysis lasers ($\lambda = 248$ nm and $\lambda = 308$ nm) and thus different initial NH(a,v'') vibrational state populations. The maximum LIF intensities of NH(X,v=0) from the NH(a) + Xe quenching process ([NH(X,v=0)]_{Xe}) were compared with the maximal LIF intensities of NH(X,v=0) from NH(a) + N₂ quenching process ([NH(X,v=0)]_{N₂}) at identical experimental conditions in other respects.



Figure 4. Potential energy curves of the photodissociation of HN₃($\mathbf{\tilde{X}}$) to NH(a,X) and N₂(X), and the deactivation of NH(a,v''=0,1) by N₂-(X), the barrier height for v''=0 and 1 estimated via $E_0 \simeq E_A - RT/2$,⁴⁰ $\Delta E_0 = 4.2$ kJ/mol, $\Delta E_1 = 3.2$ kJ/mol.

At the photolysis wavelength $\lambda_L = 308$ nm, at which NH(a) is formed only in the vibrational ground state, the ratio

$$\frac{[\mathrm{NH}(\mathrm{X},v=0)]_{\mathrm{N}_2}}{[\mathrm{NH}(\mathrm{X},v=0)]_{\mathrm{Xe}}} \approx 1.0$$

was determined. At the photolysis wavelength $\lambda_L = 248$ nm the ratio

$$\frac{[\mathrm{NH}(\mathrm{X}, v=0)]_{\mathrm{N}_2}}{[\mathrm{NH}(\mathrm{X}, v=0)]_{\mathrm{X}_e}} = 1.5 \pm 0.2$$

was observed.

The vibrational states of NH in the electronic ground state were probed by LIF for both photolysis wavelengths. In the first case at $\lambda_L = 308$ nm, NH(X,v=0) was the major product in the reaction with N₂ as well as with Xe. The population of NH(X, $v\geq1$) was below the detection limit. The intersystem crossing can be described by

and

$$\mathrm{NH}(\mathrm{a}, v''=0) + \mathrm{N}_2 \rightarrow \mathrm{NH}(\mathrm{X}, v=0) + \mathrm{N}_2$$

$$NH(a,v''=0) + Xe \rightarrow NH(X,v=0) + Xe$$

In the reaction NH(a,v'') + N₂ only NH(X,v=0) was detected, i.e., [NH(X, $v\geq1$)] was below the detection limit. In the reaction NH(a,v'') + Xe the products NH(X,v=0) and NH(X,v=1,2) were observed. The calibration of the relative concentrations, [NH-(X,v=0)], [NH(X,v=1)], etc., are underway. It can be concluded that the higher vibrational states of NH(X), i.e., NH(X, $v\geq1$) were generated by the quenching of NH(a) in higher vibrational states (v'>0) (see Discussion).

Discussion

The quenching of NH(a,v'') by $N_2(X)$ is illustrated in the correlation diagram shown in Figure 4. The discussion is divided into two parts: the first part deals with the temperature dependence of the quenching of NH(a,v'') and ND(a) by N_2 and the second part discusses the products of these quenching processes and the quenching by Xe.

The quenching of NH(a,v'') by N₂ is a slow process at room temperature, whereby NH(a,v''=0) reacts with $k_1 = 4.0 \times 10^{10}$ cm³/(mol s) (T = 293 K). The low rate constant, which agrees well with earlier determinations^{3,17} and with the results of other groups,^{1,2,6} indicates that process 1 and also process 2 may have considerable activation energies. The quenching of NH(a,v''=1)by N₂ is faster than the quenching of NH(a,v''=0) ($k_2 = 1.3 \times$ 10^{11} cm³/(mol s)). This room temperature value is in good agreement with the estimation reported by Rohrer, $k_2 = 1.1 \times$ 10^{11} cm³/(mol s),⁷ and recent direct measurements, $k_2 = 1.6 \times 10^{11}$ cm³/(mol s).^{6,17} The main part of this work is therefore the temperature dependence of the specific quenching processes.

Temperature Dependence of $NH(a, v') + N_2$. The temperature dependences of NH(a,v''=0,1) with N₂ in the temperature range $290 \le T/K \le 515$ corresponds to $E_A(NH(a,v''=0)) = 5.4 \text{ kJ/mol.}$ The preexponential factor is $A_1(NH(a,v''=0)) = 3.9 \times 10^{11}$ $cm^3/(mol s)$. This small value reflects the small transition probability from the singlet to the triplet system. In the work of Nelson et al.⁴ the temperature dependence of the rate of the reaction of NH(a) with N2 was examined in the temperature range $306 \le T/K \le 596$. The activation energy of $E_A = (5.4 \pm 0.5)$ kJ/mol, and the preexponential factor $A_1 = 4.3 \times 10^{11} \text{ cm}^3/(\text{mol})$ s), are in very good agreement with the results of this work.

For the vibrationally excited state the temperature dependence of the quenching rate constant has, to our knowledge, not yet been determined directly. The activation energy $(E_A(NH(a,v''=1)))$ = 4.4 kJ/mol) appears to be slightly smaller and the preexponential factor $(A_2(NH(a,v''=1)) = 8.6 \times 10^{11} \text{ cm}^3/(\text{mol s}))$ slightly higher than for NH(a,v''=0). Thus it can be concluded that nearly the same barrier exists for both incoming channels (see Figure 4). The NH(a,v''=1) depletion process can consist of collisional intersystem crossing and vibrational quenching.

$$NH(a,v''=1) + N_2 \rightarrow NH(X) + N_2$$

$$NH(a,v''=1) + N_2 \rightarrow NH(a,v''=0) + N_2$$
(2)

If it is assumed that k_2 is a measure of the rate constant for the formation of the $HN_3(\tilde{X})$ complex and that the rates for the formation of HN₃(\tilde{X}) from NH(a,v''=0) + N₂ and NH(a,v''=1) $+ N_2$ (reacting adiabatically over a similar barrier) are equal and if the rate of ISC is independent of whether $HN_3(\tilde{X})$ is formed from NH(a,v"=0) or NH(a,v"=1) ($k_{ISC} = 4 \times 10^{10} \text{ cm}^3/(\text{mol s})$), then a rate constant of $k_{vib} = 9 \times 10^{10} \text{ cm}^3/(\text{mol s})$ can be obtained for vibrational deactivation, a value which is in reasonable agreement with direct measurements (see Product State Distribution).

In previous works^{9,10,14,28} the activation barrier was experimentally determined or theoretically calculated from the decomposition of HN₃/DN₃. An IR MPD study was carried out with DN₃.¹⁰ The dissociation products were detected by LIF. The spin-allowed pathway to ND(a) and the spin-forbidden pathway to ND(X) are product pathways of the dissociation. ND(a) was observed in the vibrational ground state only, and the rotational temperature was determined to be $T_{\rm rot} = 425$ K. From the Doppler profiles of the NH(a) transitions it was found that NH-(a,v''=0) was translationally excited with an energy distribution that peaked at $E_{\rm tr} \simeq 1700 {\rm ~cm^{-1}} \simeq 20.3 {\rm ~kJ/mol}$. This observation was explained with a barrier in this exit path, which, however, is found to be much larger than the activation energy obtained here.

The theoretical interpretation of these results was performed by Alexander, Werner, and Dagdigian.¹³ Excited $DN_3(^3A'')$ dissociates into ND(X³ Σ^-) + N₂(X¹ Σ_g^+) on a triplet surface which is crossed by the singlet surface leading to the spin-allowed products ND($a^{1}\Delta$) + N₂(X¹ Σ_{g}^{+}). The geometry at the singlettriplet crossing point was determined by CASSCF and MCSCF-CI calculations. Some CASSCF calculations predicted a barrier in the case of a great N_2 -NH distance (0.26-0.32 nm). MCSCF-CI calculations showed only a continuous increase of the energy of the lowest singlet state with an increasing distance up to a maximum (0.24 nm). Recently, the authors examined theoretically the barrier of the exit channel $HN_3(\bar{X}^1A') \rightarrow NH(a)$ + N₂.¹⁴ A dissociation barrier ($\Delta E = 14.5 \text{ kJ/mol}$) was obtained in CAS calculations. The distance between N_2 and NH(a) was \sim 0.22 nm. These calculations give a theoretical understanding of the vibrational ground state quenching process. The barrier in the singlet exit channel results from the fact that the two π electrons, which occupy in the free NH radical either the π_x or π_{ν} orbital are squeezed into a single 2a" orbital of HN₃ when the NN-NH distance becomes smaller.

For CO(${}^{1}\Sigma^{+}$), a quencher isoelectronic with N₂(${}^{1}\Sigma_{g}^{+}$)

$$NH(a) + CO \rightarrow HNCO^* \rightarrow NH(X) + CO$$

no activation energy was observed.8 In the intermediate molecule, HNCO, the bond strength for the HN-CO bond formed is much larger and in the hypersurface for the spin-allowed channel no barrier, i.e., $\Delta E < 450$ cm⁻¹, was found in ab initio calculations,²⁸ which means that in this case the effect leading to a barrier in the NH(a)- N_2 case is less pronounced.

On the other hand, it is interesting to compare the collisioninduced intersystem crossing $NH(a-X)-N_2$ with the quenching of the species $O(^{1}D)$ and $CH_{2}(\tilde{a}^{1}A_{1})$ which are isoelectronic with NH($a^{1}\Delta$).

The quenching of O(¹D) with N₂ is also very rapid $[k = (1.7-4.2) \times 10^{13} \text{ cm}^3/(\text{mol s})^{29-32}]$. The rate constant, however, shows a negative temperature dependence. The activation energy was $E_A = -0.9 \text{ kJ/mol}$ with a preexponential factor of A = 1.2× 10^{13} cm³/(mol s) [104 ≤ $T/K \le 354$]³² in the fast reaction. The quenching to $O(^{3}P)$ proceeds over a collision complex on the lowest singlet surface of $N_2O(X^1\Sigma^+)$. The crossing from the singlet surface to the triplet $({}^{3}A' + 2{}^{3}A'')$ surface $(O({}^{3}P) + N_{2}(X^{1}\Sigma))$ happens with a high probability during the lifetime of the complex. The singlet potential surface, which was constructed, has no barrier; thus the negative temperature dependence of the rate constant can be understood.

The carbone $CH_2(\tilde{a})$ is quenched by N_2 with a rate constant in the range $(4.4-7.8) \times 10^{12} \text{ cm}^3/(\text{mol s})^{.33-37}$ The rate increases with increasing temperature $(k(T) = 4.2 \times 10^{12} (T/295 \text{ K})^{(1.0\pm0.3)}$ cm³/(mol s)) in the temperature range $210 \le T/K \le 475.^{33.34}$ This quenching rate is faster than that for NH(a). The reaction mechanism, however, is completely different from the reaction mechanism in O(¹D) and NH(a). In CH₂($\tilde{a}^{1}A_{1}$) rovibronic states with strong singlet-triplet mixing exist. The collision-induced intersystem crossing takes place via the variation of the mixing during the collision. This situation cannot be compared to NH(a)where the singlet-triplet energy gap is so large that the coupling is weak.^{36,38,39}

Product State Distribution. The vibrational states of NH(X)after collision-induced ISC were observed for NH(a) in the vibrational ground state and the vibrationally excited state for the two quenchers Xe and N_2 . For NH(a) in the vibrational ground state only NH(X,v=0) was formed by both N₂ and Xe. When NH(a), however, was vibrationally excited, the vibrational states of NH(X) after the quenching process were significantly different for N₂ and Xe. For N₂ only NH(X,v=0) was observed whereas for Xe as a collision partner NH(X,v=0,1,2) was detected. With this result a process

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$$NH(a,v''=0) + Xe \not\rightarrow NH(X,v>0) + Xe$$

can be excluded. The observation of NH(X,v>0) in the other experiment (see below) indicates that the absence of NH(X,v)cannot be explained by a rapid vibrational quenching in the electronic ground state. Thus, at least for v'' = 0 the proof can be given that the vibrational state is not changed by the collision-induced ISC with Xe, i.e., the electronic excitation energy is not converted into vibrational energy. For NH(a,v''=1) the following process

$$NH(a,v''=1) + Xe \rightarrow NH(X,v=1) + Xe$$

can be assumed, but a change in the vibrational state cannot be excluded. The reaction rate of NH(a,v''=0) with Xe ($k_4 = 7.2$ $\times 10^{12}$ cm³/(mol s))³ was nearly identical with the reaction rate of NH(a,v''=1) with Xe ($k_5 = 7.7 \times 10^{12} \text{ cm}^3/(\text{mol s})$). This indicates that vibrational quenching is of minor importance in reaction 5. The appearance of NH(X,v=0,1,2) with time was followed and compared to the NH(a,v''=0,1) depletion.⁶ To determine from these measurements the quenching mechanism, however, calibrations of [NH(a,v')] and [NH(X,v)] are needed.

For N₂ as the quenching gas, no NH(X) with v > 0 was observed in both experiments with NH(a,v''=0) and $NH(a,v''\geq 0)$. As in the case for Xe a quenching process

$$NH(a,v''=0) + N_2 # NH(X,v) + N_2$$

can be excluded. The fact that no NH(X,v>0) is observed can be explained by a fast vibrational quenching

$$NH(a,v'>0) + N_2 \xrightarrow{\kappa_{vib}} NH(a,v''=0) + N_2$$

with $k_{\rm vib} = 1.2 \times 10^{11} \,\mathrm{cm}^3/(\mathrm{mol \ s})^{17}$ This quenching process can occur very efficiently via the crossing of the ${}^{1}A'(v''=1)$ and ${}^{1}A''(v''=0)$ surfaces²⁸ as illustrated in Figure 4. Vibrational quenching contributes mainly to the depletion of $NH(a,v'\geq 1)$. The direct ISC pathway

$$NH(a,v''=1) + N_2 \rightarrow NH(X,v=0,1) + N_2$$

is of minor importance. A calibration of the [NH(X,v=1)] detection limit will give an upper limit for the rate constant. For the N₂ quenching of NH(a,v''), produced in the photolysis of HN₃ at $\lambda = 266$ nm, Adams and Pasternack⁶ detected the ratio [NH- $(X,v=1)]/[NH(X,v=0)] \le 0.02$. Since the initial vibrational population (NH(a,v')) obtained at $\lambda = 266$ nm is very similar to the population at $\lambda = 248$ nm these results can be compared directly. The results in reference⁶ and in this work are in good agreement.

It can be concluded that all experiments can be described assuming that the vibrational quantum number is unchanged during the ISC.

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First Observation of a Radical–Triplet Pair Mechanism (RTPM) with Doublet Precursor

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Absorptive CIDEP signals of nitroxide radical were first observed in fluoranthene-TEMPO, coronene-TEMPO, pyrene-TEMPO, and naphthalene-TEMPO systems by time-resolved ESR. The absorptive spin polarization was interpreted by RTPM with doublet precursor of the radical triplet pair. From the CIDEP decay profiles and triplet quenching experiments, it was concluded that the generated CIDEP in these systems is explainable by the simultaneous operation of both doublet and quartet precursor RTPMs.

Introduction

Singlet and triplet excited molecules and intermediate radicals coexist in the early photochemical stage. Interactions between these species have extensively been investigated and many interesting phenomena have been well-known, such as S₁ and T quenching by radicals, triplet-triplet annihilation, and so on. Photochemistry and photophysics of these species have been discussed based on the electron spin multiplicities because the spin angular momentum of these intermediate molecules is a good quantum number. For example, quenching of excited states by free radicals and radical recombination reactions selectively occur according to the conservation rule of the spin angular momentum, which are confirmed by magnetic field effects.^{2,3}

Chemically induced dynamic electron polarization (CIDEP) of radicals is generated through the radical pair mechanism (RPM),⁴ the triplet mechanism (TM),⁵ and the radical-triplet

pair mechanism (RTPM).^{6,7} These mechanisms are also discussed based on the spin angular momentum. RPM and RTPM are explained by magnetic interaction acting on the potential surface of spin states of radical pair and radical-triplet pair, respectively. In RTPM, randomly encountered radical and triplet pairs show quartet and doublet spin states. The quenching of triplet molecule occurs through the doublet spin states of radical-triplet pair. During the course of triplet-doublet interaction, the quartet and doublet spin states mix with each other by the zero-field splitting and hyperfine interactions. This mixing generates CIDEP of net emission (E) and an E/A (emission/absorption) multiplet pattern, which polarization is abbreviated as E^*/A .

RPM and RTPM are so far the only CIDEP mechanisms due to the interaction among the species of initial photochemical processes, but it is still unknown whether CIDEP is generated or not via radical-excited singlet and triplet-triplet pairs. As for

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