3540 SCHEME II



on analogies with related azo compounds, postulated a nonbridged isomer as responsible for the observed absorption.



However, considering that the rapid equilibrium given in eq 7 imposes the condition that TTH must be formed very rapidly as compared with the formazan, and assuming that two resonance forms should contribute to the structure of  $TT^-$  (Scheme II), a cyclic structure for TTH



also warrants serious consideration, specially if it is considered that this species could be easily transformed into 1,2-dihydrotriphenyltetrazolium chloride, observed for the TTC reduction in acid media. Further work should be performed in order to clarify the nature of these isomers.

As is apparent from the results presented in this paper, the photodisproportionation of TTC in alkaline aqueous solutions is analogous to the tetrazolium salt disproportionation observed in the dark in strongly basic media.<sup>5,12</sup> Jámbor has already noted this analogy in the early 1950s.<sup>17</sup> In both cases, the strong reducing properties of the basic forms of TT<sup>+</sup> (and perhaps TT<sup>•</sup>) play an essential role.

Opposite to our observations of a pseudo-first-order decay for the TT<sup>•</sup> radical, Bielski et al. found a second-order decay in the case of nitroblue tetrazolinyl radicals.<sup>14</sup> On the other hand, preliminary flash photolysis experiments carried out with neotetrazolium chloride indicate also a second-order behaviour.<sup>16</sup>

Assuming that the TT<sup>•</sup> radical disproportionates with a rate constant similar to the one found by Bielski et al.,  $k_{\text{disp}} \sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , and that under our experimental conditions [TT<sup>•</sup>]  $\sim 10^{-7} \text{ M}$ , the second-order process should be 100 times faster than reaction 4, indicating that the actual disproportionation rate constant for the TT<sup>•</sup> radicals should be less than  $10^7 \text{ M}^{-1} \text{ s}^{-1}$ .

This would indicate that the tetrazolinyl radicals of the ditetrazolium ions are better reducing agents than the parent tetrazolium ions. Whether this is a general rule should be a matter of further research.

Acknowledgment. We thank Dr. E. Castellano for his constructive criticism and helpful suggestions. This research project was supported by the Consejo Nacional de Investigaciones Científicas y Ténicas and by the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires.

**Registry No.** TTC, 298-96-4; F, 504-65-4; P<sup>+</sup>, 236-27-1; NTC, 13146-67-3.

# Elementary Reactions of NH( $a^{1}\Delta$ ) with Atoms and Diatomic Molecules

W. Hack\* and A. Wilms

Max-Planck-Institut für Strömungsforschung, Bunsenstrasse 10, 3400 Göttingen, FRG (Received: March 16, 1988; In Final Form: September 28, 1988)

The elementary reactions of NH( $a^{1}\Delta$ ) with the noble gas atoms Kr and Xe and with the diatomic molecules N<sub>2</sub>, O<sub>2</sub>, and NO were studied in a quasi-static laser flash photolysis cell at room temperature and low pressures. NH(a) was produced by HN<sub>3</sub> laser photolysis at  $\lambda_{L} = 248$  and 308 nm. The detection of NH(a) and of the reaction products was achieved by pulsed laser-induced fluorescence (LIF). Time resolution was obtained by the delay between photolysis and probe pulse. For the overall NH(a) depletion NH(a) + R  $\rightarrow$  products, the following rate constants were obtained at T = 296 K:  $k_1$ (Kr)  $\leq 6 \times 10^9$  cm<sup>3</sup>/(mol s);  $k_1$ (Xe) = (7.2 ± 0.7) × 10<sup>12</sup> cm<sup>3</sup>/(mol s);  $k_1$ (N<sub>2</sub>) = (5.0 ± 0.5) × 10<sup>10</sup> cm<sup>3</sup>/(mol s);  $k_1$ (O<sub>2</sub>) = (2.7 ± 0.3) × 10<sup>10</sup> cm<sup>3</sup>/(mol s);  $k_1$ (NO) = (1.8 ± 0.3) × 10<sup>13</sup> cm<sup>3</sup>/(mol s). For the reactions of NH(a) with O<sub>2</sub> and N<sub>2</sub>, the primary products OH and NH(X) were observed and the branching ratios for the corresponding product channels were determined quantitatively. The elementary processes of NH(a) are discussed and compared with the NH(X) reactions and with the reactions of the isoelectronic species O(<sup>1</sup>D) and CH<sub>2</sub>( $\tilde{a}^{1}A_{1}$ ).

#### Introduction

Elementary processes of electronically excited species are of interest from a practical and a theoretical point of view. In contrast to the other degrees of freedom like translational, rotational, or vibrational energy the change of electronic energy, as a general rule, influences the reactivity of the species significantly, due to the change of the energy surface on which the reaction proceeds. Comparison of the experimental results with the calculated potential surfaces makes detailed knowledge of the reaction dynamics feasible. In photolytic systems, for instance in atmospheric photochemistry, the reactions of electronically excited atoms and molecules are of great importance. NH radicals, which are isoelectronic with O atoms and CH<sub>2</sub> radicals, are much less studied than either of the other two. The first electronic excited state of NH is the  $(a^{1}\Delta)$  state which has a long lifetime of about  $\tau_{0} \simeq 1.7 \text{ s}^{1}$  due to the forbidden transition to the  $({}^{3}\Sigma^{-})$ -electronic ground state. The excitation energy of NH(a) of 151 kJ/mol lies between those of O({}^{1}D) and CH<sub>2</sub>( $\tilde{a}$ ). The NH radical is a suitable species for studying the effects of electronic excitation in the isoelectronic group O, NH, and CH<sub>2</sub> since both its lowest electronic states,  $(a^{1}\Delta)$  and  $(X^{3}\Sigma^{-})$ , can be detected with high sensitivity by laser-induced fluorescence (LIF).

<sup>(1)</sup> Marian, C. M.; Klotz, R. Chem. Phys. 1985, 95, 213.



Figure 1. Experimental arrangement.

The aim of this work was to study the quenching of NH(a) with the noble gases Kr and Xe and its chemical reactions with the atmospheric diatomic molecules  $N_2$ ,  $O_2$ , and NO using  $HN_3$  laser photolysis as the NH(a) source and LIF for the detection of NH(a), NH(X), and OH.

#### **Experimental Section**

Investigation of NH(a) reactions was performed in a quasi-static gas cell at room temperature ( $T = 296 \pm 3$  K). NH(a) was generated by HN<sub>3</sub> laser photolysis. NH(a) and the reaction products NH(X) and OH were detected with LIF. The experimental arrangement is shown in Figure 1 and was essentially the same as that described in ref 2 and 3.

The gas cell consisted of a cylinder measuring 7 cm in diameter and 25 cm in length. In the direction of the lasers the cell was fitted with side arms containing light baffles. A photomultiplier tube (Hammamatsu, R 955) was attached perpendicular to the laser beam path. The induced fluorescence from the observation volume in the center of the cell was focused onto the photocathode of the photomultiplier via collimating optic and glass filters for the suppression of scattered laser light. The cell was connected to a gas supply system (MKS 251, 254, and 256). The flow meters (MKS 256) was calibrated for each gas used. The gas flow in the cell was fast enough to exchange the gas in the observation volume between the laser shots. The pressure was measured with pressure heads (MKS 220, Baratron, 0–10 Torr and 0–1000 mbar).

The photolysis laser was an exciplex laser (Lambda Physik, EMG 101) used on the KrF line at  $\lambda_L = 248$  nm and the XeCl line at  $\lambda_L = 308$  nm. The photolysis laser beam was shaped by a system of lenses and apertures. In the gas cell it has a crosssectional area of  $A_L = 11 \text{ mm}^2$  and an approximately rectangular intensity profile. The photolysis pulse energy in the gas cell was measured with an energy detector (Oriel, 142 LR) and amounted typically to  $E_L = 3 \text{ mJ}$ .

The probe laser was an exciplex-pumped, frequency-doubled dye laser (Lambda Physik, EMG 200, FL 2002). It had a beam cross section of  $A_L \approx 3 \text{ mm}^2$ .

The photolysis laser and the probe laser were directed to the middle of the gas cell. The two counterpropagating laser beams overlapped collinearly. With this optical arrangement the dye laser beam path which defines the observation volume was encircled by the photolyzed gas mixture and thus the diffusion of radicals out of the observation volume was minimized. Solution of the diffusion equation for this arrangement (see e.g. ref 4) revealed that the influence of diffusion on the radical concentration in the observation volume was negligible under our experimental conditions. For a He pressure of p(He) = 30 mbar the mutual diffusion coefficient was  $D_{\text{He-NH}} \approx 30 \text{ cm}^2/\text{s}$  (derived from the

Lennard-Jones parameters of He and NH according to ref 5). With this value, after a typical reaction time of  $\Delta t = 20 \ \mu$ s the diffusive losses of radicals in the observation volume were less than 1% which is much less than the error limits of the measurements. Moreover, the errors in the value of  $k_1(R)$  are caused by the changes in the diffusive rate as [R] is altered. This result of the calculated diffusion effects was confirmed by experimental checks: (i) The observation of NH(a) in a gas mixture of p(He) = 10 mbar and a small HN<sub>3</sub> pressure of  $p(\text{HN}_3) = 2.9 \times 10^{-3} \text{ mbar gave}$  a linear correlation of ln [NH(a)] versus  $\Delta t$  even for long reaction times up to  $\Delta t = 100 \ \mu$ s. (ii) The removal rate of NH(a) in this experiment was found to be identical with the rate of collision-induced removal in the reaction NH(a) + HN<sub>3</sub>.<sup>6</sup> Thus diffusion did not contribute significantly to the decay time.

The lasers were triggered by a home-made multichannel pulse generator. The time resolution of the experiments was obtained from the variable delay between the photolysis and the probe laser. For the detection of NH(a) the P(2) line of the transition NH- $((c^{1}\Pi,v=0)-(a^{1}\Delta,v=0))$  was excited at  $\lambda_{L} = 325.6$  nm. The products NH(X) and OH were detected by the excitation of intense lines at  $\lambda_{L} = 336.2$  nm [Q<sub>1</sub> branch of NH((A<sup>3</sup>\Pi,v= 0)-(X<sup>3</sup>\Sigma<sup>-</sup>,v=0))] and at  $\lambda_{L} = 308.3$  nm [P<sub>1</sub>(1) line of OH- $((A^{2}\Sigma^{+},v=0)-(X^{2}\Pi,v=0))]$ , respectively.

The laser-induced fluorescence was monitored with the photomultiplier and recorded with a transient digitizer (Tektronix, 7912 AD) which was coupled to a minicomputer (DEC, PDP 11/34) for signal processing. Noise reduction was achieved by signal averaging over 4-64 fluorescence pulses and the radical concentration was taken to be proportional to the averaged and integrated signal. For comparison of radical concentrations in different gas mixtures (different reactants or different total pressures), instead of the integrals of the fluorescence intensity versus time, the amplitudes of the fluorescence intensity averaged over many pulses were evaluated to obtain the fluorescence intensity immediately after the dye laser excitation. The amplitudes were not affected by the different rates of collisional quenching of the fluorescing electronic state provided that the widths of the fluorescence pulses were substantially larger than the width of the exciting dye laser pulse of  $t_{L,1/2} \approx 15$  ns. If the experimental conditions were kept constant (HN<sub>3</sub> pressure, photolysis energy, detection sensitivity) and only the reactant was changed, the comparison of the signal amplitudes of a product radical gave the relative yield of the product radical in the corresponding NH(a) reaction. The branching ratios for the formation of the products NH(X) and OH were determined in this way.

For the quantitative determination of the branching to the products OH + NO in the reaction of NH(a) with  $O_2$  the absolute concentrations of the educt NH(a) and the product OH were measured. The absolute concentration of OH was obtained by calibration of the OH detection sensitivity. For this measurement, the gas cell was connected to an isothermal discharge flow reactor consisting of a Pyrex tube with a movable probe. This flow system allows the generation of OH radicals by the reaction

$$H + NO_2 \rightarrow OH + NO$$

The hydrogen atoms H were generated in a side arm of the flow reactor in a microwave discharge of H<sub>2</sub> burning in He. NO<sub>2</sub> was added in well-known concentrations with the probe. The fast and quantitative reaction of NO<sub>2</sub> with an excess of H atoms yielded defined absolute concentrations of OH and enabled calibration of the OH detection sensitivity in the observation region of the gas cell. The time between formation and detection of OH was sufficient to relax its vibrational states to the thermal distribution.

The absolute concentration of NH(a) at the start of the reaction after the photolysis pulse was obtained by evaluation of the absorption of  $HN_3$  with Lambert-Beer's law. For this evaluation the beam cross section of the photolysis laser and the pulse energy were measured directly at the observation region in the gas cell

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Figure 2. Correlation diagram of the electronic states in the system HN<sub>3</sub>  $\leftrightarrow$  NH + N<sub>2</sub> (energies are given in kJ/mol).

(energy detector: Oriel, 142 LR). The absorption coefficient of HN<sub>3</sub> amounts to  $\epsilon$ (248 nm) = 2.3 × 10<sup>-20</sup> cm<sup>2</sup>/molecule.<sup>7</sup> The quantum yield of the formation of NH(a) from the HN<sub>3</sub> photolysis is taken to be  $\phi(248 \text{ nm}) \approx 1$ , in agreement with the findings of, e.g., ref 8-12. Here, the photolysis of  $HN_3$  in the wavelength region of  $\lambda \approx 248$  nm has been reported to generate almost exclusively NH in the electronic state  $(a^{1}\Delta)$  as observable product and the fractional population of NH(a) in relation to NH in other electronic states was found to be more than 99%. NH(a) was formed in the vibrational ground state v = 0. The generation of the photodissociation products  $NH(a) + N_2$  from the photolysis of HN<sub>3</sub> is represented schematically in the correlation diagram in Figure 2.

Chemicals with the following purities were used: He 99.9996%, O<sub>2</sub> 99.998%, N<sub>2</sub> 99.999%, Kr 99.99%, Xe 99.99%, NO 99.85% (all Messer Griesheim). NO was applied to the system via a glass trap cooled to -78 °C. HN<sub>3</sub> was produced by metaling stearic acid CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>COOH with NaN<sub>3</sub>. The HN<sub>3</sub> was dried with  $CaCl_2$  and stored in a glass bulb under a pressure of  $p(HN_3) =$ 200 mbar and diluted with He to a total pressure of 1 atm. The purity of HN<sub>3</sub> was analyzed by mass spectrometry and IR absorption. No impurity bands were found in the IR spectra. Analysis by mass spectrometer showed that the possible impurities  $NH_3$  and  $N_2H_4$  amounted to less than 0.3 mol %.

#### Results

The reactions of NH(a)

$$NH(a) + R \xrightarrow{k_1(R)} products$$
(1)

were studied by monitoring the NH(a) concentration profiles after  $HN_3$  photolysis. In addition to reaction 1, the NH(a) is also consumed by the precursor:

$$NH(a) + HN_3 \rightarrow products$$

$$k_2 = 7.3 \times 10^{13} \text{ cm}^3/(\text{mol s}) \text{ [ref 6, 9, 11-15]}$$
(2)

The radiative decay of NH(a) ( $\tau_0 \simeq 1.7 \text{ s}^1$ ) and the quenching by He  $(k_1(\text{He}) < 6 \times 10^8 \text{ cm}^3/(\text{mol s})^{14})$  were slow and could

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Figure 3. Semilogarithmic plots of the NH(a) concentration profiles in the reaction NH(a) + Xe for the determination of the quenching rate constant  $k_q(Xe)$ .

be neglected in the experiments studied in this work. The NH(a) concentration is given by

 $-d[NH(a)]/dt = k_1(R)[NH(a)][R] + k_2[NH(a)][HN_3]$ (I)

The ratio of the concentration of the precursor plus reactant over the initial NH(a) concentration was in the range of  $5 \times 10^2 \le$  $cm^3$ )  $\leq 3 \times 10^{-13}$ . Thus the reactions of NH(a) with itself and the reaction products can be neglected. Since  $[NH(a)]_0$  is relative small, i.e.  $[NH(a)]_0 \ll [HN_3]_0 + [R]_0$ , eq I can be written as

$$-d[NH(a)]/dt = k^{1}[NH(a)]$$
(II)

and

$$\ln \{ [NH(a)]_t / [NH(a)]_0 \} = -k^1 \Delta t$$
 (III)

with

$$k^{1} = k_{1}(\mathbf{R})[\mathbf{R}] + k_{2}[\mathbf{HN}_{3}]$$

The pseudo-first-order rate constant  $k^1$  was obtained from the slope of the semilogarithmic plot of NH(a) versus  $\Delta t$  as shown for the reactant Xe as an example in Figure 3. The reactant pressure is varied at constant HN<sub>3</sub> partial pressure and  $k^1$  is obtained as a function of [R]. The slope of the  $k^1$  versus [R] plot obtained by a least-squares fit (see Figure 4, a and b) is taken as the second-order rate constant for the overall NH(a) depletion by the reactant. The intercepts of these plots reflect in good approximate the rate of reaction 2 for the corresponding HN<sub>3</sub> pressure. The stated error limits of the rate constants include the estimated systematic errors, arising from the uncertainty of the gas flows and the pressure in the gas cell and from the statistical errors. The error limits given here are in all cases larger than

The rate of the reaction NH(a) + Kr was found to be small and an upper limit of the rate constant was determined:

$$k_1(\mathrm{Kr}) \leq 6 \times 10^9 \mathrm{cm}^3 / (\mathrm{mol s})$$

For Xe a very fast rate is obtained with

$$k_1(\text{Xe}) = (7.2 \pm 0.7) \times 10^{12} \text{ cm}^3/(\text{mol s})$$

This is much faster than expected from the "heavy atom effect" (see Discussion).

For N<sub>2</sub> two independent experiments were performed at different photolysis wavelengths:  $\lambda_L = 248$  and 308 nm. For  $\lambda_L =$ 



**Figure 4.** Stern-Volmer plots of the NH(a) depletion: (a, top) for the reactions with Xe and NO; (b, bottom) for the reactions with  $O_2$  and  $N_2$ .

248 nm and short reaction times an increase of the NH(a) concentration was observed in the ln [NH(a)] versus  $\Delta t$  plot (see Figure 5, a and b) indicating a formation of NH(a) at short reaction times after the photolysis pulse. At longer reaction times ( $\Delta t \ge 20-50 \mu$ s, depending on the N<sub>2</sub> pressure) a single-exponential decay was observed. This time range was used to evaluate the rate constant of the NH(a) depletion reaction by N<sub>2</sub>. After photolysis of HN<sub>3</sub> at  $\lambda_L = 308$  nm a single-exponential decay of NH(a) was obtained at all reaction times. The slope of ln [NH(a)] versus  $\Delta t$  in these experiments was identical with that observed after the 248-nm photolysis at long reaction times. The NH(a) depletion rate constant from the plots is

$$k_1(N_2) = (5.0 \pm 0.5) \times 10^{10} \text{ cm}^3/(\text{mol s})$$

A possible pressure dependence of this rate constant was examined by adding He to the gas mixture up to a total pressure of  $P_{\text{total}} = 180 \text{ mbar } [p(N_2) = 30 \text{ mbar}]$ . The value  $k_1(N_2)$  from these measurements did not differ from the value obtained at low pressures without He.

To analyze the formation effect at  $\lambda_L = 248$  nm further experiments were performed. (i) Energy relaxation within the NH(a) system was checked as a possible cause of the formation of NH(a) in the observed quantum state. Rotational relaxation of NH(a) is rapid under the experimental conditions and is completed within  $\Delta t \leq 1 \ \mu$ s. This was confirmed by excitation spectra of NH(a) at  $\Delta t = 1 \ \mu$ s ( $p(HN_3) = 2.7 \times 10^{-3} \ mbar$ ,  $p(He) = 10 \ mbar$ ) exhibiting a population of rotational states according to an equilibrium distribution at room temperature. The formation of higher vibrational states (NH(a,v>0)) in the photolysis was examined for NH(a,v=1), which was detected via the transition NH(c,v=1)-NH(a,v=1) at  $\lambda = 338 \ mmodel{nm}$ . No formation of NH(a,v=1) was observed, i.e., the NH(a,v=1) was less than 1% of



Figure 5. Semilogarithmic plots of the NH(a) concentration profiles after the photolysis of HN<sub>3</sub> at  $\lambda_L = 248$  nm in presence of N<sub>2</sub>: (a, top)  $p(HN_3) = 1.7 \times 10^{-3}$  mbar,  $p(N_2) = 14$  mbar; (b, bottom)  $p(HN_3) =$  $1.7 \times 10^{-3}$  mbar,  $p(N_2) = 21$  mbar. (×) Experimental points connected by the lower line; upper line is extrapolation from long reaction times.

the NH(a,v=0) at all reactions times and all N<sub>2</sub> pressures. Quenching from the metastable electronic state NH( $b^{1}\Sigma^{+}$ ) to NH(a) was not investigated explicitly here since its formation in the photolysis of HN<sub>3</sub> has been reported to be negligible.<sup>10</sup> (ii) Multiphoton effects were examined by changing the intensity of the photolysis laser. A variation of the laser intensity by a factor of 5 did not alter the characteristics of the NH(a) profiles.

For the concentration profiles of NH(a) after photolysis at  $\lambda_L$ = 248 nm in the presence of N<sub>2</sub> neither energy relaxation within the NH state system nor multiphoton absorption of HN<sub>3</sub> or N<sub>2</sub> with consecutive reactions explains the observed time behavior at short reaction times. Further aspects of this effect are discussed in the next section.

For the atoms Kr and Xe and the other diatomic molecules no such effect was observed and the decay of NH(a) is single exponential during the whole reaction time range. The rate constant obtained for  $O_2$  is

$$k_1(O_2) = (2.7 \pm 0.3) \times 10^{10} \text{ cm}^3/(\text{mol s})$$

The rate of the NH(X) product formation in this reaction (see

TABLE I: Quenching Rate Constants for the Reactions of NH(a),  $O(^{1}D)$ , and  $CH_{2}(\tilde{a})$  with Noble Gases (in cm<sup>3</sup>/(mol s))<sup>a</sup>

	He	Ne	Ar	Kr	Xe	
O(1D)	$<1.8 \times 10^{8} (17)$	$3 \times 10^{9} (17)$	$3.0 \times 10^{11} (19)$	$3.9 \times 10^{12}$ (19)	$4.2 \times 10^{13}$ (19)	
	$<4.2 \times 10^{8}$ (18)	$6.6 \times 10^9$ (18)	$4.3 \times 10^{11}$ (18)	$9.3 \times 10^{12}$ (18)	$6.0 \times 10^{13}$ (18)	
NH(a)	$<6 \times 10^8$ (14)	. ,	$<6 \times 10^8$ (14)	$\leq 6 \times 10^{9b}$	$7.2 \times 10^{12b}$	
					$1.4 \times 10^{13}$ c	
$CH_2(\tilde{a})$	$1.9 \times 10^{12}$ (20)	$2.5 \times 10^{12}$ (20)	$3.6 \times 10^{12} (20)$	$4.2 \times 10^{12}$ (20)	$9.6 \times 10^{12} (20)$	
	$2.1 \times 10^{12} (21)$		$3.5 \times 10^{12}$ (21)	$4.8 \times 10^{12}$ (21)		

<sup>a</sup>Numbers in parentheses are reference numbers. <sup>b</sup>This work. <sup>c</sup>Derived from the relative value of  $k_q(X)$  reported in ref 22 together with the absolute value of  $k_2 = 7.3 \times 10^{13}$  cm<sup>3</sup>/(mol s).<sup>6,9,11-15</sup>

below) was found to be in agreement with this value.

The reaction of NH(a) with the stable radical NO was found to be very fast and the rate constant

$$k_1(NO) = (1.8 \pm 0.3) \times 10^{13} \text{ cm}^3/(\text{mol s})$$

was measured.

The reaction products were determined directly and quantitatively. In these experiments advantage was taken of the fact that with noble gases the only reaction product formed is NH(X)

$$\mathrm{NH}(\mathrm{a}) + \mathrm{Xe} \xrightarrow{k_{\mathrm{q}}(\mathrm{Xe})} \mathrm{NH}(\mathrm{X}) + \mathrm{Xe}$$

with  $k_a(Xe)/k_1(Xe) = 1$ . At long reaction times (i.e.,  $\Delta t[Xe]$  $\geq 4 \times 10^{-13}$  [(mol s)/cm<sup>3</sup>]) the NH(a) is almost completely converted by Xe into NH(X). The contribution of the NH(a)consumed in the reaction with HN<sub>3</sub> was minimized by applying small HN<sub>3</sub> concentrations. For the determination of the detection sensitivity of NH(X) relative to NH(a) this contribution was taken into account with the known rate constant of this reaction:

$$NH(a) + HN_3 \rightarrow NH_2(\bar{A}) + N_3$$
  
 $k_2 = 7.3 \times 10^{13} \text{ cm}^3/(\text{mol s}) \qquad (\text{ref } 6, 9, 11-15)$ 

Thus it was possible to calibrate the relative LIF sensitivity of NH(a) and NH(X). This sensitivity ratio was used to determine the branching ratio of the quenching channel in each reaction:

$$NH(a) + R \xrightarrow{k_q(R)} NH(X) + R$$
(1a)

The NH(X) concentrations were measured alternately from the reaction NH(a) + Xe and NH(a) + R, changing only the reactant and under otherwise identical experimental conditions. From the decrease in NH(X) with long reaction times  $\Delta t \gtrsim 50 \ \mu s$  in presence of Xe, He, and HN<sub>3</sub> an upper limit was obtained for the rate of the reaction of NH(X) with  $HN_3$ :

$$NH(X) + HN_3 \rightarrow products$$
  $k \le 5 \times 10^{10} \text{ cm}^3/(\text{mol s})$ 

With the small HN<sub>3</sub> pressures applied in this work the removal of NH(X) in the consecutive reaction  $NH(X) + HN_3$  is very slow.

For the reaction  $NH(a) + N_2$  it was found that NH(a) is removed completely (within the experimental error limits) by physical quenching. A branching ratio of

$$k_0(N_2)/k_1(N_2) = 1.0^{(+)} 0.2$$

was measured (photolysis wavelength  $\lambda_L = 308$  nm). At  $\lambda_L =$ 248 nm the additional formation of NH(a) at short reaction times, as described above, makes direct determination of the value  $k_0(N_2)/k_1(N_2)$  from the [NH(a)]/[NH(X)] concentration ratios impossible.

For  $O_2$  the physical quenching was found to be the main pathway for NH(a) depletion. A concentration profile of the product NH(X) formed in the reaction NH(a) +  $O_2$  is shown in Figure 6. From the quantitative comparison with the NH(X)formed in the reaction NH(a) + Xe the following branching ratio was determined:

$$k_{\rm q}({\rm O}_2)/k_1({\rm O}_2) \ge 0.6$$

Here the reaction

$$NH(X) + O_2 \rightarrow products \qquad k = 5.6 \times 10^9 \text{ cm}^3/(\text{mol s})$$
(ref 16)



Figure 6. Concentration profile of the product NH(X) formed in the reaction NH(a) + O<sub>2</sub> ( $\lambda_L$  = 248 nm,  $p(HN_3)$  = 7.9 × 10<sup>-3</sup> mbar,  $p(O_2)$ = 30 mbar). The line connects the experimental points.

was taken into account as an important NH(X) sink, since this reaction is slower than the reaction of  $NH(a) + O_2$  by only a factor of 5.

Among the chemical channels which have a contribution of  $\leq$ 40%, several specific pathways are energetically available:

$$NH(a) + O_2 \xrightarrow{\kappa_{OH}O_2} NO + OH \qquad \Delta H_r^\circ = -373 \text{ kJ/mol}$$
  

$$\rightarrow NO_2 + H \qquad \Delta H_r^\circ = -252 \text{ kJ/mol}$$
  

$$\rightarrow HNO + O \qquad \Delta H_r^\circ = -154 \text{ kJ/mol}$$

The formation of NO + OH was directly investigated by detecting  $OH(X^2II)$  with LIF. The concentration of OH relative to NH(a)was obtained by calibrating the detection sensitivity for OH and evaluating the NH(a) concentration from the HN<sub>3</sub> absorption according to Lambert-Beer's law (see Experimental Section). A small OH LIF signal was detected due to the reaction NH(a) +  $O_2$ . As an upper limit it can be stated that the reaction NH(a)  $+ O_2$  yields less than 6% OH relative to the initial concentration of NH(a):

$$k_{\rm OH}({\rm O_2})/k_{\rm q}({\rm O_2}) \le 0.06$$

From this measurement it can be concluded that the chemical channel leading to OH + NO is a minor pathway.

For NO the analysis of the products is complicated by the rapid reaction of NH(X) with NO. Preliminary results indicated that a small fraction of the NH(a) removal proceeds by physical quenching. Further studies are under way.

#### Discussion

The rate constants of the reactions

 $NH(a) + Kr, Xe \rightarrow NH(X) + Kr, Xe$ 

together with the rate constants obtained for the quenching of NH(a) by other noble gases are summarized in Table I and compared to the quenching rates of the isoelectronic species  $O(^{1}D)$ and  $CH_2(\tilde{a})$ .

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The rate of  $k_{a}(Xe)$  is in agreement with the observation of Kodama,<sup>22</sup> who found that Xe is an effective quencher and gave the ratio  $k_q(Xe)/k_2 = 0.19$ . With a value of  $k_2 = 7.3 \times 10^{13}$  cm<sup>3</sup>/(mol s)<sup>6,9,11-15</sup> a rate constant of  $k_q(Xe)$  is obtained, which is higher by a factor of 2 than that observed in this study.

In the reaction of NH(a) with noble gases the change of the quenching rate constants with the atomic mass of the quencher is most significant from Kr(Z=36) to Xe(Z=54). The observed change in  $k_{q}$  of more than 3 orders of magnitude is higher than expected from the change in the spin-orbit coupling due to the heavy atom effect.<sup>23</sup> For  $O(^{1}D)$  and  $CH_{2}(\tilde{a})$  only an increase of a factor of 6 and 2, respectively, is obtained.

The large change of  $k_q(Kr)$  to  $k_q(Xe)$  could be due to formation of an exciplex in the Xe-NH(a) reaction whereas in the Kr-NH(a) system the interaction potentials are purely repulsive with a "crossing" of the potential curves at high energies. Thus a significant positive temperature dependence of  $k_{q}(Kr)$  is expected.

For  $O(^{1}D)$  a significant change in the rate constants is observed from Ne to Ar. This is in agreement with the change from a purely repulsive  $Ne-O(^{1}D)$  interaction to an attractive potential for Ar–O(<sup>1</sup>D) as calculated for these systems.<sup>24</sup> For CH<sub>2</sub>( $\tilde{a}$ ) all quenching rates are high and only a small increase with increasing Z is observed.

For the reaction

$$NH(a) + O_2 \rightarrow products$$

two indirect measurements have been reported in the literature by McDonald et al.<sup>25</sup> and Drozdoski et al.<sup>26</sup> McDonald et al. attempted to deduce the rate from the detection of the chemiluminescence reaction NH(a) + HN<sub>3</sub>  $\rightarrow$  NH<sub>2</sub>( $\tilde{A}^2A_1$ ) + N<sub>3</sub> which proceeds in competition with the reaction  $NH(a) + O_2$ , if the  $HN_3$ photolysis is used as the NH(a) source. For the reaction NH(a) $+ O_2$  an apparent production rather than a consumption of NH(a) resulted from these measurements, indicating that this method is not suitable to the investigation of the reaction  $NH(a) + O_2$ . From the NH(X) profiles after photolyzing HNCO at  $\lambda = 193$ nm in the presence of O<sub>2</sub>, Drozdoski et al. determined a rate constant  $k_1(O_2) = 9.3 \times 10^{12} \text{ cm}^3/(\text{mol s})$ . Recently Cox et al.<sup>13</sup> remarked that they arrived at essentially the same value for  $k_1(O_2)$ from the NH(X) product profiles using  $HN_3$  photolysis as the NH(a) source. These values are more than 2 orders of magnitude higher than the rate constants obtained in this study.

The value of  $k_1(O_2) = 2.7 \times 10^{10} \text{ cm}^3/(\text{mol s})$  reported here has been determined directly from the NH(a) profiles and is to be preferred, since its determination is independent of the reaction mechanism, whereas the evaluation of the rates from NH(X)profiles assumes that NH(X) is exclusively formed in the primary reaction of NH(a).

The quenching channel

$$\mathrm{NH}(a) + \mathrm{O}_2 \xrightarrow{k_{q}(\mathrm{O}_2)} \mathrm{NH}(\mathrm{X}) + \mathrm{O}_2$$
(1a)

was found in this work to be the main reaction path with  $k_{a}(O_{2})/k(O_{2}) \geq 0.6$ . This result indicates that an additional formation of NH(X) in processes other than via reaction 1a would not occur in this system. Thus the NH(X) production and the NH(a) depletion profiles should give rise to an identical rate constant. This was actually observed in the experiments described in this work and confirms the results reported here.

It is possible that reaction 1a proceeds as an energy-transfer reaction to produce  $O_2(a^1\Delta_g, v')$  with a reaction enthalpy of  $\Delta H_r^{\circ}$ > -56 kJ/mol, whereas the production of  $O_2(b^1\Sigma_g^+)$  is endothermic  $(\Delta H_r^{\circ} > + 7 \text{ kJ/mol}).$ 

The isoelectronic species  $O(^{1}D)$  and  $CH_{2}(\tilde{a}^{1}A_{1})$  react with  $O_{2}$ in fast reactions. The main channel for  $O(^{1}D)$  is

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$$O(^{1}D) + O_{2}(X) \rightarrow O(^{3}P) + O_{2}(b^{1}\Sigma_{g}^{+})$$

with a rate of  $k(300 \text{ K}) = 2.5 \times 10^{13} \text{ cm}^3/(\text{mol s})^{27}$  whereas the rate for the reaction pathway

$$O(^{1}D) + O_{2}(X) \rightarrow O(^{3}P) + O_{2}(a^{1}\Delta_{g})$$

is at least about 2 orders of magnitude smaller  $k \le 6 \times 10^{11}$  $cm^3/(mol s)$ <sup>28</sup> The reaction of  $CH_2(\tilde{a})$  has a rate constant of  $k(300 \text{ K}) = 2.9 \times 10^{13} \text{ cm}^3/(\text{mol s})^3$  experiments to study the primary products are in progress.

The reaction of NH in its electronic ground state with  $O_2$  with  $k = 5.8 \times 10^9 \text{ cm}^3/(\text{mol s})^{16}$  is a factor of 5 slower than the reaction of NH in its first electronically excited state.

The reaction

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

is expected to be a fast reaction since NO is a molecule with an open electronic shell. To our knowledge there are no other direct determinations of the rate constant  $k_1(NO)$  reported in the literature. The reactions of  $O(^1D)$  and  $CH_2(\tilde{a})$  with NO are also very rapid with  $k = 5.1 \times 10^{13} \text{ cm}^3 / (\text{mol s})^{29}$  and  $k = 9.6 \times 10^{13}$  $cm^3/(mol s)$ ,<sup>21</sup> respectively.

For the reaction mechanism several open channels are available from the energetic point of view. The quenching channel, as indicated by preliminary results, is only of minor importance. This is understandable, since no electronic adiabatic correlation exists neither in a linear  $(C_{\infty v})$  nor in a planar  $(C_s)$  configuration. The correlation in the lowest symmetry  $(C_i)$  is of course possible.<sup>30</sup>

NH(X) reacts with NO with a rate constant of  $k = 2.8 \times 10^{13}$  $cm^3/(mol s)^{31}$  which is significantly larger than the rate constant of the reaction of the singlet excited state NH(a) + NO. An excited electronic state that reacts slower than the electronic ground state is rare, but for the reactions of NH(a), NH(X) with NO it follows if one considers the reaction NH( $X^{3}\Sigma^{-}$ ) + NO( $X^{2}\Pi$ ) as a "radical-radical" reaction, whereas the NH( $a^{1}\Delta$ ) + NO(X<sup>2</sup> $\Pi$ ) can be addressed as a "molecule-radical" reaction.

The reaction

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

is about a factor of 2 faster than the depletion of NH(a) by  $O_2$ molecules; the reaction  $NH(a) + N_2$  can proceed via the attractive potential of ground-state  $HN_3$  (see Figure 2). The rate constant  $k_1(N_2) = (5.0 \pm 0.5) \times 10^{10} \text{ cm}^3/(\text{mol s})$  determined in this work agrees, within the error limits, with the value reported recently by Bower et al.<sup>32</sup> Bower et al. measured the removal of NH(a) after photolysis of HNCO, NH<sub>3</sub>, or N<sub>2</sub>H<sub>4</sub> at  $\lambda_L$  = 193 nm and obtained a rate constant of  $k_1(N_2) = (4.5 \pm 0.4) \times 10^{10} \text{ cm}^3/(\text{mol})$ s).

The only product channel in the reaction  $NH(a) + N_2$  is the quenching to NH(X); the combination adduct  $[HN_3(X)]^*$  is not stabilized at low pressures. This was established experimentally in this study. The branching ratio of the quenching channel was found to be  $k_q(N_2)/k_1(N_2) = 1.0^{(+)} 0.2$ .

After photolysis of HN<sub>3</sub> in the presence of N<sub>2</sub> at  $\lambda_L$  = 248 nm a nonlinear decay in the plot  $\ln NH(a)$  versus  $\Delta t$  was monitored for short reaction times, indicating a delayed formation of NH(a). This nonlinear behavior was not observed for the photolysis wavelength of  $\lambda_L = 308$  nm. For long reaction times both experiments lead to the same quenching rate constant and an influence of this effect on the depletion rate measurements can be eliminated. This is confirmed by the agreement with the measurements of Bower. Nevertheless an explanation is warranted. (i) Relaxation within the NH state system cannot explain the

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formation of NH in the observed state NH( $a^{1}\Delta, v'=0, K=2$ ), since the photolysis of HN<sub>3</sub> does not generate NH in higher vibronic states and the rotational relaxation into the detected rotational state K = 2 is much faster than the observed formation (see Results). (ii) Chemical reactions of  $HN_3$  with excited  $N_2$  molecules could explain the observed profiles if they would proceed with reasonable rates. An excitation of  $N_2(X)$  to electronically excited states is possible with one photon (248 nm) only for vibrationally excited  $N_2(X)$  with  $v \ge 6$  [for the forbidden transition to the electronic state  $N_2(A^3\Sigma_u^+)$ ]. Excitation with more than one photon is possible also for  $N_2(X,v=0)$  but a dependence of the observed NH(a) formation effect on the photolysis laser intensity should be found. Our results, however, indicate that such a dependence does not exist. Further experiments at other wavelengths and attempts to admix HN<sub>3</sub> later than the irradiation of  $N_2$  are in progress.

The reaction pathways and the energetics of the reaction NH(a) $+ N_2$  are represented schematically in Figure 2. The attractive electronic ground-state  $HN_3(\tilde{X}^1A')$  potential correlates adiabatically with the  $NH(a)-N_2(X)$  initial states. Stabilization of  $[HN_3(\bar{X})]^*$  in collisions is not efficient in the pressure range used in this work. The addition of He up to 150 mbar did not change the observed quenching rate and the branching ratio of the quenching channel amounts to 100%. The quenching mechanism of the reaction  $NH(a) + N_2$  is the nonadiabatic transition from the  ${}^{1}A'$  to the  ${}^{3}A''$  potential in the HN<sub>3</sub> system. Assuming that there is no significant energy barrier on the  $NH(a)-N_2(X)$  entrance channel a  ${}^{1}A' - {}^{3}A''$  transition probability for a single crossing of  $\gamma \simeq 1.2 \times 10^{-3}$  can be derived from the value of  $k_1(N_2)$  with a Lennard-Jones parameter of  $\sigma_{LJ} = 3.3$  Å for a NH(a)-N<sub>2</sub> collision. The small value of the transition probability is in reasonable agreement with the values estimated from experiments concerned with the unimolecular decomposition of  $HN_{3}$ .<sup>33,34</sup>

Acknowledgment. We are grateful for the support and encouragement given to us by Prof. H. Gg. Wagner. Financial support of the Deutsche Forschungsgemeinschaft SFB 93 is acknowledged.

Registry No. NH, 13774-92-0; Kr, 7439-90-9; Xe, 7440-63-3; N<sub>2</sub>, 7727-37-9; O<sub>2</sub>, 7782-44-7; NO, 10102-43-9; HN<sub>3</sub>, 7782-79-8.

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# **Backward Electron Transfers within Geminate Radical Pairs Formed by** Electron-Transfer Quenching of Phosphorescent States of Tris(2,2'-bipyrazine)ruthenium(II) and Tris(4-methyl-2-(2'-pyridyl)pyrimidine)ruthenium(II)

## Takeshi Ohno,\* Akio Yoshimura, Noboru Mataga,<sup>†</sup> Shigeo Tazuke,<sup>‡</sup> Yuji Kawanishi,<sup>‡</sup> and Noboru Kitamura<sup>‡</sup>

Department of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560, Japan (Received: April 5, 1988; In Final Form: November 17, 1988)

The triplet excited states of tris(2,2'-bipyrazine)ruthenium(II) and tris(4-methyl-2-(2'-pyridyl)pyrimidine)ruthenium(II) were studied by means of nanosecond laser kinetic spectroscopy. A close similarity was found between the absorption spectra of the triplet excited state and the one-electron-reduced species of tris(2,2'-bipyrazine)ruthenium(II). The molar extinction coefficients of the excited ruthenium(II) compounds were determined by means of an energy-transfer reaction. Yields (0.55-0.88) of the primary electron-transfer (ET) products formed in the quenching by organic donors such as aromatic amines and methoxybenzenes were determined. The rates of backward ET within the geminate radical pair formed in the quenching are estimated from the yield. The  $\Delta G^{\circ}$  dependence of the backward ET rates is bell-shaped and is discussed in terms of Franck-Condon factor and electronic coupling.

## Introduction

Electron transfer (ET) is one of the most fundamental reactions in chemistry and biology. Reaction rates of bimolecular ET in condensed media have been studied theoretically and experimentally. Theories predict that reaction rates of ET increase with exergonicity to a maximum and then decrease with increasing exergonicity in the highly exergonic region.<sup>1</sup> A number of experimental studies of bimolecular ET in polar solvents have revealed that a diffusion-controlled collisional process limits the ET rate before it reaches the intrinsic maximum.<sup>2</sup> Rates of fast ET processes faster than the diffusion process have been estimated in the case of the recombination of the geminate radical ion pairs produced by bimolecular ET quenching of luminescence in solution.<sup>3-8</sup> Rates of the ET processes occurring within the geminate radical pair are estimated from the free-radical yields in the

luminescence quenching. We have studied reaction rates of backward ET occurring within a geminate radical pair which was produced in the quenching of fluorescence<sup>5-7</sup> or phosphorescence<sup>3,4,8</sup>

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<sup>&</sup>lt;sup>†</sup>Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560. <sup>‡</sup>Research Laboratory of Resource Utilization, Tokyo Institute of Tech-

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