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Product Branching Ratios of the $NH_2(X^2B_1) + NO_2$ Reaction

Ned Lindholm and John F. Hershberger*

Center for Main Group Chemistry, Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105

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The reaction of $NH_2(X^2B_1)$ with NO_2 was studied at 298 K using time-resolved infrared diode laser spectroscopy to detect N_2O and NO products. The $N_2O + H_2O$ channel was confirmed to be a rather minor contribution to the overall reaction, with a branching ratio of 0.24 ± 0.04. The branching ratio of the $NO + H_2NO$ channel was measured to be 0.76 ± 0.1.

Introduction

The NH_2 radical is an important intermediate in a variety of combustion environments including the thermal de-NO_x process[1,2] and the chemistry of nitramine propellants.[3] Reactions of NH_2 with NO_x species are therefore of great interest. The $NH_2 + NO$ reaction has been extensively studied[4−14] and is generally accepted to produce primarily $H_2O + N_2$ with a small contribution by the $OH + HN_2$ product channel. The product channels of the $NH_2(X^2B_1) + NO_2$ reaction have until recently received much less study, however. Several possible product channels are thermodynamically accessible:[15−16]

$$NH_2(X^2B_1) + NO_2 \rightarrow N_2O + H_2O \quad \Delta H = -385 \text{ kJ/mol} \tag{1a}$$

$$\rightarrow H_2NO + NO \quad \Delta H = -57.7 \text{ kJ/mol} \tag{1b}$$

$$\rightarrow N_2 + H_2O_2 \quad \Delta H = -364 \text{ kJ/mol} \tag{1c}$$

$$\rightarrow N_2 + 2OH \quad \Delta H = -146 \text{ kJ/mol} \tag{1d}$$

$$\rightarrow 2HNO \quad \Delta H = -25.1 \text{ kJ/mol} \tag{1e}$$

The total rate constant of reaction 1 has been measured by several groups.[15,17−20] Most measurements at 298 K have been in the range $k_1 = (2.1-2.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, although one study[20] reported a substantially lower value of $k_1 = 9.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Measurements at elevated temperatures[15,17,20] have all shown that this reaction has a negative temperature dependence, although there is substantial disagreement on the rate constants at high temperatures. Bulatov et al. observed no dependence of the total rate constant on pressure over the range 10−650 Torr.[15]

Literature data on active product channels of this reaction are more contradictory, however. Ab initio calculations have suggested that channels 1a and 1b are the most likely.[16] Hack et al. used mass spectrometry to detect N_2O and H_2O products.[20] Although no quantitative branching ratio was quoted, they suggested that channel 1a dominates the reaction. A recent flow reactor and kinetic modeling study of the NH_3/NO_2 system suggested that channel 1a is dominant at low temperatures but that 1b becomes important at high temperatures (∼800−1300 K).[21] In contrast to those results, two out of three recent direct studies have indicated that channel 1a is only a minor contributor to the total reaction rate. A recent study in the author's laboratory used 193 nm photolysis of NH_3 to produce NH_2 radicals followed by infrared laser detection of N_2O.[22] A branching ratio of 0.14 ± 0.02 into channel 1a at 298 K was determined. Although ammonia is a highly efficient NH_2 radical source, secondary sources of NO in that study (primarily due to reaction of photolytically produced hydrogen atoms with NO_2) prevented a quantitative determination of the yield of channel 1b. Park and Lin used mass spectrometry detection following NH_3 photolysis to obtain a branching ratio of $\phi_{1a} = 0.19 \pm 0.02$, which was found to be independent of temperature over the range 300−900 K.[23,24] Electron impact cracking of NO_2 produces a large amount of NO in their experiment, again preventing determination of ϕ_{1b}. Meunier et al., however, used a pulse radiolysis source and infrared detection, estimating $\phi_{1a} = 0.59 \pm 0.03$ and $\phi_{1b} = 0.40 \pm 0.05$ at 298 K.[25] Clearly, further work is needed.

In this work, we use an alternative method of generating NH_2. Instead of photolyzing NH_3, we first generate the CN radical by the photolysis of cyanogen iodide at a wavelength where NH_3 has negligible absorption:

$$ICN + h\nu \ (248 \text{ nm}) \rightarrow I + CN \tag{2}$$

NH_2 radicals are formed by the reaction of CN with ammonia:

$$CN + NH_3 \rightarrow HCN + NH_2 \tag{3}$$

This reaction is quite fast, with recent measurements indicating $k = (2.5-2.9) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.[26−28] By use of a bimolecular reaction to form NH_2 rather than direct photolysis, no hydrogen atoms are produced, and therefore, one can obtain a reliable yield of NO from channel 1b. This approach is similar to that of Meunier et al. in which F atoms created by pulse radiolysis react with NH_3 to form HF and NH_2.[25] The primary difference between the present study and that of ref 25 is that our study uses a much lower radical density.

Experimental Section

The experimental apparatus is similar to that used in previous product branching studies.[22,29−32] The photolysis source was an excimer laser (Lambda Physik COMPex 200) operating at 248 nm. The infrared probe beam was a lead salt diode laser (Laser Photonics) operating in the 80−110 K temperature range. Photolysis and probe beams were made collinear using a dichroic mirror and transmitted through a 146 cm single-pass absorption cell with CaF_2 windows. Iris diaphragms (6 mm diameter) were placed at each end of the reaction cell in order

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to ensure reproducible beam overlap. After the cell, the UV light was removed with a second dichroic mirror, and the IR probe beam was focused through a 0.25 m grating monochromator and onto a 1 mm InSb detector (~1 μs rise time). Transient absorption signals were averaged on a LeCroy 9310A digital oscilloscope and stored on a personal computer for further analysis.

Typical experimental conditions were 0.03−0.05 Torr ICN, 0−2 Torr NH_3, 0.05 Torr NO_2, and 1 Torr SF_6 buffer gas. SF_6 buffer gas was chosen because it is efficient at relaxing vibrational excitation of the N_2O and NO products. It is also expected to rapidly relax any internal excitation of the nascent CN and NH_2 radicals. The reaction mixture was allowed to stand for ~5 min in the cell in order to ensure complete mixing. Only 4−8 shots per transient signal were obtained in order to prevent depletion of reactants or buildup of products. All experiments were performed at room temperature (298 ± 3 K).

In some of the experiments it was necessary to estimate the initial radical concentration. This requires knowledge of the incident photolysis laser pulse energy as well as the absorption coefficient of ICN at 248 nm. A joule meter (Molectron) was therefore used to measure the photolysis energy immediately after the second iris. These measurements were taken under the following conditions: with the evacuated reaction cell in place, with the evacuated reaction cell removed from the optical path, with the second iris opening set at 6 mm, and with the second iris set fully open at 25 mm. Owing to window losses with the cell in place, and the slight beam divergence of the photolysis laser, there was about a 30% spread in the energy measurements. Therefore, the average of the four measurements was taken as the best estimate. Typical values for photolysis laser energy were ~10−20 mJ. An absorption coefficient of 0.009 cm^{-1} $Torr^{-1}$ for ICN at 248 nm[29] was used to calculate $[CN]_0$.

NH_3 and SF_6 (Matheson) were purified by repeated freeze−pump−thaw cycles at 77 K. NO_2 (Matheson) was purified at 223 K to remove NO and N_2O impurities. ICN (Aldrich) was purified by vacuum sublimation to remove dissolved air.

Several transitions were used to probe reaction products:

NO ($v = 0 \rightarrow v = 1$)	R(4.5) line at 1893.863 cm^{-1}
	R(6.5) line at 1900.071 cm^{-1}
N_2O ($00^00 \rightarrow 00^01$)	P(19) line at 2206.659 cm^{-1}
	P(23) line at 2202.744 cm^{-1}
	R(16) line at 2236.943 cm^{-1}
CO_2 ($00^00 \rightarrow 00^01$)	P(4) line at 2345.985 cm^{-1}

The experimental results were independent of which spectral line was used for a given molecule. The HITRAN database was used as an aid for the assignment of spectral lines.[33]

Results

Typical transient signals for N_2O and NO product molecules are shown in Figure 1. Off-resonant signals obtained with the infrared laser detuned ~0.02 cm^{-1} off the probed absorption lines were found to be negligible. The rise at early times is due to formation of the product molecules. The rise time is slower than would be predicted by the rate constant of the title reaction because under our conditions product molecules formed in vibrationally excited states take ~100 μs to relax to the ground vibrational state that is probed in these experiments. This phenomenon has been routinely observed in our previous product yield measurements.[22,29−32]

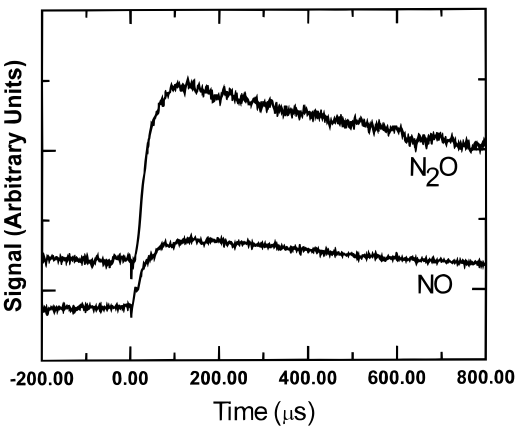

Figure 1. Transient infrared absorption signals for N_2O and NO product molecules. Probed lines are NO $v = 0$ R(4.5) and N_2O (00^00) P(23). Reaction conditions are the following: $P_{ICN} = 0.05$, $P_{NO_2} = 0.05$, $P_{NH_3} = 1.0$, and $P_{SF_6} = 1.0$ Torr.

A possible secondary source of NO products in addition to reaction 1b is direct photodissociation of the NO_2 reagent. When the ICN precursor was omitted from the reaction mixture, transient signals for NO were found to be negligible at the low NO_2 pressures used, indicating that NO_2 photodissociation is not a significant factor in these experiments.

Transient absorption signals were converted into absolute number densities using equations described in previous publications.[22,29−32] The only change is that the infrared absorption coefficients of the NO lines probed were found, by direct measurement of fractional absorption of standard NO samples, to be ~30% smaller than those tabulated in the HITRAN database. This discrepancy is probably at least partly due to instrumental broadening of the particular laser diode used for NO detection. Since the same diode was used in both the absorption coefficient and product yield experiments, it was deemed appropriate to use our absorption coefficients in the number density calculations.

The most important secondary reactions that must be considered involve reaction of photolytically produced CN radicals with NO_2 rather than the desired reaction with NH_3:

$$CN + NO_2 \rightarrow NCO + NO \quad (4a)$$

$$\rightarrow N_2O + CO \quad (4b)$$

$$\rightarrow CO_2 + N_2 \quad (4c)$$

Any NCO produced in reaction 4a would then quickly react with NO_2:

$$NCO + NO_2 \rightarrow N_2O + CO_2 \quad (5a)$$

$$\rightarrow 2NO + CO \quad (5b)$$

These reactions are fast, with $k_4 = (7.4−8.1) \times 10^{-11}$ and $k_5 = (1.8−2.7) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.[30−31,34−35] Channel 4a is the major channel in reaction 4,[30] while channel 5a dominates reaction 5.[31] Clearly, both the detected products are produced in the above sequence, and the complexity of the system combined with uncertainties in the data for reactions 4 and 5 imply that it would be difficult to obtain a reliable branching ratio for reaction 1 if these secondary reactions are occurring to a large extent. We therefore suppress reaction 4 by

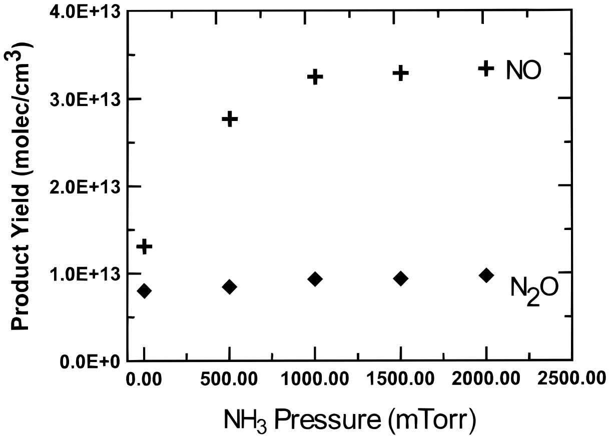

Figure 2. N_2O and NO product yields as a function of NH_3 pressure. Reaction conditions are the following: $P_{ICN} = 0.05$, $P_{NO_2} = 0.05$, P_{NH_3} = variable, and $P_{SF_6} = 1.0$ Torr.

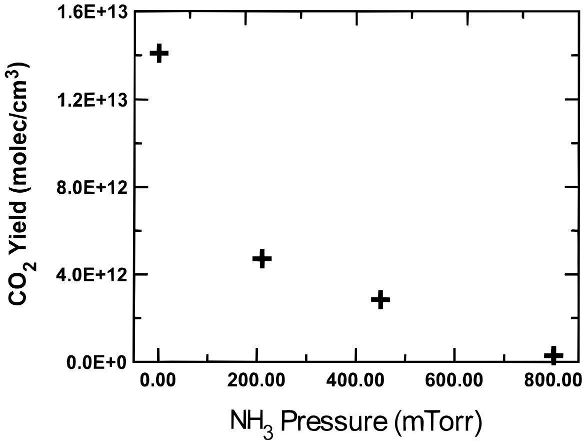

Figure 3. CO_2 product yields as a function of NH_3 pressure. Reaction conditions are the following: $P_{ICN} = 0.03$, $P_{NO_2} = 0.05$, P_{NH_3} = variable, and $P_{SF_6} = 1.0$ Torr.

performing experiments with a large excess of NH_3 over NO_2. Figure 2 shows the effect of varying the initial $[NH_3]$ on the observed yields of N_2O and NO products, while Figure 3 shows the effect on the yield of CO_2 products. Note that reaction 5a is the only plausible source of CO_2 in this system. The decay in the CO_2 yield with increasing $[NH_3]$ indicates that if the $[NH_3]/[NO_2]$ ratio is at least ~20, reactions 4 and 5 are effectively suppressed and nearly all the CN radicals are removed by reaction 3. Additional evidence for this hypothesis is apparent in the fact that the N_2O and NO yield curves (Figure 2) have leveled off at these conditions. The lower N_2O and especially NO yields at low $[NH_3]$ were somewhat unexpected, since reactions 4 and 5 should produce both NO and N_2O in high yield. Under these conditions, however, additional CN loss mechanisms (possibly CN + ICN or radical−radical reactions) may be present. Some evidence for this may be found in Figure 2 of our previous study of reaction 4,[30] which shows that CN produced in the photolysis of an ICN/buffer gas mixture decays faster than expected by diffusional processes alone. Most of the product yield studies in the present work were performed using 0.05 Torr NO_2 and 1.0 Torr NH_3. Under these conditions, secondary chemistry is largely suppressed.

Of the potential minor channels 1c−1e, channel 1d appears the most likely, although ab initio calculations have indicated that the potential energy barrier to form these products is somewhat higher than for channels 1a and 1b.[16] If significant amounts of OH radicals are produced in this reaction, the data analysis would be considerably complicated by the possible re-formation of NH_2 radicals from the reaction

TABLE 1: Branching Ratios of the $NH_2 + NO_2$ Reaction

	ϕ_{1a} ($N_2O + H_2O$)	ϕ_{1b} ($NO + H_2NO$)	ref
this work	0.24 ± 0.04	0.76 ± 0.1	
Park and Lin	0.19 ± 0.02		23, 24
Quandt and Hershberger	0.14 ± 0.02		22
Meunier, Pagsberg, and Sillesen	0.59 ± 0.03	0.40 ± 0.05	25

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

Although this reaction is rather slow, with a recommended rate constant of $k = (1.5-1.6) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ at 298 K,[36,37] it could represent a significant OH removal mechanism at the rather high NH_3 pressures used in our experiment. Since NH_2 is formed, this reaction, when combined with the title reaction, represents a possible chain mechanism. We cannot detect OH directly, but we can efficiently detect carbon dioxide formed by the reaction

$$OH + CO \rightarrow CO_2 + H \tag{7}$$

Experiments were therefore conducted with the addition of 1.0 Torr of CO to the standard reaction mixture. Under these conditions, reaction 7 should occur on a roughly ~100 μs time scale, although some OH would be removed by reaction 6 as well. No increase in CO_2 yield was observed upon addition of CO, indicating that the OH concentration in this system is negligible. We estimate an upper limit of $\phi_{1d} < 0.03$.

There are two approaches for the determination of branching ratios from our product yield data. The first method is to simply assume that all CN radicals are converted to NH_2 by reaction 3 and that all NH_2 radicals subsequently react with NO_2 and therefore report ϕ_{1a} as the ratio of N_2O formed to initial $[NH_2]_0$, and similarly for ϕ_{1b}. Alternatively, one may assume that only the detected channels 1a and 1b are active and quote $\phi_{1a} = [N_2O]/([N_2O] + [NO])$ and $\phi_{1b} = [NO]/([N_2O] + [NO])$. The first method has the advantage of determining whether channels 1c−1e contribute but is somewhat less precise than the second method because of the uncertainties in the determination of $[NH_2]_0$. Using the first method, we obtain $\phi_{1a} = 0.287$ and $\phi_{1b} = 0.92$. These numbers add up to somewhat greater than 1, indicating that our calculated $[NH_2]_0$ is underestimated by about ~20%. These data are consistent, however, with the assumption that channels 1c−1e do not contribute significantly. The second method yields $\phi_{1a} = 0.24 \pm 0.04$ and $\phi_{1b} = 0.76 \pm 0.1$ (average of six experimental runs at 1.0 Torr NH_3 pressure), where the uncertainties represent two standard deviations. We believe the second method provides the more reliable determination in this instance because all active product channels are probed.

Discussion

Table 1 shows a comparison of our results with other recent work. The branching ratio for channel 1a obtained in the present work is in reasonable, although not in outstanding agreement with the study of Park and Lin.[23,24] The value reported here is significantly higher than in our previous study using 193 nm NH_3 photolysis,[22] although the qualitative conclusion that channel 1a is a minor contribution at room temperature remains unchanged. Our results, however, differ dramatically from those obtained in the pulse radiolysis study by Meunier et al.,[25] who used the F + NH_3 reaction to form NH_2 radicals. They report $\phi_{1a} = 0.59 \pm 0.03$ and $\phi_{1b} = 0.40 \pm 0.05$. This discrepancy is especially surprising in view of the similarity of the experimental approaches in ref 25 and this work. There are two possible explanations for this discrepancy. One is that the experiments of ref 25 were performed at a total pressure of ∼30 Torr, while our data are at ∼2 Torr pressure. It is possible that the branching ratio depends on pressure, although this would be quite surprising, since the total rate constant displays no pressure dependence.[15,24] Another difference between their study and ours lies in the radical densities employed. Meunier et al. quote $[F]_0 = 5.7 \times 10^{14}$ molecules/cm^3, in contrast to our typical $[CN]_0$ of $\sim(2-4) \times 10^{13}$. At such high densities, we believe that the reaction

$$F + NH_2 \rightarrow HF + NH \qquad (8)$$

is significant in their experiments and cannot be ignored. No direct measurements of the rate constant for this reaction have been reported, although Fagerstroem et al. inferred $k_8 = 1.16 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} by fitting a kinetic model to experimental data[38] and Donaldson et al. performed energy disposal experiments on the HF products of this reaction.[39] It seems quite likely, in any case, that this reaction proceeds much faster than $F + NH_3$ (although we note that there is significant disagreement in the literature regarding the $F + NH_3$ rate constant).[40−42] Since the $[NO_2]/[F]_0$ ratio in the experiments of ref 25 was only about 10, reaction 8 may be able to compete with the title reaction for NH_2 radicals. The $NH + NO_2$ reaction has been previously estimated in our laboratory to produce $N_2O + OH$ in 41% yield.[32] The reaction $F + NH \rightarrow N + HF$ may further complicate this system. It is therefore quite possible that much of the N_2O observed in the experiments of ref 25 was due to the $NH + NO_2$ and possibly $N + NO_2$ reactions. Simple kinetic modeling calculations on their system suggest that N_2O formation from these secondary reactions can be significant, although the detailed comparisons depend on the values of the rate constants used as well as initial reagent concentrations.

The reasons for the discrepancy in our current value of ϕ_{1a} and our earlier study[22] ($\phi_{1a} = 0.14$) are more difficult to understand. It is certainly true that the experiments reported here have a greater complexity in the possible secondary chemistry for N_2O formation than those of ref 22. Simple kinetic modeling calculations using literature values of rate constants of reactions 1, 3, and 4 suggest that even the high excess of $[NH_3]/[NO_2] \approx 20$ used in our experiments is not sufficient to completely eliminate contributions from the $CN + NO_2$ reaction. This is in contrast, however, to our observation that CO_2 formation (due to the $CN + NO_2$ and $NCO + NO_2$ reactions) is almost completely suppressed under these conditions. In other words, kinetic modeling predicts a slower falloff of $[CO_2]$ vs NH_3 pressure than observed in Figure 3. Possible explanations include uncertainties in the rate constants used in the modeling as well as possible nonthermal effects due to formation of highly rotationally excited CN in the photodissociation, which may not be completely relaxed by the buffer gas. Which of our two reported values for ϕ_{1a} is most accurate is at this time an open question, although we tend to favor the determination reported here. We note that Park and Lin's value of $\phi_{1a} = 0.19$ lies almost exactly midway between our two determinations.

One significant source of uncertainty in all measurements of ϕ_{1b} is the fate of the H_2NO radicals. We are not aware of any direct kinetic measurements of this species, although Bulatov et al. estimated $k = 2.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} for the $H_2NO + O_3$ reaction from kinetic modeling of NH_3/O_3 flash photolysis data.[43] This suggests that $H_2NO + NO_2$ is also very slow and probably not a source of additional NO in our experiments. Obviously, additional experiments are necessary to resolve this issue.

Conclusions

The branching ratios of the $NH_2 + NO_2$ reaction were measured by infrared detection of products. The most important result of this study is that we believe it represents the first reliable estimate of the contribution of the major NO formation channel. This study also confirms earlier reports that $N_2O + H_2O$ formation represents only a minor channel, although the measured value of the contribution of this channel is somewhat greater than that obtained in our previous determination.

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