Infrared Chemiluminescence Studies of the H + NFCl₂ and H + NFCl Reactions

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The primary and secondary reactions in the H + NFCl₂ system have been studied by infrared chemiluminescence in a fast flow reactor at 300 K. The primary reaction is exclusively Cl atom abstraction to give HCl(v=0-4) + NFCl with a total rate constant of $(1.9 \pm 0.4) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and an inverted vibrational distribution of $P_0-P_4 = 9:20:32:27:12$. The rate constant for HF formation from H + NFCl was estimated as $(0.9 \pm 0.4) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, and the HF vibrational distribution, $P_0-P_3 = 42:34:18:6$, is characteristic of unimolecular HF elimination reactions. These data for the HF + NCl(a) product channel from the H + NFCl reaction are compared to earlier studies, which provided information about the HCl + NF(a) product channel. The latter seems to be the more important, and the total rate constant for H + NFCl is about 4 × 10^{-11} cm³ molecule⁻¹ s⁻¹ at 300 K. The dynamics of the H + NFCl reaction are discussed and compared to the H + NF₂ reaction. A small number of experiments also were done with the H + NF₂Cl reaction system.

Introduction

The reactions of H atoms with NF2 and NCl2 radicals proceed by recombination followed by unimolecular HF and HCl elimination from the chemically activated HNF₂* and HNCl₂* ground electronic state molecules. In both cases the unimolecular reactions mainly proceed with conservation of spin and the reactions provide chemical sources for useful concentrations of $NF(a^{1}\Delta)$ and $NCl(a^{1}\Delta)$ radicals.¹⁻⁵ In this work, the H + $NFCl_{2}$ reaction was used to generate NFCl radicals in a fast flow reactor in the presence of excess H atoms. The HCl(v) from the primary step and the HF(v) from the secondary step (corresponding to formation of $NCl(a^{1}\Delta) + HF$) were observed after a short reaction time by infrared chemiluminescence (IRCL) using techniques developed in the Kansas laboratory. These infrared chemiluminescence data are combined with observation of the NF- $(a^{1}\Delta - X^{3}\Sigma^{-})$ emission from the NF $(a^{1}\Delta)$ + HCl channel in order to characterize the product branching fractions from the H + NFCl reaction (see reactions 4 and 5 and Figure 1).

Infrared chemiluminescence studies6 of three-centered and fourcentered unimolecular HX elimination reactions from halomethanes and haloethanes have provided information about the energy disposal in these systems.⁷ The predominant channel for chlorofluoromethanes is HCl elimination, rather than HF elimination. The structures of the HCl and HF elimination transition states are similar, and the relative magnitudes of the RRKM rate constants are determined by the threshold energies, E_0^* . As a consequence of the difference in thermochemistry of the two exit channels, $E_0^*(\text{HCl}) < E_0^*(\text{HF})$ for the chlorofluoromethanes.⁶ However, the thermochemistry of HNFCl favors HF elimination over HCl elimination, as illustrated by Figure 1, which summarizes the exit channels for unimolecular HX elimination from HNFCl. Since the $X^{3}\Sigma^{-}$ state is the ground electronic state for NF and NCl, crossings of the singlet and triplet potentials exist in the exit channels. The central challenge for the H + NFCl reaction is to determine the branching fractions for formation of NCl($a^{1}\Delta$) and NF($a^{1}\Delta$), assuming that singlet channels are the important ones. Earlier work by Coombe and

• Abstract published in Advance ACS Abstracts, December 15, 1993.



HNFCI (X1A)

Figure 1. Schematic representation of the reaction channels and thermochemistry for the H + NFCl reaction system. The solid lines are intended to identify the main reaction pathways. The H-ClNF path to NF(a) + HCl is thought to be singlet abstraction (see text). The dashed lines connected to a^3A'' represent the triplet abstraction pathways. The dashed line from HNFCl to NF(a) + HCl is an allowed unimolecular process, but the threshold energy should be much higher than for the formation of NCl(a) + HF. The activation energy barriers for the reverse reactions, NF(a) + HCl and NCl(a) + NF, are not shown on the plot.

co-workers⁸ showed that formation of NF(a) seems to be more important than NCl(a) in contradiction to the expectation from a unimolecular elimination mechanism from HNFCl. Therefore, direct abstraction of Cl atoms to give NF(X) or NF(a) also needs to be considered in the mechanism. By analogy to the $H + NF_2$

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reaction,² direct abstraction of F atoms from NFCl is very unlikely. The H + NFCl reaction is an interesting atom + radical reaction system for both theoretical and practical reasons. The practical application is, of course, the possibility of generating high concentrations of both NF(a) and NCl(a) from a single precursor.

The instability of the halogen amines has limited their study, but Gilbert and co-workers have developed ways to synthesize small quantities of NFCl₂ and NF₂Cl and they have studied the photochemistry of these molecules.⁹ The Denver group has also examined the H + NFCl₂/NF₂Cl reactions by observing the NF-(a¹Δ,b¹Σ⁺) and NCl(a¹Δ,b¹Σ⁺) emission after reaction times of 2-10 ms.⁸ In this collaborative study, we have used the methods of the Denver laboratory to prepare NFCl₂ for study of the primary and secondary reactions for shorter reaction times (0.2-1.0 ms) in the Kansas flow reactor. The combination of the new observations at shorter time together with the prior work provides some state-to-state information about the reaction dynamics and the thermochemistry of these systems.

The thoroughly studied $H + Cl_2$ reaction was used as a reference reaction for the $H + NFCl_2$ primary reaction, and comparison of the relative HCl emission intensities for the same conditions gives the HCl(v) formation rate constant for the $H + NFCl_2$ reaction. Less extensive work also was done for the $H + NF_2Cl$ reaction system, but only the primary reaction was observed. Both of these primary reactions proceed by direct abstraction with rate constants similar to that for Cl_2 .

The thermochemistry of NFCl₂ is not well established and we used the Xe(6s, $^{3}P_{2}$) + NFCl₂ reaction to obtain an estimate for D_{0} (Cl-NFCl) from the short-wavelength limit of the XeCl-(B-X) ultraviolet emission spectrum. Since there is no assurance that all of the available energy will be released to XeCl^{*}, the measurement necessarily provides an upper limit value, but the upper limits from this technique^{10,11} normally are close to the true bond energy for halogen-containing molecules that have dissociative radical anions (e.g., formation of Cl⁻ + NFCl in this case). The D_{0} (F-NCl) and D_{0} (Cl-NF) values are discussed in order to obtain an estimate for $\Delta H_{1}^{\circ}_{0}$ (NFCl).

Experimental Methods

The NFCl₂ was synthesized following the procedures below. The reactor, a 20 cm length of 2.5 cm diameter stainless steel pipe, was filled with a mixture of clean, dry Cu shot, NH4Cl and NaCl (NH₄Cl:NaCl = 1:1). The reactor was heated to $110 \,^{\circ}$ C in a flow of nitrogen for about 4 h to dry the reactor and its contents. The reactor temperature was lowered to 55-60 °C and the temperature was maintained in this range during the synthesis. After the N_2 flow was stopped, a flow of 10% (or 20%) F_2 in He was passed through the reactor at a flow rate of about 5 cm³ min⁻¹ for 2-4 h. The products were collected in a glass trap held at liquid nitrogen temperature. The products were separated by distillation through a series of stainless steel traps held at -80 °C (CO₂/methanol), -118 °C (ethanol/liquid N₂), and -196 °C (liquid N_2). In order to further purify the products, repeated separations were performed using the -118 and -196 °C baths until pure NFCl₂ was obtained in the -118 °C trap. The purity of NFCl₂ was confirmed by the UV spectrum (absorption peak at 270nm);9 the main byproduct from the synthesis is Cl₂, which is easily identified by the UV spectrum. The best syntheses yielded about 20 Torr of NFCl₂ in a 12-L bulb. The purified NFCl₂ was diluted with Ar before being metered to the flow reactor from the 12-L Pyrex reservoir. The dilute $NFCl_2$ is stable in clean Pyrex vessels, but on occasion the NFCl₂ does decompose to Cl₂ and N_2 by catalytic action of the surface. A small amount of NF₂Cl is produced by the synthesis and it can be separated from the Cl₂-containing fraction by additional fractional distillation.

The apparatus at Kansas State University for the IRCL experiments has been described in detail before.^{6,12} The reactor is a 4 cm diameter Pyrex glass pipe pumped by a large rotary

blower and mechanical pump. The highest flow velocity is 120 m s⁻¹ for Ar pressures of 0.4-0.7 Torr. The H atoms were generated by microwave discharge in a flow of 20% H₂ in Ar, which normally gives $\sim 50\%$ dissociation in our apparatus,^{12a} and added at the front end of the reactor. The infrared emission was observed from a window located 2.5 cm downstream from the reagent inlet, which corresponds to a reaction time of 0.2 ms for the optimum pumping speed. For these conditions there is no HCl(v) vibrational relaxation providing that the [H] is less than $(1-2) \times 10^{13}$ molecules cm⁻³. The reaction time is sufficiently short that the differential rate law applies for most observations. The flow velocity was lowered by a factor of 2-3 with [H] = $(1-5) \times 10^{13}$ and with [reagent] = $(0.5-5) \times 10^{12}$ molecules cm⁻³ in order to observe the secondary reactions. The HCl infrared emission from $H + Cl_2$ reaction was recorded under the same experimental conditions as the H + NFCl₂ reaction to estimate the HCl formation rate constant for the NFCl₂ reaction and to monitor the degree of vibrational relaxation.

The IRCL spectra were collected using a Bio Rad FTS 60 Fourier transform spectrometer with 2 or 4 cm⁻¹ resolution. The vibrational distribution was obtained by dividing the peak heights of each rotational line by the Einstein coefficient^{12c} of that transition and the instrumental response function. Except for HF(v = 1 and 2) from the H + NFCl reaction, the rotational distributions were 300 K Boltzmann, so converting the rotational line intensities to relative vibrational populations is straightforward. The HCl and HF Einstein coefficients have been derived from the best available dipole function.^{12c} The Einstein coefficient for NF(a) was required for comparison with the HF(3–0) emission, and we used 6.7 s as the NF(a) lifetime.^{2,13}

A few experiments were done in a 3 cm diameter flow reactor with a smaller pumping system in order to observe the emission in the 500-850-nm region. This reactor was coated with halocarbon wax to inhibit surface quenching reactions. In this case the observations were made with a photomultiplier tube (Hamamatsu R-942-02) and monochromator in order to observe the NCl(b-X), NF(a-X), and HF(3-0) emission spectra. Observations could be made for reaction times of 0.7-5 ms in this reactor. These data are complementary to the previous study from the Denver laboratory.⁸

A metastable Xe atom flow reactor¹⁰ was used to obtain the XeCl(B,C) emission spectrum from the Xe(${}^{3}P_{2}$) + NFCl₂ reaction at 0.4 Torr of He; the metastable Xe atoms were generated by adding a small flow of Xe (about 4 mTorr) to the main He flow. The combined flows passed through a hollow cathode discharge operated at 240 V. The NFCl₂ was diluted to 10% with He and added 15 cm downstream from the discharge zone. The XeCl-(B-X) emission was observed through a LiF window with a 0.3-m monochromator equipped with a cooled Hamamatsu 955 photomultiplier tube and homemade photon counter.^{10b} The monochromator and PM tube output were interfaced to a computer that controlled the data acquisition.

Results

1. Thermochemistry. Since the thermochemistry of the chlorofluoroamines is not well established, some bond energies and enthalpies of formation were estimated in order to obtain the enthalpies of the primary and secondary reactions. The upper limit to the D_0 (Cl-NFCl) was assigned from the short-wavelength limit, λ_{min} , of the XeCl(B-X) spectrum from the Xe(${}^{3}P_{2}$) + NFCl₂ reaction; see Figure 2. A XeCl* spectrum from the Xe(${}^{3}P_{2}$) + Cl₂ reaction is included in Figure 2 for reference. The XeCl* emission from reaction 1 is strong and NFCl₂ is a good Cl atom donor, as are many other molecules with the N-Cl bond.¹¹

$$Xe({}^{3}P_{2}) + NFCl_{2} \rightarrow XeCl(B, C) + NFCl$$
 (1)



220 250 280 310 340 370 400 430 nm Figure 2. Comparison of the XeCl(B-X) emission spectra from the reactions of Xe(${}^{3}P_{2}$) atoms with NFCl₂ and Cl₂; the short-wavelength limits are 203.5 and 210 nm, respectively. The scan of the XeCl(C-A) spectrum from NFCl₂ was accidentally stopped before the spectrum was completely recorded. The carrier gas was He at 0.5 Torr pressure.

At first glance, the spectrum from NFCl₂ resembles that from Cl_2 , but close inspection shows that the oscillations in the B-X spectrum are more numerous and deeper in the $Xe({}^{3}P_{2}) + Cl_{2}$ emission, which indicates a narrower XeCl(B) vibrational distribution.^{10,11} The oscillations also are more pronounced in the C-A spectrum from the Cl_2 reaction. The upper limit to the NFCl-Cl bond energy is given by $D_0 \leq E(Xe) + nRT - E(\lambda_{\min})$. Using $E(Xe^*) = 8.32 \text{ eV}$ and $n = 3 \text{ with } \lambda_{\min} = 203.5 \text{ nm}$ gives $D_0 \leq 52.7$ kcal mol⁻¹. This method generally gives reliable estimates of bond energies for reagents that have large XeCl-(B,C) yields, since the XeCl(B) vibrational distribution extends close to the thermochemical limit for reagents with dissociative RCl⁻ ions.^{10a} The λ_{min} values of the XeCl(B-X) spectra from several chlorine-containing molecule reactions are close to the true bond energies, e.g., Cl₂, CCl₄, and COCl₂.¹⁰ The estimate for D_0 (Cl-NFCl) from Figure 2 is close to the N-Cl bond energy of several other molecules that were determined by the same method, but using Hg(³P₂) atom reactions;¹¹ $D_0(CF_3NCl-Cl) \leq$ 56, $D_0(CF_2CINCI-CI) \le 57$, $D_0(CF_2CINF-CI) \le 54$, and D_0 - $(CF_2N-Cl) \leq 56 \text{ kcal mol}^{-1}.$

In order to find $\Delta H_{f}^{\circ}_{0}$ (NFCl) an estimate for D₀(Cl-NF) is needed. Comparison of the N-Cl bond energies in NCl₃ and NCl₂ (estimated to be 31.7 and 35.6 kcal mol⁻¹)¹⁴ implies that D_0 (Cl-NFCl) will be less than D_0 (Cl-NF). This trend is consistent with the successive bond energies¹⁵ in NF₃, which are 59, 63, and 76 kcal mol⁻¹. The $\Delta H_{f_0}^{\circ}(NF)$ seems to be reasonably well established by the lastest calculations^{15b} as 55 kcal mol-1, which corresponds to $D_0(N-F) = 76.0$ kcal mol⁻¹. Therefore, $D_0(Cl-NF)$ was assumed to be 4 kcal mol⁻¹ larger than $D_0(Cl-$ NFCl), which was set as ≤ 52.7 kcal mol⁻¹ from reaction 1. From this assumption and $\Delta H_{f}^{\circ}_{0}(NF)$, $\Delta H_{f}^{\circ}_{0}(NFC)$ was calculated to be 27 kcal mol⁻¹. $\Delta H_f^{\circ}(NCl)$ is less certain than $\Delta H_f^{\circ}(NF)$. Clyne and co-workers¹⁴ estimated a value of 65.3 kcal mol⁻¹, which corresponds to $D_0(N-Cl) = 75.8 \text{ kcal mol}^{-1}$. This seems too high, since $D_0(NCl)$ should be less than $D_0(NF)$. Bettendorff and Peyerimhoff¹⁶ calculated the NF and NCl bond dissociation energies, and their value for NF is 7.7 kcal mol⁻¹ lower than the more recent calculation.^{15b} Scaling their NCl result (65.7 kcal mol⁻¹) in a similar way gives $D_0(NCl) = \sim 73$ kcal mol⁻¹ and $\Delta H_{\rm f}^{\rm o}{}_0(\rm NCl) \sim 69 \ \rm kcal \ mol^{-1}$. $D_0(\rm F-NCl)$ is 60 kcal $\rm mol^{-1}$ for $\Delta H_f^{\circ}(NCl) = 69$ kcal mol⁻¹, which compares favorably with $D(NF-F) = 63 \text{ kcal mol}^{-1}$. If Perimhoff's calculation is not scaled, $\Delta H_f^{\circ}(NCl) = 76 \text{ kcal mol}^{-1} \text{ and } D_0(F-NCl) \text{ is 66 kcal mol}^{-1}.$ We have used $\Delta H_1^{\circ}(NCl) = 74 \text{ kcal mol}^{-1}$ with $T_0(NCl(a))$ and $T_0(NCl(b))^{17}$ values of 26.5 and 43.0 kcal mol⁻¹, respectively, to evaluate the enthalpies of reaction. From the above estimates, the uncertainty in the $D_0(NCl)$ and $D_0(NFCl)$ values seems to be about ± 6 kcal mol⁻¹.

With the above thermochemical data and the accepted $\Delta H_f^{\circ}_0$ values¹⁵ (in kcal mol⁻¹) for H(51.6), Cl(28.6), HF(-65.1), and HCl(-22.0), the enthalpy changes (in kcal mol⁻¹) for the reactions are summarized below.

$$H + Cl_2 \rightarrow HCl + Cl \quad (-45) \tag{2}$$

$$H + NFCl_2 \rightarrow HCl + NFCl \quad (-49) \tag{3}$$

Reaction 3 is followed by the possible secondary reactions 4a to 5b, which are written as proceeding via the ground singlet HNFCl molecule.

$$H + NFCI \rightarrow HNFCI^* \rightarrow HF + NCl(X^3\Sigma^{-}) (-70)$$
 (4a)

$$\rightarrow$$
 HCl + NF(X³ Σ^{-}) (-47) (4b)

$$\rightarrow$$
 HF + NCl(a¹ Δ ; b¹ Σ ⁺)

$$(-43; -27)$$
 (5a)
 \rightarrow HCl + NF(a¹ Δ ; b¹ Σ ⁺)

The absolute ΔH°_{0} values for (4a) and (4b) or (5a) and (5b) depend upon the $\Delta H_{f}^{\circ}(NFCl)$; but the uncertainty in the difference of the enthalpies for these pairs of reactions depends only on the uncertainty in $\Delta H_{f_0}^{\circ}(NCl)$, since $\Delta H_{f_0}^{\circ}(NF)$ is established. The difference in enthalpies between (5a) and (5b) is even larger than for (4a) and (4b) because $T_0(NCl(a)) < T_0$ -(NF(a)). Even relatively large changes in $\Delta H_f^{\circ}(NCl)$ would not change the energy ordering of the products because of the large difference in bond energies of HCl and HF and the similarities of D_0 (F-NCl) and D_0 (Cl-NF). In principle, reactions 4a and 4b could be distinguished from (5a) and (5b), respectively, by the vibrational energy released to HF(v) or HCl(v). The dynamical details associated with crossing to the triplet potentials during transversal of the single exit channels with formation of either NF(X) or NCl(X) remains to be discussed, as does the separate question of direct abstraction pathways on singlet or triplet potentials.

The activation energies for the reverse reactions to (5a) and (5b) are not well established, but the 300 K rate constant for quenching of NF(a) by HCl is only 1.6×10^{-15} cm³ s⁻¹, so there is an appreciable energy barrier.¹³ The energy barrier for quenching of NCl(a) by HF probably is even larger. Therefore, we expect the threshold energies, E_0^{\dagger} , to be substantially larger than the enthalpies for the unimolecular decomposition of HNFCl. The $D_0(H-NFC)$ probably is in excess of 100 kcal mol⁻¹ and the enthalpies for formation of NCl(a) and NF(a) from HNFCl must be ~ 57 and ~ 86 kcal mol⁻¹, respectively. Although estimation of the activation energies for NF(a) + HCl and NCl(a) + HF is not possible, the 30 kcal mol⁻¹ difference in the enthalpies probably leads to a comparable difference in the E_0^{\dagger} values. Thus, the unimolecular decomposition of HNFCl via singlet channels should favor the formation of HF + NCl(a). This expectation from for the unimolecular reaction of HNFCl does not agree with the experimental observations, vide infra, which show that the NF(a) product is more important than the NCl(a) product. A singlet Cl-atom abstraction pathway probably needs to be included in the reaction mechanism in addition to the unimolecular elimination step written for (5b); these two mechanisms are implied by the solid lines starting from H + NFCl in Figure 1.

The primary and secondary reactions for the H + NF₂Cl reaction system are given by (6) and (7). According to some older thermochemical data,¹⁸ $\Delta H_f^{\circ}(NF_2Cl) = 0 \pm 5$ kcal mol⁻¹ and ΔH°_0 for (6) must be ~60 kcal mol⁻¹.

The $H + NFCl_2$ and H + NFCl Reactions

$$H + NF_2Cl \rightarrow HCl + NF_2 (\sim -60)$$
 (6)

$$H + NF_2 \rightarrow HNF_2^* \rightarrow HF + NF(X^3\Sigma^-) (-72.4)$$
 (7a)

→ HF + NF(
$$a^{1}\Delta, b^{1}\Sigma^{+}$$
)
(-39.7, -18.4) (7b)

The H + NF₂ reaction has been thoroughly studied²⁻⁴ and gives almost entirely NF(a¹ Δ). Although the HF(v) distribution is well established, new interpretations about the energy disposal are needed because the $-\Delta H^{\circ}_{0}$ has increased from 34 to 39.7 kcal mol⁻¹.

The average energy available to the products is given by $\langle E \rangle$ = $\Delta H_0^{\circ} + E_a + 3RT$. The rate constants for reactions 3 and 6 are similar to that of H + Cl₂, so we used the E_a for reaction 2,¹⁹ which is 1.2 kcal mol⁻¹. The E_a for (4) and (5) was taken as 2 kcal mol⁻¹. The 3RT is an estimate for the average thermal energy of the collision pair. The $\langle E \rangle$ values are summarized in Tables 2 and 4.

2. HCl(r) Distributions and Formation Rate Constant from the Primary Reactions. Only HCl(v) emission was observed from the $H + NFCl_2$ and NF_2Cl reactions for experiments with the highest flow speed, corresponding to a reaction time, Δt , of 0.2 ms, implying that Cl abstraction is the only primary reaction pathway at 300 K. This is expected because no reaction can be observed from NF₃ even for very high $[H_2]$ and large Δt . The [H₂] and reagent concentrations were varied in order to obtain representative HCl(v) vibrational distributions. Figure 3 shows that the HCl(v) distribution did not change as the [NFCl₂] was varied from 7×10^{11} to 25×10^{11} molecules cm⁻³ for [H₂] = 2.7 $\times 10^{13}$ atoms cm⁻³. Some experiments were done for a factor of 2 lower $[H_2]$, and the HCl(v) distribution was nearly the same. The average HCl(v) distribution from several experiments with this sample of NFCl₂ was $P_1 - P_4 = 22:40:30:8$. The NFCl₂ sample was specifically checked for Cl₂ impurity by taking the UV spectrum before the NFCl₂/Ar mixture was prepared; there was no Cl₂ detected in the sample. The NFCl₂ flow was replaced by a Cl_2 flow and the HCl(v) distribution was obtained from the H + Cl₂ reaction. The result was $P_1 - P_4 = 17:43:35:5$ for [H₂] = 1.3×10^{13} cm⁻³. This distribution is close, but not identical, to the accepted H + Cl_2 distribution^{12a} in the literature, which is $13 \pm 2:39 \pm 2:40 \pm 2:8 \pm 2$. The HCl(v) distribution is sensitive to the [H], because of the fast H atom exchange reaction with vibrationally excited HCl, and the rather high [H] has caused a minor amount of relaxation from v = 3 and 4 into 1 and 2. Thus, the observed HCl(v) distribution from $NFCl_2$ also may have experienced a small amount of relaxation. [See note added in proof for the best HCl(v) distribution.]

The results from a second set of experiments with an independently prepared sample of NFCl₂ are shown in Table 1. This sample of NFCl₂ was also free of Cl_2 impurity, as shown by the UV spectrum taken just before preparing the mixture with Ar. The data for 0.19 ms reaction time in Table 1 agree with the HCl(v) distribution from the first set of experiments. The overall average $P_1 - P_4$ distribution from NFCl₂ is given in Table 2. The HCl(v) distributions from several other Cl atom abstraction reactions are summarized in Table 2 for comparison; all the HCl(v) distributions are sharply inverted usually with a maximum population in v = 2, 3, or 4. The HCl(v) distributions from $CINO_2$ and CINO extend to higher v because of the larger excergicity, but the $\langle f_v \rangle$ values for all the reactions in Table 2 are similar. Since vibrational surprisal plots are nonlinear for this class of H atom reactions,²⁰ extrapolation of a surprisal plot is not an acceptable way to estimated P_0 . However, the P_0 contribution from NFCl₂ probably is not negligible, and we estimate P_0 as $\sim 1/2P_1$ from the variation of the vibrational distribution with v level.



Figure 3. Plot of the HCl(v) distribution from the H + NFCl₂ reaction vs. [NFCl₂]. The [H₂] was 2.7×10^{13} molecules cm³, the Ar pressure was 0.9 Torr, and Δt was 0.3 ms.



Figure 4. Plot of the HCl(v) relative concentrations from the H + Cl₂ and H + NFCl₂ reactions vs reagent concentration. The [H₂] was 1.7 × 10¹³ molecules cm⁻³, the Ar pressure was 0.5 Torr, and Δt was 0.2 ms.

Much less effort was spent on the NF₂Cl system because of the limited sample, but the HCl(v) distribution from one set of experiments was $P_1-P_4 = 19:40:29:10$. The distribution declines rapidly on the low v side and we estimated $P_0 = 1/_2P_1$, which gives $\langle f_v \rangle \approx 0.30$. The similarity of the HCl(v) distributions from the primary reactions is evidence that the N-Cl bond energies in NFCl₂ and NF₂Cl are about the same. This NF₂Cl sample may have had a small contamination from Cl₂ impurity and these data are not as reliable as the results for NFCl₂. Nevertheless, HF(v) emission was easily observed from reaction 7b when the reaction time was increased by a factor of 2 and the sample consisted mainly of NF₂Cl.

The HCl formation rate constant for (3) was obtained by comparing the HCl(v) emission intensity from the H + $NFCl_2$ reaction to that from the $H + Cl_2$ reaction under the same experimental conditions; i.e., the total HCl intensity from the two reactions were compared for the same $[H_2]$ and reaction time. The relative HCl(v) concentrations from the two reactions are plotted vs [reagent] in Figure 4. The slopes of the linear first order plots are proportional to the respective rate constants. The rate constant $(k_{Cl_2} = 2.06 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1})^{19}$ for the H + Cl₂ reaction at 300 K then was combined with the ratio of the slopes to calculate the HCl formation rate constant from $H + NFCl_2$, and the ratio of slopes gives $k_3 = (1.9 \pm 0.4) \times 10^{-11}$ cm³ s⁻¹. The main uncertainty in this rate constant measurement is the sample purity. If there was some Cl₂ contamintion, the data from Figure 4 would give an upper limit to the rate constant for (3). The rate constant is compared to those for ClNO₂, ClNO, and Cl₂O in Table 2; all rate constants are $\sim 2 \times 10^{-11}$ cm³ s⁻¹ except for Cl₂O, which is larger. No attempt was made to determine the HCl formation rate constant for the NF₂Cl reaction, but the

TABLE 1: HF(v) an	d HCl(v) Distribution	s for the H + N	IFCl ₂ Reaction System
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						oution, P _v					
reagent (10 ¹² molecules cm ⁻³)		[H-]		reaction	HCl(v)				HF(v) ^a		
[NFCl ₂]	[Cl ₂]	$(10^{13} \text{ molecules cm}^{-3})$	P (Torr)	time (ms)	$\overline{v_1}$	<i>v</i> ₂	v3	<i>U</i> 4	$\overline{v_1}^a$	v2	<i>v</i> 3
1.8		1.7	0.46	0.19	21	39	31	9	_	_	_
2.2		1.7	0.46	0.19	19	42	31	8	-	-	-
2.5		1.7	0.46	0.19	21	42	31	6	-	-	-
0.9		4.9	1.0	0.68	35	36	21	8	56	30	14
0.9		7.4	1.0	0.68	36	37	20	8	57	31	12
0.9		8.5	1.0	0.68	35	37	20	8	56	33	11
6.1		2.4	0.65	0.27	29	40	25	6	59	31	10
	3.1	1.7	0.46	0.19	17	46	32	5	-	_	-
	4.2	1.7	0.46	0.19	17	44	32	6	-	_	-
	4.8	1.7	0.46	0.19	18	44	32	5	-		_

^a The ratio of the J = 8-17 to 300 K Boltzmann populations for HF(v=1) was 0.11; there also was a trace of high J population for HF(v=2).

TABLE 2: Summary of HCl(v) Distributions^a

					·			
reagent $\langle E \rangle^b$	P ₁	P_2	<i>P</i> ₃	<i>P</i> ₄	P 5	P ₆	$\langle f_v \rangle$	k°
Cl ₂ (48)	13	39	40	8	_		0.37	2.06
NFCl ₂ (53)	20	41	31	8	-		0.31ª	1.9 ± 0.4
$NF_2Cl(\sim 60)$	19	40	29	10	_		~0.30ª	-
Cl ₂ O ^d (72)	9	28	41	19	3		0.32	6.4 ± 1.5
CINO ⁴ (68)	5	9	19	27	24	130	0.50	1.9 ± 0.8
CINO (73)	7	14	28	32	19	trace	0.40	2.3 ± 0.3

^a For most of these reactions P_0 can be taken as negligible; however, P_0 is estimated as $\sim^{1}/_2P_1$ for NFCl₂ and NF₂Cl. The steady-state distributions for NFCl₂ and NF₂Cl may be slightly relaxed from the nascent distributions, see note added in proof for the best distribution. ^b The available energy, $\langle E \rangle = -\Delta H^{\circ}_0 + E_a + 3RT$. ^c The rate constant for Cl₂ has been directly measured (ref 19); the other values were measured by comparison to H + Cl₂. The units are 10⁻¹¹ cm³ s⁻¹. ^d Reference 12a. ^e There also is a small population in v = 7 ($P_7 = 3$). ^f Reference 20.

emission intensity was roughly comparable to that from NFCl₂, and the rate constants must be equal to within a factor of ~ 2 .

3. HF(v) Distribution and Formation Rate Constant from the Secondary Reaction. In order to observe the HF emission, the reaction time was increased to ≥ 0.3 ms and the [H₂] was increased to $(3-8) \times 10^{13}$ molecules cm⁻³. The HF(v) distributions observed for the secondary reaction from the second set of NFCl₂ experiments are summarized in Table 1. When the reaction time was >0.3 ms with high [NFCl₂], the HCl(v) distribution had an enhanced contribution from v = 1 relative to experiments with the shorter reaction times for which no HF emission could be observed. For the longest reaction time, 0.68 ms, the HCl(v)distribution was $P_1 - P_4 = 35:37:20:8$. However, the HF(v) distributions did not change appreciably for the whole series of experiments. One comparison experiment was done with H + CF₃ (from CF₃I) for $\Delta t = 0.68$ ms. The observed HF(v) distribution was the same as the nascent HF(v) distribution reported from an earlier extensive study of H + CF₃.^{6a} Thus, the HF(v) distribution assigned to reaction 5a should not be vibrationally relaxed. The average HF(v) distribution from all experiments in Table 1 was $P_1 - P_3 = 57:31:12$. There also was a trace of emission from HF(v = 4) in accord with the thermochemistry for reaction 5a giving NCl(a), which just permits formation of HF(v = 4). Emission was observed from high rotational levels, J = 8-17, of HF(v = 1); the ratio of the high to low J population was 0.11. Very weak emission also was observed from the J = 8-14 levels from HF(v = 2). The HF(v, high J) component from H + NFCl is similar to that from the three-centered HF elimination from HCF3 generated by H + CF_{3} .^{6a} The HF(v) emission also was observed from the experiments with the first preparation of $NFCl_2$; the HF(v) distribution was the same as for the data in Table 1.

In order to confirm that HF is formed in the secondary reaction of H + NFCl, rather than from the primary reaction, the HCl and HF intensities were compared as the $[H_2]$ or [H] was increased. As can be seen from Table 3, the HF intensity increases almost twice as much as the HCl intensity, when the $[H_2]$ was

TABLE 3: Comparison of the [HCl]/[HF] Ratio vs [H]

	[HCl]/[HF]				
[H ₂] ^a (10 ¹³ molecules cm ⁻³)	expt1 ^b	simulation			
4.9	9.9	10.4			
7.4	7.2	6.8			
8.5	5.9	5.9			

^a The [H] was assumed to be equal to $[H_2]$ for the calculations. The [NFCl₂] was 9.0 × 10¹¹ molecules cm⁻³. ^b These data are the same as in Table 1, except that the $P_0(HF)$ from the linear surprisal plot was added to the experimentally observed [HF(v=1-3)] concentration to obtain the total [HF]. ^c Calculated for k_3 and k_{5a} equal to 1.9 × 10⁻¹¹ and 0.9 × 10⁻¹¹ cm³ s⁻¹, respectively, for a reaction time of 0.68 ms.

increased from 4.9×10^{13} to 8.5×10^{13} cm⁻³. The higher order dependence on [H] confirms that HF(v) is formed by a secondary reaction. Ideally the [HF(v)]/[HCl(v)] ratio should scale linearly with [H]; but the dissociation efficiency of the microwave discharge may not be constant in this high [H₂] concentration range, and we are not confident that the [H] is a constant fraction of [H₂]. The HF(v) vibrational distribution is consistent with NCl(a) being the other product in accord with the thermochemistry of reaction 5a.

The HCl(v) distribution relaxes more readily with increased [H] and reaction time than does the HF(v) distribution. Therefore, separating the possible contribution of reaction 5b, which gives HCl(v = 0,1) from relaxation of the nascent HCl(v)distribution from reaction 3 is impossible. Based upon comparisons with the HCl(v) distribution from the $H + Cl_2$ reaction as Δt and [H] are increased, some of the increase in the HCl(v =1) population shown in Table 1 must be from relaxation of the HCl(v) distributions from reaction 3. However, since the ratio of HF/HCl Einstein coefficients^{12c} for the $\Delta v = -1$ transitions is \sim 5, the data in Table 1 do not exclude a contribution from reaction 5b to the observed HCl(v) yield. A more precise probe for (4b) or (5b) is to measure the formation of NF(X) or NF(a)and this is addressed in the next section. Since emission from high v levels of HCl was not observed, the contribution from reaction 4b must be very small.

The declining HF(v) populations with increasing f_v imply that HF(v = 0) is the most important level in the distribution. In order to estimate HF(v = 0), we did a surprisal analysis with the vibrational prior distribution, $P^0(f_v)$, calculated using the full statistical model^{6a} for the HF and NCl(a) products. Figure 5 shows the vibrational surprisal plots for H + NF₂ and H + NFCl. Extrapolation of the linear plot ($\lambda_v = -2.9 \pm 0.1$) for H + NFCl to $f_v = 0$ gives P_0 , and the overall normalized distribution is P_0-P_4 = 42:34:19:6:trace. The $\langle f_v \rangle$ for this distribution is 0.21, which is typical of unimolecular HF elimination reactions that release a small amount of potential energy in the exit channel. The HF(v) distribution taken from ref 2 and summarized in Table 4 for H + NF₂ also fits a linear surprisal with $P_0-P_3 = 57:32:9:2$,



Figure 5. Surprisal plots for the HF(v) distributions from the $H + NF_2$ and H + NFCI reactions. The full statistical model with conservation of energy was used to calculate the prior distribution, $P^0(f_p)$, for forming HF + NF(a) or NCl(a). The $H + NF_2$ data are from ref 2, and the H+ NFCI data are from this work.

TABLE 4: Comparison of HF(r) Distribution fromElimination Reactions^a

molecule $(\langle E \rangle)^b$	P ₀	P ₁	<i>P</i> ₂	P 3	<i>P</i> ₄	$\langle f_v \rangle$	λυ
HNFCI (47)	42	34	19	6	trace	0.21	-2.9 € 0.1
HNF ₂ (44)	57	32	9	2	-	0.14	-1.4 ± 0.5
CF ₃ H ^d (52)	50	29	15	5	1	0.16	-5.1
CFHCl2 ^d (69)	37	30	14	11	5	0.14	-3.2
CFH2Cl4 (47)	44	34	15	5	2	0.15	-3.5

^a P_0 was obtained from extrapolation of linear surprisal plots for each case. ^b This is the available energy in kcal mol⁻¹ $\langle E \rangle = -\Delta H^o_0 + E_a + nRT$; E_a was taken as 2 kcal mol⁻¹ for H + NFCl and H + NF₂. ^c Using $\Delta H_1^{o_0}$ (NF₂) = 55 kcal mol⁻¹ and experimental data from ref 2; the rate constant for HF formation, adjusted to the P_0 given here, is 0.9×10^{-11} cm³ s⁻¹, rather than 1.3×10^{-11} cm³ s⁻¹. The value from ref 3 is $(1.5 \pm 0.2) \times 10^{-11}$ cm³ s⁻¹. ^d From ref 6a.

 $\lambda_v = 1.4 \pm 0.5$ and $\langle f_v \rangle = 0.14$ based on $\Delta H_{\rm f}^{\circ}_0(\rm NF) = 55$ kcal mol⁻¹. The exact values of λ_v are rather sensitive to the choice for $\langle E \rangle$.

In order to estimate the HF formation rate constant from the H + NFCl reaction, numerical integration of the rate equations were performed for reactions 3 and 5a. The previously determined rate constant, 1.9×10^{-11} cm³ s⁻¹, was employed for reaction 3. [NFCl₂] was fixed as 9.0×10^{11} molecules cm⁻³ and [H] was 4.9 \times 10¹³, 7.4 \times 10¹³, and 8.5 \times 10¹³ molecules cm⁻³. The rate constant for reaction k_{5a} was adjusted to make the calculated product ratio, [HCl(v = 0-4)]/[HF(v = 0-3)], match the experimental value. The contribution of P_0 to the total [HF(v)] was obtained from the surprisal analysis. Table 3 gives the comparison of the calculated concentration ratio with the experimental results for each [H]. In this way, we obtained an estimate for the rate constant, 8.7×10^{-12} cm³ s⁻¹, for (5a). The calculations showed that a change in the primary reaction rate constant, k_3 , did not seriously affect the value for k_{5a} . The simulated rate constant k_{5a} ranged only from 8.7×10^{-12} to 9.5 \times 10⁻¹² cm³ s⁻¹ when k₃ was changed from 1.8 \times 10⁻¹¹ to 6.2 \times 10^{-11} cm³ s⁻¹; this is expected since the analytic prediction (for constant [H] during the time Δt) is given by [HF]/[HCl] \simeq $(1/2)k_{5a}[H]\Delta t$, where Δt is the reaction time. On the basis of the experimental, [HF]/[HCl], [H] and Δt , we obtained k_{5a} = 6.8×10^{-12} cm³ s⁻¹ from the analytic expression, which is in agreement with the above calculated value. The greatest uncertainty in the assignment of k_{5a} is the assumption of 50% dissociation of H_2 , which has been confirmed; see note added in proof. Since the fractional dissociation of H₂ was not measured in this set of experiments, the absolute value of the rate constant could be in error by a factor of 2.

One experiment was done with high [H] and $\Delta t = 0.4$ ms for the H + NF₂Cl reaction. The HF emission from the H + NF₂ secondary reaction was observed, but not studied in detail. The



Figure 6. Comparison of the NF(a-X) and HF(3-0) emission spectra from the reaction of H + NFCl₂ for a reaction time of 0.8 ms. The scale for the HF(3-0) bands has been expanded by a factor of 10.

indications were that the HF(v) distribution was the same as from the Malins and Setser² study of $H + NF_2$.

 Comparison of NF(a-X) and HF(3-0) Emission Intensities. Since the infrared emission data cannot provide any useful information about the HCl(v) + NF(a) channel, other methods are required to obtain a better measure of the product channels from the H + NFCl reaction. The possibilities are to compare the NF(a) concentration to either the NCl(a) or HF(v) concentrations. Coombe and co-workers⁸ compared the NF(a-X) and the NCl(a-X) emission intensities. This is a difficult experiment because of the need to calibrate the response of a detector at 850 and 1150 nm and because the Einstein coefficient for the NCl(a-X) transition is not well established. Since we now know that HF(v = 3) is a product from (5b), we decided to compare the HF(3-0) and NF(a-X) emission intensities. Both emissions are in the 850-nm region and can be observed with a GaAs type photomultiplier tube; the variation of the response with wavelength of the detection system was calibrated using the HF(3-0) band generated from the F + C₂H₆ reaction. These experiments were done in the smaller reactor with a flow velocity of 50 m s⁻¹. Our general observations closely parallel those of Coombe,⁸ and we easily observed the NCl(b-X), NF(b-X), and NF(a-X) emission after a reaction time of ~ 1 ms. The NF-(a-X) emissions were present at the shortest reaction time and NF(a) must be directly formed; it cannot result from an energytransfer process involving NF(X). Although the NCl(b) also was present at the shortest observation time, the [NCl(b)] grows with time and it is not directly formed by the H + NFCl reaction. The integrated intensity ratio for NCl(b-X)/NF(a-X) was 0.3 for a reaction time of 1 ms. For a 2.5-ms lifetime of $NCl(b)^{21}$ and 6.7-s lifetime of NF(a),¹³ the concentration ratio is $\sim 1 \times$ 10⁻⁴, and NCl(b) is a very minor component of the H + NFClsystem.

The NF(a-X) and HF(3-0) emission both could be observed at 1 ms reaction time for $[H_2] \approx 2 \times 10^{13} \text{ cm}^{-3}$ and $[\text{NFCl}_2] =$ $1 \times 10^{12} \text{ cm}^3$ molecule⁻¹s⁻¹. The HF(3-0) emission was extremely weak (see Figure 6), but the P_0 , P_1 , P_2 , and P_3 transitions were observed. Integration of the band areas and utilization of the known Einstein coefficients for NF and HF(3-0) and Boltzmann factors for HF(v = 3,J) gave [HF(v = 3)]/[NF(a)] ratios of 0.020, 0.016, and 0.021 from three independent spectra. These ratios are lower limits to the nascent ratio, since there may have been some vibrational relaxation of HF(v = 3). Since HF(v =3) is only 6% of the HF(v) distribution, the total [HF]/[NF(a)] ratio seems to be ~0.3. Thus, our data do generally agree with the earlier study that compared the NF(a-X) and NCl(a-X) intensities, and the NF(a) channel is more important than the NCl(a) channel. However, our ratio of ~ 0.3 is larger than the previous measurement, which gave a ratio of 0.1. The infrared spectrum of the original NFCl₂ sample showed that NF₂Cl was not present, and the H + NFCl reaction must have been the source of NF(a).

Discussion

1. Chlorine Atom Abstraction from NFCl₂ and NF₂Cl. The energy disposal to HCl(v) from the reactions of H with $NFCl_2$ (and NF₂Cl) is as expected for direct Cl atom abstraction by H atoms on a repulsive potential surface, and the HCl formation rate constant, $(1.9 \pm 0.4) \times 10^{-11}$ cm³ s⁻¹, is close to the values for Cl₂, ClNO, and ClNO₂. The greatest uncertainty in the rate constant measurement is the sample purity, and the rate constant could be somewhat smaller, if the reacting sample contained appreciable Cl_2 (there was no Cl_2 in the prepared sample). The $\langle f_v \rangle$ value of 0.31 (for $D_0(\text{Cl-NFCl}) = 52.7 \text{ kcal mol}^{-1}$) and the shape of the distribution fit the pattern for several other wellestablished Cl atom abstraction reactions, some of which even involve the N-Cl bond. Based upon the small degree of vibrational relaxation of the H + Cl_2 distribution, the nascent HCl(v)distribution from $H + NFCl_2$ may have slightly enhanced populations for v = 3 and 4 and slightly reduced populations for v = 1 and 2, relative to the observed distribution. The utilization of higher [H] in order to compensate for the small sample of NFCl₂ is responsible for the small degree of relaxation. The narrow, inverted HCl(v) distribution from these Cl atom abstraction reactions is a consequence of the momentum constraint imposed by the light mass of the attacking H atom on a repulsive surface.^{22,12a} The $\langle E_R(HCl) \rangle$ is low for this class of H atom reactions and the remaining energy is mainly released as translational energy of the products. Our estimates for $D_0(Cl NF_2$) and $D_0(Cl-NFCl)$ should be close enough to the true values that the uncertainties do not affect the broad conclusion about energy disposal to HCl(v).

Note Added in Proof. A third set of experiments was done with higher concentrations of NFCl₂ (1.5×10^{13} cm⁻³) and lower concentrations of H₂ (8×10^{12} cm⁻³) with $\Delta t = 0.24$ ms in order to obtain a better measure of the nascent HCl(v) distribution from the H + NFCl₂ reaction. The experimental distribution was P₁-P₄ = 22:35:30:13, which corresponds to $\langle f_{o} \rangle = 0.32$ for an estimate of P₀ giving P₀-P₄ = 9:20:32:27:12. For these reaction conditions the observed distribution from H + Cl₂ agreed with the accepted nascent distribution. The fractional dissociation of H₂ also was measured to be 50% using the same method as that given in ref 12a, which confirms the [H] assumed in the text.

Since only the Cl atom is removed by the H atom reactions at 300 K, the NF₂Cl and NFCl₂ molecules could serve as chemical sources of NF₂ and NFCl radicals in flow reactors, if convenient preparations for larger amounts of pure materials could be developed. The third member of the series, NCl₃, can provide a source of NCl₂ radicals.⁵

2. The H + NFCl Reaction. The rate constant for HF + NF(a) formation²⁻⁴ from the H + NF₂ reaction, $(1.3 \pm 0.3) \times$ 10^{-11} cm³ s⁻¹ (see footnote c in Table 4), is the same, within the combined experimental uncertainties, as the rate constant for HF formation, 0.87×10^{-11} cm³ s⁻¹, from H + NFCl. The somewhat higher population in HF(v = 3) and the trace population in HF(v = 4) from H + NFCl are in accord with the larger available energy for H + NFCl, relative to $H + NF_2$, and the true $\langle E \rangle$ for the former may be somewhat larger than 47 kcal mol⁻¹. This conclusion implies that $D_0(F-NCl)$ is $\leq 66 \text{ kcal mol}^{-1}$. With the change in the $\Delta H_{f_0}(NF)$, the available energy for H + NF₂ is now 44 kcal mol⁻¹ and the surprisal plot for the data of ref 2 is more nearly linear with $\lambda_v = -1.4$ and $\langle f_v \rangle = 0.14$. The surprisal plot for H + NFCl has a larger slope ($\lambda_v = -2.9$) and larger $\langle f_v(HF) \rangle$ (0.21) than for H + NF₂. The surprisal plots (and the extrapolation to $f_v = 0$) are sensitive to $\langle E \rangle$, and more

detailed dynamical interpretations require better knowledge of the thermochemistry. The energy release pattern is consistent with results for three-centered HF elimination from CF₃H and other halogenated methanes.^{6,7} We conclude that recombination of H and NFCl followed by unimolecular HF elimination on the singlet potential giving NCl(a) is one of the important product channels for the H + NFCl reaction. On the basis of the higher (by ~30 kcal mol⁻¹) enthalpy of reaction and the similar expectation for the E_0^* value for HCl elimination, reaction 5b is not expected to be competitive with (5a). Despite this conclusion, formation of NF(a) + HCl is an important product channel, and another mechanism is needed to provide an explanation. We found no emission from high v levels of HF or HCl that would suggest the importance of reaction 4a or 4b.

Our comparison of NF(a-X) and HF(3-0) emission intensities gave a ratio for NF(a)/NCl(a) formation of \sim 3.3. The earlier measurement of the Denver group gave ~ 10 based upon comparing the NF(a-X) and NCl(a-X) intensities. On the basis of the estimated rate constant for formation of NCl(a) + HF and the ratio mentioned above, the total rate constant for H + NFCl must be $\sim 4 \times 10^{-11}$ cm³ s⁻¹. This value, which ultimately is based upon comparing the HCl(v) from reaction 3 to the HF(v)yield from (5a) together with the rate constant for (3) and the [H], probably is an upper limit value. However, numerical integration of the relevant rate equations with the two recommended rate constants and the branching ratio gave agreement with the observed time dependence for formation of NF(a) in the small reactor.²¹ The small rate constant $(2.6 \pm 0.2) \times 10^{-12} \text{ cm}^3$ s^{-1}) inferred⁸ from monitoring the decay of the NCl(b) concentration previously was associated with a rate-limiting step that was thought to be either reaction 3 or reaction 5. Our new data give much larger rate constants for the primary and secondary reactions, and the explanation for the decay rate of NCl(b), which was also observed in this study, will require additional kinetic measurements, including a reliable NCl(b) radiative lifetime.²¹ As already noted, the NCl(b) concentration is about 10⁻⁴ of the NF(a) concentration.

Formation of NF(a) from H + NFCl releases ~ 14 kcal mol⁻¹, which only can give $HCl(v \leq 1)$. This is consistent with the HClemission observed under conditions such that the H + NFClreaction was taking place. The absence of any enhancement for $HCl(v \ge 4)$ under these conditions suggests that NF(X) was not formed. On the basis of electronegativity arguments, the unpaired electron in the π -type orbital of NFCl will have considerable density on Cl, as well as on N. Possibly a favorable configuration exists on the singlet potential that begins with the coordination of H to the Cl end of NFCl. This geometry, HCl-NF, may not correspond to a true local minimum, but rather the structure may evolve directly to HCl + NF(a) like an abstraction process. This suggestion needs to be tested by ab initio calculations of the potential. Such a H atom + radical interaction on the singlet potential would be somewhat analogous to the reactions of H with CIO radical, which has the electron in a π -orbital.²³ The dissociation of HOCl to HO + Cl on the singlet HOCl potential, competes with formation of HCl + $O(^{3}P)$; the latter involves a singlet-triplet potential crossing from the HClO configuration in the exit channel.

Summary

The 300 K reaction of H atoms with NFCl₂ proceeds by direct abstraction to give an inverted HCl(v) distribution with $(f_{\rm p}({\rm HCl}))$ = 0.32 and a rate constant of $(1.9 \pm 0.4) \times 10^{-11}$ cm³ s⁻¹. The secondary reaction between H + NFCl has a rate constant of ~4 × 10⁻¹¹ cm³ s⁻¹ with the NF(a) + HCl products being preferred, even though the thermochemistry strongly favors the NCl(a) + HF channel. The NF(a) + HCl product probably results from the addition of a H atom to the chlorine end of NFCl on the singlet potential, followed by the cleavage of the N–Cl bond. The

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formation of NCl(a) + HF occurs by the more conventional atom recombination pathway involving the N atom center giving HNFCl* followed by unimolecular HF elimination. The energy disposal pattern to HF(v,J) resembles the energy released to HF-(v, J) in the more completely studied three-centered HF elimination reactions from HNF₂ and HCF₃, rather than F atom abstraction. The proposed mechanisms for the interaction of H atoms with NFCl merit additional experimental and theoretical tests. Estimates for $D_0(Cl-NFCl)$, $D_0(Cl-NF)$, and $D_0(NCl)$ are given. The H + NFCl reaction seems to be a good source of NF(a) and NCl(a) radicals in a flow reactor, since the reaction mainly proceeds on singlet potentials.

Acknowledgment. We thank Mr. Rengarajan and Dr. Zhao of the KSU laboratory for assistance with experiments. The work at KSU was supported by the Air Force Office of Scientific Research (and Strategic Defense Initiative), Grant 92-J-0275, and by the National Science Foundation, Grant CHE-9120489. Work at the University of Denver was supported by the National Science Foundation, Grant CHE-9200673, and by the Air Force Office of Scientific Research, Grant AFOSR-90-0259.

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