Studies of the amidogen-nitric oxide reaction by infrared kinetic spectroscopy

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perturbed region is now obvious. It should be noted that $[Ag^+]_0$ = 1.25×10^{-3} M as used for the simulation in Figure 4 is the same as that used by Noszticzius[8] in his experiments (Figure 1).

Even better agreement between simulations and experiment can be obtained by a fine-tuning of k_3^* and k_{O5}, but we leave this until an experimental determination of k_{O6} is available. Preliminary results performed by us using conductivity methods strongly indicate that k_{O6} will turn out to be somewhat larger than 10^4 M^{-1} s^{-1}, necessitating a further reduction of k_3^*, which in turn would decrease the difference between predicted and experimentally determined bromide ion levels. In accordance with our preliminary results, Varga and Körös[29] found recently (in a malonic acid BZ system) k_{O6} values in the order of 10^4 M^{-1} s^{-1}.

k_1^*–k_{O4} represent a subset of rate constants which describe the oxybromine chemistry in BZ systems, and the values of several of these are not known with certainty.[27,30,31b,32] Tyson[32] reports a rate constant set which in the Oregonator results in a reduction of k_3^* from 10^4 to 2×10^2 M^{-1} s^{-1}, but this latter value is probably too low.[17] However, we note that the values of k_3^* used here are well within this suggested range of values.

Also flow experiments when silver ions are used in the feed stream of a CSTR[10] or when silver ions are continuously generated by an electrochemical process[8] can be simulated as shown in Figures 1B and 5.

Critical readers still will find discrepancies between our calculations and experiment. Most obvious is that in the nonperturbed oscillating regime the calculations do not show the characteristic increase of the bromide ion selective electrode's potential when the autocatalytic oxidation of cerous ions occurs at low bromide ion concentrations. However, the electrode response in an experimental situation is due to bromide and silver ions as well as interfering species[24,25] while we only consider here the response of the electrode toward Ag^+ and Br^-. Incorporation of other interfering species, as previously done,[16] may further improve the already good agreement between calculations and experiment, but we doubt that such differences are of importance for the understanding of the mechanism and the special effect silver ions have in a BZ reaction.

Our calculations suggest important experiments to be done, first of all to find the experimental rate constant of silver bromide precipitation in the BZ system. It is also desirable to find an experimental technique to follow the bromide ion concentration in the bulk solution in the presence of excess silver ions.

Despite this lack of important experimental data, we have demonstrated that Noszticzius' 1979 experiments[8] can be understood in terms of the FKN mechanism. The existence of silver ion induced oscillations does not invalidate the FKN mechanism and the Oregonator as recently suggested[25] nor do these types of oscillations appear to be non-bromide ion controlled. Varga et al.[19] came to similar conclusions for the thallium(III)-perturbed BZ reaction. Using the Oregonator model extended by complexation reactions between thallium(III) and bromide ions they demonstrated the bromide ion control in these systems.

We therefore conclude that the concept of "non-bromide ion control" as first introduced by Noszticzius[8] and then adopted by other authors[9,10] is incorrect.

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Studies of the NH₂ + NO Reaction by Infrared Kinetic Spectroscopy

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Infrared kinetic spectroscopy using excimer laser flash photolysis and color center laser probing has been used to study the NH₂ + NO reaction. The amidogen radical, NH₂, was produced by ArF photolysis of NH₃. Infrared absorptions of OH and H₂O were measured to determine the absolute contributions of the OH and H₂O product channels. It was found that the OH channel accounts for 13 ± 2% of the reaction. Using two different pairs of NH₃ and H₂O lines, we measured values of 0.85 ± 0.09 and 0.66 ± 0.03 for the ratio of H₂O formed to NH₃ photolyzed. All of the H₂O signals exhibit a pronounced induction period suggesting that H₂O is produced in very high vibrational states. The time evolution of low-lying vibrationally excited and ground vibrational state H₂O lines is adequately simulated by a model in which a stepwise sequential loss of vibrational energy occurs with quenching cross sections for each step proportional to excess energy.

Introduction

The new powerful method of infrared kinetic spectroscopy has been applied to the investigation of the reaction between NH₂ and NO. This technique employs excimer laser flash photolysis to produce high radical concentrations, tunable infrared laser probes to provide high sensitivity and resolution, and fast infrared detectors to provide microsecond time resolution. This infrared kinetic spectroscopy combination provides a very effective and versatile technique for monitoring kinetics, determining nascent distributions, and acquiring spectra of new radicals. In previous reports[1-3] we have examined the sensitivity and advantages of the

method and have demonstrated its applicability to infrared spectroscopy. The present measurements illustrate the utility of the technique in the realm of kinetics. In a single experimental setup, the concentrations of most of the participants (OH, NH₂, H₂O, NH₃, NO) in the chemical reaction between NH₂ and NO have been followed with high time resolution compared to the time scale of the reaction.

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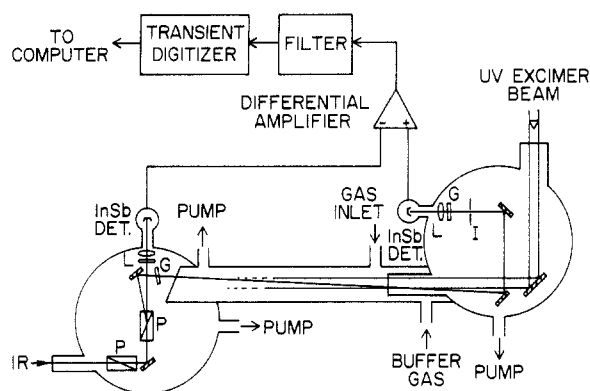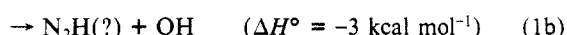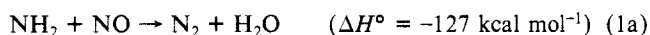†Institut für Angewandte Physik, Universität Bonn, 5300 Bonn 1, Wegelerstrasse 8, Federal Republic of Germany.

Figure 1. Experimental layout. Balance between the two liquid-N_2-cooled InSb detectors is achieved by rotating the first polarizer. The colinear IR probe and UV photolysis beams counterpropagate through the reaction cell: P, polarizer; G, germanium flat; L, lens; I, iris.

CHART I

authors	[OH]/[NH₂]	method	ref
Andresen et al.	0.65	flash photolysis/LIF	4
Silver et al.	0.40	fast flow reactor/LIF	7
Stief et al.	<0.22	flash photolysis/LIF	8

Interest in the reaction between NH_2 and NO has been kindled to some degree by its proposed central role in the industrially important "thermal DeNOx" process, in which ammonia is added to the effluent gases of power plants to convert nitrogen oxides to nitrogen. It is also an important reaction in atmospheric chemistry. The rate constant for the reaction ($\sim 1.6 \times 10^{-11}$ cm³ s⁻¹) has been measured by several workers[4-12] but a determination of the branching ratio into the various primary product channels has been more elusive. Knowledge of this ratio is very important for modeling studies[13] of the DeNOx process. Discussions of the various possible products based on thermodynamic feasibility and current experimental results have been given elsewhere,[4,7] with a general consensus that the two major product channels are

$$NH_2 + NO \rightarrow N_2 + H_2O \quad (\Delta H^\circ = -127 \text{ kcal mol}^{-1}) \quad (1a)$$

$$\rightarrow N_2H(?) + OH \quad (\Delta H^\circ = -3 \text{ kcal mol}^{-1}) \quad (1b)$$

Although both H_2O and OH have been detected in this system it has been difficult to determine the relative importance of the two pathways. Three quantitative studies of this ratio have determined significantly different values for the contribution of the channel producing OH. These results are summarized in Chart I. Observation of OH suggests that the hitherto unseen (and questionably stable) N_2H radical is also present since no H atoms have been detected as a product of this reaction.

Experimental Section

The experimental arrangement is shown in Figure 1. A Lambda-Physik EMG-101 excimer laser was used as the photolysis

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source. The fate of species formed by the 193-nm ArF excimer laser pulse (12-ns duration, 15-mJ pulse energy at the cell) or as a result of further chemical reaction is probed by a single-mode (3-MHz line width) computer-controlled Burleigh FCL-20 color center laser[14] operating from 2.3 to 3.2 μm whose frequency can be locked at an absorption feature. Species present in the 1-m-long cell are probed by a single pass of the IR laser.

A balanced detector technique was chosen in order to reduce the substantial amplitude noise of the color center laser. The difference signal from the two detectors was amplified and fed into a 20-MHz Lecroy transient digitizer (Model 2256AS) which was triggered by the photolysis pulse. Signal averaging and storage was carried out by a DEC PDP 11/23 minicomputer. Signals were typically acquired at a 12-Hz repetition rate of the photolysis laser and averaged over 1000 traces. The time constant of the complete detection system (as measured by the time response to a red F atom excimer pulse) was 1 μs.

The NH_2 radicals were generated by flash photolysis of NH_3 vapor. So that a fairly uniform concentration of products would be produced down the tube, the pressure of the precursor was adjusted for about 70% absorption of the photolysis flash. This corresponds to a pressure of about 70 mTorr of NH_3. The flow rate was adjusted so that the residence time of a gas mixture was on the order of 1 s.

The time behavior of almost all participants in the reaction could be monitored in this experiment. The IR frequencies for ground and excited vibration–rotational lines for such species were taken from published Fourier transform and difference frequency measurements (NH_3,[15] NH_2,[16] OH,[17] H_2O,[18,19] NO[20]). Computer control of our spectrometer allowed us to move between and record measurements on any two such lines, even when separated by hundreds of wavenumbers, in a matter of minutes.

The gases employed were used without further purification except for NO, which was flowed through a dry ice/acetone trap to remove all traces of NO_2 impurity as discussed below. Purities of the gases, all of which are commercially available, were as follows: NH_3 (99.99%), NO (99.0%), He (99.995%), NO_2 (99.5%), SF_6 (99.8%).

Results and Discussion

Rate Constant Check. Initially a measurement of the rate constant for the NH_2 + NO reaction was undertaken to verify our system's ability to reproduce a well-known result. A value consistent with literature values was obtained by monitoring decay curves of a ground-state NH_2 line at different NO pressures (always in excess). It is known that the 193-nm photolysis of NH_3 produces NH_2 radicals primarily in excited vibrational states of the ground electronic state.[21] To efficiently relax this vibrational excitation we performed our measurements in the presence of 8 Torr of He.[4]

Water Signal Behavior. Several absorption lines originating from the ground vibrational state of H_2O were observed in the present study. However, their appearance relative to that of the excimer flash was always delayed, sometimes by as much as 10 to 15 μs. At first this delay was interpreted as supporting a mechanism in which water was formed only as a result of secondary reactions. However, other data led us to an alternate explanation. The reaction producing H_2O (1a) is exothermic by 127 kcal mol⁻¹. Previous workers have shown that some of this

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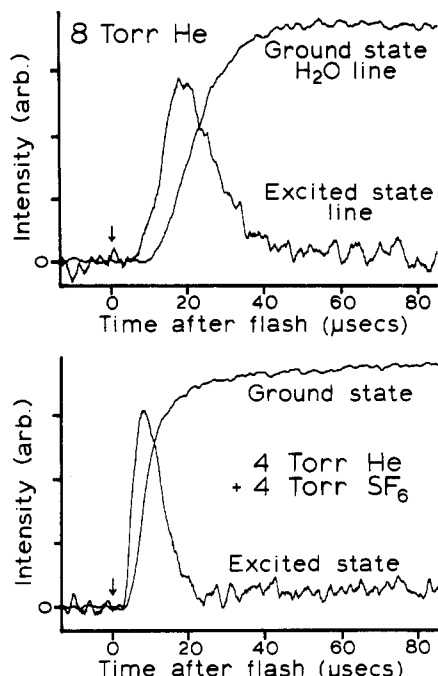(21) Donnelly, V. M.; Baronavski, A. P.; McDonald, J. R. *Chem. Phys.* **1979**, *43*, 271.

Figure 2. Time behavior of ground-state and vibrationally excited H_2O molecules formed from the reaction of NH_2 with NO. The particular transitions displayed in this figure are [(001) ← (000)P(6)] and [(002) ← (001)P(4)], respectively. Replacement of some of the He buffer gas with a more efficient relaxer such as SF_6 causes a shortening of the induction period for both signals. P_{NH_3} = 70 mTorr, P_{NO} = 1 Torr.

excess energy is channeled into vibration of the H_2O molecule, resulting in observable infrared fluorescence.[4] If the water is formed exclusively in vibrationally excited states, the delayed appearance of the ground state could result from the slowness of the relaxation processes. To explore this, we monitored an absorption line arising from vibrationally excited H_2O [(002) ← (001)P(4)]. The time behavior of this line is shown in Figure 2. The appearance of the excited H_2O line was more prompt than that of the ground-state line (although it too displayed a small induction period), and its time decay was consistent with the ground state being formed from it by relaxation processes.

In order to better identify the particular excited states produced in reaction 1a, several other excited water lines were monitored. Selected H_2O lines in the $\nu_1 + \nu_3 - \nu_1$, $\nu_1 + \nu_3 - \nu_3$, $2\nu_3 - \nu_3$, $2\nu_2 + \nu_3 - 2\nu_2$ and $\nu_2 + \nu_3 - \nu_2$ combination bands with up to 4100 cm^{-1} of energy above the origin displayed similar time behavior to the excited line shown in Figure 2. No preferred initial state, nor propensity rule for relaxation, was indicated.

To further investigate the formation and relaxation of water in its various vibrational states, a simple modeling study was undertaken. Three different relaxation models were tested. In all cases it was assumed that water was formed with 100 kcal mol^{-1} of vibrational energy and was relaxed primarily via collisions with NO (this is dramatically illustrated in Figure 6 of ref 4). Since the limited amount of experimental data did not warrant a more sophisticated treatment, only 10 distinct levels of vibrationally excited H_2O, each 10 kcal mol^{-1} apart (approximately one O–H stretch), were considered. The first model was based on a sequential step mechanism in which the excited H_2O relaxed one level at a time with equal quenching rates for each level. The second model was similar except that the quenching rates were made proportional to the amount of excess vibrational energy contained in the H_2O molecule. The third model was quite different from the others and was qualitatively similar to the adiabatic channel model proposed by Troe[22] to account for relaxation by chemically active species. In his model Troe postulates the formation of a relatively long-lived collision complex with energy redistribution occurring statistically prior to the breakup
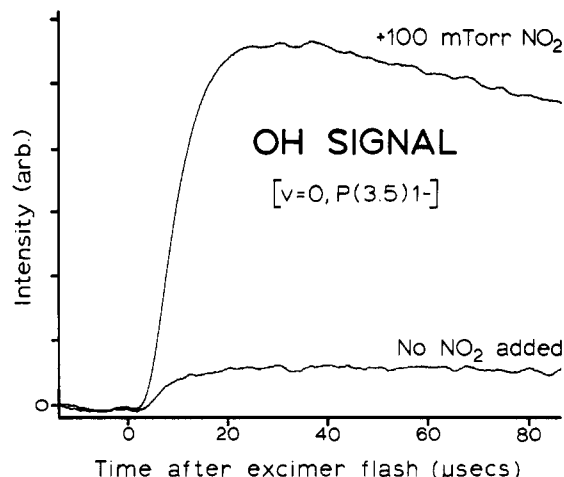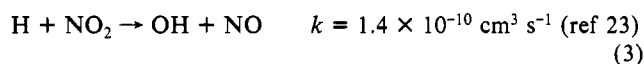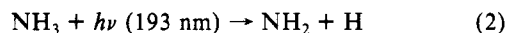

Figure 3. Measured OH signals in the presence and absence of added NO_2 after flash photolysis of NH_3 vapor with NO present. In the absence of NO_2 the signal is due to the NH_2 + NO reaction alone. The addition of NO_2 results in extra OH from the reaction of NO_2 with H atoms formed in the photolysis and is a measure of the initial NH_2 concentration (assumed equal to the H atom concentration). In both cases, P_{NH_3} = 70 mTorr, P_{NO} = 1 Torr, and P_{He} = 8 Torr.

of the complex. Our own model assumed equal rates of complex formation for all H_2O levels, and equal access to all levels below the H_2O level in question upon dissociation of the complex.

Two of these models adequately simulated even the qualitative features of the experimental observations. Both sequential step models correctly predicted a rise time for the ground-state line which was approximately equal to its induction period. This distinct feature was displayed by all of the H_2O ground-state lines studied including those obtained in the presence of an efficient relaxer such as SF_6. (With SF_6 the lines exhibited significantly shorter induction periods and correspondingly shorter rise times, but the ratio of rise time to induction period remained approximately one.) The other model predicted a more gradual increase of the ground-state H_2O population giving signal rise times distinctly longer than the induction periods. With a rate constant for quenching by NO of 2.0×10^{-11} cm^3 s^{-1}, the second sequential step model also correctly predicted the shape of the $v = 1$ line shown in Figure 2.

The observation that water is produced by reaction 1a in highly excited vibrational states is not entirely unexpected. Any attempt to construct a reasonable four- or five-center transition state for this reaction leads to one or both of the OH bonds being extended far beyond the equilibrium length at the instant of formation. The experimental observations thus tend to support a mechanism involving direct formation of H_2O via reaction 1a.

Branching Fraction into the OH Channel. The relative importance of the OH channel in reaction 1 was determined by measuring the OH signal strength both in the presence and absence of a small amount of added NO_2. The NO_2 reacts rapidly with H atoms generated in the photolysis of NH_3 to produce additional OH:

$$NH_3 + h\nu \ (193 \text{ nm}) \rightarrow NH_2 + H \qquad (2)$$

$$H + NO_2 \rightarrow OH + NO \qquad k = 1.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ (ref 23)} \qquad (3)$$

The OH signal measured under these conditions is therefore the sum of that produced in reaction 3 plus that produced in the NH_2 + NO reaction. Comparison of this signal with that obtained when the flow of NO_2 is turned off yields a value for the amount of OH formed in the NH_2/NO reaction relative to the amount of atomic hydrogen formed by the photolysis which is assumed equal to the initial amount of NH_2. Figure 3 shows a comparison of these two signals for the P(3.5)1− line of OH. Ratios were calculated from

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TABLE I: Observed Ratios of OH Signal to NH_2 Signal for Various $V = 0$ OH Lines

| transition	He, Torr	SF_6, Torr	$[OH]/[NH_2]$
P(5.5)1+	8		0.14
P(3.5)1−	8		0.13
P(1.5)2−	8		0.09
P(5.5)1−	8		0.14
P(3.5)2−	8		0.16
P(2.5)1+	8		0.14
P(5.5)1−	2.2		0.12
P(2.5)1+	2.2		0.13
P(5.5)1−	15	4	0.11

signals measured within 50 μs of the photolysis pulse, before the OH could participate appreciably in further reactions.[24]

Possible pitfalls to this approach include the fact that the initial nascent distributions for the OH produced in reactions 1 and 3 are quite different[4,25] and that the corresponding equilibrium temperatures reached may be significantly different. However, by using high pressures of He and NO, which are known to be efficient relaxers of rotationally and vibrationally excited OH, respectively,[26,27] complete relaxation was achieved in the first few microseconds after the flash. The same partial pressure of NO was used in both cases to give similar temperature rises from reaction 1a, which is highly exothermic. For the conditions of our experiments we calculated a temperature rise of 6 °C resulting primarily from the exothermicity of the NH_2/NO reaction but also from the excess energy available from the initial photolysis. The NO_2 concentration (100 mTorr) was kept small enough to minimize its participation in other reactions but large enough to give a rapid rise to the OH signal. We performed this pair of measurements over many different rotational lines of the ground vibrational state for various spin and λ components. Table I gives a summary of these measurements. Ratios determined in this manner were independent of the transition studied indicating a thermalized ground-state population of OH under the conditions of these experiments. The measured percentage of OH produced from reaction 1 was 13% with a scatter of 2% (one standard deviation):

$$NH_2 + NO \rightarrow N_2H(?) + OH \qquad 13\% \qquad (1b)$$
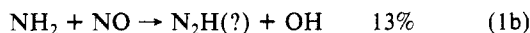
Measurements at slightly lower (3 Torr total) and at higher (20 Torr) pressures including those made in the presence of 4 Torr of SF_6 gave similar ratios. These observations are inconsistent with the theory proposing that the OH arises from dissociation of highly excited H_2O.

This measurement of the importance of the OH channel assumes that no additional H atoms are produced from the reaction of NH_2 with NO, in accordance with the claims of other authors.[4,7,28] However, in view of the dubious stability of HN_2[29] an alternative OH channel might be formulated as

$$NH_2 + NO \rightarrow N_2 + H + OH \qquad (\Delta H° = -6 \text{ kcal mol}^{-1}) \qquad (1c)$$
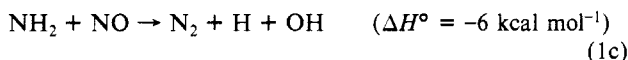
producing an extra mole of H atoms per mole of OH produced.[30] If reaction 1c is the sole source of OH then our H atom titration with NO_2 will have overestimated the amount of NH_2 produced from the photolysis step and thus underestimated the importance of the OH channel. This would necessitate a revised figure for

the percentage of OH produced from reaction 1 to 15%.

Comparison of our result for the percentage of OH formed in this reaction with that of other workers[4,7,8] is difficult since their results span almost the complete range of possibilities. However, the ability to perform this measurement with a single experimental setup under conditions of a relaxed vibrational and rotational population allowed us to estimate this percentage with confidence and with a greater accuracy.

In initial attempts at performing this measurement our NO sample was seriously contaminated with NO_2. This gave rise to a large OH signal with a short rise time due to the reaction between H and NO_2. Under conditions where the level of NO_2 impurity was greatly reduced but still significant, we noted a much slower rise to the OH signal which nevertheless attained an ultimate value comparable to that when NO_2 was added intentionally. When the NO was flowed through a 4-ft long $^1/_4$-in. diameter copper coil completely immersed in a dry ice/acetone bath, the last significant effects of the NO_2 reaction were finally eliminated. This manifested itself by a dramatic decrease in the ultimate magnitude of the OH signal, which nevertheless appeared promptly as is expected for a primary product of the NH_2/NO reaction.

Measurement of the H_2O Channel and Materials Balance. As a final check, we determined the absolute amount of H_2O produced vs. the amount of NH_3 photolyzed. These measurements were performed in 20 Torr of buffer gas to minimize the temperature rise of the system. For calibration, we determined the absorption coefficients of all of the NH_3 and H_2O lines studied directly in the experimental cell. Unfortunately, it was not convenient to measure these absorption coefficients at the same buffer gas pressure as employed in the kinetic experiments because of outgassing effects in a static cell and the difficulties in preparing calibration mixtures for a flow system. This means that H_2O/NH_3 mole ratios were calculated for Doppler-limited lines and do not take into account the effect of pressure broadening due to the buffer gas which although small (10% of Doppler width) does affect the peak absorption coefficients.

Measurements to determine the contribution of the H_2O channel were performed repeatedly for two pairs of NH_3 and H_2O lines. By acquiring the NH_3 and H_2O signals at times separated by only a few minutes we could be confident of similar experimental conditions for both. The ratio of H_2O produced to NH_3 photolyzed was measured as 0.85 ± 0.09 (one standard deviation) for one pair of lines and 0.66 ± 0.03 for the other. The quoted uncertainities arise primarily from uncertainties in the absorption coefficient measurements. The absorption coefficients for the lines were large and both species strongly adsorbed onto the glass cell making these calibration measurements difficult. The problem can be appreciated by noting that approximiately 1 mTorr of NH_3 was photolyzed by each excimer pulse.

Despite the discrepancy in the two ratios they do come close to representing a "materials balance" when the contribution of the OH channel is added. Some of the first studies of this reaction[31,32] showed a unit quantum yield of H_2O and N_2, suggesting that the oxygen-containing products from any other channel must eventually end up as H_2O. For OH this probably occurs via reactions with NH_3, NO, (third-order reaction), or with another molecule of OH. The rate of production of H_2O from these sources occurs on the same time scale as diffusion out of our IR beam and thus any additional H_2O produced by these subsequent reactions would not be seen in the present experiments.

Conclusion

The foremost advantage of the infrared kinetic spectroscopy method as it pertains to study of this reaction is that a single technique has been used to monitor the concentrations of almost all participating species. This is vividly illustrated in Figure 4.

The fraction of reactive collisions leading to the production of OH for the NH_2 + NO reaction at 298 K was measured by

(24) The most rapid removal process for OH under the conditions of these experiments (1 Torr of NO, 8 Torr of He) is the third-order reaction with NO to form HONO.

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(30) If HN_2 exists for times comparable to collision with NO ($\sim$100 ns), then it should be removed by the reaction HN_2 + NO → HNO + N_2, which is likely to be gas kinetic, rather than decomposing to H + N_2.

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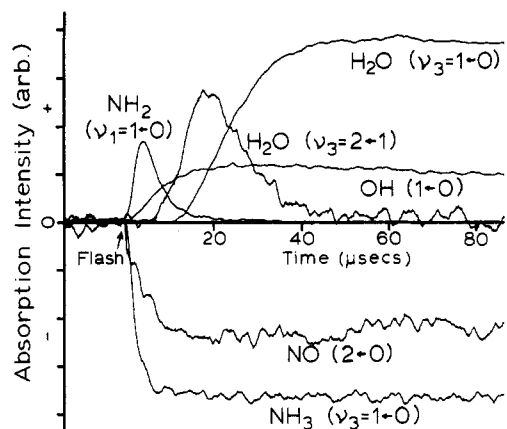(32) Serewicz, A.; Noyes, Jr., W. A. *J. Phys. Chem.* **1959**, *63*, 843.

Figure 4. Time behavior of most of the chemical species participating in the NH_2 + NO reaction for initial conditions of P_{NH_3} = 70 mTorr, P_{NO} = 1 Torr, and P_{He} = 8 Torr. Rotational levels in both ground and excited vibrational states of both transient and stable species may be probed with this infrared kinetic spectroscopy technique.

comparison of OH signals acquired in the presence and absence of NO_2. This fraction was determined as 13 ± 2% and was independent of the OH transition monitored in the pressure range studied (3 to 20 Torr). Direct cross calibration of the NH_3 and

OH signals would have been desirable but was not possible due to a lack of reliable infrared absorption cross-section data for the OH radical. A measurement of the amount of H_2O formed relative to NH_3 photolyzed in 20 Torr of buffer gas for two separate pairs of H_2O/NH_3 lines gave values of 0.85 ± 0.09 and 0.66 ± 0.03 but did not take into account the pressure broadening of the lines involved. These values were measured at times which precluded any contribution to the H_2O signal arising from further reactions of the OH present.

Investigation of both ground and excited vibrational lines of H_2O with different relaxants showed time behavior consistent with a model in which a sequential stepwise loss in energy with quenching cross sections for each step proportional to excess energy occurs from an initially highly excited H_2O molecule.

Note Added in Proof. Since this paper was submitted, we have become aware of two additional papers on this reaction. Melius, C. F.; Binkley, J. S. *Sym. (Int.) Combust., [Proc.], 20th* **1985**, 575. Dreier, T.; Wolfrum, J. *Sym. (Int.) Combust. [Proc.], 20th* **1985**, 695.

Direct Measurements of the Reactions NH_2 + H_2 ⇌ NH_3 + H at Temperatures from 670 to 1000 K

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The reactions NH_2 + H_2 → NH_3 + H (1) and H + NH_3 → NH_2 + H_2 (-1) were studied in a discharge flow system in the temperature range 673 ≤ T/K ≤ 1003 at a pressure of 4 mbar with He as the main carrier gas. Pseudo-first-order conditions $[H_2]_0 \gg [NH_2]_0$ and $[NH_3]_0 \gg [H]_0$ were applied when $[NH_2](t)$ (followed by LIF) and $[H](t)$ (followed by Lyman-α absorption), respectively, were measured. The rate constants are presented by the Arrhenius expressions $k_1(T) = 3.6 \times 10^{12}$ exp(-(38 ± 3) kJ mol^{-1}/RT) cm^3 mol^{-1} s^{-1} and $k_{-1}(T) = 8.1 \times 10^{13}$ exp(-(60.9 ± 4) kJ mol^{-1}/RT) cm^3 mol^{-1} s^{-1}. From the ratio $k_1(T)/k_{-1}(T)$ the NH_2 enthalpy of formation $\Delta H_f°$(298 K) = 192 kJ mol^{-1} at room temperature is determined.

Introduction

There have been few direct investigations of NH_2 radical reactions at high temperatures[1] in spite of the importance of these reactions to the chemistry of ammonia combustion. The systematic studies of Lesclaux[2] of reactions of NH_2 with saturated hydrocarbons and H_2 extended up to temperatures of 520 K. At very high temperatures from T = 1700 to 2200 K data are available from shock tube investigations.[3] A high-temperature discharge flow system used in the present work allows coverage of the temperature range in between.

Earlier studies by the authors[9,10] dealt with hydrogen abstraction reactions of NH_2 radicals from saturated hydrocarbons over a large temperature range and resulted in a linear empirical Evans-Polanyi relation between the activation energy for mean temperatures and the weakest C-H bond energy for C-2 to C-5 hydrocarbons. For the reaction of NH_2 with CH_4, however, some discrepancies arose at low temperatures which are partly linked to the H bond dissociation energy in NH_3.[23]

Therefore, it seemed of interest to obtain the Arrhenius parameters for the reaction

$$NH_2 + H_2 \rightarrow NH_3 + H \qquad (1)$$

and independently for the reverse reaction

$$H + NH_3 \rightarrow NH_2 + H_2 \qquad (-1)$$
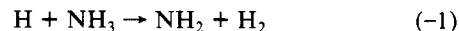
over a large temperature range for two reasons: first, to compare $k_1(T)$ to $k(NH_2+CH_4)(T)$ since the H-H bond energy in H_2 is similar to the C-H bond energy in methane and, second, since the ratio $k_1(T)/k_{-1}(T)$ enables a direct determination of the N-H bond energy in NH_3. Moreover, reverse reaction -1 is an important intermediate step in ammonia chemistry, pyrolysis, and combustion processes. Some data are available for reaction 1 in

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