J. Phys. Chem. A **2000,** *104,* 539−551

Quenching Rate Constants of NCl($a^1\Delta$) at Room Temperature

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Received: June 24, 1999; In Final Form: November 1, 1999

The total quenching rate constants for NCl($a^1\Delta$) molecules were measured at room temperature for 40 molecular reagent species and for F, H, N and O atoms. The Cl + N_3 reaction was used to provide the NCl($a^1\Delta$) molecules in a room temperature flow reactor; the azide radicals were obtained from the F + HN_3 reaction. In most cases, rate constants were obtained for both NF($a^1\Delta$) and NCl($a^1\Delta$) so that the data could be confirmed by comparison with earlier studies of NF($a^1\Delta$). The quenching rate constants for NCl($a^1\Delta$) range from $\sim 1 \times 10^{-15}$ to 4×10^{-11} cm^3 molecule^{-1} s^{-1}. Except for O_2, F, H, CH_3Cl, HCl, HBr, and HI, rate constants for the NCl($a^1\Delta$) molecule are generally smaller than or comparable to those for NF($a^1\Delta$), and NCl($a^1\Delta$) is not especially reactive at 300 K. Small rate constants were obtained for common gases, such as H_2, CO_2, and CH_4; the rate constants are larger for unsaturated hydrocarbons and they increase with the number of carbon atoms in the molecule. A correlation was found between the basicity of a series of amines and magnitudes of the quenching rate constants for NF($a^1\Delta$) and NCl($a^1\Delta$); the smaller NCl($a^1\Delta$) rate constants indicate a less acidic nature for NCl($a^1\Delta$). An unusual concentration dependent, wall-quenching process was found for $(CH_3)_2O$, CH_3OH, OCS, and saturated hydrocarbons that affected the NCl($a^1\Delta$) decay kinetics, but not those for NF($a^1\Delta$). The interaction between NCl($a^1\Delta$) and NF($a^1\Delta$) was qualitatively studied; the total bimolecular destruction rate is no larger than those for NCl($a^1\Delta$) or NF($a^1\Delta$) alone. The energy-pooling process between NF($a^1\Delta$) and NCl($a^1\Delta$) mainly gives NF($b^1\Sigma^+$) + NCl($X^3\Sigma^-$).

A. Introduction

Electronically excited molecules can serve as chemical energy storage systems provided that their radiative lifetimes are long, that the excited state can be generated via chemical means, and that the quenching rates are slow. The NCl molecule in its first electronically excited state ($a^1\Delta$, 1.15 eV) meets the first two criteria. Although the lifetime[1−3] of NCl($a^1\Delta$) is 2-3 s; the NCl(a→X) transition is sufficiently strong that the [NCl(a)] can be monitored by observation of the 1077 nm emission.[1] The generation of NCl(a) is accomplished by the reaction of Cl atoms with azide (N_3) radicals.[1,4] Energy can be extracted from the NCl(a) system by transfer to iodine atoms,[5−8] and possibly by other transfer reactions yet to be discovered. The objective of the present study was the creation of a data base for rate constants of NCl(a) quenching reactions.

The azide radical is formed by the reaction of hydrazoic acid with F atoms, which has a

$$F + HN_3 \rightarrow HF + N_3 \qquad \Delta_rH^\circ_{298} \rightarrow -180 \text{ kJ mol}^{-1} \quad (1)$$

rate constant[9] of 1.1×10^{-10} cm^3 molecules^{-1} s^{-1} and a branching fraction of 0.97.[10] The Cl + HN_3 reaction rate is too slow at room temperature to be an adequate source of N_3 in a flow reactor.[11,12] The azide radicals formed by (1) react with Cl atoms to form NCl(a) and NCl(X) or with F atoms to generate NF(a).

$$\begin{aligned} Cl + N_3 &\rightarrow N_2 + NCl(a^1\Delta) \qquad \Delta_rH^\circ_{298} = -159 \text{ kJ mol}^{-1} \\ &\rightarrow N_2 + NCl(X^3\Sigma^-) \qquad \Delta_rH^\circ_{298} = -270 \text{ kJ mol}^{-1} \end{aligned} \quad (2)$$

The thermochemistry is based upon $\Delta_fH^\circ_{298}$(NCl)[13] = 324 kJ mol^{-1}. The rate constant for (2) has been the subject of some controversy. However, recent measurements[14] utilizing laser-induced fluorescence of N_3 have determined that k_2 is $(2.1^{+1.0}_{-0.6}) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. This result is an order of magnitude smaller than the rate constant reported by Liu et al.,[9b] but in agreement with the value reported by Jourdain and coworkers[15] and with the values favored by the experimental kinetic studies of the F/Cl/HN_3 system.[1,7] The kinetics of the F/Cl/HN_3 reaction system have been thoroughly discussed, and for $\tau_{NCl(a)} = 2.0$ s the branching fraction to NCl($a^1\Delta$) is = 0.5.[1] In the present work, we used (1) and (2) to generate NCl(a) in an environment suitable for measuring the quenching rate constants in a flow reactor. We investigated 40 reagent molecules plus H, O, N and F atoms. The flow reactor always contains both NCl(a) and NF(a) molecules, and some qualitative measurements were made to characterize the bimolecular interaction between NF(a) and NCl(a). Just as for the NF(a) and NCl(a) alone, the mixed energy-pooling reaction rate is rather slow; the favored exit channel is NF($b^1\Sigma^+$) rather than NCl($b^1\Sigma^+$).

In addition to the practical need, the quenching rate constants of NCl(a) also are interesting for comparison with NF($a^1\Delta$),[16−19] $O_2(a^1\Delta_g)$,[20] and NH($a^1\Delta$).[21−26] The NCl molecule is isovalent with O_2 and the $\pi_{x^2} - \pi_{y^2}$ and $\pi_x\pi_y - \pi_x\pi_y$ components of the NCl($a^1\Delta$) state suggests acid-like or radical-like chemical reaction pathways, respectively, in addition to physical quenching. The similar electronegativities of N and Cl should lead to

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10.1021/jp9921203 CCC: \$19.00

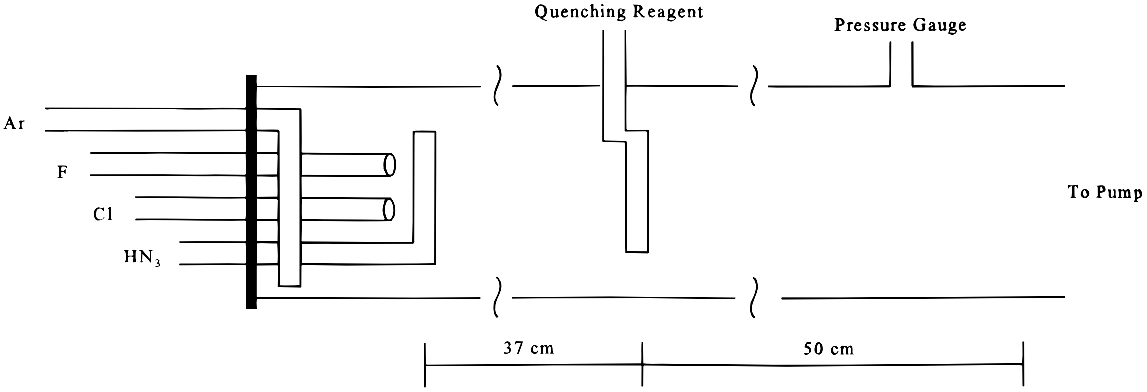

Figure 1. Schematic diagram of the 70 mm i.d. flow reactor. The Ar, HN_3, and quenching reagent inlets are perforated rings. The F and Cl atom inlets are open quartz tubes. The prereactor spans the 37-cm distance between the HN_3 inlet and the quenching reagent inlet; the main reactor is the 50-cm section after the quenching reagent inlet.

a more symmetric π electron density than for NF. Quenching of $O_2(a)$ mainly occurs by electronic-to-vibrational energy transfer with very small rate constants.[20] Chemical reactions, either insertion or addition, were argued to be the dominant quenching mechanism for NF(a),[17-19] except for some diatomic molecules containing iodine and O_2, which gave physical quenching to NF(X). The correlation between the base strength of those reagent molecules that can act as Lewis bases and the magnitude of their quenching rate constants for NF(a) suggested that the ($\pi_{x^2} - \pi_{y^2}$) component is involved in the potential surface that leads to quenching.[17] The trends for the rate constants to be reported here suggest that the quenching of NCl(a) also occurs mainly via chemical reaction pathways. The $O_2(a)$, NF(a), and NCl(a) molecules are much less reactive than NH(a).[21-26]

B. Experimental Methods

The production of NCl(a) by (2) and the subsequent quenching reactions at room temperature were studied in a large diameter reactor operated with a flow velocity of ~10 m s^{-1}. The relative concentrations of NCl(a) and NF(a) were measured by monitoring the chemiluminescence intensities of the a→X transitions at 1077 and 874 nm, respectively. Since both NF(a) and NCl(a) are present in the reactor, quenching rate constants usually were measured for both molecules to ensure that the complex environment was suitable for pseudo first-order decay measurements. Only if the data for NF(a) were reliable, were the data for NCl(a) considered. The environment is complex and this chemical system performed satisfactorily only for a narrow range of F, Cl, and HN_3 concentrations.

Flow Reactor. The flow reactor, see Figure 1, was a 120-cm long, 70-mm i.d. Pyrex tube coated with halocarbon wax (Halocarbon Products, series 600) to prevent the loss of F, Cl, N_3, and other radicals by reactions with the reactor wall. The reactor consisted of two regions; the 37-cm long prereactor where NCl(a) was generated by reactions (1) and (2), and the main reactor where the quenching reactions of NCl(a) or NF(a) were observed. The inlet tubes for the Ar carrier gas, the F atoms source (CF_4), the Cl atom source (CF_2Cl_2), and HN_3 were located in an aluminum flange, which was attached via an o-ring joint to the front of the reactor. The Ar was added through a perforated ring, the F atoms and the Cl atoms through separate 10-mm o.d. quartz tubes and the HN_3 through another perforated ring. The quenching reagent gases were added via a perforated ring injector located 37-cm downstream of the HN_3 inlet; the reagent inlet marked the starting point of the main reactor. The reactor was pumped by a mechanical pump/roots blower combination; the maximum linear flow velocity was 1200 cm s^{-1} at a pressure of 0.4 Torr. The minimum reaction time of 35 ms in the prereactor was sufficient to allow reactions (1) and (2) to proceed to completion. The reaction of NCl(a) with added quenching reagent occurred during the 47 ms that they traveled down the main reactor together. Longer reaction times could be obtained by throttling the pump.

The Ar was purified by passage through two cooled (196 K) molecular sieve filled traps. The F atoms and Cl atoms were produced by passing an Ar/CF_4, and an Ar/CF_2Cl_2 mixture, respectively, through microwave discharges in alumina tubes; the highest and most stable dissociation efficiency were obtained by using the lowest power (~20W) that would sustain the discharge. For CF_4 concentrations in the $(0.2-2.0) \times 10^{12}$ molecules cm^{-3} range, nearly complete dissociation ($2F + CF_2$) is achieved. The dissociation efficiency of CF_2Cl_2 has been measured to be 1.5 Cl atoms per CF_2Cl_2 molecule; the discharge also generates some F atoms.[11a] Using reactant concentrations of $[CF_4]_0 = 1.5 \times 10^{12}$, $[CF_2Cl_2]_0 = 2 \times 10^{12}$, and $[HN_3]_0 = 3 \times 10^{12}$ molecules cm^{-3}, the ratio of NF(a):NCl(a) intensities was ~1:3, which corresponds to [NF(a)]:[NCl(a)] = 2:5 after adjustment for the detector response and $\tau_{NF(a)}$ and $\tau_{NCl(a)}$. A spectrum of the NF(a→X) and NCl(a→X) transitions was shown in ref 1. An attempt was made to use the F + HCl reaction as the Cl atom source using the prereactor design described in ref 1. However, the additional time (length) required for the Cl + N_3 reaction to go to completion made that reactor less satisfactory than the simpler one shown in Figure 1.

For certain experiments, the reagent inlet of Figure 1 was replaced by an auxiliary flow reactor in which an independent flow of NF(a) molecules could be generated. This auxiliary reactor was a 4-cm i.d. diameter tube of 1-m length coated with halocarbon wax. About one-third of the total Ar flow was passed through this small reactor. Separate flows of HN_3 and CF_4 were added at the front of the reactor and F atoms were generated by a third microwave discharge in the CF_4 flow. The reaction time in the auxiliary reactor was sufficiently long that the 2F + HN_3 reaction could be completed; however, care must be exercised to control the starting $[HN_3]_0$, and $[F]_0$ otherwise [F], $[N_3]$, or $[HN_3]$ will be injected into the main reactor. The additional NF(a) flow could be added to the main reactor without affecting the [NF(a)] and [NCl(a)] generated in the prereactor, and the total [NF(a)] could be increased from 0.25×10^{12} up to $\sim 3-4 \times 10^{12}$ molecules cm^{-3}. The kinetic observations were made a few (10−40) centimeters downstream of the mixing zone in the main reactor. The auxiliary flow reactor was used to add H, O and N atoms to the reactor. However, F atom quenching was studied by adding F atoms from a microwave discharge in a He/F_2 mixture through the reagent inlet shown in Figure 1.

Reagents. Except for HI and HN_3, the reagents were purchased from commercial vendors. The CF_4 (Matheson) was used directly from the cylinder. The CF_2Cl_2 (PCR or Matheson) was purified via freeze−pump−thaw cycles and diluted to 20% with Ar and stored in a 12-L reservoir. The F_2 was purchased as a 10% mixture in He (Spectra Gases) and it was either used directly from the cylinder or diluted with Ar and stored in a passivated stainless steel reservoir. The ClF (Ozark Mahoning) and HF (Matheson) reagents were used directly from their cylinders. Commercial grades of O_2 and H_2 were stored in Pyrex reservoirs. High purity N_2 from Matheson was metered directly from the tank to study quenching by N_2. The condensible reagents were purified via freeze−pump−thaw cycles, and stored either pure or as mixtures in Ar in Pyrex reservoirs.

Hydrogen iodide was synthesized by adding iodine to boiling tetrahydronaphthalene,[27] purified by distillation, diluted with Ar, and stored in a 12-L reservoir. The HN_3 was prepared by the reaction of excess stearic acid with sodium azide (NaN_3) heated to 363 K under vacuum.[17] The gas was collected in a 10-L Pyrex reservoir and stored as a dilute mixture (10%) in Ar. Hydrazoic acid is explosive in nature and it should never be condensed as a liquid. The flow rate of HN_3 from the reservoir was controlled by a Teflon needle valve and measured by the pressure rise in a calibrated glass bulb. The flow rates of Ar, CF_4, and CF_2Cl_2 were controlled by needle valves and measured by precalibrated Hastings mass flow meters. The calibration of the mass flow meter on the main Ar flow was confirmed using a wet-test meter. The mass flow meters on the CF_4 and CF_2Cl_2 flow lines were calibrated using the pressure rise in a calibrated volume. The flow rates of the non-corrosive quenching reagents were controlled by a Teflon needle valve and measured by the pressure rise in a calibrated volume. The Pyrex glass manifold used for gas-handling of the quenching reagents was replaced by a stainless-steel manifold and an alumina inlet tube replaced the perforated ring inlet for the study of the corrosive gases (F_2, ClF, HF). The stainless-steel gas-handling system was passivated prior to use. The flow rates of F_2, ClF and HF were controlled by a stainless-steel needle valve and measured by the pressure rise in a stainless-steel reservoir of calibrated volume.

Detection System. The emission intensities from NCl(a) and NF(a) were monitored by a photomultiplier tube (PMT) attached to the exit slit of a 0.5-m monochromator. The PMT, which was an S-l type (Hammamatsu R1767) selected for red response, was cooled to −80 °C in a Products-for-Research housing and liquid N_2 control unit. Current leakage across the base can be a problem due to water condensation inside the cold PMT housing. This problem was prevented by applying the high voltage (−1200 V) to the PMT and allowing it to operate for ∼30 min prior to starting the cooling cycle. The monochromator was mounted on a platform that could be moved parallel to the flow reactor.

Rate Constant Measurements. Two standard methods were used to monitor the quenching reactions of NCl(a) or NF(a) under pseudo-first-order kinetic conditions: the fixed-point method and the moving-point method. The fixed-point method uses a fixed monochromator position (fixed Δt) to monitor NF(a) or NCl(a) as a function of added quenching reagent. The moving-point method measures the emission intensity from NF(a) and NCl(a) along the flow reactor for fixed concentration of added quenching reagent. The reaction time was calibrated using the known reaction rate[17] of NF(a) with NH_3. Using the fixed-point method, a plot of the natural logarithm of the NF(a) intensity vs NH_3 concentration has a slope of $k_Q\Delta t$. Dividing the slope by the rate constant for this reaction, 3.6×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, gives the reaction time. Figure 2 shows a typical NH_3 quenching plot for NF(a) and NCl(a) using the fixed-point methodology. This time can differ from the calculated plug−flow value by up to 20% because of incomplete mixing and uncertainties in flow rates. The plug flow Δt for the data shown in Figure 2 was 34 ms, while the calibrated Δt was 31 ms. The average NCl(a) quenching rate constant by NH_3 obtained via the fixed-point method was $(1.1 \pm 0.2) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} based upon the calibrated reaction time.

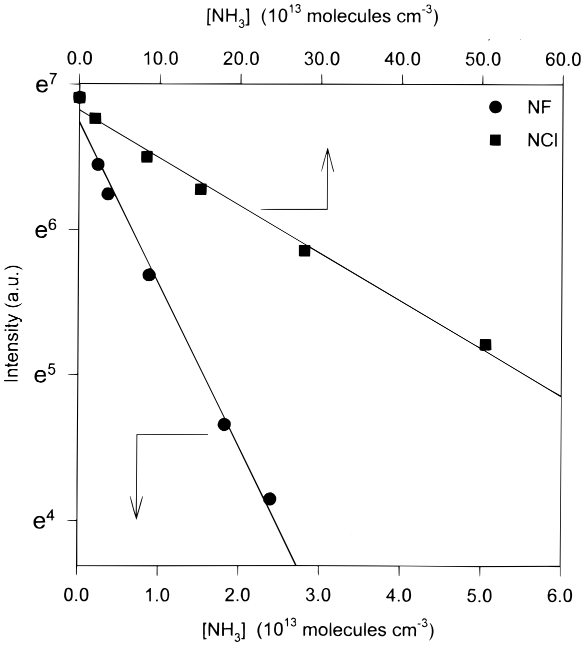

Figure 2. Pseudo-first-order quenching plots showing the removal of NF(a) and NCl(a) by NH_3 for fixed reaction time. Note that the scale for the abscissa differs by an order of magnitude for NCl(a) and NF(a). The two experiments were performed using [F] = 1.4×10^{12}, [Cl] = 1.5×10^{12}, and [HN_3] = 1.8×10^{12} molecules cm^{-3}. The NF(a) removal (●) was used to calibrate the reaction time using the known value of the rate constant, 360×10^{-14} cm^3 s^{-1}. This time, 31.1 ms, was used to calculate the NCl(a) removal rate constant (■), $(10.6 \pm 1) \times 10^{-14}$ cm^3 s^{-1}.

For the moving-point methodology, the NF(a) or NCl(a) emission intensity was measured along the length of the reactor for a given concentration of NH_3. A plot of the natural logarithm of the intensity vs time gives a slope of $k_Q[NH_3]$, and the quenching rate constants are obtained by plotting these slopes vs [NH_3]. A typical moving-point quenching plot for NF(a) and NCl(a) is shown in Figure 3; the calibrated reaction time is 9.5% smaller than the calculated plug−flow value in this experiment. The average NCl(a) quenching rate constant obtained via the moving-point methodology also was $(1.1 \pm 0.1) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. The quenching rate constant for NCl(a) by NH_3 was measured many times, and the much smaller value, relative to NF(a), is firmly established. The Δt calibrated via the NF(a) + NH_3 reaction was used to calculate all of the rate constants, except for those of the corrosive gases. In these cases, the plug−flow Δt was used due to the inability to calibrate with NH_3, since the Pyrex gas-handling system had been replaced by the stainless-steel system.

The fixed-point method has the advantage of faster data acquisition while the moving-point method demonstrates that

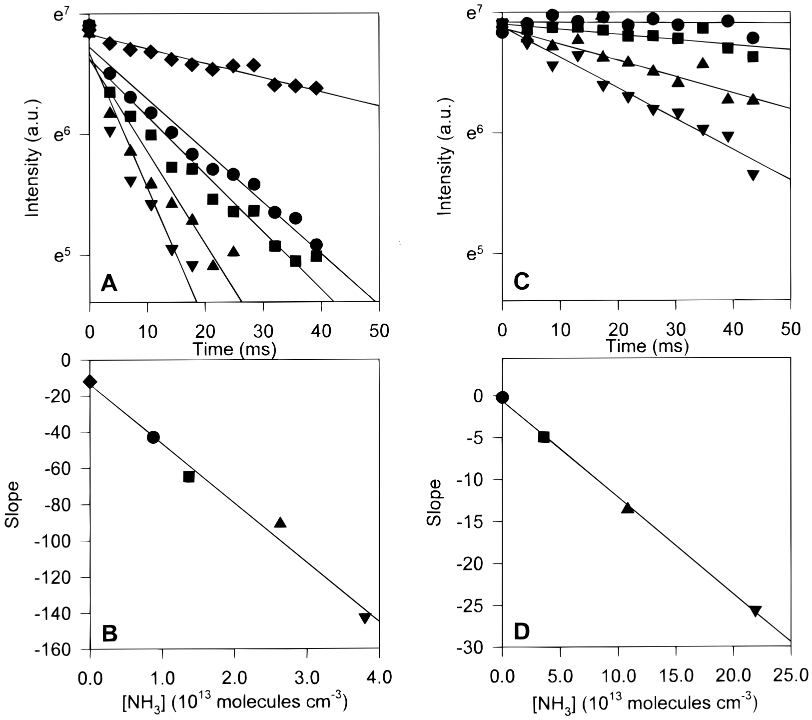

Figure 3. The pseudo first-order decay plots for NF(a) and NCl(a) obtained using the moving-point method with reaction time given by the plug−flow calculation. The data were collected using [F] = 2.2×10^{12}, [Cl] = 1.5×10^{12} and [HN_3] = 2.0×10^{12} molecules cm^{-3}. Part A shows the first-order removal of NF(a) upon addition of NH_3. A plot of the first-order slopes vs [NH_3] is shown in part B and gives a NF(a) removal rate constant of $(330 \pm 30) \times 10^{-14}$ cm^3 s^{-1}. Panel (C) shows the first-order removal of NCl(a) upon addition of NH_3. Plotting these slopes vs [NH_3] in panel (D) gives $(11.5 \pm 1) \times 10^{-14}$ cm^3 s^{-1}. The reaction time used in panels (A) and (C) may be adjusted so that the NF(a) rate constant obtained in panel (B) equals 360×10^{-14} cm^3 s^{-1}; the NCl(a) rate constant then becomes $(13 \pm 1) \times 10^{-14}$ cm^3 s^{-1}.

the quenching actually follows pseudo first-order kinetics with respect to time. In principle, the moving-point method can be used to separate competing first-order loss processes. The total first-order loss rate constant is given by

$$k_{\mathrm{total}} = \tau^{-1} + k_{\mathrm{surface}} + k_{\mathrm{R}}[\mathrm{R}] + k_{\mathrm{Q}}[\mathrm{Q}] \qquad (3)$$

where τ^{-1} is radiative decay, k_{suface} is quenching by the flow reactor walls, $k_{\mathrm{R}}[\mathrm{R}]$ is quenching from residual impurities including radical fragments from the discharges, and $k_{\mathrm{Q}}[\mathrm{Q}]$ is the quenching constant that is desired to be measured. This method fails if any of the terms are not constant along the flow reactor. The removal of NCl(a) by CF_4, CF_2Cl_2, and HN_3 has been previously measured to be negligible; the rate constants are $\leq 1 \times 10^{-15}$, $\leq 1 \times 10^{-15}$, and $\leq 1 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}, respectively.[28] An additional complication can be bimolecular self-removal at high [NCl(a)] concentrations. This was avoided by using [NCl(a)] $\leq 3 \times 10^{12}$ molecules cm^{-3}. The data for [NF(a)] and [NCl(a)] shown in Figures 2 and 3 demonstrate that the decay is small in the absence of reagent, and the conditions given by $[HN_3]_0 = 3 \times 10^{12}$, $[CF_4]_0 = 1.5 \times 10^{12}$, and $[CF_2Cl_2]_0 = 2 \times 10^{12}$ molecules cm^{-3} provide a satisfactory environment for measuring k_{Q}.

C. Experimental Results

C-1. Interactions between NF(a) and NCl(a) and between NF(a) and NCl(X). The flow reactor has approximately equal concentrations of both NF(a) and NCl(a), and the concentration of NCl(X) also may be similar to that for NCl(a). This situation presents several interesting questions regarding the interaction of NF(a) with NCl(a) and with NCl(X); the three questions to be addressed here are (i) the nature of the mixed energy-pooling reaction giving either NCl(b) or NF(b). (ii) the magnitude of the mixed total bimolecular quenching rate, and (iii) the possible generation of NCl(a) by the reaction between NCl(X) and NF(a) with rate constant k_{x}.

$$\mathrm{NCl}(X^3\Sigma^-) + \mathrm{NF}(a^1\Delta) \rightarrow \mathrm{NCl}(a^1\Delta) + \mathrm{NF}(X^3\Sigma^-) \qquad \Delta_{\mathrm{r}}H^{\circ}_{\mathrm{o}} = -26\ \mathrm{kJ\ mol^{-1}} \quad (4)$$

If the rates of the NCl(a) + NF(a) bimolecular quenching or (4) are fast, interpretation of the quenching data from the NCl(a) and NF(a) experiments could be affected. These experiments were done using the configuration with the auxiliary flow reactor so that an independent NF(a) concentration could be added to the main flow reactor. The NF(a) and NCl(a) concentrations were monitored with the 0.5-m monochromator described in the experimental section; the NCl(b-X)-665-nm and NF(b-X)-529-nm transitions were monitored with a second monochromator, which was a 0.3-m McPherson instrument with a Hamamatsu 955 photomultiplier tube. The two monochromators were placed side-by-side.

The first set of experiments were designed to identify the products of the energy-pooling reaction.

$$\mathrm{NCl}(a^1\Delta) + \mathrm{NF}(a^1\Delta) \rightarrow \mathrm{NF}(b^1\Sigma^+) + \mathrm{NCl}(X^3\Sigma^-) \qquad \Delta_{\mathrm{r}}H^{\circ}_{\mathrm{o}} = -21.6\ \mathrm{kJ\ mol^{-1}}$$

$$\rightarrow \mathrm{NF}(X^3\Sigma^-) + \mathrm{NCl}(b^1\Sigma^-) \qquad \Delta_{\mathrm{r}}H^{\circ}_{\mathrm{o}} = -67.9\ \mathrm{kJ\ mol^{-1}} \quad (5)$$

Since the NF(a) and NCl(a) reactants individually give NF(b) and NCl(b), respectively, in their self-energy-pooling reactions, the yields of NCl(b) and NF(b) must be correlated with variation of [NCl(a)] and [NF(a)] to assign products from (5). Visual observation indicated that addition of small concentrations of

NCl(a) to a flow of NF(a) greatly enhanced the green (529 nm) emission, but any enhancement of the NCl(b) red (665 nm) emission was difficult to see in the strong green background. A calibration of NF(b) emission intensity vs [NF(a)] was made using the F/HN_3 reaction system. A similar, but less reliable, calibration was made for the NCl(b) emission intensity vs [NCl(a)] using the F/CI/HN_3 reaction system to generate NCl(a); the calibration was less satisfactory because some [NF(a)] always was present. Two kinds of experiments were done. First, the enhanced NF(b) and NCl(b) emissions were observed as the fraction of [NCl(a)] was increased for a given [NF(a)] using a changing F/Cl/HN_3 composition in the main reactor. These experiments showed that the energy-pooling process favored formation of NF(b). Comparison of the NF(b) emission intensity for a range of NF(a) and NCl(a) concentrations showed that the rate constant for (5a) was 10−20 times larger than that for the self-energy-pooling by NF(a) with itself. The second experiment involved adding a flow of NF(a) from the auxiliary reactor to the main reactor with a preset [NF(a)] and [NCl(a)]. In this case, any enhancement of NCl(b) yield from the mixed reaction could be directly observed. These experiments required great care because the addition of the second flow often generated vibrationally excited HF from the F with HN_3 reaction, since either can be in slight excess in the main or auxiliary reactors. The vibrationally excited HF will generate NF(b) and NCl(b) from reaction with NF(a) and NCl(a).[1,29] By careful adjustment of the flow rates, the generation of HF(v) was eliminated. We found substantial enhancement of NF(b) beyond that expected from the NF(a) self-energy-pooling, but no change in NCl(b), upon addition of the [NF(a)] from the auxiliary reactor. Thus, the mixed energy-pooling process does not compete effectively with the NCl(a) self-reaction to give NCl(b). The self-energy-pooling rate constants for NF(a)[17] and NCl(a)[1] have been reported as 0.06 and 1.5×10^{-13} cm^3 s^{-1}. Thus, the mixed energy-pooling rate constant for reaction (5) is 10−20 times larger than that for NF(a) and comparable to the NCl(a) energy-pooling rate constant. Because of the residual NCl(b) generated from NCl(a) alone, we are unable to set a limit for (5b), but the rate constant probably is no more than 20−30% of that for self-energy-pooling by NCl(a). Our observations are consistent with observations by Benard et al.[30] from experiments in which ClN_3 and FN_3 were thermally dissociated and enhanced NF(b) emission was observed.

The possible conversion of NCl(X) to NCl(a) by (4) was investigated by generating equal concentrations ($\sim 0.5 \times 10^{12}$ molecules cm^{-3}) of NF(a) and NCl(a) in the prereactor and then adding O_2 to the main reactor to quench the NCl(a) to NCl(X). The O_2 flow was added through the HN_3 inlet. We then searched for enhancement of NCl(a) emission intensity in the mixing zone from addition of the auxiliary NF(a) concentration. The rate constant for quenching NCl(a) by O_2 is 2.6×10^{-12} cm^3 s^{-1}. Since the quenching rate constant for NF(a) is much smaller (0.7×10^{-14} cm^3 s^{-1}), adding O_2 had the desired effect of reducing [NCl(a)] without changing the [NF(a)]. A series of experiments were done with various initial [NCl(a)] in the main reactor, different degrees of quenching of NCl(a) by O_2, a range of added [NF(a)] and several reaction times. We never observed enhancement of the [NCl(a)] following the addition of [NF(a)] to the reactor for any of the conditions (providing F atoms were not added to the main reactor together with the auxiliary NF(a) flow). For the following experimental conditions, a limit can be set on k_x. Without added O_2, the [NCl(a)] was 0.5×10^{12} and the total [NF(a)] was 2×10^{12} molecules cm^{-3}. This NCl(a) concentration was reduced by a factor of 4 with addition of O_2 giving NCl(a) = 0.12×10^{12} and NCl(X) = 0.4×10^{12} molecules cm^{-3} for $[O_2] = 5 \times 10^{12}$ molecules cm^{-3}. To get a limit for k_x, we used the differential rate law for NCl(a) at the observation zone.

$$-d[\mathrm{NCl(a)}]/dt = k_{O_2}[\mathrm{NCl(a)}][O_2] - k_x[\mathrm{NF(a)}][\mathrm{NCl(X)}] \quad (6)$$

Since the [NCl(a)] was not enhanced upon increasing [NF(a)] from 0.5 to 2.0×10^{12} molecules cm^{-3}, we can use the NCl(X), NCl(a), O_2, and NF(a) concentrations given above to obtain

$$k_x < k_{O_2}[O_2][\mathrm{NCl(a)}]/[\mathrm{NF(a)}]\,[\mathrm{NCl(X)}]$$

$$k_x < 2 \times 10^{-12}\ \mathrm{cm^3\ molecules^{-1}\ s^{-1}}$$

The only way to significantly improve our limit for k_x is to increase the NCl(X) concentration, which was impossible using a microwave discharge in CF_2Cl_2 as the Cl atom source. The experiment is based upon the assumption that quenching of NCl(a) by O_2 gives NCl(X) and O_2(a); however, recent work[31] in which NCl(X) was monitored in photodissociation experiments of ClN_3/O_2 mixtures supports this assumption. Energy transfer need not be the only outcome from (4); chemical reaction with formation of N_2 + F + Cl also is a possibility.

An attempt to measure the rate constant for the total bimolecular destruction between NCl(a) and NF(a) was made by monitoring the decay of NCl(a) as excess NF(a) was added from the auxiliary reactor. The [NCl(a)] was $\sim 0.5 \times 10^{12}$ molecules cm^{-3} and [NF(a)] could be increased to $(2-3) \times 10^{12}$ molecules cm^{-3}. Conditions were adjusted so that [NCl(a)] was nearly constant over a 40−50 cm length of reactor beyond the inlet of the auxiliary reactor. Upon the addition of NF(a) to the reactor, no quenching of [NCl(a)] was observed that could be correlated with the [NF(a)]. These experiments show that the total bimolecular rate constant for NF(a) + NCl(a) is no larger than 4×10^{-12} cm^3 s^{-1}. The bimolecular rate constants[17,30,32] for 2NCl(a) or 2NF(a) → products have been reported as $(5-7) \times 10^{-12}$ cm^3 s^{-1}.

C-2. Quenching Rate Constants by Stable Molecules. The quenching rate constants of NCl($a^1\Delta$) were measured at room temperature for the reagents shown in Table 1. These molecules can be divided into six broad categories: (1) the common gases and unsaturated hydrocarbons; (2) the halogens, (3) the hydrogen halides, (4) some partly halogenated methanes, (5) the amines, and (6) some molecules for which rate constants were difficult to obtain because the k_{suface} term in (3) apparently was not constant. In most cases, a direct comparison between the NCl(a) and NF(a) reactions was made by measuring both rate constants simultaneously. The NCl(a) and NF(a) were generated using initial reactant concentrations of $[F]_0 \approx [Cl]_0$, $[HN_3]_0 \approx (1-5) \times 10^{12}$ molecules cm^{-3} with $[F]_0 \approx [HN_3]_0$. For these NF(a) and NCl(a) concentrations, the bimolecular self-destruction rates are not important, and the NF(a) and NCl(a) concentrations were nearly constant along the main reactor. The uncertainties given for the rate constants are the standard deviations from multiple experiments. For a few cases only one or two experiments were done and the uncertainty is set as ±30%. Systematic error associated mainly with the chemical complexity of the environment is the limiting factor to the reliability of the data.

a. Common Molecules. Except for oxygen and the unsaturated hydrocarbon molecules, this group has small, or even very small, rate constants. Four fixed-point and one moving-point experiment was performed for O_2 and one of the fixed-point determinations is shown in Figure 4. The average value for the

TABLE 1: Quenching Rate Constants for NCl($a^1\Delta$) by Molecular Reagents at Room Temperature

	NCl($a^1\Delta$) (10^{-14} cm^3 molecule^{-1} s^{-1})		NF($a^1\Delta$) (10^{-14} cm^3 molecule^{-1} s^{-1})		$O_2(a^1\Delta_g)^c$
molecule	current[a]	previous	current[a]	previous[b]	(10^{-18} cm^3 molecule^{-1} s^{-1})
O_2	260 ± 40	250 ± 20[d]	0.5 ± 0.2	0.70 ± 0.07	1.9 ± 0.5
N_2	$\lesssim$0.10 ± 0.05			≤0.0012	0.1
NO	~0.4 ± 0.2			≤0.15	40 ± 10
CO	0.34 ± 0.07		0.6 ± 0.1	0.36 ± 0.04	9.0 ± 3.0
CO_2	0.11 ± 0.02			0.006 ± 0.002	<0.5
SO_2	12 ± 3		4.0 ± 0.5	4.3 ± 0.5	0.004 ± 0.001
H_2	≤0.1	68 ± 7[d]		0.007 ± 0.002	4.5 ± 0.5
CH_4	≤0.1		<0.1	≤0.01	1.4 ± 0.3
C_2H_2	1.4 ± 0.3		18 ± 3	23 ± 2	6.0 ± 0.6
C_2H_4	2.5 ± 0.5		29 ± 4	32 ± 3	2.0 ± 0.2
C_3H_6	18 ± 3		145 ± 20	150 ± 20	2.2 ± 0.2
C_4H_6	62 ± 6		230 ± 30	270 ± 30	10 ± 5
cis-C_4H_8	134 ± 10		330 ± 30		20 ± 10
trans-C_4H_8	162 ± 15		310 ± 30		
C_6H_6	128 ± 15		39 ± 4		5.3
F_2	3.4 ± 0.7	25 ± 11[g]	3.4 ± 0.3	3.2 ± 0.3[e]	
Cl_2	40 ± 10	1800 ± 300[d] 2900 ± 600[g]	56 ± 4	58 ± 6[f]	
Br_2	1400 ± 400	14000 ± 2000[g]	2100 ± 400	3800 ± 600[f]	
ClF	1060[h]		760[h]	760 ± 100[f]	
HF	0.5 ± 0.3	82 ± 12[d]	0.2 ± 0.1	0.3[e]	140 ± 50
HCl	1.5 ± 0.4[j]	490 ± 70[d]	0.20 ± 0.05	0.16 ± 0.03	4 ± 3
HBr	180 ± 30		9.0 ± 2.0		8 ± 4
HI	2900 ± 500		380 ± 50		<20
HN_3		≤1.0[i]			
CH_3Cl	10 ± 2		1.1 ± 0.3	1.1 ± 0.2	5 ± 2
CH_2Cl_2	18 ± 2			0.71 ± 0.08	
CH_3Br	7.2 ± 0.4		20 ± 4	26 ± 4	30 ± 15
CH_3I	81 ± 8		246 ± 25	230 ± 20	40 ± 20
CF_3I	60 ± 10		25 ± 3	24 ± 3	<0.5
CF_2Cl_2	≤0.1				
CF_2ClBr	0.3 ± 0.1		0.5 ± 0.1	0.59 ± 0.06	
NH_3	11 ± 2		360[k]	360 ± 20	4.41 ± 0.46
NH_2CH_3	240 ± 40		1230 ± 100	1250 ± 200	13 ± 2
$NH(CH_3)_2$	1040 ± 100		1840 ± 200	1750 ± 100	93 ± 6
$N(CH_3)_3$	1960 ± 200		2500 ± 300	2600 ± 200	3200 ± 200
C_2H_6	*l*			0.07 ± 0.02	
C_4H_{10}	≤0.5[m]		1.5 ± 0.5		
$(CH_3)_2O$	35 ± 6[m]		145 ± 30	130 ± 15	
CH_3OH	*l*		8 ± 2	11 ± 1	
H_2S	2.7 ± 0.4[m]		65 ± 10	61 ± 6	2.0 ± 1.5
COS	*l*		5 ± 1		2 ± 1

[a] This work, see text. Note that the rate constants for O_2(a) are 4 orders of magnitude smaller than those for NCl(a) and NF(a). [b] Reference 17. [c] Reference 20b if reported, otherwise from ref 20a. [d] Reference 33. [e] Reference 16. [f] Reference 18. [g] Reference 32. [h] The rate constants for ClF have been scaled to match the previously determined NF(a) rate constant, see text for details. Even without scaling, $k_{\mathrm{ClF}} > 500 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. [i] Reference 1. [j] The smaller rate constant for HCl reported here is favored over the value given in ref 34; the rate constant for quenching NBr(a) by HCl given in ref 34 also may be too large. [k] The rate constant for NH_3 was set equal to 360×10^{-14} cm^3 molecule^{-1} s^{-1} in order to accurately determine the reaction time. If the time was calculated by assuming plug flow, the average rate constant was $(320 \pm 20) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. [l] Reproducible data were not obtained, see text. [m] Two decay processes were observed, an extremely fast decay followed by a slow decay. The listed result is from analysis of the slow decay process.

O_2 rate constant is $(260 \pm 40) \times 10^{-14}$ cm^3 s^{-1}. The quenching rate constant for NF(a) with oxygen was checked; the value $(0.5 \pm 0.2) \times 10^{-14}$ cm^3 s^{-1} compares favorably with the previously determined value[17] ($(0.70 \pm 0.07) \times 10^{-14}$ cm^3 s^{-1}).

High concentrations $\leq 1.5 \times 10^{15}$ molecules cm^{-3} and long Δt was required to observe any quenching by N_2, and $(\approx 0.10 \pm 0.05) \times 10^{-14}$ cm^3 s^{-1} was the estimated rate constant. Our value could be too large because of residual O_2 impurity, but direct comparisons of [NCl(a)] and [NF(a)] did show quenching for NCl(a) but not for NF(a). A single fixed-point measurement for CO gave a NCl(a) rate constant of $(0.34 \pm 0.07) \times 10^{-14}$ cm^3 s^{-1} and a NF(a) rate constant of $(0.6 \pm 0.1) \times 10^{-14}$ cm^3 s^{-1}. The latter is 1.7 times larger than the previously more carefully determined value.[17] The rate constant for SO_2 is considerably larger than for NO or CO_2; the small degree of quenching limits the reliability of the last two cases to a factor of 2.

We were unable to measure any significant removal of NCl(a) for H_2 or CH_4 concentrations up 1×10^{15} molecules cm^{-3}, which corresponds to an upper limit for the rate constant of 1×10^{-15} cm^3 s^{-1}. We also observed no quenching of NF(a), which is in agreement with the previous determination.[17]

The average from 5 experiments with C_2H_4 gave $k_{C_2H_4} = (2.5 \pm 0.5) \times 10^{-14}$ cm^3 s^{-1}; the average NF($a^1\Delta$) rate constant was $(29 \pm 4) \times 10^{-14}$ cm^3 s^{-1}, which agrees with the work of Du.[17] A series of experiments were done with acetylene, propene, *cis*- and *trans*-butene-2, butadiene and benzene in order to test whether the rate constants increased with reduction of the ionization energy of the reagent in the same way as for NF(a).[17] Some of the data using the fixed-point method are shown in Figure 5. The quenching plots for NCl(a) are well-behaved, and the average rate constants from three experiments are given in Table 1 for each molecule. The butene-2 and benzene rate constants for NF(a) were not previously reported. The NCl(a)

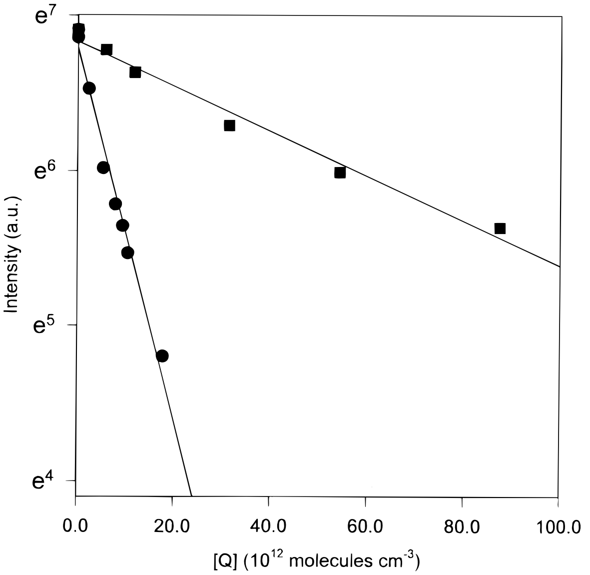

Figure 4. Pseudo first-order quenching plots for the removal of NCl(a) by oxygen (●) and chlorine (■). The starting concentrations in the pre-reactor for the O_2 experiment were [F] = 2.6×10^{12}, [Cl] = 1.5×10^{12}, and [HN_3] = 3.2×10^{12} molecules cm^{-3} with a reaction time of 37.5 ms. The experiment with Cl_2 used [F] = 1.4×10^{12}, [Cl] = 1.5×10^{12} and [HN_3] = 1.8×10^{12} molecules cm^{-3} and a reaction time of 33.7 ms.

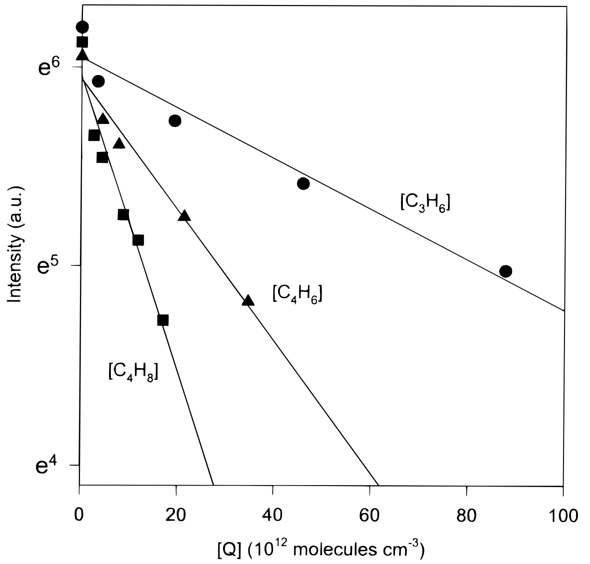

Figure 5. Pseudo-first-order quenching plot showing the removal of NCl(a) by propene, *cis*-butene and butadiene. The starting concentrations in the prereactor were [F] = 2.5×10^{12}, [C] = 1.0×10^{12}, and [HN_3] = 3.0×10^{12} molecules cm^{-3}.

rate constants are consistently smaller than those for NF(a), but both increase systematically from C_2H_2 to C_4H_8. The quenching constant of NF(a) by benzene is anomalously small, but two independent experiments confirmed the difference between NF(a) and NCl(a).

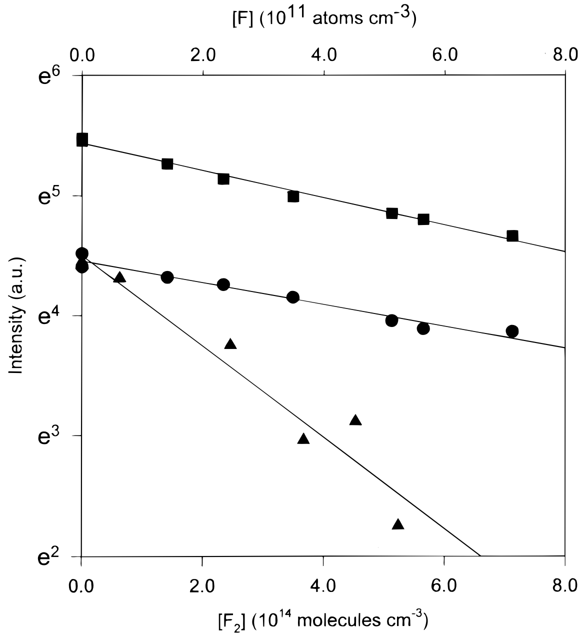

Figure 6. Pseudo-first-order quenching plots showing the removal of NF(a) (■) and NCl(a) (●) by F_2 and NCl(a) by F atoms (▲). The starting concentrations in the prereactor were [F] = 2.2×10^{12}, [Cl] = 0.8×10^{12}, and [HN_3] = 3.3×10^{12} molecules cm^{-3} with a reaction time of 34 ms for the F_2. Fore the F atom experiment, the concentrations in the prereactor were [F] = 2.6×10^{12}, [Cl] = 0.8×10^{12}, and [HN_3] = 2.3×10^{12} molecules cm^{-3} with a reaction time of 91 ms. The F atom concentration should be read from the upper scale.

b. Halogen Molecules. The quenching of NCl(a) and NF(a) by F_2 are compared using the fixed-point method in Figure 6. The average rate constant for NCl(a) was $(3.4 \pm 0.7) \times 10^{-14}$ cm^3 s^{-1}. The current rate constant measurement for NF(a) agrees with the accepted value.[16] Within the experimental uncertainty, the rate constants for quenching NCl(a) and NF(a) by F_2 are the same. Chlorine was studied three times by the fixed-point method over a twelve month period with different reactors and with chlorine from different tanks; one set of data is shown in Figure 4. The average rate constants are $(40 \pm 10) \times 10^{-14}$ and $(56 \pm 4) \times 10^{-14}$ cm^3 s^{-1} for NCl(a) and NF(a), respectively; the latter agrees with the previous result.[18] Our NCl(a) rate constant is significantly smaller then the value determined[32,33] using photolysis of ClN_3 as the NCl(a) source. This difference will be considered in the Discussion section. The bromine reaction was studied by the fixed-point method in four independent experiments. Bromine readily removes NCl(a) and NF(a) with rate constants of $(1400 \pm 400) \times 10^{-14}$ and $(2100 \pm 400) \times 10^{-14}$ cm^3 s^{-1}, respectively. The NF(a) rate constant is ~50% smaller than the value measured by Du and Setser,[18] which is acceptable given the difficulty of handling and metering Br_2.

Chlorine monofluoride was studied using both the fixed-point and moving-point methods. The moving-point method gave a rate constant of $(550 \pm 50) \times 10^{-14}$ cm^3 s^{-1}, while the fixed-point experiment, made ~6 months later using ClF from the same tank, gave a rate constant of $(340 \pm 40) \times 10^{-14}$ cm^3 s^{-1}. The discrepancy between these measurements arises from two separate experimental problems. The first moving-point experiment with freshly purchased ClF was done with a tube injector, which later was shown to give poor mixing. Thus, the plug−flow time Δt was too long and this rate constant is a lower limit. The other problem is the uncertainty in the ClF concentration. Fluorine monofluoride undergoes decomposition during storage in the cylinder with formation of Cl_2 (the F_2 seems to react with the cylinder); thus, the ClF concentration in the second measurement is an upper limit to the actual concentration. These problems can be partly circumvented by using the rate constants for quenching of NF(a) that were simultaneously measured with NCl(a). The quenching of NF(a) by ClF was previously studied and the rate constant[17,18] was determined to be $(760 \pm 70) \times 10^{-14}$ cm^3 s^{-1}. For the moving-point method with the injector that gave poor mixing, the rate constant for NF(a) was (360 ±

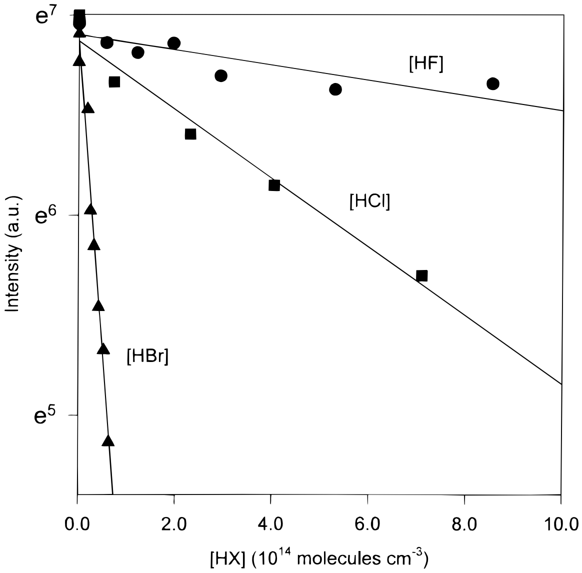

Figure 7. Pseudo-first-order quenching plots for the removal of NCl(a) by HF (●), HCl (■), and HBr (▲). The starting concentrations for the for HF and HCl experiments were $[F] = 4.5 \times 10^{12}$, $[Cl] = 2.7 \times 10^{12}$, and $[HN_3] = 6.0 \times 10^{12}$ molecules cm^{-3} with a reaction time of 67 ms. For the HBr experiment, $[F] = 2.1 \times 10^{12}$, $[Cl]\ 1.7 \times 10^{12}$, and $[HN_3] = 4.0 \times 10^{12}$ molecules cm^{-3} and the reaction time was 35.7 ms.

40) × 10^{-14} $cm^3\ s^{-1}$, a factor of 2 lower than that of Du's determination. The fixed-point experiment gave a rate constant of (260 ± 30) × 10^{-14} $cm^3\ s^{-1}$, a factor of 3 lower than Du's value.[17,18] However, the ratio of the NF(a) and NCl(a) rate constants is the same for both of our experiments. Assuming that Du's results for NF(a) is correct and that the discrepancy is the result of incorrect Δt and/or [ClF] concentration in the present experiment, the measured rate constants may be scaled and the recommended NCl(a) quenching rate constant becomes $\approx 1100 \times 10^{-14}$ $cm^3\ s^{-1}$.

c. Hydrogen Halides. Representative experiments for HF, HCl, and HBr are compared in Figure 7 for fixed-point experiments. The average rate constants from two HF experiments for NCl(a) and NF(a) were (0.5 ± 0.3) × 10^{-14} and (0.2 ± 0.1) × 10^{-14} $cm^3\ s^{-1}$, respectively. Due to the small degree of quenching, the uncertainty in the rate constants for HF are estimated to be ±50%. The NF(a) rate constant is ~30% smaller than the previously determined value,[17] but well within the combined uncertainties. Hydrogen fluoride is always present in the flow reactor from (1), but the concentration is too low to be important.

Many experiments were performed for HCl with three different reactors. The best results from a high purity tank was (1.5 ± 0.4) × 10^{-14} $cm^3\ s^{-1}$. However, the variation among different experiments was significant and hence the 25% uncertainty in Table 1. The average NF(a) quenching rate constant was (0.20 ± 0.05) × 10^{-14} $cm^3\ s^{-1}$, which agrees, within the combined uncertainties, of the value determined by Du.[17] Our rate constant for NCl(a) is more than a 100 times smaller than the value reported by Ray and Coombe.[33]

The quenching of NCl(a) and NF(a) by HBr was measured in five individual experiments; the residual Br_2 was removed before the HBr/Ar mixtures were prepared. The average quenching rate constants of NF(a) and NCl(a) were (9.0 ± 2.0) × 10^{-14} and (180 ± 30) × 10^{-14} $cm^3\ s^{-1}$, respectively. The data for NF(a) with HBr were reported previously.[34] The HI sample was distilled multiple times until no residual I_2 could be detected, and then a dilute mixture in Ar was prepared. The quenching rate is fast and quenching was followed over a reduction in [NCl(a)] by a factor of five. Three determinations of the rate constants yielded average values of (2900 ± 500) × 10^{-14} and (380 ± 50) × 10^{-14} $cm^3\ s^{-1}$ for NCl(a) and NF(a), respectively. The quenching of NF(a) by HI has not been previously reported.

d. Halogenated Methanes. All samples were distilled to remove possible halogen impurities and the fixed-point method was utilized to measure the rate constants. Four experiments performed for CH_3Cl, and the rate constants for NCl(a) and NF(a) were (10 ± 2) × 10^{-14} and (1.1 ± 0.3) × 10^{-14} $cm^3\ s^{-1}$, respectively. Three determinations of the removal of NCl(a) by methyl bromide were made for two separately prepared CH_3Br/Ar mixtures. The average rate constants for NCl(a) and NF(a) were (7.2 ± 0.4) × 10^{-14} and (20 ± 4) × 10^{-14} $cm^3\ s^{-1}$, respectively. The NCl(a) rate constant appears anomalously low compared to the methyl chloride and methyl iodide rate constants. However, the NCl(a) rate constants for the three separate experiments were self consistent, and the NF(a) rate constants for both CH_3Cl and CH_3Br agree with Du's measurements.[17] Two experiments with CH_2Cl_2 gave a rate constant of (18 ± 2) × 10^{-14} $cm^3\ s^{-1}$. The quenching rate constant for CF_2Cl_2 was too small to measure ($\leq 1 \times 10^{-14}$ $cm^3\ s^{-1}$); the rate constant for CF_2ClBr also is small, but values of (0.3 ± 0.1) × 10^{-14} and (0.5 ± 0.1) × 10^{-14} were obtained for NCl(a) and NF(a), respectively. Methyl iodide was studied five times over a period of $1^1/_2$ years; the rate constants are (81 ± 8) × 10^{-14} and (246 ± 25) × 10^{-14} $cm^3\ s^{-1}$ for NCl(a) and NF(a), respectively, and the latter agrees with the earlier report.[17] Quenching by CF_3I also was studied to provide another iodine containing molecule. Three experiments gave 60 × 10^{-14} $cm^3\ s^{-1}$ for NCl(a) and 25 × 10^{-14} $cm^3\ s^{-1}$ for NF(a).[17] In contrast with NF(a), the quenching rates of NCl(a) by CH_3I and CF_3I are about the same. For the CF_3I (and CH_3I) experiments, the $[HN_3]_0 > [F]_0 \cong [Cl]_0$ in order to avoid the generation of IF or ICl from reactions of F or Cl atoms with CF_3I.

e. Amines. As previously noted, ammonia was used as the reference reaction to determine the reaction time. More than 30 experiments, both fixed and moving-point in three different reactors, were performed with $[NH_3]$. The average NCl(a) quenching rate constant was (11 ± 2) × 10^{-14} $cm^3\ s^{-1}$, 35 times smaller than the reaction between NF(a) and NH_3. Methyl amine was studied via the moving-point method; the average of three experiments gave a rate constant of (240 ± 40) × 10^{-14} and (1230 ± 100) × 10^{-14} $cm^3\ s^{-1}$ for NCl(a) and NF(a), respectively. Both rates increase relative to NH_3, but the increase for NCl(a) is a factor of 20, whereas the NF(a) rate increases only 4-fold. Dimethylamine and trimethylamine were each examined twice using the moving-point method. The rate constants obtained for dimethylamine were (1040 ± 100) × 10^{-14} and (1840 ± 200) × 10^{-14} $cm^3\ s^{-1}$ for NCl(a) and NF(a), respectively. The NCl(a) and NF(a) rate constants obtained for trimethylamine were (1960 ± 200) × 10^{-14} and (2500 ± 300) × 10^{-14} $cm^3\ s^{-1}$, respectively. The incremental increases in the rate constants per methyl group for the amines are larger for NCl(a) than for NF(a), and the two rate constants for trimethylamine are nearly equal. The values of the NF(a) rate constants obtained for mono-, di-, and trimethylamine are all in agreement with those determined by Du and Setser.[17]

f. Other Molecules. Quenching experiments were attempted for representative saturated hydrocarbons and oxygen containing organic molecules. However, neither series gave well-behaved, pseudo-first-order decay plots. Four molecules, C_2H_6, C_4H_{10}, CH_3OH, and $(CH_3)_2O$ were studied multiple times in more than

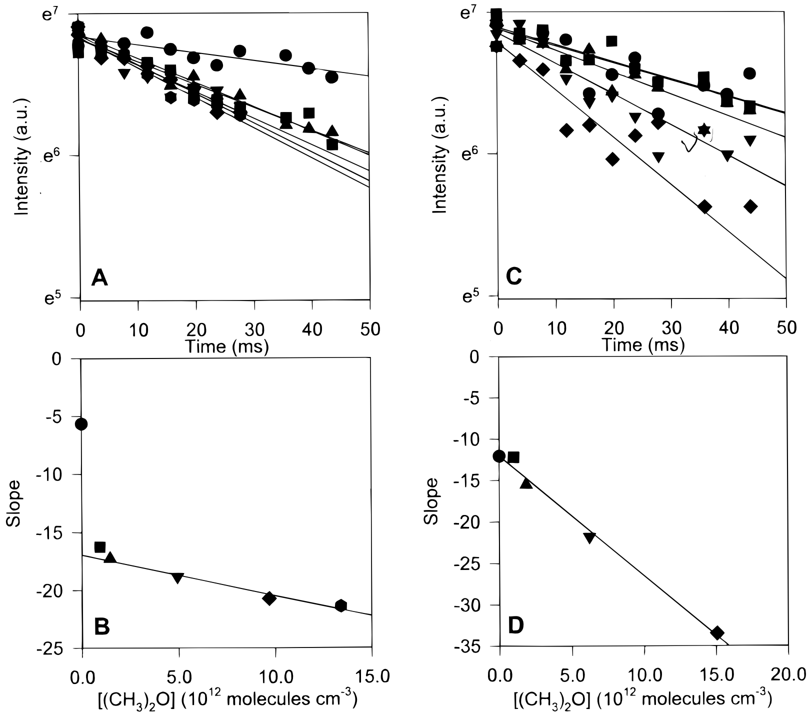

Figure 8. Kinetic plots for removal of NCl(a) and NF(a) by dimethyl ether. The starting concentrations were $[F] = 2.7 \times 10^{12}$, $[Cl] = 2.3 \times 10^{12}$, and $[HN_3] = 3.0 \times 10^{12}$ molecule cm^{-3}. Part (A) shows the first-order removal of NCl(a) upon addition of $(CH_3)_2O$. The plot of the first-order slopes vs $[(CH_3)_2O]$ in part B clearly shows the presence of two or more processes. Assuming that the slow decay is the removal of NCl(a) from gas phase quenching by $(CH_3)_2O$, the NCl(a) removal rate constant is $(35 \pm 6) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}. Parts C and D show the first-order removal of NF(a) upon addition of $(CH_3)_2O$.

one reactor using both the fixed-point and moving-point methods. In fact, the halocarbon coating on the reactor walls was completely removed, and a new coating applied without any noticeable improvement. Experiments also were done with H_2S and OCS as representative sulfur-containing compounds.

Two decay regimes were observed in the kinetic plots for the removal of [NCl(a)] by both butane and dimethylether. Figure 8 shows data for one of the four moving-point experiments for $(CH_3)_2O$. For even low $[(CH_3)_2O]$, a rapid decay was observed; however, further increase of the $[(CH_3)_2O]$ above 2×10^{12} molecules cm^{-3} hardly changed the decay rate. The first-order time plots were always well-behaved for the full range of $[(CH_3)_2O]$, but the derived pseudo-first-order constants had an anomalous dependence on $[(CH_3)_2O]$. If the values of k_{total} $[(CH_3)_2O]$ from Figure 8A are plotted vs $[(CH_3)_2O]$, a linear correlation is found (Figure 8B) for concentrations greater than 1×10^{12} molecules cm^{-3}, and the rate constant is 35×10^{-14} cm^3 s^{-1}. In contrast to NCl(a), the decay of NF(a) with added $(CH_3)_2O$ was well-behaved, and the moving-point experiments gave the pseudo-first-order rate constants shown in Figure 8. The NF(a) rate constant derived from these data, $(145 \pm 30) \times 10^{-14}$ cm^3 s^{-1}, is in agreement with the value determined by Du.[17] However, the NCl(a) data always showed, at least, two separate decay regimes. A rapid drop in [NCl(a)] could be caused[16,17] by backstreaming for high concentration of quenching reagents with removal of F and Cl atoms before NF(a) or NCl(a) can be formed. For such a complication, the observed fast decay would occur for both NF(a) and NCl(a) and this is not the case. Replacing the halocarbon wax coating on the flow reactor and carefully cleaning (replacing) the reagent gas-handling manifold did not eliminate the fast decay process for NCl(a). We concluded that a $[(CH_3)_2O]$ dependent, surface-quenching process for NCl(a) was the likely cause of these anomalous observations. If the actual homogeneous gas-phase quenching of NCl(a) corresponds to the slow decay component, $(35 \pm 6) \times 10^{-14}$ cm^3 s^{-1} is obtained as the rate constant for $(CH_3)_2O$.

Results similar to the experiments just described with $(CH_3)_2O$ were obtained with butane. Only an upper limit of $\leq 0.5 \times 10^{-14}$ cm^3 s^{-1} could be determined for the NCl(a) rate constant, because the dependence of the quenching rate on $[C_4H_{10}]$ was low for the high concentration regime. The quenching data for NF(a) by butane were normal, and the average rate constant from six separate experiments was $(1.5 \pm 0.5) \times 10^{-14}$ cm^3 s^{-1}. In order to obtain more information about the source of the curvature of the pseudo-first-order constants vs $[C_4H_{10}]$, a mixture still was made of butane and ethene in the ratio of 1.2: 1.0. The fixed-point determination of the NCl(a) decay rate from this mixture still showed curvature. Since C_2H_4 would remove the reactive radicals, we conclude that the curvature is due to the presence of butane and not from a reactive species derived from butane.

Four moving-point and two fixed-point experiments were attempted with $[CH_3OH]$. However, the slow decay components gave apparent NCl(a) rate constants that varied by an order of magnitude. On the other hand, the NF(a) data gave well-behaved kinetics with an average rate constant of $(8 \pm 2) \times 10^{-14}$ cm^3 s^{-1}, which is, within the combined uncertainties, equal to the value measured by Du.[17] Experiments with C_2H_6 gave curved NCl(a) decay plots, and the slower decay component did not reach a reproducible limit. Near the end of the study, experiments also were attempted with H_2S and OCS. The H_2S data resembled those for dimethyl ether; the NF(a) results were well-behaved, but the NCl(a) data exhibited two decay regimes. The high $[H_2S]$, or slow decay domain, gave a rate constant of $(2.7 \pm 0.4) \times 10^{-14}$ cm^3 s^{-1}. These data are sufficient to show that hydrogen abstraction from H_2S by NCl(a) is not particularly fast and that the quenching rate is slower than for NF(a). The

TABLE 2. Rate Constants[a] for Quenching $NCl(a^1\Delta)$ by Atoms

atom	$NCl(a^1\Delta)$	$NF(a^1\Delta)$
F	$(4.0 \pm 0.5) \times 10^{-11}$ $(2.2 \pm 0.7) \times 10^{-11}$ [b]	$(4 \pm 2) \times 10^{-13}$ [c]
N	$(9 \pm 4) \times 10^{-13}$	$(5 \pm 2) \times 10^{-13}$ [c]
O[e]	$(7 \pm 3) \times 10^{-12}$	$(6 \pm 2) \times 10^{-12}$ [c]
H	$(21 \pm 5) \times 10^{-13}$	$(3.1 \pm 0.6) \times 10^{-13}$ [d]
Cl	$(1.0 \pm 1.0/-0.5) \times 10^{-12}$ [b]	$(6 \pm 2) \times 10^{-13}$ [b]

[a] In units of cm^3 $molecule^{-1}$ s^{-1}. [b] From ref 1. [c] From ref 19. [d] From refs 38 and 39. [e] The O + NCl(x) reaction has a rate constant of $(1.2 \pm 0.6) \times 10^{-10}$ cm^3 s^{-1}; ref 41b.

quenching by OCS gave curved quenching plots for all ranges of [OCS]. Although not nearly so serious, the data for quenching of NF(a) by OCS also has problems.[17]

We concluded that the $k_{surface}$ term in (7) is not zero in the presence of these reagents, and furthermore, it must depend upon the reagent concentration.

$$k_{surface} = f[Q]\frac{surface}{P} \tag{7}$$

However, we have no explanation for why NCl(a) is so much more sensitive to the surface of the reactor than NF(a). Exhaustive tests were made to check whether F or Cl atoms or other fragments from the discharge could react with these molecules and generate a reactive quenching species. However, none of the tests identified such reactions. The difficulties encountered in experiments with these molecules prevented an accurate determination of the NCl(a) quenching rate constants. However, based upon the upper limits for the methane and butane, the saturated hydrocarbons have small gas-phase rate constants. The estimated rate constant for $(CH_3)_2O$ suggest that organic molecules containing oxygen will have smaller NCl(a) quenching rate constants than NF(a). This trend is expected if NCl(a) is less acidic than NF(a).

C-3. Quenching Rate Constants for F, N, O, and H Atoms. Fluorine atoms were generated by passing the F_2/He mixture plus added Ar through a microwave discharge and added via the quenching reagent inlet shown in Figure 1. The dissociation efficiency of F_2 was measured by titrating the [F] with CF_3I and monitoring the [F] from the HF(v=3) emission intensity generated by the reaction of F with H_2S or C_2H_6.[17] One of the quenching measurements is shown in Figure 6. From three separate experiments, the NCl(a) quenching rate constant was found to be $(4.0 \pm 0.5) \times 10^{-11}$ cm^3 s^{-1}. This value is 1.8 times larger than the value determined by Manke and Setser[1] (see Table 2), who produced F atoms via a microwave discharge through CF_4 or SF_6. Some concern existed that the value they determined might be too large due to removal of NCl(a) by CF_3 and CF_2 or SF_5 generated from the CF_4 or SF_6 dissociation, respectively. The current measurement using the dissociation of F_2 to generate F atoms confirms the large rate constant for F atoms. The factor of 2 difference in k_F for the two studies is probably related to the difficulty of accurately measuring [F]. Several experiments were used in the determination by Manke,[1] and the most reliable rate constant presumably is an overall average and we recommend ~3.1×10^{-11} cm^3 s^{-1}.

The experimental configuration employing the auxiliary reactor was used to study the removal rates of $NCl(a^1\Delta)$ by N, O, and H atoms. The NF(a) and NCl(a) molecules were generated in the main reactor in the way already described. The concentration range for the atoms, $(0.2-2.0) \times 10^{13}$ atoms cm^{-3}, was obtained by a microwave discharge in a flow of either N_2 or H_2. The N atom concentration could be converted to an equivalent O atom concentration by adding a slight excess of NO to the entrance of the auxiliary reactor. The N (and O) atom concentrations were determined by the titration reaction of N by NO. The details of the calibration procedure for N atom concentration are described in ref 18 where the study of the reactions of N and O atoms with NF(a) were reported. The NCl(a) concentration was not affected by the flow of H_2, N_2 or the slight excess of NO required to convert the [N] to [O].

The concentration of H atoms was determined from the degree of dissociation of a known flow of H_2, which was found from the reduction of the HF(3-0) emission intensity at 872 nm in the main reactor from reaction 8 when the microwave discharge was ignited.

$$F + H_2 \rightarrow HF(v = 0\text{-}3) + H \tag{8}$$

The distribution[35] for HF(v = 0-3) is 3:15:53:29, and the HF(3-0) emission could be observed with the 0.5-m monochromator at the entry region of the flow from the auxiliary reactor into the main reactor. The latter contained $[F] \cong 1 \times 10^{13}$ atoms cm^{-3} from a discharge through CF_4. The reaction time and [F] was adjusted so that the HF(3-0) intensity was proportional to the $[H_2]$ that was added from the auxiliary reactor. The fractional dissociation of H_2 by the discharge was found to be ~60%, as we have usually observed.[36]

Whenever possible, we compared the removal rate of NCl(a) with that for NF(a) for the same concentration of N, O, and H atoms. Since the NF(a) rate constants are established,[18,37-40] this measurement provided an immediate identification of the magnitude of the NCl(a) rate constants. This strategy proved to be very useful for the H and O reaction, but not for N atoms. Due to the overlap of the N_2(B-A) and NF(a-X) emission bands and to a persistent residual concentration of N_3 in the main reactor for conditions such that NF(a) and NCl(a) were simultaneously in the main reactor, we were unable to study the N + NF(a) reaction under such conditions. The N + NF(a) reaction could, of course, be studied if excess [F] was used in the main reactor so that only NF(a) was present. The N + NCl(a) reaction could be studied because the N_2(B-A) and NCl(a-X) emission in the 1070 nm region are not directly overlapped. Background emission in the H + NCl(a) or NF(a) experiments was not a problem. All quenching measurements were made 50 cm downstream from the atom inlet using the fixed-point observation method.

The current data seemed to favor slightly smaller values for the N and O atom rate constants with NF(a) relative to the older data.[18] However, we did not do the extensive calibrations required for careful measurement of [N], and the former rate constants were assumed to be more reliable. In the present work, individually fixed [N] = [O] were selected and the degree of quenching of NCl(a) and NF(a) were measured. The experiments showed that the quenching rate constants for NCl(a) and NF(a) were comparable, but the values for NCl(a) seem to be slightly larger than for NF(a). We recommend $k_N = (9 \pm 4) \times 10^{-13}$ and $k_O = (7 \pm 3) \times 10^{-12}$ cm^3 s^{-1} as room temperature rate constants for quenching of NCl(a). The ±40% uncertainty is associated with the difficulty of assigning the concentrations of O and N atoms. Just as for NF(a), see Table 2, the rate of reaction of O atoms with NCl(a) is an order of magnitude larger than for N with NCl(a). The ultimate products from the N and O atom reactions with NF(a) are N_2(X) and NO(X); but, they can be either directly produced or generated by secondary reactions from NF(X).[37] The situation is similar for NCl(a), because the reaction of NCl(X) with O atoms is fast.[41b] The products from N and O reacting with NH(a) are mainly NH(X) and NO(X), respectively.[23] However, the O atom + NH(a) reaction also gave 20% physical quenching and 15% formation of OH + N(^{4}S).

Piper and co-workers[38,39] reported a room temperature rate constant for H + NF(a) of $(3.1 + 0.6) \times 10^{-13}$ cm^3 s^{-1}; the products are N(^{2}D) and HF. The N(^{2}D) subsequently can react rapidly with another NF(a) molecule to give N_2(B). Initial experiments with $[H] \approx 2 \times 10^{13}$ molecule cm^{-3} showed that the quenching rate for NCl(a) by H atoms was substantially larger than for NF(a). A set of experiments then was designed to measure the quenching of both molecules for a range of H atom concentrations that gave a satisfactory quenching plot. These experiments were done by changing the H_2 flow rate, measuring the reduction of both NF(a) and NCl(a), and then subsequently measuring the fractional dissociation of the H_2 in a separate experiment. Our rate constant for NF(a) was in good agreement with Piper, and we will accept his result of $(3.1 \pm 0.6) \times 10^{-13}$ cm^3 s^{-1}. A complete fixed-point plot for quenching of NCl(a) by [H] was obtained, and the NCl(a) total removal rate constant was $(21 \pm 5) \times 10^{-13}$ cm^3 s^{-1}.

For high concentrations of NF(a), strong N_2(B-A) emission could be observed from the H + NF(a) mixing zone from the N(^{2}D) + NF(a) secondary reaction,[39] which has a very large rate constant of $(2.5 \pm 1.1) \times 10^{-10}$ cm^3 s^{-1}. Similar N_2(B-A) emission spectra were observed in an experiment with a 2:1 ratio of NCl(a) and NF(a) concentrations, and the N(^{2}D) + NCl(a) reaction also seems to occur. Given the large rate constant for this secondary step, the k_H values given in the preceding paragraph should be considered as upper limits to the rate constant of the primary step. In Piper's experiment, the H_2 concentration was much larger than the NF(a) concentration and most of the N(^{2}D) atoms should have been quenched by H_2. In our experiment the H_2 concentration was only $(0.6-3.0) \times 10^{13}$ molecules cm^{-3}; however, several other species are present, which may compete for N(^{2}D), and we do not know the rate constant for N(^{2}D) + NCl(a). Thus, we can only report a total removal constant with recognition that $(21 \pm 5) \times 10^{-13}$ cm^3 s^{-1} may be an upper limit for the H + NCl(a) elementary reaction.

D. Discussion

Only a few quenching rate constants had been measured before we began our systematic study of NCl(a) using the flow-reactor technique. Except for oxygen, our rate constants are several orders of magnitude smaller than the values inferred from the photolysis of ClN_3 as the NCl(a) source.[32,33] Taking Cl_2, as an example, Ray and Coombe[32] found $(1800 \pm 300) \times 10^{-14}$ cm^3 s^{-1}, whereas our rate constant is $(40 \pm 10) \times 10^{-14}$ cm^3 s^{-1}. Similar discrepancies exist for H_2 and HCl; the differences for F_2 and Br_2 are somewhat smaller. Independent experiments in another laboratory have confirmed the differences in the rate constants measured in the flow reactor vs those from photolysis of ClN_3 for several reagents.[7,32] The environment in the flow reactor is complex. If formation processes giving NCl(a) occur in the quenching zone of the reactor, our measured rate constants would be too small. We explicitly tested for such a complication from reaction (4), and we found no evidence that NCl(X) could be converted to NCl(a). Since the [NCl(a)] is constant or slightly decreasing along the reactor in the absence of reagent, the presence of processes giving NCl(a) seem unlikely. Since the NF(a) rate constants measured in the present reactor agreed with those measured in the much simpler 2F + HN_3 chemical system, we believe that the rate constants for NCl(a) in Table 1 must be correct to within the quoted uncertainties. Furthermore, the rate constants measured for NCl(a) have a sensible relationship relative to those accepted for NF(a) for several classes of reagent molecules. In our opinion, experimental complications must exist in the photochemical experiments using ClN_3 as the NCl(a) source. The photolysis laser could cause photodecomposition of the quenching reagent in addition to photodissociating the ClN_3. However, the room temperature quenching rate constants for H and Cl atoms are $\lesssim 2 \times 10^{-12}$ cm^3 s^{-1} and photodissociation of the reagent cannot explain the discrepancy for Cl_2 or HCl. Since the NCl(a-X) emission was observed through a filter in the photodissociation experiments,[32,33] possibly other emission interfered with the NCl(a) signal.

Oxygen removes NCl(a), or NBr(a),[34] with a much larger rate constant than for NF(a). Excitation-transfer is expected between NCl(a), or NBr(a), and O_2.

$$NCl(a^1\Delta) + O_2(X^3\Sigma^-) \rightarrow NCl(X^3\Sigma^-) + O_2(a^1\Delta) \quad (9)$$

The energy defect for excitation-transfer between NF(a) and O_2 is 3553 cm^{-1}, while the defect for (9) is 1398 cm^{-1}, and the smaller defect for NCl(a) and NBr(a) is the cause of the larger rate constant. The observation[31] of enhanced NCl(X) formation from photolysis of ClN_3 in the presence of O_2 tends to confirm the excitation−transfer mechanism, as does the experiment of Clyne and MacRobert[41] in which O_2(a) was observed by mass spectrometry. Furthermore, they[41c] added O_2 in order to study the reaction between NCl(x) and NO, and they obtained a much larger ($1.4 \pm 1.0 \times 10^{-11}$ cm^3 s^{-1}) rate constant than our value for NCl(a). Given the sizeable rate constant for (9), one might have expected (4) with an energy defect of 2155 cm^{-1} to occur. Our upper limit to the rate constant is only $\leq 2 \times 10^{-12}$ cm^3 s^{-1}, so perhaps the reaction does occur. However, chemical reaction also could occur with formation of N_2 + Cl + F.

A comparison of the NCl($a^1\Delta$) quenching rate constants with those for NF($a^1\Delta$) and $O_2(a^1\Delta_g)$ is informative. For example, quenching of NF(a) by CO proceeds over a small potential barrier giving vibrationally excited FNCO, which subsequently dissociates to F + NCO;[42] a similar mechanism is expected for NCl(a). Although the quenching constant of NCl(a) by N_2 is very small, the estimated rate constant is larger than the rate constant for quenching of NF(a) (assuming that the O_2 impurity level in the N_2 was sufficiently low to have no influence on the NCl(a) data). These N_2 quenching processes are the reverse of the reactions of F and Cl atoms with N_3. The larger quenching rate constant for NCl(a) + N_2 implies a lower potential energy barrier for association to Cl−N_3 than for F−N_3, and a competition between redissociation on the singlet surface and crossing to the triplet surface of ClN_3. This competition is consistent with the lower branching fraction[1] for reaction (2a) vs that for F + N_3. It should be noted that our inference about the barrier heights for dissociation of the ClN_3 and FN_3 molecules is at variance with the discussion of Benard.[30] The reactions of NH(a) with N_2 and CO at room temperature have rate constants of 6.6×10^{-14} and 2.0×10^{-11} cm^3 s^{-1}, respectively. The N_2 reaction proceeds via HN_3 formation and redissociation to NH(X) + N_2, and the CO reaction gives mainly (88%) H + NCO.[22,24] The NCl(a) and NF(a) reactions with NO have much smaller rate constants than the rate constant of the NH(a) reaction (3.0×10^{-11} cm^3 s^{-1}), which gives N_2O + H and NH(X) in similar amounts plus some N_2 + OH.[23]

The increase in the NF(a) and NCl(a) rate constants upon methyl substitution of NH_3 implies that NF(a) and NCl(a) interact with the electron pair, which becomes increasingly basic in the amine series. A good correlation is observed in a plot of

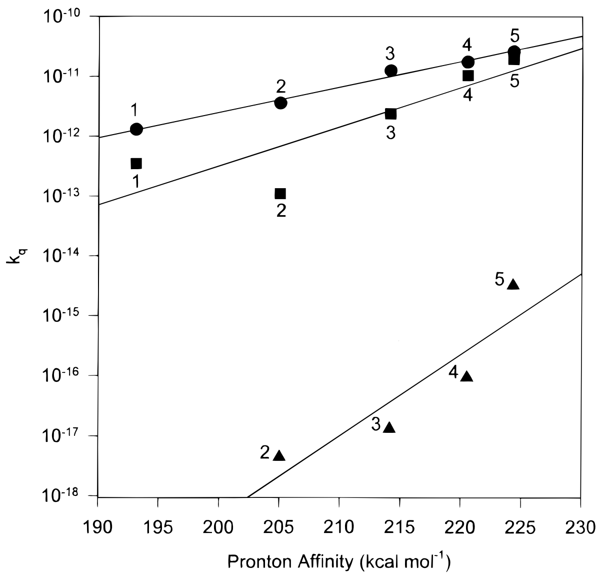

Figure 9. Plot of the quenching rate constants vs the proton affinities[43] of some reagent molecules: (1) $(CH_3)_2O$, (2) NH_3, (3) NH_2CH_3, (4) $NH(CH_3)_2$, and (5) $N(CH_3)_3$. Correlations are shown for NF($a^1\Delta$) (●), NCl($a^1\Delta$) (■), and O_2($a^1\Delta$g) (▲). If the $(CH_3)_2O$ point is deleted from NCl(a) set, the correlation would be improved and the plot much steeper.

the log of the rate constants vs proton affinity,[43] but the compression in scale from the log k_Q plot of Figure 9 should be remembered. This correlation suggests the importance of a Lewis acid–base type interaction between the $\pi_{x^2}-\pi_{y^2}$ components of NF(a) and NCl(a) and the electron pair of the reagent in determining the reaction barrier height. The correlation of NCl(a) rate constants and the basicity of the reagent could not be explored more fully because of the surface-enhanced quenching found for alcohols and ethers.

The increase of rate constants with reduction of the ionization energy for the unsaturated hydrocarbons holds for both NF(a) and NCl(a), but the increase is more marked for the series with NCl(a). The addition of butenes to the series extends the correlation formerly noted for NF(a).[17] This trend normally is indicative of a mechanism involving radical addition to the double bond. The rate constant for benzene fits the trend for NCl(a), since the ionization energies of benzene and butene-2 are nearly the same (9.1 eV). However, the rate constant for quenching of NF(a) by benzene is anomalously low. This may reflect a difference in the decomposition vs redissociation pathways for the NF and NCl adducts.

Other types of chemical reactions for nitrenes and carbenes are insertion and abstraction. By analogy with methylene, Du inferred that NF(a) reacts with halogen atoms of the methyl halides in an abstraction-like reaction. The rate constants for the reactions of NCl(a) and NF(a) with methyl halides are similar and presumably the mechanisms also are similar. The reduction in rate constant with F substitution (except for CF_3I) is quite marked, and this may be a consequence of reduced electron density on the halogen atom. Given the small rate constants for butane and H_2S, hydrogen atom abstraction is a slow process at room temperature for both NF(a) and NCl(a). The reactions with halogens and hydrogen halides probably proceed by insertion; the intermediates for Cl_2 and HCl would be the $NFCl_2$ (NCl_3) and HNClF($HNCl_2$) molecules. The temperature dependence[44] of the HCl and Cl_2 rate constants support a chemical quenching mechanism. The $NFCl_2$ and NCl_3 molecules carry excess vibrational energy, and they can dissociate by rupture of the N–Cl bond. Clyne and MacRobert[41] observed NCl_2 formation by mass spectrometry from the NCl(a) + Cl_2 reaction. The HCl, HBr, and HI rate constants are larger for NCl(a) than for NF(a), and the difference increases in the series. The larger rate constant for NCl(a) with HCl suggests that exit channels other than HCl elimination (with conservation of spin) must exist from vibrationally excited $HNCl_2$. This result reinforces the need to better understand the unimolecular reactions of vibrationally excited $HNCl_2$ and HNClF molecules.[45]

E. Conclusions

Room temperature quenching rate constants for NCl($a^1\Delta$) have been measured for 40 molecular reagents and for F, O, N, and H atoms in a flow reactor. For most reagents, the rate constants for NF($a^1\Delta$) also were simultaneously measured as a check on the experimental method. Rate constants for several reagents with NF(a) that previously were not studied also are reported. In most cases, the NCl($a^1\Delta$) rate constants are smaller than or similar to those of NF($a^1\Delta$), but several exceptions (F, H, O_2, CH_3Cl, and hydrogen halides) exist. The reaction with O_2 proceeds by excitation–transfer to give O_2($a^1\Delta$). The rate constants for amines and olefins increase with increase of the proton affinity and reduction of ionization energy, respectively, of the reagents. Most reactions probably proceed by chemical interaction, and the next step in understanding reactions of NF($a^1\Delta$) and NCl($a^1\Delta$) is to identify the primary reaction products. The recent study of the bonding properties of CH_2-($\tilde{a}^1\Delta$,) with N_2 may provide some insight about adduct formation involving NCl($a^1\Delta$) or NF($a^1\Delta$) with stable molecules.[46] An upper limit of 4×10^{-12} cm^3 s^{-1} was set for the bimolecular, self-destruction rate constant between NF($a^1\Delta$) and NCl($a^1\Delta$). The rather large F atom quenching rate constant should be remembered for chemical systems using F atoms to generate NCl(a). The H atom rate constant is 7 times larger for NCl(a) than that for NF(a), but the H atom quenching rate constant is still 20 times smaller than the rate constants for F atoms. Further study of the reaction kinetics of the mixed NX($a^1\Delta$), X = F, Cl, Br, and O_2($a^1\Delta_g$), systems seems worthwhile with searches for possible utilization of the stored chemical energy.

Acknowledgment. This work was supported by the U.S. Air Force under Grant F49620-96-1-0110 from the Air Force Office of Scientific Research.

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