Rate and mechanism of the NH($a^{1}\Delta$) + Cl₂ reaction

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The reaction of NH(a $^{1}\Delta$) with Cl₂ was studied by pulsed photolysis of HN₃/Cl₂/Ar mixtures with the 248 nm output of a KrF laser. The rate constant for NH(a $^{1}\Delta$) quenching by Cl₂ was determined to be $(6.8\pm0.4)\times10^{-11}$ cm³ s⁻¹. A major product channel for this reaction is production of NCl(a $^{1}\Delta$) and vibrationally excited HCl, suggesting that the reaction proceeds by an insertion mechanism via an amine-like intermediate similar to that of the H+NCl₂ reaction.

1. Introduction

The dynamics of processes involving the imidogen radical are of considerable interest because of the relatively simple structure of this species and its tractability as a subject for computational study. Previously in our laboratory, we have studied reactions [1-3] of the isoelectronic species O(¹D) with HN₃, HNCO, and CINCO. These processes were observed to proceed by either insertion (as in $O(^{1}D)$ + HNCO, which generates [2] NH($a^{1}\Delta$) and CO₂ as domiproducts) abstraction (as nant or in $O(^{1}D) + CINCO$, which generates [3] CIO + NCO). In this Letter, we describe observations of the reaction of NH($a^{1}\Delta$) radicals with molecular chlorine. This reaction may proceed by abstraction or by insertion as follows:

 $NH(a^{1}\Delta) + Cl_{2} \rightarrow HNCl + Cl, \qquad (1)$

$$\Delta H \approx -36 \, \text{kcal/mol} \,, \tag{1}$$

 $NH(a^{1}\Delta) + Cl_{2} \rightarrow [HNCl_{2}]^{+} \rightarrow NCl + HCl_{1}$

$$\Delta H = -63 \, \text{kcal/mol} \,. \tag{2}$$

The insertion process, reaction (2), is particularly interesting since its dichloroamine-like intermediate may be very similar to that formed in the $H+NCl_2$ reaction [4]. $H+NCl_2$, like its analogous [5] $H+NF_2$ and H+NFCl, is thought to proceed by an amine-like intermediate which eliminates the hydrogen halide, leaving the halogen nitrene. Such reactions proceed on the ground state singlet potential energy surface of the amine intermediate, such that the products (e.g., NCl+HCl) are formed in singlet states. Indeed H+NCl₂, H+NF₂, and H+NFCl have all been shown [4-7] to produce NCl($a^{1}\Delta$) or NF($a^{1}\Delta$) in high yield. If the NH($a^{1}\Delta$)+Cl₂ reaction were to proceed by insertion involving an intermediate similar to that of H+NCl₂, the products of the reaction would be expected to be NCl($a^{1}\Delta$) and HCl, the latter with some vibrational excitation.

In this Letter, we present measurements of the rate constant for $NH(a^{1}\Delta)$ quenching by Cl_{2} and a determination of the dominant product channel.

2. Experimental

In these experiments, the NH (imidogen) radical was generated by 248 nm photolysis of HN₃. This process has been studied in detail by Bohn and Stuhl [8]. Preparation of HN₃ was carried out as described previously [9]. The HN₃ was collected in an evacuated 5 l pyrex bulb to a pressure of ≈ 30 Torr and then diluted to a 10% mixture with helium. Purity and concentration of the mixture were determined with UV and IR spectroscopy [9,10]. The only apparent impurity was a trace amount of CO₂. Chlorine (Matheson 99.99%) was diluted in helium in a passivated stainless steel vessel to a 10%-30% mixture.

Chlorine azide was generated by passage of Cl_2/Ar

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mixtures over H₂O-moistened NaN₃ suspended on glass wool at 273 K, in a synthesis described previously [11]. The ClN₃ density in the effluent of the generator was monitored by IR absorption of the molecule near 2050 cm⁻¹. The effluent was collected in a pyrex bulb previously passivated with Cl₂. The concentration and purity of the ClN₃ in the bulb were measured using IR and UV spectroscopy [11,12]. The only observable impurity in the mix was a small amount of Cl₂.

The experimental apparatus consisted of a simple pyrex photolysis cell with the observation window at 90° to the counter-propagating photolysis and probe laser beams. Imidogen radicals were formed by photolysis of HN₃/diluent mixtures at 248 nm. The KrF photolysis beam was stopped down with an iris to a diameter of about 1 cm and propagated through the glass photolysis cell. Typical KrF laser fluences were 50-100 mJ/cm². The NH product was detected by LIF on the $(a^{1}\Delta \rightarrow c^{1}\Pi)$ transition of this radical [13]. The LIF probe beam was the frequency-doubled output of a XeCl excimer-pumped dye laser (Lambda Physik LPX100/FL3001, PRA L-2X). The probe beam was variably delayed from the photolysis pulse using a delay generator (SRS DG535) triggered by the photolysis laser. The resulting fluorescence signal was detected using a cooled GaAs photomultiplier tube in combination with a bandpass filter (Acton Research Corp.). The signal from the photomultiplier tube was amplified, digitized, and stored using a gated boxcar integrator (SRS 250/ 245/240) triggered by the probe pulse.

Reagents were flowed through calibrated mass flow meters (Tylan) and mixed 15 cm upstream of the photolysis cell. There was no evidence of pre-reaction during this period. Research grade argon (General Air) was flowed into the cell at a rate to give a background pressure of about 6 Torr. The argon buffer was used in order to increase the flow velocity through the cell, and to minimize losses due to diffusion out of the photolysis zone. The buffer also ensured thermalized rotational and translational distributions in the photolysis products produced from either HN₃ or ClN₃. The total cell pressure ranged from 6 to 8 Torr.

The NCl($a^{1}\Delta$) product was sought by looking for the near-infrared emission from this radical [14]. The NCl($a \rightarrow X$) emission at 1.076 µm was detected using an intrinsic germanium detector (North Coast Scientific Corp.) cooled to 77 K, in combination with an interference filter (Acton Research Corp.). The filter had a transmission maximum near 1.08 μ m with 10 nm fwhm. The time decay of this emission was amplified, averaged, and digitized over 1000 successive pulses using a Nicolet 1270 data acquisition system. The resulting time profiles were then analyzed with a curve-fitting program on a microcomputer.

Infrared emission from vibrationally excited HCl was observed using a cooled InSb detector (EG&G Judson) with an interference filter with peak transmittance at 3.4 μ m. The resulting signals were also averaged for 1000 shots using the Nicolet 1270 and analyzed on a microcomputer.

3. Results and discussion

3.1. Rate constant for NH($a^{1}\Delta$) quenching by Cl_{2}

The time profile of the NH($a^{1}\Delta$) radical was monitored by LIF of the $(a^{1}\Delta \rightarrow c^{1}\Pi)$ transition between 325 and 327 nm, and monitoring the subsequent $(c \rightarrow a)$ fluorescence through a bandpass filter with a 50% transmittance at 325 nm. The probe laser was tuned to the Q(3) line of the NH(c, v'=0 \leftarrow NH(a, v''=0) transition and the photolysis-to-probe delay was varied from 5 to 500 µs. The rate constant for NH($a^{1}\Delta$) quenching by Cl₂ was determined by monitoring the time dependence of the NH($a^{1}\Delta$) LIF intensity for fixed HN₃ densities and variable chlorine densities. Given the photolysis fluence and the absorption cross section [11] of HN₃ $(\sigma_{248} = 2.49 \times 10^{-20} \text{ cm}^2), \approx 0.5\%$ of the HN₃ was photolyzed to NH(a). Therefore, the experimental conditions were such that the Cl_2 was in large excess over the excited NH produced by photolysis. In this environment, the NH($a^{1}\Delta$, v=0) time decays were exponential and were found to grow shorter with increasing Cl₂ flow rates. The rate of decay of the NH radical for these conditions is given by

$$\lambda_{\text{decay}} = k_{\text{Cl}_2}[\text{Cl}_2] + k_{\text{HN}_3}[\text{HN}_3] + k_{\text{Q}}[\text{Q}], \qquad (3)$$

where decay by radiation or diffusion out of the observation zone are both too slow to be significant. The term $k_0[Q]$ in the above expression is the quenching rate by species other than the Cl_2 and the HN₃ parent molecule, such as the Ar diluent and any impurities that may be present in the cell. By fitting the observed temporal profiles to an equation of the form $I = I_0 \exp(-\lambda_{decay} t)$, the decay rate, λ , for the reaction was determined. Plotting the decay rates versus the Cl₂ density yields a Stern-Volmer plot such as that depicted in fig. 1. We recorded nine independent data sets such as that shown in the figure with reproducable results. The intercept in the figure corresponds to the sum of the second and third terms of eq. 3. Averaged over the nine data sets, the intercept indicates a rate constant for quenching by species other than Cl_2 of 1.2×10^{-10} cm³ s⁻¹. This measured value is in good agreement with the published rate constant [13,15] $k_{\rm HN3} = 9.3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, suggesting the primary loss of NH(a) in the absence of Cl₂ is due to quenching by the HN₃ parent. The data also indicate a rate constant for NH($a^{1}\Delta$) quenching by Cl₂, $k_{Cl_2} = (6.8 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. The reported uncertainty combines the statistical uncertainty (1σ) in the slopes of the individual plots with the variance in the slopes of the nine plots.

Although the present data reflect quenching of the NH(a, v=0) state, it has been shown [16] that 248 nm HN₃ photolysis generates NH($a^{1}\Delta$) in the (v=0, 1, 2, 3) vibrational states. Bohn and Stuhl [8] have studied the analogous HN₃, HNCO+NH(a, v=0, 1, 2) reactions and found no rate dependence for the



Fig. 1. Stern-Volmer plot of the first-order decay rate of NH($c \rightarrow a$) LIF intensity versus [Cl₂]. For the data shown, [HN₃]= 3.7×10^{13} cm⁻³.

various vibrational levels in these rapid processes. In light of the magnitude of the measured rate constant for NH(a, v=0)+Cl₂, we expect that this rate constant will also have a negligible dependence on the NH($a^{1}\Delta$) vibrational states. Further, it seems unlikely that non-reactive quenching (i.e. energy transfer to Cl₂ resulting in relaxation of NH from the a $^{1}\Delta$ state to the $X^{3}\Sigma^{-}$ state) makes a significant contribution to the observed quenching rate. E to V, R or E to T processes are likely to be very much slower than the observed rate. Although spin-allowed E to E energy transfer might be fast, generation of the lowest-lying excited electronic state of Cl₂ (the A' ${}^{3}\Pi_{2}$ state) would be endothermic by 12.8 kcal/mol. Hence, it seems very likely that reactive quenching processes like (1) and (2) above dominate. This conclusion is borne out by observations of reaction products, described below.

3.2. Observation of reaction products

As noted above, the products from the reaction may include NCl and HCl. In the H+NCl₂ reaction [4], the predominant products are electronically excited NCl and vibrationally excited NCl. If the $NH(a^{1}\Delta) + Cl_{2}$ reaction proceeds by a similar intermediate, the HCl product should also be excited in this case. From the thermochemistry of the reaction, HCl might be excited to levels as high as v=4(assuming an NCl($a^{1}\Delta$, v=0) co-product). Consequently, we sought emission from this species in the 3.4 µm region. This emission was readily observed. The emission required the presence of both HN₃ and Cl_2 in the flow, and its intensity varied linearly with the density of NH(a $^{1}\Delta$), the limiting reagent. A typical time profile of the HCl(v) emission is depicted in fig. 2. For the conditions of our experiments, the very fast rise of the emission is correlated with the NH(a $^{1}\Delta$) quenching rate, and the decay represents the rate of collisional quenching of HCl(v).

NCl($a^{1}\Delta$) may be detected by observing its radiative relaxation to the ground state, which produces an emission at 1.08 µm with a radiative lifetime [17,18] of τ =1.4 s. The NCl ($a \rightarrow X$) emission was readily observed using the Ge detector and narrowband filter described above. Like the HCl(v) emission, it required the presence of both the HN₃ and Cl₂ flows, and its intensity varied linearly with



Fig. 2. Typical time profile of the HCl(ν >0) emission at 3.4 μ m with [HN₃]=6.8×10¹³ cm⁻³, [Cl₂]=2.0×10¹⁶ cm⁻³, and [Ar]=2.4×10¹⁷ cm⁻³.

the initial NH($a^{1}\Delta$) density. A minor complication in this experiment is the residual amount of HN₃ parent molecule which is known [9,13,15] to react with NH(a ¹ Δ) to produce excited NH₂ $\tilde{A}(^{2}A_{1})$. This molecule subsequently chemiluminesces to the $\tilde{X}(^{2}B_{1})$ state with a broad emission extending from 600 nm to more than 1.1 μ m. Any such NH₂ emission at 1.08 µm would appear as a background undemeath the NCl $(a \rightarrow X)$ emission. The NH₂ background was measured by sampling the 1.08 µm emission signal in the absence of Cl₂. The intensity from the NH₂ background was about 20% of the signal from NCl(a). The signal-to-noise of the experiments was sufficient to simply subtract the background signal. Since the HN₃ density was held constant in these experiments, the NH₂ background contribution should also be constant.

Fig. 3 shows a background-corrected 1.08 μ m emission profile from NCl(a). The loss of NCl(a) is dominated by quenching by residual Cl₂ in the cell, present at a density of $\approx 3 \times 10^{15}$ cm⁻³. The rate constant for NCl(a) quenching by Cl₂ has been measured [19] in our laboratory, and was found to be $k_{Cl_2} = (1.8 \pm 0.3) \times 10^{-11}$ cm³ s⁻¹. Hence, the rate of formation of NCl(a¹ Δ) quenching by Cl₂) should be about four times faster than its rate. The rise of the signal should therefore reflect the production of NCl(a) from the NH+Cl₂ reaction, and the decay is the loss of NCl(a) from the cell. The factor of four



Fig. 3. Time profile of the NCl($a \rightarrow X$) emission at 1.08 µm with [HN₃]=1.8×10¹⁴ cm⁻³, [Cl₂]=2.4×10¹⁵ cm⁻³, and [Ar]=2.2×10¹⁷ cm⁻³.

between the rise and decay time is not observed because of the time constant of the Ge detector. Given the rate constant of NH($a^{1}\Delta$) quenching reported above, and the reagent densities in the cell, the calculated 1/e formation time is substantially shorter that the relatively long electronic time constant ($\tau \approx 13 \ \mu s$) associated with the Ge detector.

3.3. Branching fraction for NCl(a)+HCl(v)

In order to determine the branching fraction for the production of NCl and HCl, the NCl(a) emission intensity was calibrated against a standard. This was accomplished using photolysis of ClN₃, a known source of excited singlet NCl [11,20]. ClN₃ was introduced into the cell with the same buffer gas density as the previously described experiments. Densities of NCl(a) produced by the photolysis pulse were calculated from the known densities of ClN₃ in the photolysis cell, the absorption cross section [11] of this molecule at 248 nm, and the measured fluence of the incident laser radiation. Although the quantum yield for production of NCl(a) from the photolysis is not specifically known, we expect it to be near unity given the propensity for nitrene $(a^{1}\Delta)$ production from photolysis of other azides [13,21] in analogous bands. The NCI(a) quantum yields was therefore assumed to be unity for these calculations.

Fig. 4 shows representative emission profiles from NCl(a) generated by photolysis of ClN₃. Although



Fig. 4. Time profile of the $(a \rightarrow X)$ emission of NCl generated by 248 nm photolysis of ClN₃. (a) $[ClN_3] = 1.4 \times 10^{13} \text{ cm}^{-3}$; (b) $[ClN_3] = 5.6 \times 10^{13} \text{ cm}^{-3}$. In both cases, the density of the Ar diluent was $2.1 \times 10^{17} \text{ cm}^{-3}$.

the NCl(a) is a direct photoproduct of the ClN_3 photolysis, there is a rise time associated with the emission profile. This is due to the fact that our filter/detector combination is sensitive only to emission by NCl(a) from the (v=0) vibrational level. The observed rise in fig. 4 represents population of NCl(a, v=0) from relaxation of higher lying levels in collisions with the Ar buffer. The NCl(a, v=0) emission intensity is observed to increase with increasing Ar densities, leveling off for Ar pressures greater than about 6 Torr. We assume that for such pressures, all excited levels are relaxed to v=0 at long times. The decay of the NCl(a, v=0) is very slow as shown in the figure. By extrapolating the long decay to the intercept and assuming unity quantum yield, the effective density of NCl(a, v) at time t=0 can be calculated.

In the NH+Cl₂ reaction, we can then associate the NCl($a^{1}\Delta$, v=0) emission intensity with a density of the NCl fragment in this state. As mentioned above, the time response of the Ge detector affected the observed signal. In this situation, the indicated intensity of the signal is smaller than the actual intensity since the detector response approaches the true signal intensity exponentially according to the detector RC time constant. The time response of the Ge detector was measured by inputting a square-wave signal pulse of known duration and measuring the output with the data acquisition system. In this way, both

the intrinsic time constant, τ_{RC} , of the detector, as well as the extent of dimunition of the observed intensity when the duration of the input signal is less than τ_{RC} were measured. By taking data at several different pulse widths, it was possible to map out a response curve for the detector. The observed signal was then multiplied by a scaling factor as determined from this response curve. This procedure gives a more appropriate value for the observed signal intensity. Using the above described detector response curve, we find the observed signal at 10 μ s is $\approx 40\%$ of the actual signal. Applying this correction factor to the NCl(a) signal, the data indicate that $NH(a^{1}\Delta) + Cl_{2}$ reaction produces a density of NCl(a, v=0) which is roughly equivalent (to within the substantial uncertainties of the calibration) to the initial density of NH($a^{1}\Delta$). For the conditions of our experiment (a large excess of Cl_2), only about 10% of the excited NH reacts with the HN₃ parent. Although this calibration is not sufficiently quantitative to precisely the yield of NCl($a^{1}\Delta$) from the reaction, the data do indicate that production of $NCl(a^{1}\Delta) + HCl(v)$ is surely the dominant channel.

4. Conclusions

The data presented above indicate that the $NH(a^{1}\Delta)+Cl_{2}$ reaction is very rapid, and that it proceeds primarily via an insertion mechanism to produce $NCl(a^{1}\Delta)$ and vibrationally excited HCl. These products are in accord with angular momentum conservation rules, and suggest that the reaction does indeed proceed via an intermediate similar to that of the $H+NCl_{2}$ reaction.

A finer measure of the dynamics of such processes, in particular the nature of the transition state, lies in the internal energy distributions of the product hydrogen halides. This energy distribution is well known for HF formed by the H+NF₂ reaction [22] and for HF/HCl formed by H+NFCl [7]. In the latter process, the HF/HCl branching fraction is also a fine measure of the dynamics. Hence, a more direct comparison might be made if such distributions were determined for the analogous NH($a^{1}\Delta$)+F₂ and NH($a^{1}\Delta$)+ClF reactions. We are studying these processes at present.

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