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THE REACTION OF NH$_2$ WITH NO$_2$

by

R. K. M. Jayanty, R. Simonaitis and Julian Heicklen

July, 1976

IONOSPHERE RESEARCH LABORATORY

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$$H + NO_2 \rightarrow HO + NO$$

1

The other measured products of the reaction were N_2 and N_2O with respective quantum yields of 0.94 ± 0.10 and > 0.3 in the presence of small amounts of He (~ 5 torr) and 0.65 ± 0.15 and > 0.13 in the presence of a large excess of He. The quantum yield for NO_2 consumption was 6.0 ± 2.0 in the absence of He. These results are explained in terms of the reactions

$$NH_2 + NO_2 \rightarrow N_2O + H_2O \qquad\qquad 4a$$
$$\rightarrow N_2 + 2OH \qquad\qquad 4b$$
$$\rightarrow N_2 + H_2O_2 \qquad\qquad 4c$$
$$\rightarrow 2HNO \qquad\qquad 4d$$

$$\rightarrow \text{solid or undetected product} \atop \text{ultimately} \qquad\qquad 4e$$

The relative importance of the reaction channels are $(k_{4a} + k_{4d})/(k_{4b} + k_{4c}) > 0.3$ in the presence of small amounts of He (5 torr) and > 0.20 in the presence of a large excess of He. The ratio $k_{4b}/k_4 \simeq 0.34$ if $k_{4c} = 0$ or $k_{4c}/k_4 \simeq 0.42$ if $k_{4b} = 0$. Reaction channels 4a-4d account for $> 65\%$ of the reaction. The overall rate coefficient for reaction 4 is larger than for the NH_2-NO reaction, i.e. $> (2 \pm 1) \times 10^{-11}$ cm^3 sec^{-1}.

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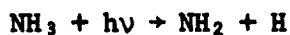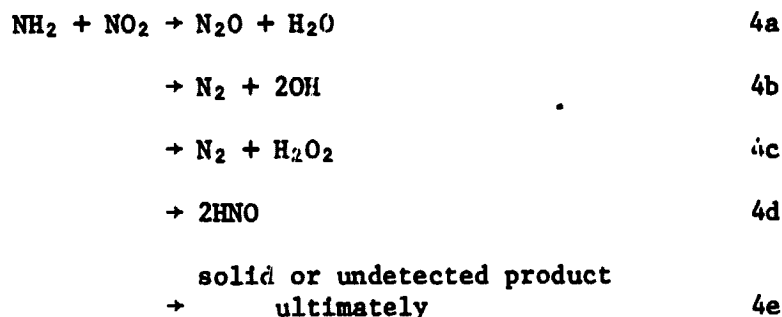
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Abstract

NH$_3$ was photolyzed at 213.9 nm in the presence of NO$_2$ at 25°C in order to study the reactions of NH$_2$ with NO$_2$.

$$NH_3 + h\nu \rightarrow NH_2 + H$$

The products included NO, with a quantum yield of 1.0, and it can be attributed to the reaction

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Introduction

The reaction of NH_2 radicals with NO_2 has been, so far as we know, the subject of only one study. Bedford and Thomas (1) studied the thermal reaction of NH_3 and NO_2 in the temperature range of 615-660°K. The kinetics of the reaction was consistent with an abstraction between NH_3 radicals and NO_2

$$NH_2 + NO_2 \rightarrow NH + HNO_2 \qquad\qquad 1a$$

The reaction

$$NH_2 + NO_2 \rightarrow N_2O + H_2O \qquad\qquad 1b$$

was found to be unimportant. In this note we report on a brief study of the photolysis of NH_3 in the presence of NO_2 at 213.9 nm. The object was to study the reaction of NH_2 radicals with NO_2 at room temperature.

Experimental

A conventional high vacuum line utilizing Teflon stopcocks with Viton "O" rings was used. Pressures were measured with a dibutylphthalate manometer and a Wallace and Tiernan gauge. The reaction vessel was a cylindrical quartz cell 10 cm long and 5 cm in diameter.

The N_2O, NH_3, and NO_2 were Matheson C.P. grade. The N_2O was degassed at -196°C and distilled in Vacuo from a dry ice-acetone bath. The NH_3 was degassed at liquid nitrogen temperatures and purified by distillation from -96°C to -130°C. The NO_x was degassed at -196°C and diluted with helium.

Irradiation was from a Phillips Zn resonance lamp TYP 93106E. The effective radiation was at 213.9 nm. After irradiation the gases non-condensable at -196°C were expanded into a calibrated volume and analyzed for N_2 by gas chromatography using a 10 ft. long, 1/4 inch O.D. copper column packed with 5Å molecular sieves. The condensables were then analyzed for N_2O using a 24 ft. long, 1/4 inch O.D. copper column packed with Poropak Q. These columns were operated at room temperature. The carrier gas in all cases was helium.

NO production in the NH_3-NO_x system was determined using a chemiluminescent detector described earlier (?). The lower limit of the detector sensitivity was about 10 ppb, but the NH_3-NO_2 system always gave a background signal corresponding to about 4 mTorr of NO. NO_2 removal rates were determined by differential absorption spectroscopy. The limit of NO_2 detection was $\sim$ 15 mTorr. Formation of products after photolysis was also checked by infrared absorption using a Perkin Elmer 521 spectrometer, but none were detected.

Actinometry was done by photolysis of an optically equivalent amount of N_2O. The quantum yield of N_2, $\Phi\{N_2\}$, for this system is known to be 1.41 (3) at 213.9 nm. The relative value for the absorption coefficient of NH_3 to that of N_2O is 50 ± 5 (4).

Results

The photolysis of NH_3 in the presence of NO_2 ($\lesssim 0.2$ torr) at 213.9 nm and 25°C leads to the production of N_2, NO, N_2O, and a solid product, presumably NH_4NO_3 or possibly NH_4NO_2. The results for the photolysis are given in Table I. The range of concentration conditions which could be used was severely restricted by a dark reaction giving the same products (5). This dark reaction becomes dominant for $[NO_2] > 0.2$ mtorr and $[NH_3]$ > 2 torr. Much lower concentrations of NO_2 could not be employed because of the need to produce sufficient product yields for analysis. The product quantum yields were all corrected for the accompanying dark side reaction. The maximum corrections for the conditions employed were N_2O, $\leq 25\%$; N_2, $\leq 30\%$; NO_2, $\leq 10\%$; NO, $\leq 30\%$. The effect of absorbed light intensity, I_a, and irradiation time was determined only for $\Phi\{NO\}$. For the other products the effect of I_a and time of irradiation was not determined, because of experimental restrictions. The results indicate that $\Phi\{N_2\} = 0.94 \pm 0.2$, and $-\Phi\{NO_2\} = 6.0 \pm 2.0$, where the uncertainties are the estimated errors in the measurements. Only a lower limit to $\Phi\{N_2O\} \gtrsim 0.3$ was estimated, because a significant dark background of N_2O required extended irradiation such that most of the NO_2 was consumed. $\Phi\{NO\} \sim 1.0$ over an extended time of irradiation, but declines in the later stages, either due to secondary reactions, or to the fact that the sampling capillary is plugged by solid NH_4NO_2 or NH_4NO_3 reducing gas flow into the chemiluminescent detector. Photolysis of NO_2 in the absence of NH_3 also gives NO ($\sim 10\%$ of the NO produced with NH_3 present). The NO quantum yields in Table I are corrected for the NO produced from NO_2 photolysis. Plots of [NO] vs irradiation time are shown for one run, and for separate runs at different times in Fig. 1.

In most runs a significant amount of NO_2 was consumed, up to 100% if $-\phi\{NO_2\}$ remains constant, but there does not appear to be a significant dependence of $\phi\{NO\}$ on $[NO_2]$.

In Table II are results in the presence of a large excess of He. $\phi\{NO\}$ remains at 1.0, but both $\phi\{N_2\}$ and $\phi\{N_2O\}$ are reduced; the former to 0.65 ± 0.13, and the later to ≥ 0.13.

Discussion

The initial step in the photolysis of NH_3 leads to the production of NH_2 and H

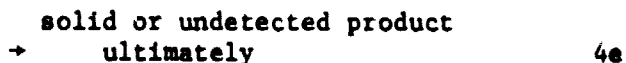$$NH_3 + h\nu \ (213.9 \text{ nm}) \rightarrow NH_2 + H \qquad \qquad \text{Rate} = I_a$$
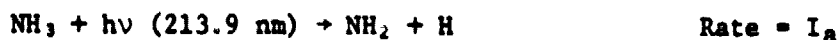
The H atom produced in the primary act can react only with NO_2.

$$H + NO_2 \rightarrow OH + NO \qquad \qquad 1$$

The OH produced in reaction 1 can react with either NH_3 or NO_2, the relative proportion depending on the total pressure and the $[NH_3]/[NO_2]$ ratio.

$$OH + NH_3 \rightarrow H_2O + NH_2 \qquad \qquad 2$$

$$OH + NO_2 \ (+M) \rightarrow HONO_2 \ (+M) \qquad \qquad 3$$

The $HONO_2$ produced reacts further with NH_3 to give solid NH_4NO_3. There are several possible reactions of NH_2 with NO_2

$$NH_2 + NO_2 \rightarrow N_2O + H_2O \qquad \qquad 4a$$

$$\rightarrow N_2 + 2OH \qquad \qquad 4b$$

$$\rightarrow N_2 + H_2O_2 \qquad \qquad 4c$$

$$\rightarrow 2HNO \qquad \qquad 4d$$

$$\rightarrow \begin{array}{l} \text{solid or undetected product} \\ \text{ultimately} \end{array} \qquad \qquad 4e$$

$$\rightarrow NH + HNO_2 \qquad \qquad 4f$$

Reaction 4f is 13.5 kcal/mole endothermic (1). Therefore the upper limit for k_{4f} at 300°K is about 10^{-20} cm^3 sec^{-1}; thus it may be neglected at 300°K, but apparently it is important at higher temperatures (1). Reactions 4a – 4c are formally analogous to the well known fast reaction

$$NH_2 + NO \rightarrow N_2 + H_2O \qquad \qquad 5$$

The observed N_2 production must occur by reaction 4b or 4c, because the alternate route to N_2 production via the secondary process consisting of reactions 1 and 5 cannot be important since $\phi\{NO\} = 1.0$ and NO is produced

with a constant rate up to [NO] = 36 mtorr (Fig. 1). The only source of NO appears to be reaction 1. Since NO production is linear up to [NO]/[NO₂] ∿ 0.4, reaction 5 cannot compete with reaction 4 up to this value of the ratio. Thus $k_4 > (2 \pm 1) \times 10^{-11} cm^3 sec^{-1}$, since $k_5 = (2 \pm 1) \times 10^{-11}$ cm³ sec⁻¹ (6). The large quantum yield of NO_2 removal, $-\Phi\{NO_2\} = 6$ in the absence of He, can be accounted for by the fact that HO radicals propagate a chain, and NO_2 is known to react with H_2O_2 to regenerate the HO radical (7).

$$H_2O_2 + NO_2 \rightarrow HONO_2 + HO \qquad\qquad 6$$

The source of the N_2O is probably reaction 4a, but the unlikely reaction 4d followed by

$$2HNO \rightarrow N_2O + H_2O \qquad\qquad 7$$
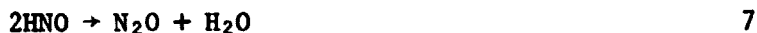
cannot be ruled out from the present data. If HNO is produced it must always be removed by reaction 7. Reaction with NO_2

$$HNO + NO_2 \rightarrow HONO + NO \qquad\qquad 8$$

can be ruled out, because then $\Phi\{NO\}$ would exceed 1.0 contrary to the observations.

Since $\Phi\{N_2\} = 0.94$ and $\Phi\{N_2O\} > 0.3$ in the presence of small amounts of He, $(k_{4a} + k_{4d})/(k_{4b} + k_{4c}) > 0.32$. Similarly in the presence of excess He, $\Phi\{N_2\} = 0.65$ and $\Phi\{N_2O\} > 0.13$; $(k_{4a} + k_{4d})/(k_{4b} + k_{4c}) > 0.20$. Based on the mechanism consisting of reactions 1-4 and 6-7, the rate law expressions for $\Phi\{N_2\}$ and $-\Phi\{N_2O\}$ are

$$\Phi\{N_2\} = \frac{k_{4b} + k_{4c}}{k_4} \left[1 + \frac{\beta(1 + \alpha)}{(1 - \beta\alpha)} \right] \qquad\qquad a$$

$$-\Phi\{NO_2\} = 2 + \frac{k_{4c}}{k_4} + \frac{[(1 - \beta) + \beta(1 + k_{4c}/k_4)](1 + \alpha)}{1 - \beta\alpha} \qquad b$$

where $\alpha \equiv (2k_{4b} + k_{4c})/k_4$

$\beta \equiv k_2[NH_3]/(k_2[NH_3] + k_3[NO_2])$

Values of β can be computed from the known rate coefficients [$k_2 = 2 \times 10^{-13}$ cm^3 sec^{-1} (8) and $k_3 \simeq 1.0 \times 10^{-12}$ cm^3/sec ([He] = 5 torr) (8) and $k_3 \simeq 4 \times 10^{-12}$ cm^3/sec ([He] $\approx$ 400 torr) (8)] and the mean value of the NO_2 pressure ($\sim$ 0.19 torr). Thus β $\simeq$ 0.67 when [He] = 5 torr and $\simeq$ 0.35 in the presence of $\sim$ 400 torr He.
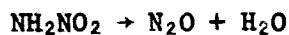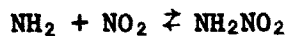
We fit the values found for $\Phi\{N_2\}$ to obtain the branching ratios for reaction 4. With [He] = 5 torr, $k_{4b}/k_4 = 0.34$ if $k_{4c} = 0$ or $k_{4c}/k_4 = 0.41$ if $k_{4b} = 0$. Either combination gives a computed value for $-\Phi\{NO_2\} = 4.9$ in fair agreement with the observed value of 6.0 ± 2.0. With [He] $\simeq$ 400 torr $k_{4b}/k_4 = 0.36$ if $k_{4c}/k_4 = 0$ or $k_{4c}/k_4 = 0.42$ if $k_{4b}/k_4 = 0$. The combinations give computed values for $-\Phi\{NO_2\} = 3.7$ and 4.0, respectively. Takit r the low and high He pressure values the average values of k_{4b}/k_4 = 0.34 if $k_{4c} = 0$, and the average value of $k_{4c}/k_4 = 0.42$ if $k_{4b} = 0$. Combining the values for k_{4c}/k_4 with the ratios $(k_{4a} + k_{4d})/(k_{4b} + k_{4c})$ determined above, the probabilities of the sum of channels 4a, 4c and 4d are > 0.70 and > 0.60 for the low and high He pressures, respectively. If $k_{4c}/k_4 = 0$ the lower limits are slightly lower. A small additional loss of NH_2 via channel 4e is possible.

In a detailed study of the thermal reaction between NH_3 and NO_2 in the temperature range of 615 - 660°K, Bedford and Thomas (1) concluded that the exclusive reaction between NH_2 and NO_2 is reaction 4f. They obtained the ratio $k_5/k_{4f} = 10^{-2.3}$ exp(6400/RT). At room temperature k_5/k_{4f} extrapolates to 2×10^2, and since k_5 is now known to be $(2 \pm 1) \times 10^{-11}$ cm^3 sec^{-1} at 300°K (6), $k_{4f} = 1 \times 10^{-13}$ cm^3 sec^{-1} at 300°K. This value is nearly 7 orders of magnitude greater than the maximum predicted from the endothermicity of reaction 4f.

Bedford and Thomas suggested that reaction 4f is an abstraction reaction. Thus it could become more important at high temperatures than

channels 4a-4e, if these channels proceed through an adduct which can also decompose reversibly, i.e.

$$NH_2 + NO_2 \rightleftarrows NH_2NO_2$$

$$NH_2NO_2 \rightarrow N_2O + H_2O$$

$$\rightarrow N_2 + 2OH$$

$$\rightarrow N_2 + H_2O_2$$

$$\rightarrow 2HNO$$

$$\rightarrow solid$$
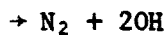
At high temperatures, these reactions become unimportant because the adduct preferentially reverts to reactants, and reaction 4f could become the dominant reaction path.

It is interesting to note that NO_2 does not abstract an H atom from HO_2 to form HNO_2 and O_2, but proceeds via the pernitric acid to the same products (9). Evidence for adduct formation has also been obtained for the reactions of NH_2 with NO (6b) i.e. reaction 5, which is closely related to reaction 4.

Table II

Photolysis of NH₃-NO₂ Mixtures at 213.9 nm and 25°C

in the Presence of He[a]

[He], Torr	Irradiation time, min	[NO] mtorr	$\Phi\{NO\}$	$\Phi\{N_2\}$	$\Phi\{N_2O\}$
280	3.0	-	-	0.62	-
280	5.0	-	-	0.63	-
280	4.0	-	-	-	> 0.13
300	4.0	-	-	-	> 0.12
300	4.0	-	-	0.68	-
500	4.0	-	-	0.66	-
730[b]	2.0	4.3	1.07	-	-

a) $[NH_3] = 2 \pm 0.3$ Torr, $[NO_2] = 195 \pm 11$ mtorr, $I_a = 10.5 \pm 0.4$ mtorr/min.

b) $[NH_3] = 1.46$ torr, $[NO_2] = 109$ mtorr, $I_a = 2.0$ mtorr/min.

List of Figures

Figure 1