Infrared chemiluminescence Evidence for adduct formation in the H + CH₂XI reaction and studies of the N + CH₂X (X = Cl/F/I/H) reactions

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Infrared chemiluminescence from a flow reactor has been used to study the H + CH₂XI and N + CH₂X (X = Cl, F, I, H) reactions at 300 K. Both the HI + CH₂Cl and HCl + CH₂I channels were identified for the H + CH₂ClI reaction. The HCl channel involves adduct, HICH₂Cl, formation as confirmed by the D + CH₂ClI reaction, which gave both HCl and DCI products. The nascent HCl(v) distribution from the H + CH₂ClI reaction was P₁–P₅ = 25 : 29 : 26 : 13 : 7. The rate constant for the HCl(v) formation channel is estimated to be 4 times smaller than that for the H + Cl₂ reaction. The highest HCl(v) level observed from the H + CH₂ClI reaction implies that the C–Cl bond energy is 50.2 kJ mol⁻¹ lower than that of the Cl–CH₃ bond, which is in modest agreement with recent theoretical estimates. The H + CH₂FI reaction gave a HF(v) distribution of P₁–P₃ = 77 : 15 : 8. The C–F bond energy in CH₂FI is estimated to be < 460.2 kJ mol⁻¹, based on the highest HF(v) level observed, the upper bound being the same as that of F–CH₃. When N atoms are added to the flow reactor, the HCl(v) emission intensities from CH₂FII increased by up to 2-fold, which is attributed to the N + CH₂ClI → HCl + HCN reaction. Concomitant weak emission from HCN and HNC could also be observed; however, the main product channel is thought to be NCH₂ + Cl. Strong visible CN(A–X) emission was also observed when H/N/CH₂XI were present in the reactor. If the CH₂X radicals were produced by the F + CH₂X reaction in the presence of N atoms, similar results were obtained. The N + CH₂N reaction is proposed as the first step that leads to CN(A) formation with NCN as an intermediate.

I. Introduction

This paper reports the results of infrared chemiluminescence (IRCL) studies of the H + CH₂XI and N + CH₂X (X = Cl/F/I/H) reactions. Our initial interest in the H + CH₂ClI reaction was to use it to produce CH₂Cl in the flow reactor for subsequent studies of the N + CH₂ClI reaction. Iodine atom abstraction reactions by H atoms are usually fast and the N atom reaction could also be an important sink for CH₂ClI. Reversible adduct formation has also been observed for Cl + CH₃I and F + CH₂BrCl. For reactions of H atoms with IX compounds (X = Cl/F), an H migration step following adduct formation has long been recognized. In the present study infrared chemiluminescence from HCl(v) was observed from the H + CH₂ClI reaction, and an adduct seems to facilitate HCl formation. At least two channels are possible:

H + CH₂ClI → HI + CH₂Cl (−104.6) (R1)
H + CH₂ClI → HICH₂Cl → HCl + CH₂I (−108.8) (R2)
→ HI + CH₂Cl  (−104.6) (R1)

The thermochemistry is not well established, but the enthalpies of reaction (in kJ mol⁻¹) based upon our thermochemical estimates, vide infra, are given in parentheses. The HI formation could be either direct or via the adduct, but the HCl formation is thought to proceed only through adduct formation. Direct CI abstraction from chloroalkanes has a large activation barrier and this reaction has not been observed at 300 K in a flow reactor. The D + CH₂ClI and H/D + CH₂FI reactions were also investigated to elucidate the adduct formation mechanism.

Our interest in the N + CH₂Cl reaction arose because of the importance of the N + CH₂Cl reaction in planetary atmospheres and combustion processes. For this reaction, the product channels have been actively discussed.

N (4S) + CH₂(X=Cl) → CH₂N(X=Cl)
CH₂N(X=Cl) + H → CH₂N(X=Cl) + H
→ CH₂N(X=Cl) + H → CH₂N(X=Cl) + H
→ CH₂N(X=Cl) + H → CH₂N(X=Cl) + H
→ CH₂N(X=Cl) + H → CH₂N(X=Cl) + H
→ CH₂N(X=Cl) + H → CH₂N(X=Cl) + H
→ CH₂N(X=Cl) + H → CH₂N(X=Cl) + H

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The N + CH₃ reaction was proposed to account for the presence of HCN in Titan’s atmosphere. However, laboratory studies of this reaction showed that the most exothermic channel, (R4), is not the dominant channel. In fact, the CH₂N + H channel accounts for 90% of the reaction and the HCN + H₂ (or 2H) channel is estimated to contribute ≈ 10%. The HCN can also be formed by the disproportionation reactions, H + CH₂N → HCN + H₂ or N + CH₂N → HCN + NH. The N + CH₃ reaction presumably proceeds by recombination giving the triplet methyl nitrene radical, which then dissociates. The triplet CH₃N radical (X-A₂) requires a spin change to give HCN + H₂. Sadaygov and Yarkony evaluated the intersystem crossing between the CH₂N (X-A₂) and (1A) states and identified a zero-barrier path for (R4). During the course of investigating the IRCL from (R2) and (R8) can both be observed by IRCL, if the products are adducts. If one assumes that the C–H bond energies in CH₃N and CH₂ClN are similar, the enthalpy of reaction for (R7) can be calculated, but no attempt has been made to look for HCN by IRCL from this reaction. HCN infrared chemiluminescence, which is relatively easy to observe, has been used to study the dynamics of several reactions.

It is well known that unimolecular H₂ elimination processes from ground state molecules have high barriers, e.g. 376.6 kJ mol⁻¹ for CH₃SiH₃. Thermal dissociation of C₂H₆ is dominated by C–C bond breaking, but unimolecular HCl elimination, with a barrier of 230.1 kJ mol⁻¹, is the dominant reaction for CH₂CH₂Cl. Could the HCN+HCl channel be more important for the N + CH₂Cl reaction than the HCN + H₂ channel for N + CH₂? By analogy with the N + CH₃ reaction, one could envisage the following steps:

\[
\begin{align*}
N + CH₂Cl & \rightarrow CH₃N + Cl (−242.7) \quad (R6) \\
\rightarrow CHCIN + H & (−167.4?) \quad (R7) \\
\rightarrow HCN + HCl & (−554.4) \quad (R8) \\
\rightarrow HCN + H + Cl & (−126.8) \quad (R9)
\end{align*}
\]

For (R7), the enthalpy of reaction is given with a question mark as there is no experimental or theoretical estimate of the enthalpy of formation of CHCIN. The C–Cl and C–H bond energies in CH₂Cl are nearly the same. However, the C–Cl bond may be weaker than the C–H bond in the NCH₂Cl adduct. If one assumes that the C–H bond energies in CH₃N and CH₂ClN are similar, the enthalpy of reaction for (R7) should be closer to that of (R3) (−167.4 kJ mol⁻¹) and (R7) is certainly less exothermic than (R6). In our experiments, (R6) and (R7) are not directly followed. The HCN and HCl from (R8) can both be observed by IRCL, if the products are vibrationally excited. In the present work, CH₂Cl was added to a flow reactor in which both H and N atoms were present, and the additional infrared chemiluminescence from the N + CH₂Cl reaction was studied in the presence of the H + CH₂Cl reaction. The F + CH₃X reactions were also used as a precursor for CH₂ radicals. Although HCN is a minor product, it was observed, and the HNC formation channel needs to be added to the N + CH₂X mechanism:

\[
\begin{align*}
N + CH₂ & \rightarrow HNC + H₂ (−429.3) \quad (R10) \\
N + CH₂Cl & \rightarrow HNC + HCl (−493.7) \quad (R11)
\end{align*}
\]

During the course of investigating the IRCL from (R2) and (R8), the intense yellow CN(A⁻→X⁻Σ⁺⁺) chemiluminescence was clearly evident whenever CH₂Cl was added to the flow reactor containing both H and N atoms. The same visible emission was observed on adding CH₂Cl to the reactor containing F and N atoms. In fact this CN(A-X) emission was observed for several CH₂XI molecules with H and N atoms and for several CH₂X molecules with F and N atoms. This CN emission has been commonly observed when halogenated hydrocarbons are added to active nitrogen. However, even though investigations spanning four decades, the excitation-mechanism remains poorly characterized. In the present work, the generation of CH₂X radicals in the presence of N atoms, by the F or H atom primary reactions greatly intensifies the CN formation and is also part of the N + CH₂X chemistry. The chemiluminescence in the N + CH₂X reaction system is discussed and related to the proposed CN excitation mechanisms of the early work.

II. Experimental methods

The IRCL apparatus at Kansas State University has been described previously and only the pertinent details associated with the addition of N atoms to the flow reactor are given here. The H/F/N atoms were produced in microwave discharges of H₂, CF₃, and N₂ diluted in Ar carrier gas. The H₂, N₂ and CF₄ were taken directly from tanks. Quartz discharge tubes, treated with phosphoric acid, were used for H₂ and N₂ and an alumina discharge tube was used for CF₄. The atoms were generated at the entrance of the flow reactor (4 cm diameter Pyrex tube), and the CH₂Cl or the other reagent was added 30 cm downstream via a 4-jet inlet. A few experiments were done with CH₄, CH₂Cl, CH₃Br, CH₃I and CH₂I₂ by metering these reagents as gases from the reservoirs. The infrared emission was observed through a NaCl window, which was located 2.5 cm from the reagent inlet. The reaction time between CH₂Cl and the atoms could be varied from 0.2 to 2 ms by varying the pumping speed with a throttling valve. The reagents, CH₂Cl and CH₃F, were introduced to the flow reactor by flowing Ar over the pure liquid kept at 273 K or by flowing the gas from a reservoir containing the liquid and gas in equilibrium. The concentrations of the reagents and the atoms were in the range 10¹⁴ to 10¹⁵ molecules cm⁻³. All the experiments were carried out at room temperature at a pressure in the range 0.6–2.0 Torr. The CH₃F₁ was synthesized by the method described in the literature. The purity of the CH₂F₁ samples was confirmed by GC-MS to be >90%. The CH₂Clᵢ samples were purchased from Aldrich Chemical Company or from TCI America Inc. (>98% pure) and the purity confirmed by NMR spectra. All the reagents were subjected to several freeze–pump–thaw cycles before use.

The infrared chemiluminescence at 2 cm⁻¹ resolution was observed using a Biorad FTS-60 with a liquid-N₂ cooled InSb detector. The HF/DF/HCl/DCl emission spectra were rotationally resolved and the vibrotational distributions were calculated from the peak heights of the P and R branch lines using the Einstein coefficients for the given transition and the instrumental response function. The rotational distribution corresponded to 298 K Boltzmann distribution. The relative vibrational population was obtained by averaging all the P and R branch lines from the same vibrational level. The Einstein coefficients for the (R₂₁, (CH stretch) 1→0 transitions in HCN (77 s⁻¹) and HNC (385 s⁻¹) are much larger than that for HCl (40 s⁻¹), but the HCN/HNC signals were much weaker than that of HCl. The rotational structure of the HCN/HNC spectra was not resolved, and the area under the band was used to estimate the relative [HCN/o].

The CN(A → X) emission was recorded at 1.1 Torr pressure from the F + N + CH₄/CH₂Cl reaction system in a second flow reactor with a reaction time of typically 5 ms. The emission was observed through quartz windows with a 0.5 m monochromator fitted with a cooled S-1 photomultiplier tube. This flow reactor and the spectroscopic detection equipment are described in ref. 43.

III. Results

III.1 Thermochemistry

In order to interpret the IRCL data, accurate thermochemistry is required. If the thermochemistry is unknown, the highest
observed HX(ϵ, J) level can be used to set a lower limit on the enthalpy of reaction. Experimental enthalpies of formation, ΔfH°, are not available for CH2ClI and CH2FI. However, a theoretical ΔfH° is available for the CH2ClI (13 kJ mol⁻¹) calculated at the MP2/3-21 + G(2d,2p) level. The ΔfH° for CH2I calculated at this level was 218.4 kJ mol⁻¹, in close agreement with the experimental value of 217.6 kJ mol⁻¹.

These enthalpies of formation, along with that of Cl (119.62 ± 0.05 kJ mol⁻¹), lead to a C–Cl bond energy of 326.4 kJ mol⁻¹ in CH2ClI compared to 351.5 ± 4.2 for CHClI. Using ΔfH° (HCl, −92.0 ± 0.5 kJ mol⁻¹), the enthalpy of reaction for (R2) is estimated as given below:

\[ \text{H} + \text{CH}_2\text{Cl}_2 \rightarrow \text{HCl} + \text{CH}_2\text{I} \quad (\text{R2}) \]

The average energy available to the products from a reaction is calculated as:

\[ (E) = \Delta H_0 \quad (0 \text{ K}) + E_{\text{th}} + E_a \]

where \( E_a \) is the activation energy for the reaction and \( E_{\text{th}} \) is the thermal energy of the reactants. The activation energy for this reaction has not been measured. However, comparison of HCl(ϵ) emission intensities from reaction (R2) and H + Cl₂ suggest that the rate constant for (R2) (side infra) is 4 times smaller than for the latter reaction. ϵ₁₂, \( E_a \) for (R2) is, probably, higher than that (4.8 kJ mol⁻¹) of H + Cl₂. We take the \( E_a \) to be \( \approx 17 \) kJ mol⁻¹. The thermal energy of CH₂XI at 300 K was calculated to be 12.6 kJ mol⁻¹. Hence, the \( (E) \) for (R2) should be about 133.9 kJ mol⁻¹. This is sufficient to produce HCl(ϵ = 4) from (R2), but the highest observed level is \( ϵ = 5 \). Fig. 1 shows the HCl(ϵ) IRCL spectrum, highlighting unambiguously the lines from \( ϵ = 5 \). The additional energy needed for producing \( ϵ = 5, J = 0 \) is 25.1 kJ mol⁻¹. The rotational distribution observed was thermal Boltzmann and HF(ϵ = 5, J = 0) can be used as the limit. The uncertainty in the theoretical thermochemistry and/or reactive collisions from the high energy tail of the Boltzmann distribution could be the cause of this observation. If HF(ϵ = 5) is used to fix the available energy from (R2), then the C–Cl bond energy in CH₂ClI will be 301.2 kJ mol⁻¹, 25.1 kJ mol⁻¹ less than the theoretical estimate. Inspection of the D(C–Cl) values from several CH₂ClX molecules supports a trend of lower bond energies relative to CH₂ClI.

The HCl (ϵ = 5) emission led us to consider reactions that could take place in the reactor in addition to (R2).

\[ \text{H} + \text{CH}_2\text{Cl} \rightarrow \text{CH}_2\text{Cl}^+ \rightarrow \text{HCl} + \text{CH}_2 \quad (\text{a}^{-1} \text{A}_1) \quad (\text{R12}) \]

\[ \text{CH}_2\text{Cl} + \text{CH}_2\text{Cl} \rightarrow \text{CH}_2\text{CICH}_2\text{Cl}^- \rightarrow \text{HCl} + \text{CH}_2\text{CHCl} \quad (-305.4) \quad (\text{R13}) \]

The asterisk indicates a chemically activated species. Reaction (R12) is thermoneutral and it cannot account for HCl(ϵ) emission. Reaction (R13) could certainly contribute to HCl(ϵ) emission. Kinetic simulation was done with the following steps to determine the importance of (R13):

\[ \text{H} + \text{CH}_2\text{Cl} \rightarrow \text{HI} + \text{CH}_2\text{Cl}; \]

\[ k_1 = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \rightarrow \text{HCl} + \text{CH}_2; \]

\[ k_2 = 0.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

\[ 2\text{CH}_2\text{Cl} \rightarrow \text{HCl} + \text{CH}_2 = \text{CHCl}; \]

\[ k_{13} = 2.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

The \( k_1 \) and \( k_2 \) are taken from our results (side infra) and the value of \( k_{13} \) is from ref. 49. After 1 ms, the [CH₂=CHCl] [HCl] produced from (R13) was found to be 10% of the total [HCl]. For the actual reaction time of 0.4 ms, the [CH₂=CHCl] was even less at 3% of [HCl]. Hence, the contribution from (R13) to HCl(ϵ) emission should be minimal. Moreover, the HCl(ϵ) distribution from unimolecular elimination reactions declines monotonically with very little population in higher ϵ levels. Hence, (R12) and (R13) are ruled out as possible sources of the observed HCl(ϵ) emission, especially from ϵ ≳ 4. Finally, the first-order dependence of the HCl(ϵ) intensity on [H] and [CH₂ClI] was verified as proof that (R2) was the major source for HCl emission, see Fig. 2. It is concluded that the ab initio estimate of the C–Cl bond energy in CH₂ClI, 326.4 kJ mol⁻¹, is an upper limit and it could be as low as 301.3 kJ mol⁻¹.

For CH₂FI, no theoretical estimate of D(C–F) is available. Hence, the highest HF(ϵ) level observed is used to estimate the lower limit for the C–F bond energy. The HF(ϵ = 3, J = 0) was used as the limit. With this limit, \( (E) \) is estimated to be \( \geq 138.1 \) kJ mol⁻¹. The \( E_a \) for (R12) was assumed to be 21 kJ mol⁻¹, consistent with the slower reaction rate compared to (R2). This leads to a C–F bond energy of \( \leq 460.2 \) kJ mol⁻¹ and the enthalpy of reaction is \( \leq -104.6 \) kJ mol⁻¹:

\[ \text{H} + \text{CH}_2\text{FI} \rightarrow \text{HICH}_2\text{F}^- \rightarrow \text{HF} + \text{CH}_2\text{I} \quad (\leq -104.6) \quad (\text{R14}) \]

![Fig. 1](image-url) The HCl(ϵ) emission spectrum observed from the H + CH₂Cl reaction at 0.8 Torr for the reaction time of 0.4 ms. [H] = 2.1 × 10¹³ and [CH₂ClI] = 2.5 × 10¹⁴ molecules cm⁻³. The asterisk indicates the strong lines of the ϵ = 5 → 4 band.

The IRCL experiments do not give the population of the $v=0$ level directly. Linear surprisal analysis has been used to estimate the HCl($v=0$) populations for the analogous H + ICl reaction. The surprisal plot (with model 3 prior which takes all the degrees of freedom for HCl and the other product CH$_3$I) for H + CH$_2$Cl was linear with a correlation coefficient of 0.958. The HCl($v$) distribution obtained was $P_0/P_2=1.3 : 24.7 : 31.6 : 24.7 : 10.8 : 6.9$ which implies that the $P_0$ is almost negligible. The fraction of available energy going into HCl vibration, $\langle f_v \rangle$, is calculated to be 0.48. If we assume the $P_0$ to be 1/2 of $P_1$, then $\langle f_v \rangle$ is 0.44. The available energy was taken as 167.4 kJ mol$^{-1}$ in surprisal calculations consistent with the highest HCl($v, J$) level observed in the reaction.

The rate constant for the HCl($v$) formation channel was estimated by comparing the [HCl($v$)] produced from H + CH$_2$Cl with that of H + Cl$_2$ for the same [H] and reaction time. Fig. 3 shows the [HCl($v$)] vs. [CH$_3$I] and [Cl$_2$]. The ratio of the slopes of the two lines gives the ratio (0.25) of the rate constants for these two reactions. The rate constant$^{47,48}$ for H + Cl$_2$ is $2.0 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. From this, the HCl($v$) formation rate constant for (R2) is estimated to be $5 \pm 2 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The total rate constant for H + CH$_2$Cl has not been measured yet. As noted in the Introduction, the H + CH$_3$I reaction has a rate constant$^5$ of $8.3 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and that$^6$ for H + CF$_2$I is $1.4 \times 10^{-11}$. The C-I bond in CH$_3$I is about 12.6 kJ mol$^{-1}$ weaker than that for CH$_3$I. Hence, the total rate constant for the H + CH$_2$Cl reaction should be $\geq 2 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The HCl($v>0$) formation, probably, accounts for $\leq 25\%$ of the total reaction.

The D + CH$_2$Cl reaction gave both HCl($v$) and DCl($v$) emission, see Fig. 4. The DCl($v$) emission was weak due to the much smaller ($\approx 1/4$ of that of HCl) Einstein coefficient. In order to get a better signal to noise ratio, these experiments were done at longer observation time (0.8 ms) and higher concentrations; both [D$_2$] and [CH$_3$I] were $5 \times 10^{-13}$ molecules cm$^{-3}$. Under these conditions, the HCl($v$) distribution from H + CH$_2$Cl was somewhat relaxed with a distribution of $P_0/P_2=55 : 31 : 11 : 3$. Compared to the nascent distribution reported in Table 1. From the D + CH$_3$I reaction, the distributions were $P_0/P_2=36 : 33 : 24 : 7$ for DCl($v$). The ratio of DCl($v>1$)/HCl($v>1$) concentrations observed in the experiments was about 1.1.

**Table 1.** HX($v$) distribution from various reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Percentage</th>
<th>$\langle f_v \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H + CH$_2$Cl$^x$</td>
<td>25</td>
<td>0.29</td>
</tr>
<tr>
<td>H + CH$_3$I$^x$</td>
<td>76</td>
<td>0.16</td>
</tr>
<tr>
<td>H + IC$^x$</td>
<td>6</td>
<td>0.12</td>
</tr>
<tr>
<td>H + NCl$^x$</td>
<td>34</td>
<td>0.13</td>
</tr>
<tr>
<td>H + CF$_2$I$^x$</td>
<td>58</td>
<td>0.27</td>
</tr>
</tbody>
</table>

$^x$ This work: [H$_2$] = $2.0 \times 10^{13}$ and [CH$_3$I] = $4.4 \times 10^{12}$ molecules cm$^{-3}$; $P = 1.0$ Torr, reaction time = 0.4 ms. See text for $P_0$. $^x$ This work: [H] = $6.0 \times 10^{13}$ and [CH$_3$I] = $4.2 \times 10^{13}$ molecules cm$^{-3}$. See text for $P_0$. $^x$ Ref. 2. $^x$ Except for H + NCl$_3$, the $\langle f_v \rangle$ are based on the surprisal estimates for the amount of $P_0$. Halogen abstraction reactions do not give a linear surprisal and for H + NCl$_3$, the amount of $P_0$ was assumed to be half that of $P_1$.
At larger reagent concentration, this ratio was reduced to 0.7. This may be the result of more efficient DCI(v) relaxation compared to HCl(v) relaxation, with more DCI(v = 0) being present. The HCl formation from D + CH2ClI with a similar distribution to that for H + CH2ClI shows that extensive H/D exchange occurs in the DICH2Cl adduct. The other possibility could be elimination from both the iodine and carbon atom sites. But, then one would expect more different HCl(v) and DCI(v) distributions.

### III.3 HF(v) distribution from H + CH2FI

The amount of CH2FI sample was very limited and only a few experiments could be done. The HF(v) emission from the H + CH2FI reaction could be seen only with reduced pumping speed, thus the reaction time was 0.7 ms for [H] and [CH2FI] = 5 × 10^13 molecules cm⁻³. The HF(v) distribution observed was P(v = 0) = 77 : 15 : 8. In general, HF(v) relaxation is slower than HCl(v) relaxation due to the larger energy spacings. Hence, vibrational relaxation is unlikely to be the main reason for the much lower HF(v) excitation than HCl(v) excitation from H + CH2ClI. Comparison of [HF(v)] with [HCl(v)] from H + CH2I implies that the HF(v) formation rate is about 20 times slower than the H + Cl2 reaction. This indicates that the adduct formation followed by HF formation is a small part of the total H + CH2FI reaction. A casual look at HF(v ≥ 0) distribution suggests similarity to that of addition–elimination reactions, except for the fact that the energy available to the HF(v) products is much smaller than the HX(v) elimination reactions reported in ref. 1 and 2. This is evident from the results of surprisal analysis (which had a correlation coefficient slightly smaller than for (R2) at 0.943). The HF(v) distribution obtained was P(v) = 0.7 : 75.4 : 15.9 : 7.9 and the (P0) was 0.44. Although, this estimate is an upper limit, the (P0) seems to be comparable to that for the H + CH2ClI reaction.

The D + CH2FI reaction gave both HF and DF emission. The HF(v) distribution appeared to indicate a smaller (P0) with P(v = 0) = 87 : 13 : 0, compared to that of H + CH2FI discussed above. The DF(v) distribution was 71 : 21 : 8. The [HF(v)] was about 2 times smaller than the [DF(v)]. As already pointed out, the CH2FI sample was very limited and more experiments to get the nascent distribution from this reaction could not be performed. However, these results are significant in establishing H/D exchange unambiguously, as found for the D + CH2ClI reaction.

### III.4 N + CH2X reactions: HX + HCN channel

The changes in HX(v) distribution and intensity were monitored on addition of N atoms to the H + CH2XI and F + CH2X reaction systems. In order to demonstrate the effect of N atoms and N2, reference spectra were taken at the same pressure without a N2 flow. In the second step spectra were obtained with added N2 and finally the N/N2 experiment was done; the reaction time was 0.8 ms and the pressure was 1.7 Torr. Results for the H + CH2ClI are shown in Table 2 (entries 1–3). The HCl(v) distribution observed under these conditions (without added N2) was P0–P4 = 37 : 32 : 22 : 9, which shows the effects of some relaxation. When N2 was added with the microwave discharge off, there was very little change in the HCl(v) distribution or the total emission intensity. When the N2 discharge was turned on, the HCl(v) intensity nearly doubled for the most favorable experimental conditions and the distribution became P0–P4 = 45 : 28 : 18 : 9. In addition, the HCN (001 → 000) emission could be observed. This large increase in the F-HCl is not necessarily a contradiction because the H + CH2ClI reaction probably gives more CH3Cl (+ H) radicals than CH4 (+ HCl) radicals in the primary step. The increase in HCl(v) intensity and the observation of concomitant HCN emission in the presence of N atoms are convincing evidence for (R8). The overall HCl(v) distribution showed very little change, on addition of N atoms. It is likely that the HCl(v) distribution from the N + CH2ClI reaction is similar to that of the H + CH2ClI reaction. It should be noted that the H + CH2ClI (k ≈ 2 × 10⁻¹¹ cm⁻³ molecule⁻¹ s⁻¹) and N + CH2ClI (k ≈ 8 × 10⁻¹¹ cm⁻³ molecule⁻¹ s⁻¹) are in competition. However, as already pointed out, the formation of HCl from H + CH2ClI is thermonuclear and cannot be observed.

Similar observations were made with the D + N + CH2ClI system. The IRCL spectrum showing HCl, DCI, and HCN emission from this system is shown in Fig. 4. When no N atoms are present in the reactor, only HCl and DCI emission is observed. With added N atoms, HCl and DCI intensities both increase and weak HCN emission is observed. Entries 4–9 in Table 2 summarize our observation. The HCl(v) distribution

<table>
<thead>
<tr>
<th>No</th>
<th>Atom/CHCI(v)</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
<th>ΣHCl(v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H/CHI</td>
<td>36.6</td>
<td>32.3</td>
<td>22.2</td>
<td>8.9</td>
<td>0.057</td>
</tr>
<tr>
<td>2</td>
<td>H/CHCl + N</td>
<td>38.0</td>
<td>33.5</td>
<td>20.3</td>
<td>8.2</td>
<td>0.063</td>
</tr>
<tr>
<td>3</td>
<td>H/CHCl + N</td>
<td>45.4</td>
<td>27.1</td>
<td>17.7</td>
<td>8.0</td>
<td>0.093</td>
</tr>
<tr>
<td>4</td>
<td>DC/Cl</td>
<td>35.6</td>
<td>32.8</td>
<td>24.3</td>
<td>7.3</td>
<td>0.092</td>
</tr>
<tr>
<td>5</td>
<td>DC/Cl + N</td>
<td>35.5</td>
<td>29.2</td>
<td>24.8</td>
<td>7.7</td>
<td>0.082</td>
</tr>
<tr>
<td>6</td>
<td>DC/Cl + N</td>
<td>57.1</td>
<td>27.7</td>
<td>8.4</td>
<td>6.7</td>
<td>0.115</td>
</tr>
<tr>
<td>7</td>
<td>DC/Cl + N</td>
<td>56.8</td>
<td>30.5</td>
<td>10.7</td>
<td>2.0</td>
<td>0.172</td>
</tr>
</tbody>
</table>

* Experiments 1–3 had [H] = 6 × 10⁻¹⁰,[CH2ClI] = 1.5 × 10¹⁵ molecules cm⁻³ and [N2] = 2.3 × 10⁻⁸. Pressure = 1.7 Torr and the reaction time was 0.8 ms. For experiments 4–9, high [CH2ClI] was needed, 1.9 × 10¹⁴ molecules cm⁻³ to obtain a good signal to noise ratio for the DCI(v) emission. At these concentrations, the HX(v) distribution showed some relaxation compared to that given in Table 1 and emission from v = 5 was absent due to relaxation. (see text).


55
did not change significantly with the presence of \( N_2 \) or \( N \). However, the \( \text{DCI} \) distribution showed a detectable difference in the presence of \( N \) atoms but not with \( N_2 \) alone. From the above observations, it appears that the \( \text{DCI} \) and \( \text{HCl} \) distributions from the \( N + \text{CH}_2\text{Cl}/\text{CHDCI} \) may be peaking at lower \( v \). For both \( \text{HCl} \) and \( \text{DCI} \), the change in distribution is rather subtle and it is not possible to make any more meaningful quantitative interpretation.

The addition of \( N \) atoms to the \( \text{H/D + CH}_2\text{FI} \) system led to an increase in \( \text{HF}(v) \) and \( \text{DF}(v) \) emission intensity along with weak \( \text{HNC}(v) \) emission. Separate experiments were done for the \( \text{H + CH}_2\text{I}_2 + N \) and \( \text{H + CH}_2\text{I}_1 + N \) reactions. All experiments gave weak \( \text{HNC}(v) \) emission and even weaker \( \text{HNC} \) emission, as shown in Fig. 5. Thus, the \( N + \text{CH}_2\text{X} \) reactions do have some general nature for \( X = H, \text{Cl}, \text{F} \) and I. The \( \text{HCN} \) emission observed from these reactions (for \( X = \text{Cl} \) and \( F \)) mainly consisted of the \( (001) \) reactions. Unfortunately the strong \( \text{HF}(v) \) charge products from \( \text{CF}_4 \) and \( \text{N}_2 \) interacted as evidenced by the build-up of much more \( F \) atoms from the \( \text{N} \). The additional \( \text{HF} \) is probably due to the production of \( \text{HFCI} \) radicals. This also rules out the \( \text{CF}_4 \) species, which may be present in the \( \text{CF}_4 \) discharge, as the only sources of \( \text{CN} \). At our flow velocities and concentrations, the \( N/\text{N}_2 + \text{CH}_2\text{I}_X \) reactions alone gave no emission that was visible to the eye or the IR detector. Benson and coworkers \(^{55} \) have studied the \( N + \text{CHCl}_3 \) reaction in a very low pressure reactor for longer reaction time (a few seconds) and reported a rate constant of \( 1 \times 10^{-13} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) for the primary step. This is consistent with our observation of no \( \text{CN} \) chemiluminescence in the absence of any added \( F \) or \( H \) atoms. In our reactors, the \( \text{CN} \) emission began at the reagent inlet as soon as the \( F \) or \( H \) atom discharge sources were activated and the onset of the chemiluminescence seems to depend on the mixing rate of the reagent into the gas flow. In the absence of \( \text{CH}_2\text{X} \), the discharge products from \( \text{N}_2 \) and \( \text{CF}_4 \) reacted, generating a weak unidentified emission, in the pre-reactor section of the flow reactor for high \( N_2 \) and \( \text{CF}_4 \) flows. However, this unidentified reaction must be relatively slow, and the emission extended over the whole length of the reactor. The addition of \( \text{CH}_2\text{X} \) reagents to the \( N/\text{F/CF}_4 \) flow gave much stronger emission, which obscured this weak emission. Another observation was the build-up of \( (\text{CN})_\text{s} \) polymer on the flow reactor beyond the reagent inlet, as \( \text{CN} \) radical sources are prone to do. \(^{26,27} \) This suggests that the \( \text{CN} \) concentration is not negligible, and that the \( N + \text{CH}_2\text{X} \) reaction system must include \( \text{CN} \)-generating steps.

The emission spectra and measurements of the dependence of the \( \text{CN} \) emission intensity were taken in the reactor that permitted the \( [N] \) to be measured by titration with \( \text{NO} \) and the \( [F] \) to be measured by titration with \( \text{CF}_3\text{I} \). The various emission

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**Fig. 5** The \( \text{HCN}(v) \) and \( \text{HNC}(v) \) infrared emission spectra observed from \( \text{H + N + CH}_2\text{I}_3 \) reactions. The pressure was 1.8 Torr and the reaction time was 0.8 ms. \([H] = 6 \times 10^{-3}\). Both \( \text{HCN} \) and \( \text{HNC} \) emission are thought to result from the \( N + \text{CH}_3\text{I} \) reaction.
titration with NO by observation of the N2(B-A) emission intensity to reaction system as a function of [N]. The [N] was determined by titration with CH3Cl so large as to deplete the reagent with the fixed concentration. For fixed [F] providing that the variable concentration was not for a fixed [N] concentration, the CN emission intensity decreased with [F] and [N] = 0.5–5 × 10^12 atoms cm^-3. For a fixed [N] concentration, the CN emission intensity increased linearly with [F] for fixed [CH2Cl] and with [CH2Cl] for fixed [F] providing that the variable concentration was not so large as to deplete the reagent with the fixed concentration. An experiment to test the order dependence for [N] was done with [CH2Cl] = 4 × 10^13 and [F] = 2 × 10^12 molecule cm^-3. The results, shown in Fig. 6, demonstrate apparent first-order kinetics for [N] = 1–5 × 10^12 atoms cm^-3.

IV. Discussion

IV.1 The H + CH2Cl and CH2FI reactions

The H + CH2Cl reaction at room temperature has several surprising aspects. Foremost was the HCl(r > 0) product channel with a rate constant of 5 ± 2 × 10^-12 cm^3 molecule^-1 s^-1 at 300 K, which is much larger than that for H + CH2Cl or CH2Cl2. A second surprise was the observation of both HCl and DCI formation from D + CH2ClII. Finally the HCl(r) distribution was rather flat with strong emission from HCl(r ≤ 4) and weak emission from r = 5, which indicates a low D(Cl-CH2Cl) as already discussed. All of these aspects are consistent only with addition of the H atom to the iodine molecule with a low activation energy followed by partial exchange of the H atoms between the iodine and carbon atom with subsequent formation of HCl. The mechanism may be somewhat similar to the H + IX reaction systems, which have a direct interaction channel giving HX, plus an indirect channel involving addition to iodine atom followed by H-atom migration to the X atom. Attack at the iodine atom serves as a way of circumventing the energy barrier for direct abstraction. The HCl(r) distribution gives (f_r(HCl)) = 0.48, which is much larger than most 3- or 4-centred unimolecular elimination reactions. The linear vibrational surprisal and the large f_r are additional evidence for a different mechanism (i.e. neither direct abstraction nor addition-elimination) and the term addition-migration reaction may be a better description. The Cl and O atom reactions with CH2CI, F with CH2BrCl and Cl with CHI also involve an addition pathway. Since iodine forms stable molecules with 10 or 12 electrons around the central iodine atom, free radical addition to give a 9-electron adduct of iodine should not be so surprising. In fact, ab initio calculations for the adducts with Cl atoms do find bent C–Cl–I structures of CH2I and CH2ClI with weak 1–Cl bonds (55 kJ mol^-1). The H atom exchange pathway and the HCl or HF formation mechanisms are less easy to visualize. The trajectory calculations for H + ICl may provide some clues.19 After the H atom bonds to the I atom, the H makes many large excursions while the heavy CI atom begins to depart. In some cases the H atom has an encounter, either repulsive or attractive, with the Cl atom. For attractive encounters, the H atom is passed to the Cl atom. If the /HIC is not linear, as theoretically found for /CHIC, large amplitude motions can bring the H atom closer to the Cl and C atoms. For the latter, a synchronous motion of one of the H bound to C toward the I atom lead to exchange of H atom positions i.e., the Cl2 atoms originally bound to I and C interchange geometrically by a rearrangement pathway. Recently, Holmes and coworkers have identified such an unusual 1,2-FCl rearrangement pathway in CF3CICCF2CH3, which facilitates 4-centered HCI elimination through CF3CFCICCF4. Is the HI formation, (R1), process always direct or can it be an exit channel from the adduct? Certainly the 0 atom addition mechanism seems to be fairly general for alkyl iodides.13,14 The HCl(r) and DCI(r) intensities reported in Table 2 offer some important clues. Intensities of both HCl(r) and DCI(r) increase on N atom addition to the D + CH2Cl reaction system. If DI formation occurs through direct abstraction only, then one would expect the HCl(r) intensity alone to increase by the contribution from N + CH2Cl, with no change in DCI(r). The fact that both increase implies that H/D exchange occurs before the HI/DI formation and that both CH2Cl and CHDCl radicals are produced. The DCI(r) (from N + CHDCl) emission was weak and a more quantitative interpretation is not possible.

IV.2 The N + CH2X reaction (X = H, Cl, F, I)

The primary interaction between N(S) atom and CH2X radicals is association to give the CH2XN triplet ground-state nitrone radical. The nitrone radical has enough energy for dissociation and (R6) or (R7) is the most important product channel. The CHXN radical probably lacks sufficient energy to overcome the barrier for loss of a second H atom, but dissociation of a carbon–halogen bond might be possible. The (R4) (or (R8)) step requires intersystem crossing to the singlet nitrone potential surface and this seems to be the rate limiting step. Our IRCL data confirm that (R8) does occur in competition with (R6) (or (R7)) for several CH2X type radicals. The HCl(r) distribution appears similar to that of the H + CH2Cl reaction. However, the HCl formation mechanism is not established and both internal conversion and structural isomerization of NCH2Cl may occur prior to HCl elimination. The IRCL results do show that the vibrational energy released to HCl and HCN is a small part of the available energy from (R8). The HCN emission was always weak, but there was some indication that this emission was stronger from molecules with weaker C–X bonds. The singlet methyl nitrone radical has the possibility for isomerization to CH2NH or even CHNH2 and, according to the calculations, 1,1-elimination of H2 is preferred over 1,2-elimination. Thus, some HNC formation could be expected, as we observed. Our data, unfortunately, cannot be placed on a quantitative basis and we cannot assign branching ratios to dissociation of triplet CH2XN vs. the elimination step giving HX and HCN (or HNC). The IRCL spectra do show that HCN and HNC have little vibrational excitation.

Secondary reactions must be responsible for the CN chemiluminescence because N + CH2 does not provide sufficient energy to give CN(A) + HX + H. Since the radical species from the primary steps seem reasonably well established and since...
the thermochemistry can be estimated, a discussion of the mechanism responsible for the chemiluminescence in the N + CH2X reaction seems worthwhile. Since the CN(X) and CN(A) states are rapidly interconverted80–82 by collisions with Ar, it may not really matter whether high vibrational levels of CN(X) or CN(A) are initially formed. Therefore, we will just search for reactions with sufficient exothercity to give CN(A), $e' = 8$. As a consequence of early work on the subject, several excitation steps have been discussed. These include: (i) the N(S) + CX(X$^*$A) reaction, (ii) excitation by an electronic energy-transfer step, (iii) CN acting as a third body in atomic (N or O) recombination, (iv) more complex CN-forming reactions, such as N + NCN. Dorth and coworkers55 have isolated the N + CCl reactions and confirmed that (i) does give CN(A) with the $P_2$ type vibrational distribution, as suggested by Thrush and Setser.34,64 The original argument84 in support of this type of reaction was based on the fact that the CN(A) potential lies below the CN(X) potential at long distance. However, these reactions probably proceed by addition of N to the radical to give a stable triplet adduct that subsequently dissociates,65 rather than by direct X atom abstraction from an attacking N atom. Thus the CN bond is probably formed before the X atom leaves. For example, the N + C + M reaction, the three-body recombination mechanisms can be discounted because nowadays it is established that the two-body reactions of O and N atoms with CN are very fast.33 Benson and coworkers55 have suggested the following sequence to explain the CN emission from the N + CHCl reaction system:

$$
N + CCl_3 \rightarrow ICN + Cl + Cl \quad (R15)
$$

$$
N + ICN \rightarrow N_2 + CCl \quad (R16)
$$

$$
N + CCl \rightarrow CN(A) + Cl \quad (R17)
$$

The N + ICN reaction is very slow in the absence of ‘active nitrogen’,34,64 and the second step is doubtful. In our systems, we do not see how CIICl(X$^*$II) or CH(X$^*$II) radicals can be generated, and the electronic transfer steps also do not seem feasible. We believe that the N atoms must react with the product (CH2N or CHXN) from the N + CH2X reaction. Although easily visible, the CN chemiluminescence is probably associated with a minor channel of the N + CHXN chemistry. We suggest the following sequence of reactions, with the thermochemistry based on $X = H$ and $\Delta H^0$ (CH2N)$^{38}$ 238.5 and $\Delta H^0$ (NCN)$^{67}$ 456.1 kJ mol$^{-1}$:

$$
N + CHXN \rightarrow NH + XCN (-221.8) \quad (R18a)
$$

$$
\rightarrow NCN + HX (-280.3) \quad (R18b)
$$

$$
\rightarrow N_2 + CHX (-322.2) \quad (R18c)
$$

$$
N(S) + NCN(X$^*$1) \rightarrow N_2 + CN(-506.3) \quad (R19)
$$

The formation of NCN would be in competition with several other possible product channels as given in (R18). Moreover, it may occur through a complex mechanism involving more than one step. Steidt and coworkers83 have identified (R18a) as a dominant channel for X = H. A direct route from CHXN to CN would be more desirable; however, formation of CN from N + CH2N seems unlikely. The isomerization of CH2N to HCNH or CHN2 has calculated barriers$^{57}$ of 188.3 and 288.7 kJ mol$^{-1}$ and they are unlikely candidates. Since the CH2N and NCN radicals are formed and removed by steps involving N atoms, the CN concentration will be approximately first order in [N], in accord with the experimental observations. It is worth noting that McFadden and coworkers85 observed CN formation when monitoring the products from the N + CF3 reaction by mass spectrometric detection. Most spectroscopic studies of NCN radicals have used the N2/CIF3/He microwave discharge as the source for NCN.$^{69}$ and formation of NCN in our reaction systems and that of McFadden and coworkers68 could be expected. The mechanism proposed above can explain the very general finding of CN formation from the interaction of a variety of halomethyl radicals with N atoms.

V. Conclusions

Infrared chemiluminescence in a fast flow reactor has been used to identify HCl($e' > 0$) formation from the H + CH2Cl reaction with a rate constant of $5 \pm 2 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at room temperature. The D + CH2Cl reaction gives both HCl and DCI products, which strongly suggests a mechanism in which H/D exchange occurs in an adduct. The HCl($e'$) distribution has a linear surprisal with $\langle f \rangle = 0.48$, which suggests an analogy to the dynamics for the addition-migration channel of the H + IC1 reaction. From the highest observed HCl($e' = 5$) level, DCl(CH2I) is estimated to be $\leq 301.2$kJ mol$^{-1}$ compared to a theoretical estimate of 326.4 kJ mol$^{-1}$. The H + CH2FI reaction is similar to the H + CH2ClI and the highest observed HFI($e' = 3$) level from the H + CH3FI reaction implies that the C–F bond energy is $\leq 460.2$kJ mol$^{-1}$. The lower D(C–Cl), relative to that of CH2ClI, is consistent with the bond energies of other CH2XCl molecules. In contrast, multiple halogen substitution does not seem to affect the D(3–F) values very much. The I atom in the CH2XI molecules provides a reaction pathway to access the Cl or F atoms with a lower energy barrier compared to direct N abstraction. The H/D exchange was identified by the inference of CH2ClI and CHDClI product as well, which suggests that the HI formation channel also arises via the adduct.

The addition of N atoms to the reactor containing CH2ClI radicals gave additional HCl($e'$) emission plus weak HCN and HNC emission. These observations identify a singlet exit channel from the N + CH2ClI reaction, although the spin-conserving triplet channel giving Cl + CH2N products is probably the dominant one. Fast secondary reactions starting with N + CH2N reaction must lead to CN formation, in part, as identified by the CN(A) chemiluminescence from several F/CH2X/N and H/CH2XI/N reaction systems. One possibility for the CN(A) forming step is N + NCN. However, the products from the N + CH2N reaction need to be identified before this possibility could be confirmed.

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References
