Energetics of Halogen Amine Reactions with Triplet Metastables: $NFCl_2$ with $Ar(^3P_{0,2})$, $He(2^3S)$, and $N_2(^3\Sigma^+_u)$ and NF_2Cl and NCl_3 with $Ar(^3P_{0,2})$

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The collisions of $NFCl_2$ with the metastable species $Ar(^3P_{0,2})$, $He(2^3S, 2^1S)$, and $N_2(^3\Sigma^+_u)$ and of NF_2Cl and NCl_3 with $Ar(^3P_{0,2})$ were carried out using a discharge flow system, and diatomic product channels were identified on the basis of emission from the fragments. The mechanisms for these reactions were determined from the emission spectra of the products, the energy available in the reacting species and released in the fragments, and the conservation of spin angular momentum. To carry out the energy analysis, the ΔH_{form}'s of NF_2Cl, $NFCl_2$, and NCl_3 were calculated using G1 and G2 methods with Gaussian 94, yielding average theoretical values of −5.3, 23.0, and 48.3 kcal/mol, respectively. These values are compared to estimated experimental ΔH_{form}'s which have been reported for NF_2Cl and NCl_3.

Introduction

Halogen amines are a fascinating class of compounds that have been studied in our laboratory for several years. In particular, the series NCl_3, $NFCl_2$, and NF_2Cl have been of interest to us because of the changes observed in stability as chlorine atoms are replaced with fluorine atoms and because of the ease with which excited state fragments can be generated both chemically and photolytically from the parent amines (for example, the $a^1\Delta$ and $b^1\Sigma^+$ states of NF and NCl and the D′ states of Cl_2 and ClF).[1−5] It has been observed that conservation of spin angular momentum directs the product formation in the photolytic and chemical processes of these compounds studied to date.

Pertinent to the work presented here are the results from the gas phase and low-temperature matrix photolysis experiments of $NFCl_2$, NF_2Cl, and NCl_3.[1,3,5,6] The UV absorption spectra of these compounds consist of structureless features, characteristic of dissociated electronic states. $NFCl_2$ has two maxima at 275 and 190 nm,[3,7] which are accessible with KrF (249 nm, 4.98 eV) and ArF (193 nm, 6.42 eV) excimer laser wavelengths. When gas mixtures of $NFCl_2$ in argon were photolyzed at 249 nm, both UV and visible emissions were observed, with features at 258, 284, and 440 nm.[3] The UV emission peaks were assigned to the $D' \rightarrow A'$ transitions in Cl_2 and ClF, respectively. The weak visible emission at 440 nm observed in the 249 nm photolysis study was tentatively assigned to NFCl, an assignment that was later confirmed by low-temperature matrix isolation experiments.[8] Photolysis of $NFCl_2$ at 193 nm resulted in UV emission bands at 201, 209, 216, 225, 234, and 284 nm, with no emission in the visible region.[3] The 284 nm band was assigned to $ClF(D' \rightarrow A')$. When the pressure of argon was increased from 2 to 26 to 54 Torr, the bands between 200 and 235 nm were quenched and $Cl_2(D' \rightarrow A')$ emission at 258 nm emerged, indicating that these were emission from high-lying electronic states of Cl_2 (electronic states above the D′ state). For both photolysis wavelengths, the species responsible for the emission were determined to be initially formed photofragments, and an energy balance analysis indicated that a two-photon process was responsible for the formation of the ion pair states of Cl_2 and ClF. The proposed mechanism is shown here for the formation of $Cl_2(D')$ at 249 nm, but analogous mechanisms can be written for the formation of ClF(D′) and for the formation of the high-lying electronic states in the 193 nm experiments.

$$NFCl_2 + h\nu \rightarrow NFCl_2^* \tag{1a}$$

$$NFCl_2^* \rightarrow Cl_2(A'^3\Pi_{2u}) + NF(X^3\Sigma^-) \tag{1b}$$

$$Cl_2(A') + h\nu \rightarrow Cl_2(D') \tag{1c}$$

These data complement the results obtained from photolysis studies of $NFCl_2$ in low-temperature argon matrices, where the formation of NF was observed.[1]

The UV absorption spectrum of NF_2Cl contains two broad structureless features with maxima at 185 and 235 nm.[1,7] Photolysis at 193 nm was used to probe the 185 nm feature, and emission was observed at 284 nm, the $D' \rightarrow A'$ emission of ClF, and at 215 nm, emission from ClF originating from an ion pair state above the D′ state.[5] A two-photon mechanism, analogous to the mechanism of reactions 1a−1c was proposed for the 193 nm photolysis in which $ClF(A'^3\Pi)$ and $NF(X^3\Sigma^-)$ were formed via the absorption of the first photon, with the second photon promoting ClF to the high-lying excited triplet ion pair states.

The UV absorption spectrum of NCl_3 displays an intense maximum at 220 nm and a somewhat weaker feature at 260 nm with a red tail that extends weakly into the visible.[2,9] When NCl_3 was photolyzed at 308 nm (4.03 eV) and 249 nm (4.98 eV) with XeCl and KrF excimer lasers, respectively,[6] no emission from diatomic fragments was observed, in contrast with $NFCl_2$ and NF_2Cl.[1,29] Visible emission was observed and has since been assumed to be from NCl_2 generated in the photolysis pulse. The excited electronic states of NF_2Cl, $NFCl_2$, and NCl_3 generated in the photolysis experiments were assigned as singlets since the ground state is a singlet, and in the case of the first two, they are easily observed in absorption.

This paper describes a set of experiments in which $NFCl_2$, NF_2Cl and NCl_3 were reacted with triplet metastable species. $NFCl_2$ was reacted with metastables $Ar(^3P_{0,2})$, $He(2^3S)$, and $N_2(^3\Sigma^+_u)$ to examine the product formation as a function of metastable energy. NF_2Cl and NCl_3 were reacted with $Ar(^3P_{0,2})$ to compare the product channels with those of $NFCl_2$. Spectroscopic studies have shown that reactions between singlet

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ground state molecules and triplet metastables usually excite the molecule to the triplet state manifold.[10] Consequently, triplet states of the halogen amines should be accessed in these reactions, and the dissociation products will be different from those of the singlet states produced in the photolysis work. Similar studies were carried out by Zhao and Setser with PF_3, and emission from PF and from the PF_2 radical was observed, indicating diatomic and triatomic dissociation channels.[11] In a separate set of experiments, Zhao and Setser generated NCl($b^1\Sigma^+$) via the reaction of $NFCl_2$ with He metastables and measured its radiative lifetime and several quenching rate constants.[12] For the experiments reported here, it was anticipated that similar products would be formed, and while no emission from triatomic radicals was detected, there was identifiable emission from diatomic fragments NF, NCl, and Cl_2 in the $NFCl_2$ and NF_2Cl studies and from NCl and Cl_2 in the NCl_3 studies. Mechanisms for the formation of these fragments are proposed on the basis of the electronic states of the fragments identified via their emission spectra, the energetics of the systems for which the ΔH_{form}, using G1 and G2 methods with Gaussian 94, were calculated,[13−17] and the spin constraints of the system.

Experimental Section

The discharge-flow method described by Zhao and Setser[11] was used to study the reactions of gaseous $NFCl_2$, NF_2Cl, and NCl_3 with the various metastables. The flow of metastables was produced by passing Ar, N_2, or He gas through the high-voltage zone of the discharge cell. A 180 kohm resistor was placed in series with the discharge, and the voltage between the two tantalum electrodes was 400, 450, and 890 V to generate N_2*, Ar*, and He*, respectively. Passing pure N_2 gas through a dc discharge generates what is known as “active nitrogen”, which contains reactive species in addition to $N_2(A^3\Sigma_u^+)$, including atomic nitrogen, $N_2(C^3\Pi_u)$, $N_2(B^3\Pi_g)$, and vibrationally excited $N_2(X^1\Sigma_g^+)$. The effect of these other species in the flow system will be addressed.

$NFCl_2$ and NF_2Cl were synthesized and purified as described in ref 1 and 4. Briefly, a stainless steel reactor tube (30 cm long and 1.8 cm o.d.) was filled with 14 g each of NH_4Cl and NaCl and clean, dry copper shot. The charged reactor was heated to 110 °C for 4 h while passing dry N_2 gas through it to completely dry the contents. The reactor was cooled (to 55 °C to optimize the $NFCl_2$ production or to 35 °C to optimize the NF_2Cl production), and the synthesis was started by passing a 20% mixture of F_2 in helium (Spectra Gases) through the reactor. The net chemical reaction has been proposed to be[18]

$$2NH_4Cl + 3NaCl + 7F_2 \Longrightarrow NFCl_2 + NF_2Cl + 8HF + 3NaF + Cl_2 \quad (2)$$

The reaction products were collected in a Teflon U-trap submerged in liquid N_2. $NFCl_2$ or NF_2Cl was separated from the other products by vacuum distillation techniques, and Pyrex bulbs containing between 5 and 10% $NFCl_2$ or NF_2Cl in argon were prepared. UV absorption spectra, taken with a 7.5 cm Pyrex cell equipped with fused quartz windows and a Milton Roy Spectronic 3000 array spectrometer, were used to verify the presence of $NFCl_2$ or NF_2Cl in the prepared bulbs.

NCl_3 was synthesized following the method described in ref 6 in which a gaseous mixture of Cl_2 and argon was passed through an aqueous solution of $(NH_4)_2SO_4$ in 1M H_2SO_4. Due to its high vapor pressure and low solubility in water, NCl_3 was swept out of the solution with the argon and the excess chlorine and was condensed as an amber-colored liquid in a cold trap submerged in a methanol/dry ice bath. The cold bath was removed, and any condensed Cl_2 was allowed to evaporate. Then, the NCl_3 vapor was carried by the flow of argon through $^1/_4$ in. black Teflon tubing to the discharge flow cell. Black tubing was used to minimize the photodecomposition of NCl_3. A Teflon metering valve, placed before the cell, allowed a small fraction of the NCl_3/Ar gas mixture to enter the gas discharge system, and the rest was returned to the hood. It should be noted that NCl_3 can explosively decompose and should be used with adequate safety precautions.

Halogen amine/Ar or halogen/Ar gas mixtures were admitted to the stream of metastables through a perforated circular Pyrex ring placed inside the dc discharge-flow cell and located 1 cm below the lower electrode. The pressure in the system was monitored with an MKS Baratron gauge (Model 122A), and for the data presented here, the total pressure in the flow dc discharge cell was 5.8 Torr for the Ar* and N_2*experiments and 15 Torr for the He* experiments. Reagent (with the exception of NCl_3, which decomposes upon passing through a flow meter) and carrier gas mass flows were measured with calibrated MKS mass flow meters, and the linear flow velocity of the system was 200 cm s^{-1} at the pressures used in these experiments. The reagent densities in the flow cell were calculated from the reagent flows, the carrier gas flow, and the total pressure. The $NFCl_2$ or NF_2Cl density varied between 0.56×10^{14} and 1.1×10^{14} molecules/cm^3, and the density of metastables in the dc discharge was assumed to be 0.01% of the total density of Ar, He, or N_2.[10]

A circular 2.54 cm o.d. fused quartz viewing port was located 4 cm below the Pyrex ring on the side of the dc discharge flow tube (2.54 cm o.d.). For a second series of experiments, the circular viewing port was removed, a rectangular opening extending from 1 to 5 cm below the Pyrex ring was cut into the side of the Pyrex tube, and a fused quartz window was glued over the rectangular opening. Ultraviolet and visible emissions were dispersed by a Jarrell Ash 0.275 m monochromator with a 2 nm band-pass, and detected with a cooled GaAs photomultiplier tube (Hamamatsu R943-02). A cooled indium detector was used in place of the photomultiplier tube to look for infrared emission. The signal from the detector was transformed into a voltage signal with an electrometer (Keithley Instruments, Model 610C) and visualized with a strip-chart recorder (Alltech Associates). In some experiments, a yellow glass filter was placed between the viewing port of the discharge cell and the entrance slit of the monochromator to block second-order UV emission lines in the visible region.

Results

The energies of the excited metastables $Ar(^3P_{0,2})$, $N_2(A^3\Sigma_u^+)$, and $He(2^3S, 2^1S)$ are listed in Table 1. Also included in Table 1 is a summary of the emitting products detected when $NFCl_2$ was admitted to a stream of each of these metastables. In the Ar metastable experiments, both visible and UV emission were observed. The visible emission appeared to the eye as a very intense orange flame, and its spectrum is shown in Figure 1B. To achieve the spectral resolution in Figure 1B, the bandwidth of the monochromator was reduced to 1 nm. The single blue degraded peak with a maximum at 530 nm is identified as the $\Delta v = 0$ sequence band of the $b^1\Sigma^+ \rightarrow X^3\Sigma^-$ transition in NF. The emission bands between 710 and 535 nm are assigned to the $b^1\Sigma^+ \rightarrow X^3\Sigma^-$ transition in NCl. The most intense peak at 664 nm is part of the $\Delta v = 0$ sequence band, and the other sequence bands are assigned as indicated in the figure, with the individual band maxima listed in Table 2. These data are in good agreement with previously reported NCl emission data

TABLE 1: States and Energies (*E*) of He, Ar, and N_2 Metastable Species and the Emission Observed upon Reaction of These Metastables with $NFCl_2$

species	state	*E*, cm^{-1}	*E*, kcal/mol	*E*, eV	emission observed
He^a	2^1S	166 272	475.3	20.6	$NF(b^1\Sigma \rightarrow X^3\Sigma)$; $\Delta v = 0$
	2^3S	159 850	457.0	19.8	$NCl(b^1\Sigma \rightarrow X^3\Sigma)$; $\Delta v = 0$
					Cl_2 emission at 258, 246, 236, 226, 216 nm
Ar^a	$^3P_0$	94 554	270.3	11.7	$NF(b^1\Sigma \rightarrow X^3\Sigma)$; $\Delta v = 0$
	$^3P_2$	93 144	266.3	11.5	NCl $(b^1\Sigma \rightarrow X^3\Sigma)$; $\Delta v = -1, 0, +1, +2, +3$
					Cl_2 $(D' \rightarrow A')$ at 258 nm, secondary reaction
					Cl_2 emission at 198 nm, secondary reaction
N_2^b	$^3\Sigma_u^+$	50 934	145.7	6.31	$NF(b^1\Sigma \rightarrow X^3\Sigma)$; $\Delta v = 0$

[a] See Table 1 in ref 10 for state assignments and energies. [b] $N_2(^3\Sigma_u^+)$ energy calculated from $[T_e + \omega_e/2]$ from ref 30.

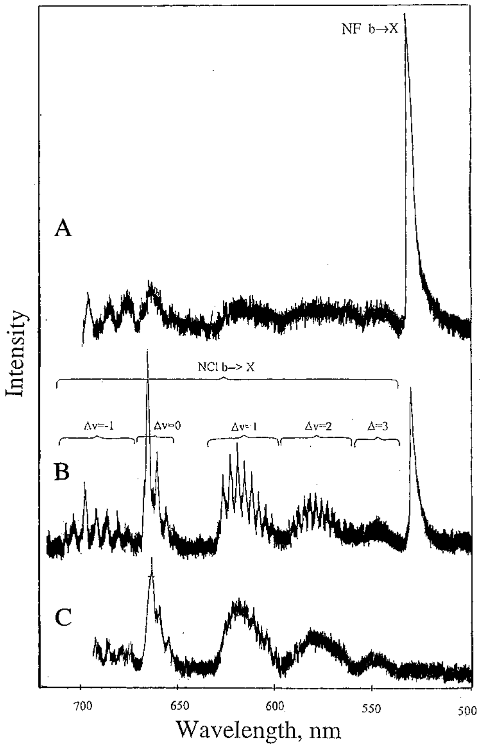


Figure 1. Visible emission spectrum observed when (A) NF_2Cl, (B) $NFCl_2$ and (C) NCl_3 were added to a stream of $Ar(^3P_{0,2})$ metastables. The bandwidth of the emission monochromator was 2 nm for (A) and (C), and 1 nm for (B).

by Colin et al.[19] and by Pritt and Coombe and co-workers.[20,21] When Cl_2 was reacted with the argon metastables, no such emission was observed.

Since the $NFCl_2 + Ar(^3P_{0,2})$ reaction generates the $b^1\Sigma^+$ states of NF and NCl, the possibility that the $a^1\Delta$ states of NF and NCl were also produced was explored. When the PMT was replaced with the cooled indium detector to probe the infrared region, the only emission that was observed was from the $B^3\Pi_g \rightarrow A^3\Sigma_u^+$ transition in N_2,[22] with no evidence of the $a^1\Delta \rightarrow X^3\Sigma^-$ transitions in NCl (at 1080 nm) and NF (at 874 nm).[20,23] The nitrogen source was determined to be a small air leak.

The spectrum of the UV emission, shown in Figure 2A, consists of two features with maxima at 258 and 198 nm. Both bands were also observed when a 5% mixture of Cl_2 in argon was admitted to the stream of argon metastables as shown in Figure 2B. The 258 nm band is the well-known transition between the D'($^3\Pi$ 2g) and A′($^3\Pi$ 2u) states of Cl_2.[24] Cl_2 emission at 198 nm has been reported, and although the specific electronic states involved are debated, it is likely that this transition originates from an ion pair state at a higher energy than the D′ state.[25] The C → A transition of ArCl has been observed in the 198 nm spectral region, and there is certainly a possibility of direct abstraction of Cl by an $Ar(^3P_{0,2})$ in these systems.[26] However, at the pressures used in these experiments, this emission should be effectively quenched according to the data provided in ref 26. Consequently, this emission is assigned to Cl_2. The D′ → A′ transition in ClF is a blue degraded band which is known to lie at 284 nm.[27] A band at 284 nm is observed in Figure 2A; however, it is red degraded and is also observed in Figure 2B and in Figure 2C (the spectrum of the emission from the argon discharge with no added reagents), so is associated with emission from the discharge. As is apparent in Figure 2, this emission is greatly attenuated when either $NFCl_2$ or Cl_2 is added to the system.

The spectra of Figures 2A,B appear to be nearly identical, and the question arose as to whether or not Cl_2 contamination in the $NFCl_2$ sample was responsible for the UV emission. Cl_2 is a product of the synthesis, as shown in reaction 2, and the separation of $NFCl_2$ from Cl_2 requires that the last step in the vacuum distillation procedure be repeated many times. It is judged to be complete when the Cl_2 absorption at 330 nm does not appear in the UV spectrum of the sample. The small extinction coefficient of Cl_2 (60 L mol^{-1} cm^{-1} at 330 nm)[28] and the fact that the tail of the $NFCl_2$ absorption peak at 270 nm extends weakly into the 330 nm region makes it possible, however, that some Cl_2 was present in all of the samples used in this study. To address this problem, experiments were run in which Cl_2/Ar samples were admitted to the Ar metastables, and the emission intensity at 258 and 198 nm as a function of Cl_2 density was monitored. Calibration plots of the intensity vs Cl_2 density were prepared from these data, and the plot obtained for the 258 nm emission is shown in Figure 3A. Figure 3B is a plot of the Cl_2 emission observed when an $NFCl_2$/Ar sample was added to the stream of argon metastables. (The $Cl_2 + Ar(^3P_{0,2})$ were performed on the same day as the $NFCl_2 + Ar(^3P_2)$ experiments to reduce the possibility that the metastable density had changed for the Cl_2 and the $NFCl_2$ runs.) An upper limit on the Cl_2 contamination in the $NFCl_2$/Ar sample was calculated from the UV absorption spectrum of the $NFCl_2$ sample, and the Cl_2 emission intensity expected for this density of Cl_2 was read from the calibration plots. It was assumed that this intensity could be subtracted from the total Cl_2 emission intensity observed in the $NFCl_2$/Ar experiments. However, the decays observed in Figure 3 indicate that quenching of the Cl_2 emission becomes important when the reagent density gets larger than about 1.5×10^{13} molecules cm^{-3}, and this complicates the correction of the Cl_2 emission intensity in the $NFCl_2$ experiments for Cl_2 contamination. Consequently, only $NFCl_2$ data in the low-density regime, where the intensity increases with density, could be corrected for Cl_2 contamination. Curve A of Figure 4 shows the total Cl_2 emission intensity in the $NFCl_2$ experiment, and curve B shows the Cl_2 emission intensity corrected for the Cl_2 contamination. Clearly, some of the Cl_2 emission observed in the $NFCl_2$ experiment can be ascribed to the presence of Cl_2 contamination in the sample, but not all of it. For example, at $NFCl_2$ densities of 6×10^{12} molecules/

TABLE 2: Individual Band Maxima (in nm) for the NCl ($b^1\Sigma^+ \rightarrow X^3\Sigma^-$) Emission Shown in Figure 2

sequence $\Delta v = -1$	assignment v', v''	sequence $\Delta v = 0$	assignment v', v''	sequence $\Delta v = +1$	assignment v', v''	sequence $\Delta v = +2$	assignment v', v''
703	0, 1	664	0, 0	626	1, 0	589	3, 1
697	1, 2	660	1, 1	619	2, 1	587	4, 2
691	2, 3	665	2, 2	619	3, 2	584	5, 3
686	3, 4			615	4, 3	581	6, 4
680	4, 5			611	5, 4	578	7, 5
674	5, 6			608	6, 5	575	8, 6
				604	7, 6	572	9, 7
				600	8, 7	569	10, 8
						566	11, 9
						563	12, 10

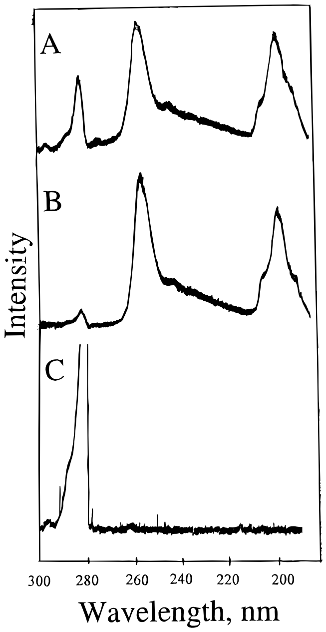


Figure 2. UV emission spectra observed upon the addition of (A) $NFCl_2$ and (B) Cl_2 to a stream of $Ar(^3P_{0,2})$ metastables. The bands at 258 and 198 nm are assigned to Cl_2. (C) UV spectrum of the Ar discharge.

cm^3, one-half to two-thirds of the Cl_2 emission is from $NFCl_2$ and the remainder is attributed to the Cl_2 contamination. The same analysis was performed for the 198 nm emission feature, with a similar result. Since the Cl_2 density calculations were upper limits, these analyses give lower limits on the contribution that $NFCl_2$ gives to the Cl_2 emission at both 198 and 258 nm.

Although the quenching process in these experiments has not been identified, it is not direct quenching of the Cl_2 ion pair states because Cl_2 ion pair state lifetimes are on the order of 10 ns in the system, and the gas kinetic collision rate is 8 μs^{-1} $Torr^{-1}$. Therefore, under the conditions of these experiments a Cl_2 molecule in an ion pair state will see less than one collision before it emits. The quenching process must, however, involve a species that leads to the formation of Cl_2 in its ion pair state and could be quenching of $Ar(^3P_{0,2})$ atoms due to changes in the walls as the reagents are introduced into the system.

No emission from ClF was observed in these experiments. To ascertain whether this was due to an experimental problem or due to the fact that no emitting states of ClF were generated in the $NFCl_2$ plus metastable reactions, a tank of ClF was obtained (which unfortunately was contaminated with Cl_2), and a bulb of ClF in argon was prepared and added to the stream of metastables. Still, no ClF emission was observed. With the idea that perhaps the ClF emission was too weak to see 4 cm (0.019 ms) downstream of the mixing zone, the rectangular viewing port described in the Experimental Section was installed, allowing the emission 1 cm below the mixing region to be viewed. All of the ClF and $NFCl_2$ reactions were repeated, but no emission from ClF emission was observed in any of the experiments, and the conclusion is that ClF emission cannot be detected in this system.

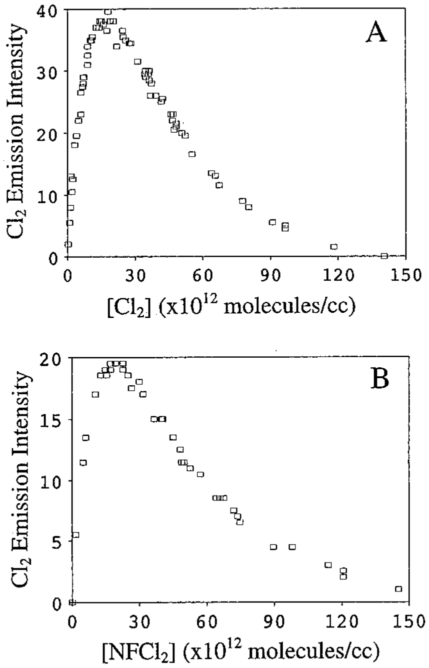


Figure 3. (A) Cl_2 emission intensity at 258 nm as a function of Cl_2 density upon the addition of a 5% mixture of Cl_2 in argon to the stream of $Ar(^3P_{0,2})$ metastables. (B) Cl_2 emission intensity at 258 nm as a function of $NFCl_2$ density upon the addition of a 5% sample of $NFCl_2$ in argon to the stream of $Ar(^3P_{0,2})$ metastables.

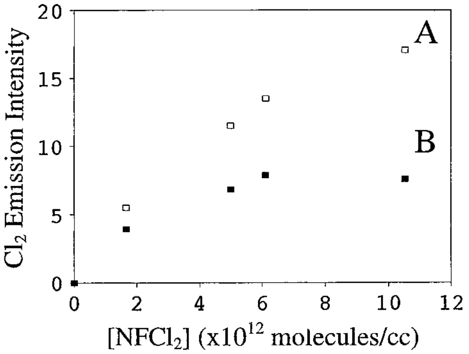


Figure 4. (A) Total Cl_2 emission intensity at 258 nm as a function of $NFCl_2$ density from Figure 3A. (B) Cl_2 emission intensity at 258 nm corrected for Cl_2 contamination plotted as a function of $NFCl_2$ density. An upper limit on the Cl_2 contamination in the $NFCl_2$ sample was calculated as described in the text.

The spectrum of the emission produced when N_2 was passed through the dc discharge with no added reagent consisted of $N_2(B^3\Pi_g \rightarrow A^1\Sigma_u^+$, first positive) emission in the visible, and

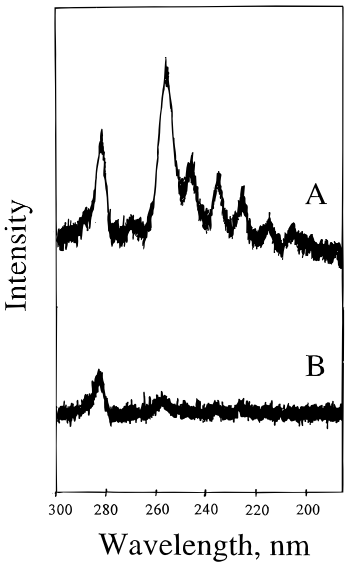


Figure 5. UV emission spectra observed upon the addition of (A) $NFCl_2$ and (B) Cl_2 to a stream of He(2^3S, 2^1S) metastables. The band at 284 nm is assigned to the He discharge since it was observed when no reagent was added to the system and looked very similar to the feature that appears in Figure 2C. The other bands are assigned to Cl_2 (see text).

$N_2(C^3\Pi_u \rightarrow B^3\Pi_g$, second positive) and NO($A^2\Sigma^+ \rightarrow X^2\Pi$, γ band) emission in the UV.[22] When $NFCl_2$ was added, the NF($b^1\Sigma^+ \rightarrow X^3\Sigma^-$) emission at 528 nm appeared in the visible, and there was a general decrease in the intensity of the N_2 first positive and of the NO γ band emission. No UV emission from Cl_2 or ClF was observed, however, from the addition of either $NFCl_2$ or Cl_2. Visible and UV emission were observed when $NFCl_2$ was reacted with He metastables. Two visible bands at 528 and 664 nm were assigned to the $\Delta v = 0$ sequence bands of the $b^1\Sigma^+ \rightarrow X^3\Sigma^-$ transitions in NCl and NF. The UV emission spectrum is shown in Figure 5A and consists of a peak with a maximum at 258 nm assigned to $Cl_2(D' \rightarrow A')$ and a series of bands at shorter wavelengths with individual band maxima at 246, 236, 226, 216, and 206 nm. These bands correlate well with the short wavelength bands observed in the 193 nm photolysis of $NFCl_2$ and are assigned to transitions originating from high lying electronic states Cl_2.[3,24] The relative intensity and the distinct nature of these UV bands were a function of the He pressure, and to see them well required helium pressures of 15 Torr. The emission observed when Cl_2 was added to the flow of He metastables is shown in Figure 5B. Zhao and Setser reported NCl(b→X) emission from the reaction of $NFCl_2$ with He metastables; however, since they were only interested in the NCl emission, they did not report any other emission that they may have observed.[12]

Emitting fragments generated in the NF_2Cl or NCl_3 plus Ar metastable rare gas atom reactions are summarized in Table 3, with the $NFCl_2$ reactions for comparison. When NF_2Cl was admitted to the stream of Ar metastables, the emission appeared to the eye as an emerald green flame. Consistent with this observation, the spectrum, shown in Figure 1A, reveals an intense single blue degraded peak at 528 nm assigned to the b → X transition in NF. The weak emission features in the 650−570 nm region are the $\Delta v = 1$, 2, and 3 sequence bands of the NCl(b→X) transition. Nitrogen first positive emission appears in the 650−700 nm region and obscures the NCl(b→X) $\Delta v = 0$ sequence band. The UV emission spectrum was virtually identical to the $NFCl_2 + Ar(^3P_{0,2})$ UV emission spectrum with Cl_2 features at 258 and 198 nm. Since Cl_2 cannot be formed in a direct reaction of NF_2Cl with Ar metastables, the observed UV emission must be due to residual chlorine present in the sample as a contaminant. Cl_2 is a product of both the synthesis and NF_2Cl thermal decomposition, and it is, consequently, nearly impossible to completely eliminate Cl_2 from the sample. Again, as in the $NFCl_2$ experiments, no ClF emission was detected in this experiment. When the Ar pressure was reduced to 2.0 Torr, a peak at 192 nm assigned to the B → X transition in ArF appeared as a second maximum just to the blue of the 198 nm Cl_2 feature.[26]

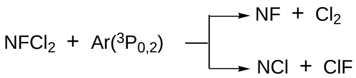
TABLE 3: Emission from Fragments Generated in the Reactions of $Ar(^3P_{0,2})^a$ with $NFCl_2$, NF_2Cl, and NCl_3

molecule	emission observed
$NFCl_2$	$NF(b^1\Sigma^+ \rightarrow X^3\Sigma^-)$; $\Delta v = 0$
	$NCl(b^1\Sigma^+ \rightarrow X^3\Sigma$-); $\Delta v = -1, 0, +1, +2, +3$
	$Cl_2(D' \rightarrow A')$ at 258 nm, secondary reaction
	Cl_2 emission at 198 nm, secondary reaction
NF_2Cl	NF $(b^1\Sigma^+ \rightarrow X^3\Sigma^-)$; $\Delta v = 0$
	$NCl(b^1\Sigma^+ \rightarrow X^3\Sigma^-)$; $\Delta v = +1, +2, +3$ (weak)
	$ArF(^2B \rightarrow X)$ at low pressures of argon
NCl_3	$NCl(b^1\Sigma^+ \rightarrow X^3\Sigma^-)$; $\Delta v = -1, 0, +1, +2, +3$
	$Cl_2(D' \rightarrow A')$ at 258 nm, secondary reaction
	Cl_2 emission at 198 nm, secondary reaction

Addition of the NCl_3 sample below the argon discharge generated an intense orange emission flame similar to that observed for the $NFCl_2 + Ar(^3P_{0,2})$ reaction, and the spectrum (Figure 1C) indicates the $\Delta v = 0$, +1, +2, and +3 sequence bands of the $b^1\Sigma^+ \rightarrow X^3\Sigma^-$ transition in NCl. The UV emission was again essentially the same as that observed in the $NFCl_2$ and NF_2Cl reactions and was similarly assigned to ion pair transitions in Cl_2.

Discussion

When molecular species react with metastable argon atoms, Penning ionization, associative ionization, neutral excitation, neutral dissociation, and neutral dissociative excitation may occur.[10] The last of these, neutral dissociative excitation, is assumed to be responsible for the production of excited state diatomic fragments in the $Ar(^3P_{0,2})$ reaction systems. On the basis of the product emissions observed in the $NFCl_2$ system, there are two pathways leading to diatomic fragments by which the reaction proceeds, as shown here.



(3a)

(3b)

Analogous diatomic pathways can be written for the $NF_2Cl/Ar(^3P_{0,2})$ system, and for the $NCl_3/Ar(^3P_{0,2})$ system, a single channel leading to the formation of NCl and Cl_2 can be written. Two aspects of this process will be analyzed here, the energetics and the spin constraints.

To examine the energetics of the reactions requires that the ΔH_{form} values for the products and reactants and the energies of the excited states of the products be known. For $NFCl_2$, the only ΔH_{form} available is the experimental lower limit of −10 kcal/mol determined from the $NFCl_2$ gas-phase photolysis experiments.[3] Therefore, G1, G2-MP2, and G2-MP4 methods were used with Gaussian 94 to compute the energies of $NFCl_2$, N_2, F_2, and Cl_2.[13−17] These energies were used together with the formation reaction to compute the ΔE_{form} for $NFCl_2$. The ΔH_{form} was calculated from $\Delta E_{form} + \Delta nRT$ where Δn is the change in the number of moles in the formation reaction. The results of the three calculations are included in Table 4 and show about a 5% variation. To estimate the reliability of the calculated ΔH_{form} of $NFCl_2$, ΔH_{form}'s were calculated for NF_3, NCl_3, and NF_2Cl, species for which experimental values have been reported. These values are also included in Table 3. For

TABLE 4: Theoretical and Experimental ΔH_{form}'s in kcal mol^{-1} for NF_3, NF_2Cl, $NFCl_2$, and NCl_3

molecule	G1	G2-MP2	G2-MP4	av theor	exptl
NF_3	−35.36	−38.38	−38.29	−37.55	−31.43[a]
NF_2Cl	−3.94	−5.90	−6.16	−5.33	+5[b]
$NFCl_2$	+24.12	+22.61	+22.28	+23.00	+29.1[c]
NCl_3	+49.54	+47.67	+47.59	+48.32	+63[d]

[a] Reference 37. [b] Reference 29. [c] Predicted experimental value assuming that the average theoretical ΔH_{form} is 21% too low. [d] Reference 9.

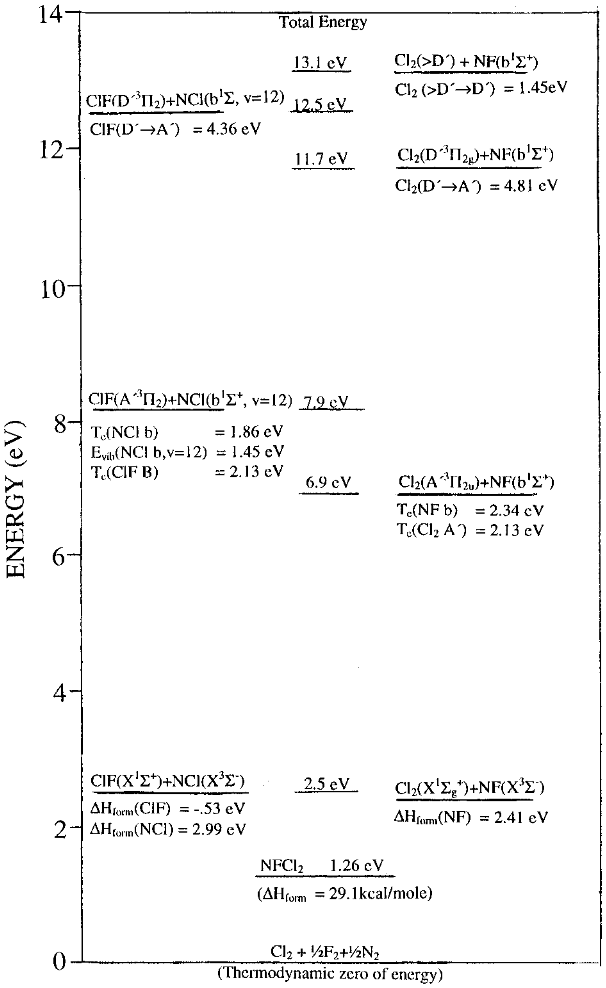


Figure 6. Energy level diagram for $NFCl_2$ and the diatomic channels NF + Cl_2 and NCl + ClF. The energies listed under "Total Energy" were calculated from the energies of the diatomic fragments for each channel indicated.

NF_3 and NCl_3, the average calculated ΔH_{form}'s are 19 and 23% lower, respectively, than the experimental values. (It is noted, however, that there is significant uncertainty in the experimental ΔH_{form} of NCl_3.) Assuming that the theoretical value for $NFCl_2$ is 21% too low predicts an "experimental" value of 29.1 kcal/mol. The theoretical and experimental values of ΔH_{form} for NF_2Cl were not used in this analysis because the validity of the experimental value is debatable.[29] The results of the G1, G2-MP2, and G2-MP4 methods gave very similar ΔH_{form}'s for NF_2Cl and yield an average value of −5.33 kcal/mol.

Figure 6 is an energy level diagram for $NFCl_2$ and the diatomic dissociation channels. The right side of the diagram shows the energetics of the NF plus Cl_2 pathway using the known energies for $NF(b^1\Sigma^+)$, $Cl_2(D')$, and $Cl_2(A')$, converted to electronvolts.[24,30] Using the adjusted ΔH_{form} for $NFCl_2$, the diagram indicates that there is sufficient energy in the reaction with Ar $^3P_2$ atoms (11.7 eV) or with Ar $^3P_0$ (11.5 eV) to generate $NF(b^1\Sigma^+)$ and $Cl_2(D')$. To generate the Cl_2 state that is responsible for the emission at 198 nm, however, would require an additional 4.15 kcal/mol in the reaction involving the more energetic $Ar(^3P_0)$ or 8.75 kcal/mol in the reaction with $Ar(^3P_2)$.

As noted above, the spectrum of the Cl_2 emission observed in the $NFCl_2$ + $Ar(^3P_{0,2})$ experiments is virtually identical to that observed in the Cl_2 + $Ar(^3P_{0,2})$ experiments. It is very unlikely that these reactions would generate identical Cl_2 emission spectra in view of the energetics of the two cases, particularly since according to our calculations, there is insufficient energy to produce the 198 nm Cl_2 emission in the $NFCl_2$ reaction. It is, however, possible that the Cl_2 ion pair states are not direct products of the $NFCl_2$ + $Ar(^3P_{0,2})$ reaction but are formed in a secondary step as shown here.

$$NFCl_2 + Ar(^3P_2) \rightarrow NF + Cl_2 \qquad (4a)$$

$$Cl_2 + Ar(^3P_2) \rightarrow Cl_2(\text{ion pair states}) \qquad (4b)$$

The electronic states of the diatomic species in this mechanism can be analyzed on the basis of the observed emission and spin constraints. Since reactions between singlet ground state molecules and triplet metastable atoms usually excite the molecule to the triplet state manifold, then for our system an intermediate triplet state of $NFCl_2$ is produced in step 4a. The emission data indicate that a channel exists in which the NF fragment is produced in an excited singlet state, so spin conservation rules predict that the Cl_2 fragment will be a triplet. There are three low lying $^3\Pi$ states of Cl_2, the $B(0u^+)$, the A(1u), and the A′(2u) states.[30] The B state generates well-known red/orange emission which was not observed in these experiments. No emission corresponding to the A and A′ states was observed, although none would be expected due to their long lifetimes and the high probability of collisional quenching in the system.[31] A "dark" dissociation channel in which the ground state fragments $NF(X^3\Sigma^-)$ and $Cl_2(X^1\Sigma_g^+)$ are generated also correlates with the triplet $NFCl_2$ intermediate state, and this channel is the likely source of the ground state Cl_2 for step 4b, since it would generate identical emission to what is observed when Cl_2 is added to the stream of Ar metastables.

The NCl + ClF channel can also be analyzed, and the left side of the energy diagram (Figure 6) shows the energetics of this channel using the known energies in electronvolts for $NCl(b^1\Sigma^+)$ and ClF(D′).[19,20,24] Since the energy of the ClF(A′) state is not established, it was assumed to have the same energy as the $B^3\Pi$ state because the analogous states are very close in energy in Cl_2 and F_2.[30] Spin constraints predict that the ClF will be generated in a triplet state with $NCl(b^1\Sigma^+)$, similar to the $NF(b^1\Sigma^+)$ + Cl_2(triplet state) case above, and the energy diagram indicates that there is sufficient energy in the $NFCl_2$ + $Ar(^3P_{2,0})$ reaction for the production of ClF(D′) with $NCl(b^1\Sigma^+)$. There is also a spin and energetically allowed "dark" dissociation channel possible leading to the formation of ground state NCl and ClF.

The reactions of $NFCl_2$ with N_2 metastables (6.31 eV) and He (19.8 eV) probes dissociating triplet states at energies lower and higher than the state produced in the Ar metastable (11.7 eV) studies. For the reactions with N_2 metastables, neutral dissociative excitation is assumed to be responsible for the production of excited state diatomic fragments as in the Ar metastable reactions. The NF(b→X) emission at 528 nm shows that the NF channel is open; however, no emission from Cl_2 was observed. There are several reactive species in active N_2, and these must all be considered regarding their possible participation in the production of NF($b^1\Sigma^+$) from $NFCl_2$. For nitrogen atoms to be involved would require that the N atom extract an F atom from the $NFCl_2$ directly or break apart the $NFCl_2$ molecule to produce electronically excited NF. This seems very unlikely, particularly since the density of nitrogen atoms below the discharge is quite small in typical systems. The visible and UV spectra of the active nitrogen indicate the presence of several excited electronic states of N_2, $A^3\Sigma_u{}^+$, $B^3\Pi_g$, and $C^3\Pi_u$.[22] Of these, only the A state has a sufficiently long lifetime to suffer enough collisions with $NFCl_2$ to be an important contributor to product formation. Figure 6 shows that there is sufficient energy in the reaction with a 6.3 eV $N_2(A^3\Sigma_u{}^+)$ metastable to generate NF($b^1\Sigma^+$) plus Cl_2 in a low-lying triplet state and NCl($b^1\Sigma^+$) plus ClF in a low-lying triplet state. The details of the potential surface of the dissociating $NFCl_2$ state must be responsible for the fact that the NCl($b^1\Sigma^+$) channel is not observed, even though it is not prohibited by the energetics of the reaction. Dark channels are possible both energetically and by spin considerations as in the argon metastable reactions. The fact that no $D' \rightarrow A'$ emission was observed when either $NFCl_2$ or Cl_2 was added is consistent with the fact that there is insufficient energy in the N_2 metastable to promote ground state Cl_2 to the D′ state and does not preclude the dark channels.

The He metastables are the most energetic of the metastables used in this study, and are the only ones with both triplet and singlet components at 19.8 and 20.6 eV, respectively. Since the $\Delta v = 0$ sequence band of the NCl($b^1\Sigma^+ \rightarrow X^3\Sigma^-$) transition and emission from several high-lying electronic triplet states of Cl_2 were observed, spin constraints predict that the dissociating state of $NFCl_2$ is generated in the reaction with He metastables is a triplet. The high-lying ion pair states of Cl_2 are a product of the dissociating excited triplet state of $NFCl_2$ since only the $D' \rightarrow A'$ emission at 258 nm was observed when the Cl_2/Ar sample was reacted with He metastables. This is in contrast to reactions of $NFCl_2$ with Ar or N_2 metastables where the Cl_2 emission at 258 and 198 nm was assigned to secondary reactions with ground state Cl_2. The $\Delta v = 0$ sequence band of the NF($b \rightarrow X$) emission was also observed in the He metastable reactions, so the NF + ClF channel is open; however, as in the other metastable reactions, no information regarding the electronic state of the product ClF is available from the data. In the $NFCl_2$ + He($^{1,3}S$) studies done by Zhao and Setser,[12] it was proposed that $NFCl_2$ is ionized in the collision, and then NCl(b) is formed following the recombination of the parent ion with an electron. It is not possible to verify whether this mechanism or direct excitation of a triplet state of $NFCl_2$ is responsible for the excited state product formation from the data available. In either case, however, the dissociating state of $NFCl_2$ must be a triplet state because of the spin multiplicity of the products. Furthermore, if the excited triplet state of $NFCl_2$ is generated in a direct reaction with He, then it can be assigned to a reaction involving He(^3S) atoms rather than He(^1S). This is reasonable in view of the fact that there is a much larger density of He(^3S) generated in the discharge than of He(^1S).[10]

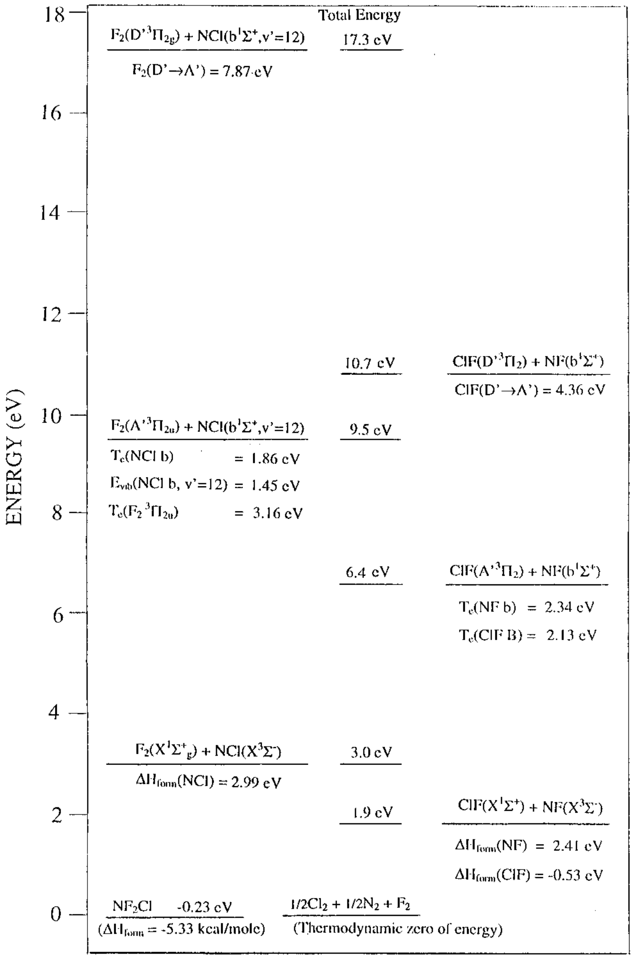


Figure 7. Energy level diagram for NF_2Cl and the diatomic channels NF + Cl_2 and NCl + ClF. The energies listed under "Total Energy" were calculated from the energies of the diatomic fragments for each channel indicated.

The NF_2Cl/Ar($^3P_{0,2}$) and NCl_3/Ar($^3P_{0,2}$) were carried out to compare the processes in these chemically related systems to those observed in the $NFCl_2$/Ar($^3P_{0,2}$) system. An energy diagram for the NF_2Cl system is shown in Figure 7. Since, as mentioned above, the experimental ΔH_{form} value for NF_2Cl is not well established, the average theoretical value from Table 4 is included in the diagram. The experiment shows that the NF($b^1\Sigma^+$) fragment is formed in the reaction. Thus, assuming that an excited electronic triplet state of NF_2Cl is formed in the NF_2Cl + Ar($^3P_{0,2}$) reaction, the spin constraints predict that the second fragment, ClF, must be produced in a triplet state. There is sufficient energy to generate ClF(D′), as shown in the energy level diagram, although no ClF($D' \rightarrow A'$) emission was observed. There are also other low-lying triplet states that are energetically accessible, the B($^3\Pi_0{}^+$) and A′($^3\Pi_2$) states. A "dark" channel leading to the production of the ground state fragments, NF($X^3\Sigma^-$) and ClF($X^1\Sigma^+$), also correlates with a triplet intermediate state of NF_2Cl. The left side of the energy level diagram represents the energetics of the NCl + F_2 channel. Spin rules dictate that production of NCl($b^1\Sigma^+$) must be accompanied by production of the F_2 fragment in a triplet state. However, generation of the D′ state of F_2 is not possible when the energetics of the NCl + F_2 channel are examined. This channel would yield a lower limit for the ΔH_{form} of NF_2Cl of 135 kcal/mol, an unreasonably high value and certainly out of the question compared to the ΔH_{form}'s of Table 4. The formation of one of the low-lying triplet states of $F_2(^3\Pi^+{}_{0u}$ or $^3\Pi_{2u})$ plus the $b^1\Sigma^+$ state of NCl and the "dark" channel leading to NCl($X^3\Sigma^+$) + $F_2(X^1\Sigma^+{}_g)$ are allowed product channels based on spin and energy considerations.

The formation of ArF(^2B) was observed in the Ar($^3P_{0,2}$) + NF_2Cl reaction when the argon pressure was reduced to 2 Torr. This product is allowed by the spin constraints of the system, and there are several possible mechanisms by which it could be generated. First, direct abstraction of a fluorine atom from NF_2Cl could lead to the ArF(^2B) formation, leaving a doublet NFCl as the other reaction product, although NFCl was not detected in these studies. Ground state $F_2(X^1\Sigma^+{}_g)$ generated in the "dark" channel is also a candidate for a secondary reaction

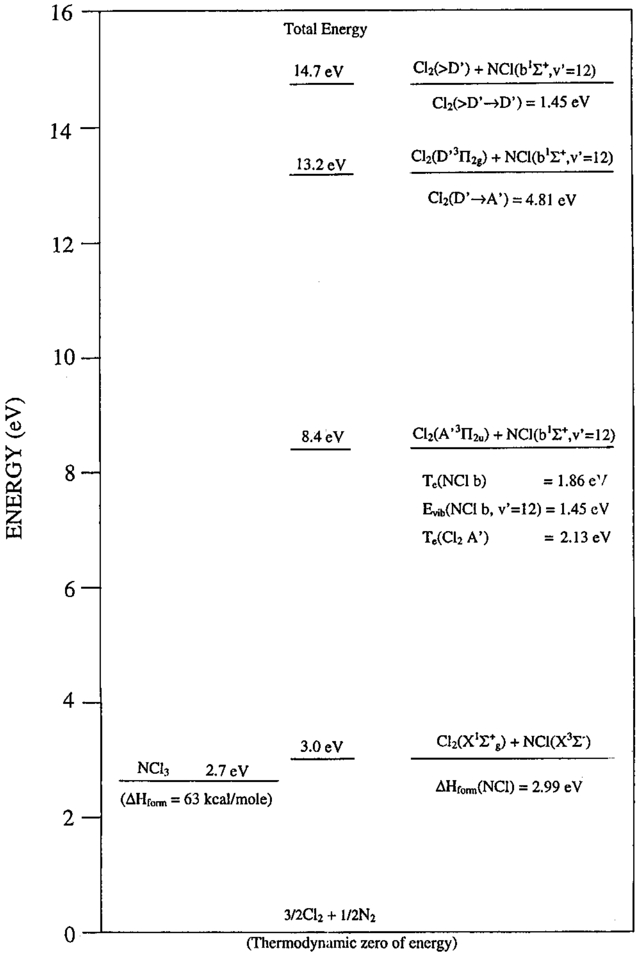


Figure 8. Energy level diagram for NCl_3 and the diatomic channel $NCl + Cl_2$. The energies listed under "Total Energy" were calculated from the energies of the diatomic fragments for each channel indicated.

with $Ar(^3P_{0,2})$ leading to the $ArF(^2B) + F(^2P)$ production. Finally, the mechanism of excimer formation via an excited molecular halogen channel has been reported for the $Cl_2^* +$ Xe(Kr), $Br_2^* +$ Xe, and $IBr^* +$ Xe reactions.[27] By analogy with these reactions, it is possible that $ArF(^2B)$ could also be formed via an excited molecular fluorine channel where an excited triplet state of fluorine acts as a precursor.

An energy level diagram constructed for the $NCl_3 + Ar(^3P_{0,2})$ reaction system is given in Figure 8. As can be seen from the diagram, a sufficient amount of energy is present in the reaction with either 11.7 or 11.5 eV Ar metastables to generate Cl_2 emission at 258 nm. To generate the 198 nm emission, however, an additional 6.92 or 11.5 kcal/mol is needed in a reaction with a $Ar(^3P_0)$ or $Ar(^3P_2)$ metastable, respectively. Therefore, analogous to the $NFCl_2$ case, a two-step mechanism is proposed to account for the generation of chlorine emission. The dissociating state of NCl_3 formed as an intermediate in the $NCl_3(^1X) + Ar(^3P_{0,2})$ reaction correlates with two pathways both leading to the production of diatomic fragments. The $NCl(b^1\Sigma^+)$ and Cl_2(low-lying triplet state) fragments are generated in channel one. Presumably, the ground states $NCl(X^3\Sigma^-)$ and $Cl_2(X^1\Sigma^+{}_g)$ are formed in the second, "dark", dissociation channel. The ion-pair states of chlorine are assumed to be formed via a secondary reaction between the ground state of Cl_2 formed in the "dark" channel and argon metastables.

The vibrational excitation of the nitrene products is a reflection of the geometry of the dissociating halogen amine, assuming no vibrational or electronic quenching of the $b^1\Sigma^+$ states of NF and NCl. To check this assumption, the visible spectra were run at different amine densities. Since the vibrational distributions were observed to not depend on the amine densities, this assumption is valid. For the $NFCl_2/Ar(^3P_{0,2})$ and the $NF_2Cl/Ar(^3P_0)$ systems, only the $\Delta v = 0$ sequence band is observed in the NF(b → X) emission spectrum, implying that the majority of the NF fragments are emitting from the $v = 0$ level of the $b^1\Sigma^+$ state. Quenching of $NF(b^1\Sigma^+)$ is generally inefficient,[32] and quenching of $v' > 0$ levels would require a polyatomic or diatomic species with a near-resonant vibrational mode. Potential collision partners in the flow system are argon atoms, the diatomic species NF, NCl, ClF, or Cl_2, and parent molecules. Of these, only argon is present at high enough densities for a sufficient number of collisions, but it would not be an efficient vibrational quencher of $NF(b^1\Sigma^+,v'>0)$. It is concluded, therefore, that the dissociating states of $NFCl_2$ and NF_2Cl produce $NF(b^1\Sigma^+,v'= 0)$ directly and that the NF bond of the dissociating state is approximately the same length as r_e of $NF(b^1\Sigma^-)$, 1.2998 Å.[30] The length of the NF bond in the ground electronic state of both $NFCl_2$ and NF_2Cl is reported to be 1.382 Å, so the dissociating state has a shorter NF bond than does the ground state in both amines.[33,34] Vibrational excitation up to $v' = 12$ was observed in the NCl(b→X) emission spectra observed in all three amine systems (NF_2Cl, $NFCl_2$, and NCl_3). Therefore, using the same reasoning, the NCl bond of the dissociating parent amine must be longer than the bond length of the b state of NCl ($r_e = 1.5714$ Å).[30] For comparison, the NCl bond length of the ground state of both NF_2Cl and $NFCl_2$ is 1.730 Å and of the ground state of NCl_3 is 1.759 Å.[33,34] Applying this analysis to the $NFCl_2 + N_2(^3\Sigma^+)$ reaction, the fact that only $\Delta v = 0$ sequence bands were observed in the b → X emission of both NF and NCl indicates that the N−F and N−Cl bonds in the dissociating state are very similar to the r_e values of the b states of NF and NCl.

For the metastable reactions of $NFCl_2$ in which both NF and NCl b → X emission was observed, the [NCl(b)]/[NF(b)] ratio was evaluated with the following expression.

$$\frac{[\mathrm{NCl(b)}]}{[\mathrm{NF(b)}]} = \frac{[\sum_{\lambda} (S_{\mathrm{NCl(b\to X)}} q_{\mathrm{NCl}})]A_{\mathrm{NF}}}{[\sum_{\lambda} (S_{\mathrm{NF(b\to X)}} q_{\mathrm{NF}})]A_{\mathrm{NCl}}}$$

where the sum is over the wavelength range of the NCl or NF emission, S is the signal intensity of the NCl or NF b → X emission at wavelength λ, q is the system response at each wavelength, and A is the Einstein A coefficient. A halogen quartz lamp with known output was used to measure the system response as a function of wavelength. Two values for the lifetime of the $NCl(b^1\Sigma^+)$ have been reported, 0.63 and 2.0 ms, which yield Einstein A values of 1.59×10^3 and 5.0×10^2 s^{-1}, respectively,[21,35] and the Einstein A coefficient for $NF(b^1\Sigma^+)$ is 44.3 s^{-1}.[36] In the $NFCl_2$ plus Ar metastable reactions, the [NCl(b)]/[NF(b)] ratio is 5/4 using 630 ms for the NCl(b) lifetime (or 4/1 using 2 ms for the NCl(b) lifetime). For the $NFCl_2 +$ He metastable reaction, the choice of the $NCl(b^1\Sigma^+)$ lifetime changes the [NCl(b)]/[NF(b)] ratio from unity for the shorter τ to 3/1 for the longer τ, but for either lifetime, the NF(b) channel is not the preferred pathway. Comparison of the visible emission spectrum observed in the $NF_2Cl/Ar(^3P_{0,2})$ system (Figure 6A) with that observed in the $NFCl_2/Ar(^3P_{0,2})$ system (Figure 1) indicates that, in the NF_2Cl case, the NCl to NF ratio is lower. Although the ratio was not calculated because of the difficulty in resolving the NCl(b→X) emission in the NF_2Cl experiment, it appears that there is a preference for NF(b) over NCl(b) production. Statistically, one would expect this to be the case, and apparently the potential curves do not select against the statistical expectation.

Conclusion

The studies reported here have yielded new information on excited electronic states of $NFCl_2$, NF_2Cl, and NCl_3 via reactions of these amines with excited triplet metastable species. Excited singlet states of these amines had been probed via photolysis experiments carried out previously, and information on excited triplet states is now available from the data presented here. For $NFCl_2$, two excited singlet states had been observed in the 249 nm (4.98 eV) and 193 nm (6.42 eV) photolysis experiments, and evidence for three excited triplet states was observed following the reaction of $NFCl_2$ with triplet metastables of energy 6.3, 11.7, and 19.8 eV. All five of these excited electronic states have dissociation pathways leading to the formation of diatomic fragments which can be understood on the basis of conservation of spin angular momentum. Only in the 249 nm photolysis was a nondiatomic dissociation pathway producing NFCl observed. The direct production of ion pair states of the diatomic halogens appears to be possible only in the reactions of $NFCl_2$ with He metastables; otherwise, low-lying triplet states of the halogens are generated.

The singlet and triplet electronic states of $NFCl_2$ observed to date can be classified according to the preferred diatomic dissociation channel. The NF + Cl_2 channel is the favored dissociation pathway for both the lowest excited singlet state pumped at 4.98 eV and the triplet state accessed at 6.3 eV. Dissociation of the second excited singlet state pumped at 6.42 eV and of the triplet states observed at 11.7 and 19.8 eV generally favor the NCl + ClF over the NF + Cl_2 channel.

The results of the $NF_2Cl/Ar(^3P_{0,2})$ and the $NCl_3/Ar(^3P_{0,2})$ reaction systems are similar to those of the $NF_2Cl/Ar(^3P_{0,2})$ system, which is not surprising since these molecules are closely related to each other. There are again diatomic dissociation channels which are easily understood on the basis of spin constraints and energetics. The variations observed in the NX species generated are also not unexpected for the series NF_2Cl, $NFCl_2$, and NCl_3. In the NF_2Cl system, both NF(b) and NCl(b) are generated with an apparent preference for NF(b). In the $NFCl_2$ system, again, both NF(b) and NCl(b) are generated, but with a preference for NCl(b). Of course, only NCl(b) is observed in the NCl_3 system. As a part of this work, the ΔH_{form}'s for NF_3, NF_2Cl, $NFCl_2$, and NCl_3 were computed. The experimental value for NF_3 is fairly well established, and the calculated value was 19% lower. For NCl_3, an experimental value had been reported, and the calculated value was similarly too low (by 21%). This suggests that the experimental ΔH_{form} for $NFCl_2$ is ~20% higher than the computed value. The trend observed in the calculated ΔH_{form}'s for the series NF_3, NF_2Cl, $NFCl_2$, and NCl_3 (−31.4, −5.3, 23.0, and 48.3 kcal/mol, respectively) conforms to expectations regarding the stability of these compounds. As the F atoms are replace by Cl atoms, the stability decreases.

Computations of the electronic states are planned and, with the information obtained from the metastable studies presented here and the previously reported photolysis studies, will improve our understanding of the excited electronic states of these intriguing molecules.

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