Photodissociation of Gaseous NCl_3 at 193 and 249 nm[†]

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The optical absorption spectrum of gaseous NCl_3 was measured from 170 to 350 nm, and experiments were performed in which this molecule was irradiated with a pulsed laser at 193 nm and 249 nm. Photodissociation channels accessible at these wavelengths can produce fragments in singlet, doublet, or triplet manifolds of states. Photodissociation at 249 nm produces prompt banded emission in the visible and near-IR spectral regions that is tentatively ascribed to transitions in NCl_2, suggesting that the dissociation channel leading to doublet fragments (NCl_2 and Cl) is operative at this photolysis wavelength. The absence of emission from excited singlet states of NCl or excited triplet states of Cl_2 suggests that the singlet and triplet dissociation channels are not important at 249 nm. For photolysis at 193 nm, prompt emission is observed from both the $a^1\Delta$ and $b^1\Sigma^+$ excited states of NCl. No emission is observed from either NCl_2 or excited triplet states of Cl_2. A measure of the quantum yield for $NCl(a^1\Delta)$ production by the 193 nm photodissociation of NCl_3 was determined by observing the transfer of energy from excited NCl to iodine atoms in the pulsed photolysis system. This method suggests that the yield has a value of 0.8 ± 0.2.

Introduction

Nitrogen trichloride has been studied by many researchers since its identification by Davy[1] in the early nineteenth century, and much of this work has been focused on reactions in solution or in the gas phase[2−4] and on the mechanism of the autodecomposition of this highly energetic species.[5] Very little is known about the photochemistry of NCl_3 apart from the UV absorption spectrum reported by Clark and Clyne,[2] and results of exploratory work by Gilbert and co-workers[6] on the photodissociation of NCl_3 at 249 and 308 nm. Recently, NCl_3 has once again become a subject of interest, this time as a chemical source of electronically excited $NCl(a^1\Delta)$. Excited $NCl(a^1\Delta)$ has been shown to effectively transfer energy to iodine atoms,[7,8] and both pulsed and cw lasers operating on the $5^2P_{1/2} \rightarrow 5^2P_{3/2}$ transition in iodine have been demonstrated based on this mechanism.[9,10] Gaseous $NCl(a^1\Delta)$ might be generated from NCl_3 by either reactions or photodissociation. Exton and co-workers[3] have shown that excited $NCl(a^1\Delta)$ is produced when NCl_3 reacts with either H or D atoms, and Schwenz, et al.[11] have demonstrated the efficient production of excited $I(5^2P_{1/2})$ when HI is added to an NCl_3/H reactive flow. Work on the autodecomposition of NCl_3 has produced no evidence of the production of excited NCl, nor was this species found in the work by Gilbert and co-workers[6] on photolysis at 249 and 308 nm.

The NCl_3 absorption spectrum published by Clark and Clyne[2] exhibits a strong absorption with a maximum near 220 nm and a long, lower absorbance tail extending into the visible. The latter feature is responsible for the golden yellow appearance of pure liquid NCl_3. Optical excitation of ground state (singlet) NCl_3 produces an excited singlet that can dissociate to two singlet, two doublet, or two triplet fragments as follows

$$NCl_3^* \text{ (singlet)} \rightarrow NCl(a^1\Delta, b^1\Sigma^+) + Cl_2(X^1\Sigma_g^+) \quad (1)$$

$$\rightarrow NCl_2(\text{doublet states}) + Cl\ (^2P) \quad (2)$$

$$\rightarrow NCl(X^3\Sigma^-) + Cl_2(^3\Pi \text{ states}) \quad (3)$$

In the previous work by Gilbert, et al.,[6] for photolysis at 249 and 308 nm, the principal result was the observation of strongly banded emission in the visible region that was thought to arise from excited states of either NCl_2 (channel (2) above) or the parent NCl_3. In the present work, we report additional, more extended observations of NCl_3 photolysis at 249 nm, and new results from photolysis of the molecule at 193 nm. The data indicate the operation of both channels (1) and (2) above, and we present a measurement of the quantum yield for channel (1) for photolysis at 193 nm, based on the observation of emission from excited $I(5^2P_{1/2})$ when an iodine atom precursor is added to the system.

Experimental Details

NCl_3 was generated in a shielded apparatus in a fume hood by passing gaseous Cl_2 through an acidified solution of $(NH_4)_2SO_4$, using techniques that have been described in detail previously.[3,6] The NCl_3 was collected in a trap at 193 K, and subsequently allowed to warm to room temperature to allow any Cl_2 in the trap to evaporate into a stream of Ar. At room temperature, the residual NCl_3 is a golden yellow liquid. Once the NCl_3 was generated, it was entrained in a flowing stream of Ar, and the proportion of gaseous NCl_3 in the flow was determined by passage of the flow through a 1 cm absorption cell and measurement of the absorbance of 254 nm light from a low-pressure Hg lamp.

A small portion of the NCl_3/Ar flow was admitted to a photolysis cell through a passivated stainless steel metering valve. The remainder of the flow was returned to the fume hood.

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The photolysis cell was constructed from a stainless steel block with 2.54 cm diameter channels for the flow of gases, the passage of the photoylsis laser beam, and the observation of emissions from the photolysis zone. The photolysis laser beam passed through the cell via 15 cm long sidearms that were baffled to reduce the effects of light scattering. The windows attached to the ends of these sidearms were UV grade fused silica. Near-IR emission from photolysis products was viewed at 90° to the axis of the laser beam via a polished KCl window. IR emissions were observed either directly through the window by a cooled intrinsic Ge detector equipped with appropriate filters, or by transmitting the emission via an optical fiber to a 0.25 m monochromator that dispersed the emission before its detection. Emission in the visible region was observed through a second fused silica window, also at 90° to the axis of the laser beam, with an optical fiber/monochromator/photomultiplier apparatus. The photolysis cell was pumped with a mechanical pump, and flows were such that the total pressure in the cell was varied from 0.1 to 1.5 Torr. The pressure in the cell was measured with a capacitance manometer. For most measurements, the pump was throttled such that the residence time of the flowing gases in the observation zone of the cell was at least 8 ms.

The gases flowing through the cell were irradiated by the pulsed emission from an excimer laser (Questek) operated at 1 Hz on either the ArF or KrF transitions at 193 and 249 nm, respectively. The fluence of the laser pulses was varied between 8 and 116 mJ cm^{-2}. Spectra of emissions produced by the photolysis were obtained by scanning the monochromator noted above as the photolysis laser was repetitively pulsed, with data being acquired using a gated integrator (Stanford Research Systems) set for various gate widths and delays. Time profiles of individual emission features were recorded with a digital oscilloscope (LeCroy). Both the gated integrator and digital oscilloscope were interfaced to a computer for data display and analysis.

UV/VUV absorption spectra of NCl_3 were recorded using a VUV absorption spectrometer (Acton Research) equipped with a deuterium lamp and a photomultiplier tube with a sodium salicylate phosphor. A flowing stream of NCl_3 diluted in Ar (generated as described above) was passed through a 1.0 cm path length cell mounted between the exit slit of the monochromator and the photomultiplier tube. Absorption spectra were determined by manual, point-by-point analysis of background and sample spectra.

Results

1. Absorption Spectrum of NCl_3. The absorption spectrum of NCl_3 reported by Clark and Clyne[2] indicates a major feature with a maximum near 220 nm, but does not include data for wavelengths below about 210 nm. Because the present experiments employed photolysis radiation at 193 nm, it was first necessary to measure the absorption spectrum of the molecule at shorter wavelengths. Figure 1 shows the spectrum recorded using the method described above, along with the spectrum measured by Clark and Clyne. The two spectra are in good agreement, as expected since the densities of NCl_3 in the present experiments were determined by optical absorption at 254 nm, using the extinction coefficient at that wavelength from the Clark and Clyne spectrum.

From the present data, it is clear that the very strong absorption with a maximum at 220 nm extends well below 200 nm. The absorption cross section at 193 nm is 4.5×10^{-18} cm^2. Further, a second maximum is observed at 210 nm, suggesting a second optical transition. This feature was very reproducible.

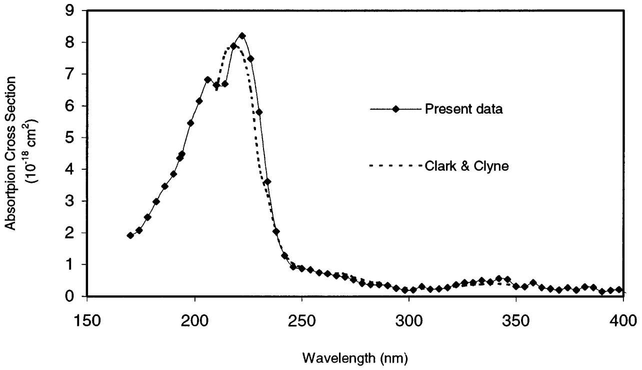

Figure 1. Absorption spectrum of gaseous NCl_3. Broken line, data from ref 2; (◆) and solid line, present data normalized to ref 2 data at 254 nm.

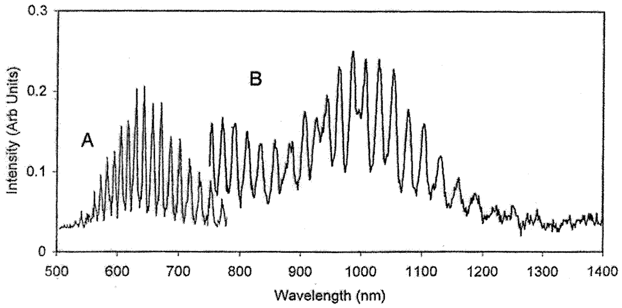

Figure 2. Spectra of emissions in the visible and near-IR regions produced by 249 nm photolysis of an NCl_3/Ar mixture (approximately 2% NCl_3) at a total pressure of 0.88 Torr. Spectrum A (500−800 nm) is from ref 6. Spectrum B (from 750 to 1400 nm) is from present data. For spectrum B, the delay time from the laser pulse was 15 μs and the gate width was 15 μs.

2. Photodissociation at 249 nm. Experiments with photolysis at 249 nm were performed in an effort to reproduce and extend the data previously reported by Gilbert and co-workers.[6] Previous data consisted of spectra of banded emission extending from roughly 500 to 775 nm. The features of this spectrum (thought[6] to be associated with excited states of NCl_2 or NCl_3) were found to have emission lifetimes on the order of 3 μs (for NCl_2) and 34 μs (for NCl_3). In the present experiments, we recorded spectra from 700 to 1500 nm using the 0.25 m monochromator (equipped with a grating blazed at 2.0 μm and used in second order) in combination with the cooled Ge detector, for a variety of delays from the photolysis pulse and a gate width of 15 μs. Figure 2 shows the spectrum recorded for a delay of 15 μs, along with the spectrum reported by Gilbert and co-workers. Clearly, the banded spectrum of the present data is the extension of that reported by Gilbert, et al., with the features at 752 and 768 nm common to both data sets.

Time profiles for the banded emission features of the present spectrum were observed using the digital oscilloscope. The features were observed to have rapid rise and decay times limited by the time response of the Ge detector (13 μs), consistent with the shorter lifetime reported by Gilbert, et al.[6] Further, the intensities of individual features (recorded with the Ge detector across the full wavelength range of the emission) were all found to increase linearly with the incident laser fluence. These results indicate that the emitter of the banded spectrum is a direct fragment of one-photon photodissociation of NCl_3 at 249 nm.

The emission spectra recorded in these experiments exhibited no evidence of the presence of either excited NCl or excited Cl_2, corresponding to photodissociation channels 1 and 3 above.

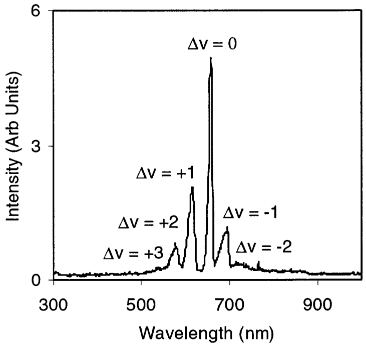

Figure 3. Spectrum of emission in the visible region produced by 193 nm photolysis of an NCl$_3$/Ar mixture (approximately 2% NCl$_3$) at a total pressure of 0.40 Torr. For the data shown, the delay time from the laser pulse was 500 μs, and the gate width was 15 μs. Vibrational sequences of the b$^1\Sigma^+ \rightarrow$ X$^3\Sigma^-$ transition in NCl are indicated.

In scans of the near-IR and visible regions with a variety of delays up to 1.0 ms, there was no evidence of emission from either the a$^1\Delta$ or b$^1\Sigma^+$ states of NCl, which emit at 1076 and 665 nm, respectively. Emission from NCl(a$^1\Delta$) was sought by using the Ge detector coupled with a narrow band-pass filter centered at 1080 nm. Emission from NCl(b$^1\Sigma^+$) was sought by recording spectra in the visible region with the GaAs photomultiplier tube and monochromator (in this case used in first order with a grating blazed at 500 nm).

Excited Cl$_2$($^3\Pi$) has a characteristic banded emission spectrum in the red visible and near-IR, and is produced[5,6] by the auto-decomposition of NCl$_3$. This emission is easily distinguished from the emission shown in Figure 2, or from the red emission of the NCl(b$^1\Sigma^+ \rightarrow$X$^3\Sigma^-$) transition by either visual observation or spectral scans, as was noted by Gilbert and co-workers.[6] There is no evidence of emission from excited Cl$_2$ in the spectrum shown in Figure 2. In the present experiments, we were able to induce the auto-decomposition flame by throttling the pump such that the photoysis cell was not fully purged between laser pulses. In this case, the spectrum in the red visible (recorded with the photomultiplier tube) clearly revealed features attributable to Cl$_2$($^3\Pi$), with a detector-limited rise and a decay over a few μs.

3. Photodissociation at 193 nm. Photolysis of NCl$_3$/Ar mixtures at 193 nm with the same experimental conditions as employed for the experiments at 249 nm gave different results. Gated spectra recorded in the visible and near-IR with the GaAs photomultiplier tube and Ge detector, respectively, exhibited none of the bands shown in Figure 2. Further, there were no bands attributable to emissions from Cl$_2$($^3\Pi$) states. Instead, the spectrum of emission in the visible region exhibited the features shown in Figure 3. These features are clearly identified as the sequences of the b$^1\Sigma^+ \rightarrow$ X$^3\Sigma^-$ transition[12] in NCl, with the most intense band at 665 nm corresponding to the $\Delta v = 0$ sequence of this transition. Features corresponding to the $\Delta v = \pm 1$, ± 2, and $+3$ sequences are also evident, and their intensities indicate that the excited NCl(b$^1\Sigma^+$) is formed with considerable vibrational excitation.[12,13] The intensity of the emission varied linearly with the fluence of the photolysis laser, suggesting that NCl(b$^1\Sigma^+$) is produced directly by the single photon photodissociation of NCl$_3$.

Emission from NCl(a$^1\Delta$) produced by the photolysis at 193 nm was observed by using the cooled Ge detector combined with a narrow band filter centered at 1080 nm. The transmission band of the filter was sufficiently narrow such that only the $\Delta v = 1$ band of the emission was transmitted. Figure 4 shows the time profile of the NCl (a$^1\Delta$, $\Delta v = 0$) emission. The profile exhibits a rise limited by the bandwidth of the detector (77 kHz) followed by a slow decay over several ms. The intensity of this emission from NCl(a$^1\Delta$) also varied linearly with the fluence of the photolysis laser. The decay time of the emission and the density of NCl$_3$ in the system (1.0×10^{14} cm^{-3}) suggest that collisional quenching of the excited NCl(a$^1\Delta$) by the residual parent NCl$_3$ has a rate constant no greater than 2.5×10^{-12} cm^{3}s^{-1}. In fact, we believe the rate constant to be substantially smaller than this value, since for the conditions of Figure 4 (total pressure 0.16 Torr) the loss of NCl(a$^1\Delta$) is likely to be dominated by collisions with the vessel wall.

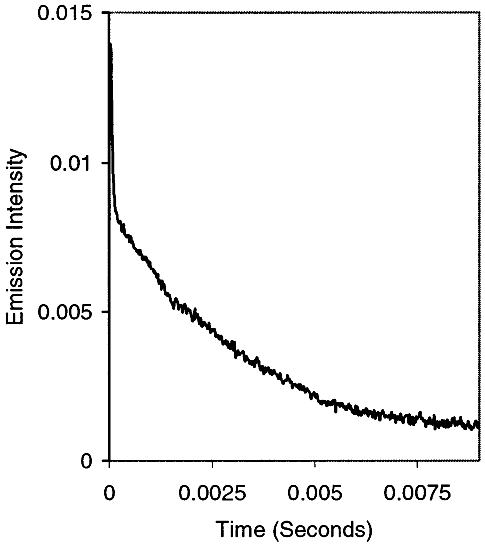

Figure 4. Time profile of the emission from NCl(a$^1\Delta$, $v = 0$) produced by 193 nm photolysis of an NCl$_3$/Ar mixture (2.0% NCl$_3$) at a total pressure of 0.16 Torr.

4. Excitation of Iodine Atoms. In previous experiments performed in our laboratory,[7] emission from I(5^{2}P$_{1/2}$) produced by excitation in collisions with NCl(a$^1\Delta$) was observed from the pulsed photolysis of mixtures of ClN$_3$ and CH$_2$I$_2$ at 193 nm. Photodissociation of ClN$_3$ at this wavelength produces NCl(a$^1\Delta$) with a branching fraction[14] of at least 0.7, and photodissociation of CH$_2$I$_2$ produces CH$_2$I and I atoms. Of the I atoms produced from the dissociation of CH$_2$I$_2$, 95% are in the ground 5^{2}P$_{3/2}$ state and 5% are in the excited 5^{2}P$_{1/2}$ state.[15] The collisional excitation of the ground-state iodine atoms by the NCl(a$^1\Delta$) present is easily observed in the time profile of the iodine emission at 1315 nm. The excited iodine produced by direct photolysis of CH$_2$I$_2$ has a detector limited rise followed by a slow exponential decay over several ms. The excited iodine produced by collisional excitation appears as an emission signal rising over a few hundred μs to a ms after the laser pulse (depending on the densities of the collision partners), followed once again by a slow decay over a few ms. Because the rate constant for excitation of iodine atoms to the 5^{2}P$_{1/2}$ state by collisions with NCl(a$^1\Delta$) is known,[7,8] and the enhancement in the absolute number density of I(5^{2}P$_{1/2}$) caused by such collisional excitation can be experimentally determined from the I(5^{2}P$_{1/2}$) emission time profile (by using the time profile of excited iodine emission from phototdissociation of CH$_2$I$_2$ as a standard), observation of the production of excited iodine atoms by 193 nm photolysis of mixtures of CH$_2$I$_2$ and NCl$_3$ offers a means of determining the density of NCl(a$^1\Delta$) present, and hence the quantum yield for its production by photodissociation of NCl$_3$.

Figures 5A, B, and C show time profiles of 1315 nm iodine emission produced by the 193 nm photodissociation of CH$_2$I$_2$

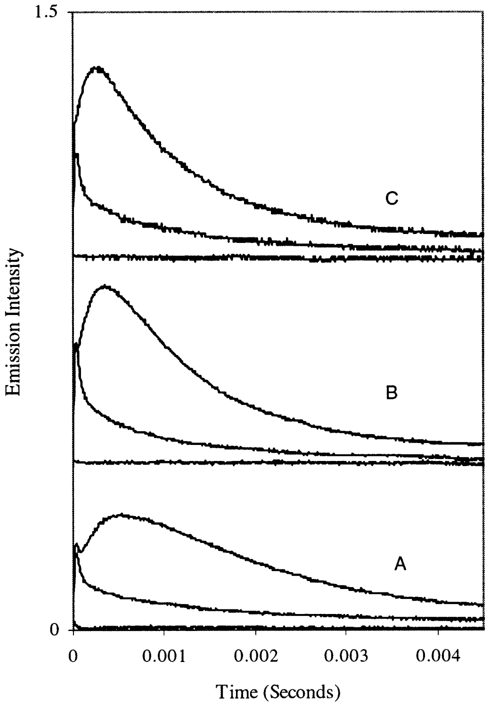

Figure 5. Time profiles of emission from excited iodine atoms produced from the pulsed photolysis of either CH_2I_2/Ar or CH_2I_2/NCl_3-Ar mixtures, for three different conditions. For each case, a baseline is shown for photolysis of Ar diluent alone. (A) Lower trace, emission from $I(5^2P_{1/2})$ produced by 193 nm photolysis of a CH_2I_2/Ar mixture; initial density of excited iodine atoms is 2.0×10^{11} cm^{-3}. Upper trace, emission from $I(5^2P_{1/2})$ produced by 193 nm photolysis of a CH_2I_2/NCl_3/Ar mixture. The initial density of excited iodine atoms is 2.0×10^{11} cm^{-3}, and the density of NCl_3 removed by the photolysis is 5.1×10^{13} cm^{-3}. (B) Lower trace, emission from $I(5^2P_{1/2})$ produced by 193 nm photolysis of a CH_2I_2/Ar mixture; initial density of excited iodine atoms is 3.3×10^{11} cm^{-3}. Upper trace, emission from $I(5^2P_{1/2})$ produced by 193 nm photolysis of a CH_2I_2/NCl_3/Ar mixture; initial density of excited iodine is 3.3×10^{11} cm^{-3}, and the density of NCl_3 removed by the photolysis is 1.6×10^{14} cm^{-3}. (C) Lower trace, emission from $I(5^2P_{1/2})$ produced by 193 nm photolysis of a CH_2I_2/Ar mixture; initial density of excited iodine atoms is 3.1×10^{11} cm^{-3}. Upper trace, emission from $I(5^2P_{1/2})$ produced by 193 nm photolysis of a CH_2I_2/NCl_3/Ar mixture; initial density of excited iodine atoms is 3.1×10^{11} cm^{-3}, and the density of NCl_3 removed by the photolysis is 2.8×10^{14} cm^{-3}.

(diluted in Ar) and mixtures of CH_2I_2 and NCl_3 (also diluted in Ar) under three different experimental conditions. As noted in the figure caption, the densities of photofragments are smallest for Figure 5A and largest for 5C. In each figure, the bottom trace is a baseline produced by photolysis of Ar alone. The middle trace corresponds to emission from excited iodine produced by photodissociation of CH_2I_2/Ar. In the middle trace of Figure 5A, for example, the laser fluence, the initial density of CH_2I_2, the CH_2I_2 absorption cross section, and the known $I(5^2P_{1/2})/I(5^2P_{3/2})$ ratio[15] are such that the initial densities of excited state and ground-state iodine atoms for these conditions are calculated to be 2.0×10^{11} and 3.8×10^{12} cm^{-3}, respectively. The short initial "spike" observed in the time profile corresponds to emission from I_2 present in the CH_2I_2 as an impurity. The longer decay over several ms corresponds to quenching of the excited iodine atoms by collisions with other species present in the mixture or the cell walls.

The upper trace in each figure corresponds to emission from excited iodine atoms with NCl_3 added to the CH_2I_2/Ar mixture. In the upper trace of Figure 5A, the excitation of the iodine atoms by collisions with $NCl(a^1\Delta)$ is clearly evident in the rise of the emission signal to a maximum at 440 μs after the laser pulse, followed by a decay over several ms. The maximum intensity of the emission produced from the NCl_3/CH_2I_2/Ar mixture is a factor of 2.8 greater than the initial intensity of the emission from CH_2I_2/Ar, shown in the middle trace, indicating that the densities of excited and ground-state iodine at the time of the maximum are 5.6×10^{11} and 3.5×10^{12} cm^{-3}, respectively.

At the maximum, the steady-state expression for the density of excited iodine atoms is

$$[I(5^2P_{1/2})] = k_e[I(5^2P_{3/2})][NCl(a^1\Delta)]/k_q \tag{4}$$

where k_e is the second-order rate constant for excitation of iodine atoms in collisions with $NCl(a^1\Delta)$ and k_q is a first-order rate constant for the overall quenching of the excited iodine atoms. This expression can be rearranged to give the density of excited NCl at the steady state, as follows

$$[NCl(a^1\Delta)] = (k_q/k_e)([I(5^2P_{1/2})]/[I(5^2P_{3/2})]) \tag{5}$$

For the conditions of Figure 5A, $[I(5^2P_{1/2})]/[I(5^2P_{3/2})] = 0.16$ at the steady state. The value of k_e is known[7,8] to be $1.6 \times 10^{-11} cm^3 s^{-1}$ at room temperature, and k_q is determined from either the rise or the decay of the iodine emission signal shown in the figure, depending on which corresponds to the quenching rate. If, for example, the signal decay (360 s^{-1}) were to correspond to the quenching rate, then the density of $NCl(a^1\Delta)$ at the steady state would be determined to be 3.6×10^{12} cm^{-3} from eq 5. This cannot be the case, though, because for such a density the rate of excitation of the iodine atoms (using $k_e = 1.6 \times 10^{-11}$ cm^3s^{-1}) would be only 58 s^{-1}, far slower than the rate implied by the rise of the signal shown in the figure. On the other hand, if the rise of the signal (at a rate of 5000 ± 500 s^{-1}, determined by a fit to the data) were to correspond to the decay of the excited iodine, then eq 5 would suggest the density of $NCl(a^1\Delta)$ at the steady state to be 5.0×10^{13} cm^{-3}. For this density the pseudo-first-order rate of excitation of the iodine atoms would be 800 s^{-1}, significantly faster than the observed decay of the emission signal (360 s^{-1}). Because the density of $NCl(a^1\Delta)$ is far greater than the density of ground-state iodine atoms, and the rate of excitation of the iodine atoms is much slower than the rate of quenching of the excited iodine, we infer that the observed decay in fact corresponds to the rate of removal of $NCl(a^1\Delta)$ from the system. Hence, the rise of the signal would indeed appear to correspond to the rate of decay of the excited iodine atoms, and the density of excited NCl at the steady state is determined to be 5.0×10^{13} cm^{-3}. This value may be compared to the density of NCl_3 dissociated by the 193 nm laser pulse, 5.1×10^{13} cm^{-3}, to give an apparent quantum yield for the production of $NCl(a^1\Delta)$ of 0.98.

The data shown in Figure 5B,C correspond to substantially higher densities of NCl_3 photofragments. A treatment analogous to that described above results in calculated $NCl(a^1\Delta)$ quantum yields of 0.56 and 0.46, respectively, for these data. These values are substantially lower than that calculated from the data of Figure 5A, and the difference suggests that quenching of $NCl(a^1\Delta)$ by photofragments in the time between the laser pulse and the maximum of the iodine emission signal may have an effect. Taken together, the three results suggest that the intrinsic quantum yield for production of $NCl(a^1\Delta)$ at 193 nm is 0.8 ± 0.2.

Discussion

The branching fractions among the singlet, doublet, and triplet photodissociation channels are quite different for photolysis at

249 and 193 nm. The channel leading to singlet photofragments (eq 1) is clearly open at 193 nm, with a high quantum yield for the production of NCl($a^1\Delta$). Because emission from excited $Cl_2(^3\Pi)$ states was not observed for either 193 or 249 nm photolysis, it would appear that dissociation of NCl_3 to triplet fragments (eq 3) is not open at these wavelengths. As noted above, emission from excited Cl_2 is readily observed when the NCl_3 auto-decomposition flame is ignited by throttling the pump. It is interesting to note that emission from excited NCl($a^1\Delta$, $b\Sigma^+$) is not observed in the auto-decomposition flame, and indeed emission from excited I($5^2P_{1/2}$) produced by the photodissociation of CH_2I_2/NCl_3/Ar mixtures at 193 nm is quenched when the auto-decomposition flame is ignited. These observations are consistent with the auto-decomposition mechanism proposed by Rubtsov,[5] in which Cl atoms are among the principal products. These atoms are efficient quenchers[16,17] of both NCl($a^1\Delta$) and I($5^2P_{1/2}$).

While the present data offer a much extended spectrum of the banded emission produced by photodissociation of NCl_3 at 249 nm (Figure 2), few conclusions can be drawn beyond those reported by Gilbert and co-workers.[6] The exponential decay times for the new bands observed between 750 and 1400 nm appear to be short, in accord with those expected for excited states of NCl_2. The bands observed by Gilbert et al.[6] at shorter wavelengths had longer lifetimes and were thought to correspond to excited states of the parent NCl_3. Gilbert and Smith[18] have shown that the near UV broadband photolysis of NCl_3 trapped in a low-temperature Ar matrix generates NCl and Cl_2. These authors speculate, though, that the initial photofragments are NCl_2 and Cl and that the NCl arises from either further photolysis or reaction of the NCl_2 in the matrix cage.

The measurements described above suggest that the channel producing NCl($a^1\Delta$) is dominant in NCl_3 photodissociation at 193 nm. While production of $Cl_2(X^1\Sigma_g{}^+)$ as a cofragment (eq 1) seems reasonable, molecular chlorine would not make a significant contribution to the quenching processes observed in the system, in particular the rapid quenching of excited I($5^2P_{1/2}$) observed in the rise of the signals in Figure 5 or the quenching of NCl($a^1\Delta$) reflected in the decay of those signals. It seems likely that the excited NCl is quenched primarily by collisions with ground-state iodine atoms and by collisions with other NCl($a^1\Delta$) molecules. For example, the data of Figure 5A exhibit a decay rate of 360 s^{-1}. From the value of k_e and the density of ground-state I($5^2P_{3/2}$) in the system, NCl($a^1\Delta$) quenching by iodine atoms should contribute about 60 s^{-1} to this observed rate. If the NCl($a^1\Delta$) density in the system were constant at its initial value (4.0×10^{13} cm^{-3}, assuming a quantum yield of 0.8), then NCl($a^1\Delta$) self-quenching, with a rate constant[19] of 7.2×10^{-12} cm^3s^{-1}, would account for another 290 s^{-1}. Hence the total quenching rate should be about 350 s^{-1}, in very good agreement with the observed result. For the conditions of Figure 5, this self-quenching process should be dominant in the removal of excited NCl and the observed decays should in fact be second order.

The rapid loss of excited I($5^2P_{1/2}$) from the system, exhibited by the rise of the signals in Figure 5, is more difficult to account for. The most likely quencher would appear to be the residual NCl_3 in the system. To account for the observed rates, I($5^2P_{1/2}$) quenching by NCl_3 would have to have a rate constant of roughly 3×10^{-11} cm^3s^{-1}. This value is similar to that reported by Ray and Coombe[7] for I($5^2P_{1/2}$) quenching by ClN_3. Current experiments in our laboratory are directed toward exploring the rates of energy transfer processes in the I($5^2P_{1/2}$)/NCl($a^1\Delta$)/NCl_3 system.

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