

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

E. Arunan,^{*a} S. P. Vijayalakshmi,^a R. Valera^b and D. W. Setser^b

^a Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India. E-mail: arunan@ipc.iisc.ernet.in

^b Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, USA

Received 14th September 2001, Accepted 26th October 2001

First published as an Advance Article on the web 6th December 2001

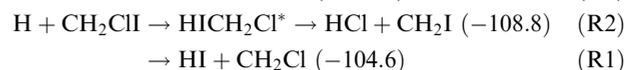
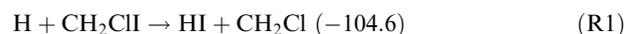
Infrared chemiluminescence from a flow reactor has been used to study the H + CH₂XI and N + CH₂X (X = Cl, F, I, H) reactions at 300 K. Both the HI + CH₂Cl and HCl + CH₂I channels were identified for the H + CH₂CII reaction. The HCl channel involves adduct, HICH₂Cl, formation as confirmed by the D + CH₂CII reaction, which gave both HCl and DCl products. The nascent HCl(*v*) distribution from the H + CH₂CII 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 + CH₂CII 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 H + CH₂CII increased by up to 2-fold, which is attributed to the N + CH₂Cl → 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 + CH₃X 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 + CH₂CII reaction was to use it to produce CH₂Cl in the flow reactor for subsequent studies of the N + CH₂Cl reaction. Iodine atom abstraction reactions by H atoms are usually fast and the Kansas State Laboratory has successfully used the reaction of iodoalkanes with H atom as precursor for various radicals.^{1–4} For example, the rate constants for the H + CF₃I/CH₃I reactions^{5–7} are both about 1 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹. As the investigation proceeded, it was realized that the primary reaction, H + CH₂CII, was interesting and needed to be characterized on its own merit. The chemistry of iodine-containing molecules is important in the earth's atmosphere.⁸ Major sources for I atoms in the atmosphere are CH₃I and CH₂CII.⁸ Photodissociation of these iodocompounds^{9,10} and their reactions with Cl^{11,12} and O¹³ atoms have been studied as possible sinks for CH₂CII in the atmosphere. As pointed out above, H atoms rapidly react with iodoalkanes and the H atom reaction could also be an important sink for CH₂CII. No study of this reaction has yet been reported, to the best of our knowledge.

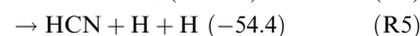
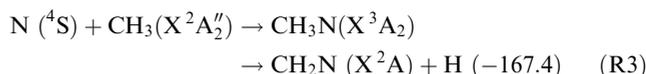
Reactions of O atoms¹³ and Cl atoms¹² with CH₂CII appear to proceed *via* bound intermediates. Leone and co-workers¹⁴ have shown that the mechanism for O + C₂H₅I and larger alkyl iodides involves a bound intermediate that gives HOI. Reversible adduct formation has also been observed for Cl + CH₃I¹⁵ and F + CH₂BrCl.¹⁶ For reactions of H atoms

with IX compounds (X = Cl/F), an H migration step following adduct formation has long been recognized.^{17–19} In the present study infrared chemiluminescence from HCl(*v*) was observed from the H + CH₂CII reaction, and an adduct seems to facilitate HCl formation. At least two channels are possible:



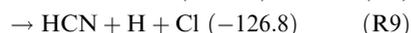
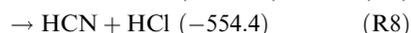
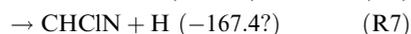
The thermochemistry is not well established, but the enthalpies of reaction (in kJ mol⁻¹) based upon our thermochemical estimates, *vide infra*, are given in parentheses. The HI formation could be either direct or *via* the adduct, but the HCl formation is thought to proceed only through adduct formation. Direct Cl abstraction from chloroalkanes has a large activation barrier and this reaction has not been observed at 300 K in a flow reactor.² The D + CH₂CII 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 + CH₃ reaction in planetary atmospheres and combustion processes.^{20–25} For this reaction, the product channels have been actively discussed.

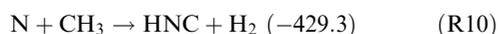


The $N + CH_3$ reaction was proposed to account for the presence of HCN in Titan's atmosphere.²⁰ However, laboratory studies of this reaction showed that the most exothermic channel, (R4), is not the dominant channel.²² In fact, the $CH_2N + H$ channel accounts for 90% of the reaction and the $HCN + H_2$ (or $2H$) channel is estimated to contribute $\approx 10\%$. The HCN can also be formed by the disproportionation reactions, $H + CH_2N \rightarrow HCN + H_2$ or $N + CH_2N \rightarrow HCN + NH$.²³ The $N + CH_3$ reaction presumably proceeds by recombination giving the triplet methyl nitrene radical, which then dissociates. The triplet CH_3N radical (X^3A_2) requires a spin change to give $HCN + H_2$. Sadygov and Yarkony²⁰ evaluated the intersystem crossing between the CH_3N (X^3A_2) and ($1^1A'$) states and identified a zero-barrier path for (R4). Due to the large exoergicity, the HCN product could be vibrationally excited. As far as we know, 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.^{26–28}

It is well known that unimolecular H_2 elimination processes from ground state molecules have high barriers, *e.g.* $376.6 \text{ kJ mol}^{-1}$ for CH_3SiH_3 .²⁹ Thermal dissociation of C_2H_6 is dominated by C–C bond breaking, but unimolecular HCl elimination,^{30,31} with a barrier of $230.1 \text{ kJ mol}^{-1}$, is the dominant reaction for CH_3CH_2Cl . Could the $HCN + HCl$ channel be more important for the $N + CH_2Cl$ reaction than the $HCN + H_2$ channel for $N + CH_3$? By analogy with the $N + CH_3$ reaction, one could envisage the following steps:



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 CHClN. The C–Cl and C–H bond energies in CH_2Cl are nearly the same.³² However, the C–Cl bond may be weaker than the C–H bond in the NCH_2Cl adduct. If one assumes that the C–H bond energies in CH_3N and CH_2ClN are similar, the enthalpy of reaction for (R7) should be closer to that of (R3) ($-167.4 \text{ kJ mol}^{-1}$) and (R7) is certainly less exoergic 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, CH_2ClI was added to a flow reactor in which both H and N atoms were present, and the additional infrared chemiluminescence from the $N + CH_2Cl$ reaction was studied in the presence of the $H + CH_2ClI$ reaction. The $F + CH_3X$ reactions were also used as a precursor for CH_2X radicals. Although HNC is a minor product, it was observed, and the HNC formation channel needs to be added to the $N + CH_2X$ mechanism:



During the course of investigating the IRCL from (R2) and (R8), the intense yellow $CN(A^2\Pi-X^2\Sigma^+)$ chemiluminescence was clearly evident whenever CH_2ClI was added to the flow reactor containing both H and N atoms. The same visible emission was observed on adding CH_3Cl to the reactor containing F and N atoms. In fact this $CN(A-X)$ emission was observed for several CH_2XI molecules with H and N atoms and for several CH_3X molecules with F and N atoms. This CN emission has been commonly observed when halogenated hydrocarbons are added to active nitrogen,^{33–38} but despite investigations spanning four decades, the excitation-mechanism remains poorly characterized. In the present work, the

generation of CH_2X radicals in the presence of N atoms, by the F or H atom primary reactions greatly intensifies the CN emission intensity, and CN formation is also part of the $N + CH_2X$ chemistry. The chemiluminescence in the $N + CH_2X$ reaction system is discussed and related to the proposed CN excitation mechanisms of the early work.^{33–38}

II. Experimental methods

The IRCL apparatus at Kansas State University has been described previously^{1–4} 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 H_2 , CF_4 , and N_2 diluted in Ar carrier gas. The H_2 , N_2 and CF_4 were taken directly from tanks. Quartz discharge tubes, treated with phosphoric acid, were used for H_2 and N_2 and an alumina discharge tube was used for CF_4 . The atoms were generated at the entrance of the flow reactor (4 cm diameter Pyrex tube), and the CH_2ClI or the other reagent was added 30 cm downstream *via* a 4-jet inlet. A few experiments were done with CH_4 , CH_3Cl , CH_3Br , CH_3I and CH_2I_2 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 CH_2ClI and the atoms could be varied from 0.2 to 2 ms by varying the pumping speed with a throttling valve. The reagents, CH_2ClI and CH_2FI , 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 10^{12} to 10^{13} molecules cm^{-3} . All the experiments were carried out at room temperature at a pressure in the range 0.6–2.0 Torr. The CH_2FI was synthesized by the method described in the literature.³⁹ The purity of the CH_2FI samples was confirmed by GC-MS to be $> 90\%$. The CH_2ClI 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- N_2 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 coefficients⁴⁰ 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 ν_3 (CH stretch) $1 \rightarrow 0$ transitions in HCN (77 s^{-1})⁴¹ and HNC (385 s^{-1})⁴² 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 $[HCN(v)]$.

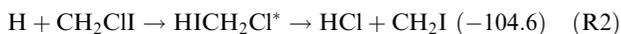
The $CN(A \rightarrow X)$ emission was recorded at 1.1 Torr pressure from the $F + N + CH_4/CH_3Cl$ reaction system in a second flow reactor with a reaction time of typically 5 ms. The emission was observed through quartz windows with a 0.5 m monochromator fitted with a cooled S-1 photomultiplier tube. 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 $\text{HX}(v, J)$ level can be used to set a lower limit on the enthalpy of reaction.⁴⁴ Experimental enthalpies of formation, $\Delta_f H^\circ$, are not available for CH_2ClI and CH_2FI . However, a theoretical $\Delta_f H^\circ$ is available for the CH_2ClI (13 kJ mol^{-1})¹² calculated at the MP2/3-21++G(2d,2p) level. The $\Delta_f H^\circ$ for CH_2I calculated¹² at this level was $218.4 \text{ kJ mol}^{-1}$, in close agreement with the experimental value of $217.6 \text{ kJ mol}^{-1}$. These enthalpies of formation, along with that of Cl ($119.62 \pm 0.05 \text{ kJ mol}^{-1}$),⁴⁵ lead to a C–Cl bond energy of $326.4 \text{ kJ mol}^{-1}$ in CH_2ClI compared to 351.5 ± 4.2 for CH_3Cl .⁴⁶ Using $\Delta_f H^\circ$ (HCl , $-92.0 \pm 0.5 \text{ kJ mol}^{-1}$),⁴⁵ the enthalpy of reaction for (R2) is estimated as given below:

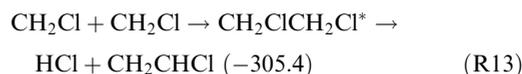


The average energy available to the products from a reaction is calculated as:

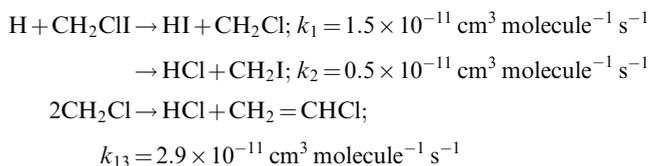
$$\langle E \rangle = \Delta H_0(0 \text{ K}) + E_{\text{th}} + E_a$$

where E_a is the activation energy for the reaction and E_{th} is the thermal energy of the reactants. The activation energy for this reaction has not been measured. However, comparison of $\text{HCl}(v)$ emission intensities from reaction (R2) and $\text{H} + \text{Cl}_2$ suggest that the rate constant for (R2) (*vide infra*) is 4 times smaller than for the latter reaction.^{47,48} The E_a for (R2) is, probably, higher than that ($4\text{--}8 \text{ kJ mol}^{-1}$) of $\text{H} + \text{Cl}_2$. We take the E_a to be $\approx 17 \text{ kJ mol}^{-1}$. The thermal energy of CH_2ClI at 300 K was calculated to be 12.6 kJ mol^{-1} . Hence, the $\langle E \rangle$ for (R2) should be about $133.9 \text{ kJ mol}^{-1}$. This is sufficient to produce $\text{HCl}(v=4)$ from (R2), but the highest observed level is $v=5$. Fig. 1 shows the $\text{HCl}(v)$ IRCL spectrum, highlighting unambiguously the lines from $v=5$. The additional energy needed for producing $v=5$, $J=0$ is 25.1 kJ mol^{-1} . The rotational distribution observed was thermal Boltzmann and $\text{HF}(v=5, J=0)$ 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 $\text{HF}(v=5)$ is used to fix the available energy from (R2), then the C–Cl bond energy in CH_2ClI will be $301.2 \text{ kJ mol}^{-1}$, 25.1 kJ mol^{-1} less than the theoretical estimate.¹² Inspection of the $D(\text{C–Cl})$ values from several CH_2ClX molecules supports a trend of lower bond energies relative to CH_3Cl .⁴⁶

The $\text{HCl}(v=5)$ emission led us to consider reactions that could take place in the reactor in addition to (R2).



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



The k_1 and k_2 are taken from our results (*vide infra*) and the value of k_{13} is from ref. 49. After 1 ms, the $[\text{CH}_2=\text{CHCl}]$ ($[\text{HCl}]$) produced from (R13) was found to be 10% of the total $[\text{HCl}]$. For the actual reaction time of 0.4 ms, the $[\text{CH}_2=\text{CHCl}]$ was even less at 3% of $[\text{HCl}]$. Hence, the contribution from (R13) to $\text{HCl}(v)$ emission should be minimal. Moreover, the $\text{HCl}(v)$ distribution from unimolecular elimination reactions declines monotonically with very little population in higher v levels.^{1,2} Hence, (R12) and (R13) are ruled out as possible sources of the observed $\text{HCl}(v)$ emission, especially from $v \geq 4$. Finally, the first-order dependence of the $\text{HCl}(v)$ intensity on $[\text{H}]$ and $[\text{CH}_2\text{ClI}]$ was verified as proof that (R2) was the major source for HCl emission, see Fig. 2. It is concluded that the *ab initio* estimate¹² of the C–Cl bond energy in CH_2ClI , $326.4 \text{ kJ mol}^{-1}$, is an upper limit and it could be as low as $301.3 \text{ kJ mol}^{-1}$.

For CH_2FI , no theoretical estimate of $D(\text{F–CH}_2\text{I})$ is available. Hence, the highest $\text{HF}(v)$ level observed is used to estimate the lower limit for the C–F bond energy. The $\text{HF}(v=3, J=0)$ was used as the limit. With this limit, $\langle E \rangle$ is estimated to be $\geq 138.1 \text{ kJ mol}^{-1}$. 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 $\leq 460.2 \text{ kJ mol}^{-1}$ and the enthalpy of reaction is $\leq -104.6 \text{ kJ mol}^{-1}$:

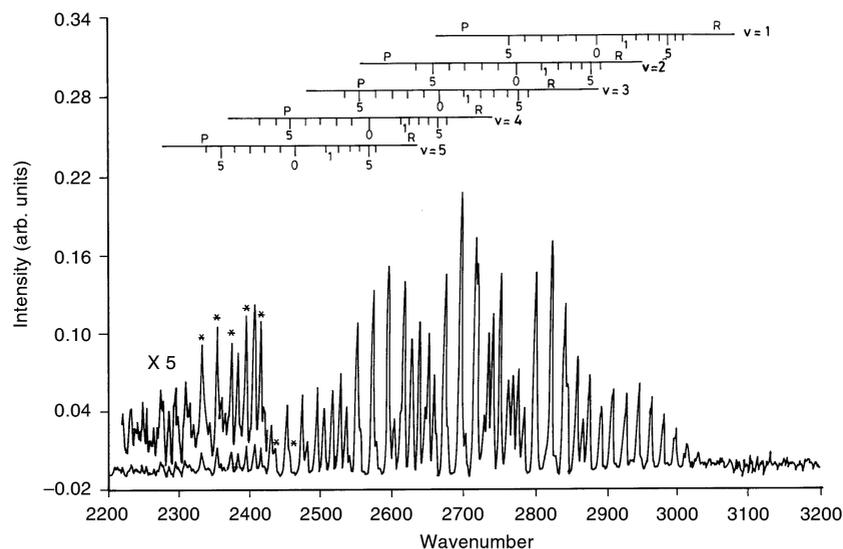


Fig. 1 The $\text{HCl}(v)$ emission spectrum observed from the $\text{H} + \text{CH}_2\text{ClI}$ reaction at 0.8 Torr for the reaction time of 0.4 ms. $[\text{H}] = 2.1 \times 10^{13}$ and $[\text{CH}_2\text{ClI}] = 2.5 \times 10^{13} \text{ molecules cm}^{-3}$. The asterisk indicates the strong lines of the $v=5 \rightarrow 4$ band.

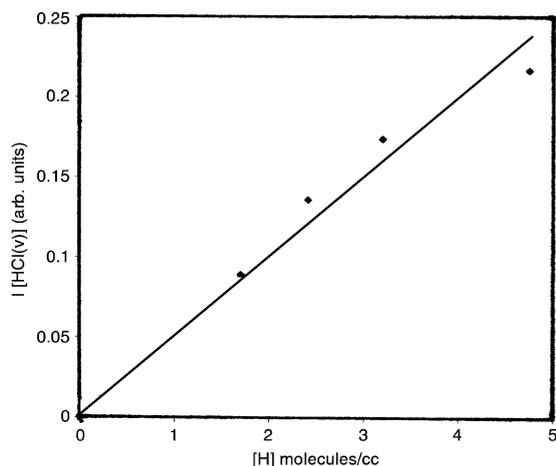


Fig. 2 The $\text{HCl}(v)$ intensity *vs.* $[\text{H}]$ showing the first-order dependence. The pressure (1.6 Torr), reaction time (0.8 ms) and $[\text{CH}_2\text{ClI}]$ (4.5×10^{13} molecules cm^{-3}) were kept constant.

The $D(\text{F}-\text{CH}_2\text{Cl})$ ⁵⁰ and $D(\text{F}-\text{CH}_3)$ ⁵¹ are ~ 460.2 kJ mol^{-1} and halogen substitution does not seem to affect the C–F bond dissociation energy of halofluoromethanes.

III.2 $\text{HCl}(v)$ distribution and $\text{HCl}(v)$ formation rate constant for $\text{H}/\text{D} + \text{CH}_2\text{ClI}$

The $\text{HCl}(v)$ emission could be observed at 0.6 Torr pressure with the maximum pumping speed corresponding to a reaction time of 0.4 ms for $[\text{H}]$ and $[\text{CH}_2\text{ClI}] \leq 3 \times 10^{13}$ molecules cm^{-3} . Under these conditions,^{1,2,52,53} there is very little $\text{HCl}(v)$ relaxation and the observed distribution is the nascent $\text{HCl}(v)$ distribution from the $\text{H} + \text{CH}_2\text{ClI}$ reaction. The nascent $\text{HCl}(v)$ distribution is $P_1\text{--}P_5 = 25 : 29 : 26 : 13 : 7$ obtained as the average of several experiments (Table 1). The $\text{HCl}(v)$ distribution was reproducible when experiments were repeated under the same conditions using several different commercial samples of CH_2ClI . The distribution is nearly flat for $v = 1\text{--}3$ and it is similar to the $\text{HX}(v)$ distribution observed from the $\text{H} + \text{IX}$ reactions.^{17–19} For comparison, the HX distributions from $\text{H} + \text{ICl}$, NFCl_2 , CF_3O and CF_2Cl are included in Table 1. The $\text{H} + \text{CF}_2\text{Cl}$ and CF_3O reactions give stable molecules before unimolecular HX elimination occurs. In these unimolecular elimination processes, the $\text{HCl}(v)$ distribution declines monotonically and $\langle f_v \rangle = 0.15$.¹ The $\text{H} + \text{NFCl}_2$

Table 1 $\text{HX}(v)$ distribution from various reactions

Reaction	Percentage					$\langle f_v \rangle^g$
	P_1	P_2	P_3	P_4	P_5	
$\text{H} + \text{CH}_2\text{ClI}^a$	25	29	26	13	7	0.48
$\text{H} + \text{CH}_2\text{FI}^b$	76	16	8	—	—	0.44
$\text{H} + \text{ICl}^c$	6	12	15	16	18 ^c	0.61
$\text{H} + \text{NFCl}_2^d$	20	41	31	8	—	0.31
$\text{H} + \text{CF}_3\text{O}^e$	34	30	20	10	6	0.14
$\text{H} + \text{CF}_2\text{Cl}^f$	58	27	10	5	—	0.13

^a This work: $[\text{H}_2] = 2.0 \times 10^{13}$ and $[\text{CH}_2\text{ClI}] = 4.4 \times 10^{12}$ molecules cm^{-3} ; $P = 1.0$ Torr, reaction time = 0.4 ms. See text for P_0 . ^b This work: $[\text{H}] = 6.0 \times 10^{13}$ and $[\text{CH}_2\text{FI}] = 4.2 \times 10^{13}$ molecules cm^{-3} . See text for P_0 . ^c Ref. 17 The distribution extends to $v = 7$ and the percentage of $P_6 = 19$; and of $P_7 = 14$. ^d Ref. 52. ^e Ref. 53. ^f Ref. 2. ^g Except for $\text{H} + \text{NFCl}_2$, 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 $\text{H} + \text{NFCl}_2$, the amount of P_0 was assumed to be half that of P_1 .

reaction⁵² is representative of direct abstraction reactions for which sharply peaked distributions that do not extend to the thermochemical limit are found. The distributions from $\text{H} + \text{IX}$ are thought to be the sum of a direct abstraction plus an addition migration step. In this case, the distributions do extend to the thermochemical limit.⁴⁴

The IRCL experiments do not give the population of the $v = 0$ level directly. Linear surprisal analysis has been used to estimate the $\text{HCl}(v = 0)$ populations for the analogous $\text{H} + \text{ICl}$ reaction.⁴⁴ The surprisal plot (with model 3 prior which takes all the degrees of freedom for HCl and the other product CH_2I) for $\text{H} + \text{CH}_2\text{ClI}$ was linear with a correlation coefficient of 0.958. The $\text{HCl}(v)$ distribution obtained was $P_0\text{--}P_5 = 1.3 : 24.7 : 31.6 : 24.7 : 10.8 : 6.9$ 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 $\text{HCl}(v, J)$ level observed in the reaction.

The rate constant for the $\text{HCl}(v)$ formation channel was estimated by comparing the $[\text{HCl}(v)]$ produced from $\text{H} + \text{CH}_2\text{ClI}$ with that of $\text{H} + \text{Cl}_2$ for the same $[\text{H}]$ and reaction time. Fig. 3 shows the $[\text{HCl}(v)]$ *vs.* $[\text{CH}_2\text{ClI}]$ and $[\text{Cl}_2]$. 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 $\text{H} + \text{Cl}_2$ is 2.0×10^{-11} cm^3 molecule $^{-1}$ s^{-1} . From this, the $\text{HCl}(v)$ 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 $\text{H} + \text{CH}_2\text{ClI}$ has not been measured yet. As noted in the Introduction, the $\text{H} + \text{CH}_3\text{I}$ reaction has a rate constant⁶ of 8.3×10^{-12} cm^3 molecule $^{-1}$ s^{-1} and that⁵ for $\text{H} + \text{CF}_3\text{I}$ is 1.4×10^{-11} . The C–I bond in CH_2ClI ¹² is about 12.6 kJ mol^{-1} weaker than that for CH_3I . Hence, the total rate constant for the $\text{H} + \text{CH}_2\text{ClI}$ reaction should be $\geq 2 \times 10^{-11}$ cm^3 molecule $^{-1}$ s^{-1} . The $\text{HCl}(v > 0)$ formation, probably, accounts for $\leq 25\%$ of the total reaction.

The $\text{D} + \text{CH}_2\text{ClI}$ reaction gave both $\text{HCl}(v)$ and $\text{DCl}(v)$ emission, see Fig. 4. The $\text{DCl}(v)$ 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 $[\text{D}_2]$ and $[\text{CH}_2\text{ClI}]$ were $5\text{--}10 \times 10^{13}$ molecules cm^{-3} . Under these conditions, the $\text{HCl}(v)$ distribution from $\text{H} + \text{CH}_2\text{ClI}$ was somewhat relaxed with a distribution of $P_1\text{--}P_4 = 55 : 31 : 11 : 3$ compared to the nascent distribution reported in Table 1. From the $\text{D} + \text{CH}_2\text{ClI}$ reaction, the distributions were 57 : 31 : 10 : 2 for $\text{HCl}(v)$ and 36 : 33 : 24 : 7 for $\text{DCl}(v)$. The ratio of $\text{DCl}(v \geq 1)/\text{HCl}(v \geq 1)$ concentrations observed in the experiments was about 1.1.

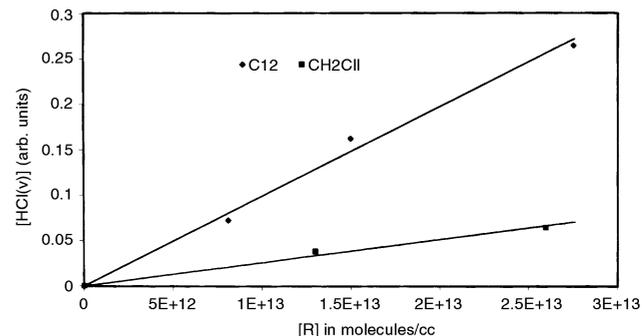


Fig. 3 The $[\text{HCl}(v)]$ *vs.* $[\text{R}]$ for $\text{R} = \text{Cl}_2$ and CH_2ClI . The $[\text{HCl}(v)]$ is the total concentration of $[\text{HCl}(v)]$ obtained from the observed intensities corrected for Einstein coefficients and the instrumental response function for all $v > 0$. From the slopes of the two graphs, the rate constant for the CH_2ClI reaction is determined to be one quarter of that for the Cl_2 reaction *i.e.* the rate constant for $\text{H} + \text{CH}_2\text{ClI} \rightarrow \text{HCl}(v > 0) + \text{CH}_2\text{I}$ is $5 \pm 2 \times 10^{-12}$ cm^3 molecule $^{-1}$ s^{-1} .

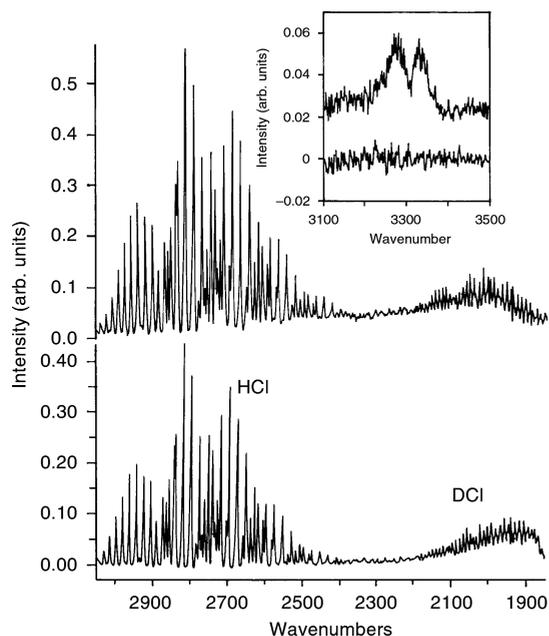


Fig. 4 The IRCL spectrum from the $D + CH_2ClI$ reaction with (upper) and without (lower) N atoms. The reactor pressure was 1.6 Torr for the lower spectrum and 1.7 Torr for the upper spectrum. Both $[H]$ and $[CH_2ClI] \approx 5 \times 10^{13}$ molecules cm^{-3} . Reaction time was 0.8 ms.

At larger reagent concentration, this ratio was reduced to 0.7. This may be the result of more efficient $DCl(v)$ relaxation compared to $HCl(v)$ relaxation, with more $DCl(v=0)$ being present. The HCl formation from $D + CH_2ClI$ with a similar distribution to that for $H + CH_2ClI$, shows that extensive H/D exchange occurs in the $DICH_2Cl$ 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 $DCl(v)$ distributions.

III.3 HF(v) distribution from $H + CH_2FI$

The amount of CH_2FI sample was very limited and only a few experiments could be done. The $HF(v)$ emission from the $H + CH_2FI$ reaction could be seen only with reduced pumping speed, thus the reaction time was 0.7 ms for $[H]$ and $[CH_2FI]$ in the range $5\text{--}10 \times 10^{13}$ molecules cm^{-3} . The $HF(v)$ distribution observed was $P_1\text{--}P_3 = 77 : 15 : 8$. 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 $H + CH_2ClI$. Comparison of $[HF(v)]$ with $[HCl(v)]$ from $H + Cl_2$ implies that the $HF(v)$ formation rate is about 20 times slower than the $H + Cl_2$ reaction. This indicates that the adduct formation followed by HF formation is a small part of the total $H + CH_2FI$ reaction. A casual look at $HF(v > 0)$ distribution suggests similarity to that of addition-elimination reactions,^{1,2} 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 $P_0\text{--}P_3 = 0.7 : 75.4 : 15.9 : 7.9$ and the $\langle f_v \rangle$ was 0.44. Although, this estimate is an upper limit, the $\langle f_v \rangle$ seems to be comparable to that for the $H + CH_2ClI$ reaction.

The $D + CH_2FI$ reaction gave both HF and DF emission. The $HF(v)$ distribution appeared to indicate a smaller $\langle f_v \rangle$ with $P_1\text{--}P_3 = 87 : 13 : 0$, compared to that of $H + CH_2FI$ 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 CH_2FI 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 $D + CH_2ClI$ reaction.

III.4 N + CH_2X reactions: $HX + HCN$ channel

The changes in $HX(v)$ distribution and intensity were monitored on addition of N atoms to the $H + CH_2XI$ and $F + CH_3X$ reaction systems. In order to demonstrate the effect of N atoms and N_2 , reference spectra were taken at the same pressure without a N_2 flow. In the second step spectra were obtained with added N_2 and finally the N/N_2 experiment was done; the reaction time was 0.8 ms and the pressure was 1.7 Torr. Results for the $H + CH_2ClI$ are shown in Table 2 (entries 1–3). The $HCl(v)$ distribution observed under these conditions (without added N_2) was $P_1\text{--}P_4 = 37 : 32 : 22 : 9$, which shows the effects of some relaxation. When N_2 was added with the microwave discharge off, there was very little change in the $HCl(v)$ distribution or the total emission intensity. When the N_2 discharge was turned on, the $HCl(v)$ intensity nearly doubled for the most favorable experimental conditions and the distribution became $P_1\text{--}P_4 = 45 : 28 : 18 : 9$. In addition, the $HCN(001 \rightarrow 000)$ emission could be observed. This large increase in the I_{HCl} is not necessarily a contradiction because the $H + CH_2ClI$ reaction probably gives more $CH_2Cl(+HI)$ radicals than $CH_2I(+HCl)$ 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 $N + CH_2Cl$ reaction is similar to that of the $H + CH_2ClI$ reaction. It should be noted that the $H + CH_2Cl$ ($k \approx 2\text{--}4 \times 10^{-11}$ cm^3 molecule $^{-1}$ s $^{-1}$)⁵⁴ and $N + CH_2Cl$ ($k \approx 8 \times 10^{-11}$ cm^3 molecule $^{-1}$ s $^{-1}$)²¹ are in competition. However, as already pointed out, the formation of HCl from $H + CH_2Cl$ is thermoneutral and cannot be observed.

Similar observations were made with the $D + N + CH_2ClI$ system. The IRCL spectrum showing HCl , DCl and HCN emission from this system is shown in Fig. 4. When no N atoms are present in the reactor, only HCl and DCl emission is observed. With added N atoms, HCl and DCl intensities both increase and weak HCN emission is observed. Entries 4–9 in Table 2 summarize our observation. The $HCl(v)$ distribution

Table 2 $HCl(v)/DCl(v)$ distribution and total observed emission intensity from $H/D + CH_2ClI$ with/without N_2/N in the reactor^a

No	Atom/ $XCl(v)$	Percentage				$\Sigma HCl(v)$
		P_1	P_2	P_3	P_4	
1	H/HCl	36.6	32.3	22.2	8.9	0.057
2	H/HCl + N_2	38.0	33.5	20.3	8.2	0.063
3	H/HCl + N	45.4	27.1	17.7	8.0	0.093
4	D/DCl	35.6	32.8	24.3	7.3	0.092
5	D/DCl + N_2	38.3	29.2	24.8	7.7	0.082
6	D/DCl + N	57.1	27.7	8.4	6.7	0.115
7	D/HCl	56.9	31.0	10.1	2.0	0.135
8	D/HCl + N_2	54.0	33.7	10.2	2.1	0.124
9	D/HCl + N	56.8	30.5	10.7	2.0	0.172

^a Experiments 1–3 had $[H] = 6 \times 10^{13}$, $[CH_2ClI] = 1.5 \times 10^{13}$ molecules cm^{-3} and $[N_2] = 2.3 \times 10^{15}$. Pressure = 1.7 Torr and the reaction time was 0.8 ms. For experiments 4–9, high $[CH_2ClI]$ was needed, 1.9×10^{14} molecules cm^{-3} , to obtain a good signal to noise ratio for the $DCl(v)$ 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).

did not change significantly with the presence of N_2 or N. However, the $DCI(v)$ 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 $DCI(v)$ and $HCl(v)$ distributions from the $N + CH_2Cl/CHDCI$ may be peaking at lower v . For both HCl and DCl, 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 $H/D + CH_2FI$ system led to an increase in $HF(v)$ and $DF(v)$ emission intensity along with weak $HCN(v_3)$ emission. Separate experiments were done for the $H + CH_2I_2 + N$ and $H + CH_3I + N$ reactions. All experiments gave weak $HCN(v_3)$ emission and even weaker HNC emission, as shown in Fig. 5. Thus, the $N + CH_2X$ reactions do have some general nature for $X = H, Cl, F$ and I . The HCN emission observed from these reactions (for $X = Cl$ and F) mainly consisted of the $(001) \rightarrow (000)$ transition with little evidence for any bending or CN stretch excitation. However, the $H + CH_2I_2 + N$ reaction system did generate additional vibrational excitation in HCN, see Fig. 5. For the $H + N + CH_2ClI$ reaction system, the $[HCN(v)]$ was estimated from the area under the curve, correcting for the Einstein coefficient and instrument response function. The $[HCN(v_3 = 1)]$ was 10% of the increase in $[HCl(v)]$. If the increase in $HCl(v)$ and $HCN(v)$ are due to the same reaction (R8), then one would expect equal amounts of $HCl(v)$ and $HCN(v)$. It is likely that most of the HCN product is produced in the vibrational ground state. However, this is just a speculation, since our experiment cannot directly determine the ground state population for HCN or HCl.

Experiments also were done with $N + CH_3$, $N + CH_2Cl$ and $N + CH_2Br$ using the $F + CH_4$, CH_3Cl and CH_3Br as primary reactions. Unfortunately the strong $HF(v, J)$ emission overlaps any weak HCN emission. Under favorable conditions, the HCN emission could be clearly observed underneath the $HF(v, J)$ emission as a shift in the base line. We attempted to observe an increase in HCl emission from $F + N + CH_3Cl$ compared to $F + CH_3Cl$. The latter reaction system gives both HF from the $F + CH_3Cl$ primary reaction and HCl from the $F + CH_2Cl$ secondary reaction.¹ The experiments were inconclusive because of several problems. We were unable to obtain $[F]$ above $3-4 \times 10^{12}$ molecule cm^{-3} . Thus, the CH_2Cl was lower than in the H atom experiments. In addition, the discharge products from CF_4 and N_2 interacted as evidenced from a chemiluminescence in the pre-reactor. Moreover, both $HF(v)$ and $HCl(v)$ intensities increased when N atoms were added. The additional HF is probably due to the production of more F atoms from the $N + CF_n$ reactions. However, the CN

chemiluminescence seemed to be of normal intensity, which implies that the (N) was normal. Observation of both HCN and CN emission (next section) provides evidence for the $N + CH_2X$ reaction in these systems.

III.5 $N + CH_2X$ reactions: CN emission

Both $H + N + CH_2XI$ and $F + N + CH_3X$ ($X = H, F, Cl, Br$ and I) reaction systems gave strong CN ($A \rightarrow X$) emission that was readily visible in a slightly darkened room. An emission spectrum was recorded for the $F + CH_3Cl/CH_4 + N$ reaction systems, using the second flow reactor. The vibrational distribution resembles the P_2 distribution characterized by Bayes³⁶ but with somewhat higher relative populations in the low v levels. This emission is the peach-colored flame observed when halogenated hydrocarbons are added to active nitrogen.^{33,36} The $H + CH_2XI$ and $F + CH_3X$ systems both led to the CN emission, clearly indicating that the F/H atoms do not have any role except to produce the CH_2X radicals. This also rules out the CF_n species, which may be present in the CF_4 discharge, as the only sources of CN. At our flow velocities and concentrations, the $N/N_2 + CH_3X$ or CH_2IX reactions alone gave no emission that was visible to the eye or the IR detector. Benson and coworkers⁵⁵ have studied the $N + CHCl_3$ reaction in a very low pressure reactor for longer reaction time (a few seconds) and reported a rate constant of 1×10^{-16} cm^3 molecule⁻¹ s⁻¹ for the primary step. This is consistent with our observation of no CN chemiluminescence in the absence of any added F or H atoms. In our reactors, the 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 CH_3X , the discharge products from N_2 and CF_4 reacted, generating a weak unidentified emission, in the pre-reactor section of the flow reactor for high N_2 and 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 CH_3X reagents to the $N/F/CF_x$ flow gave much stronger emission, which obscured this weak emission. Another observation was the build-up of $(CN)_x$ polymer on the flow reactor beyond the reagent inlet, as CN radical sources are prone to do.^{26,27} This suggests that the CN concentration is not negligible, and that the $N + CH_2X$ reaction system must include CN-generating steps.

The emission spectra and measurements of the dependence of the CN emission intensity were taken in the reactor that permitted the $[N]$ to be measured by titration with NO and the $[F]$ to be measured by titration with CF_3I . The various emission

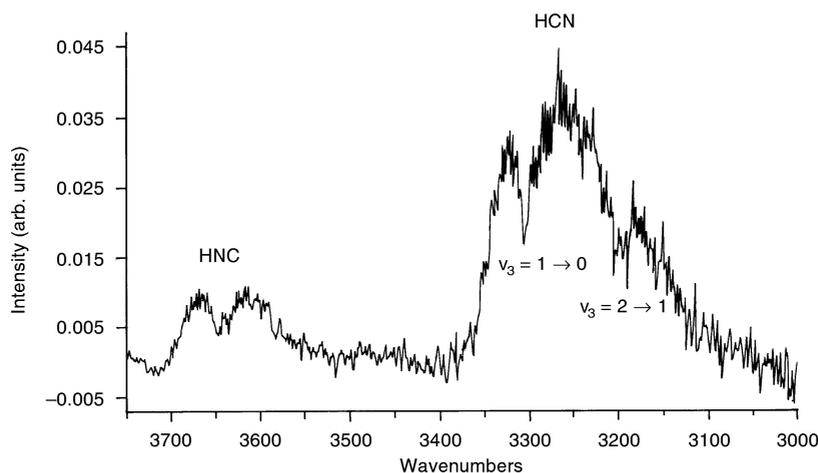


Fig. 5 The $HCN(v)$ and $HNC(v)$ infrared emission spectra observed from $H + N + CH_2I_2$ reactions. The pressure was 1.8 Torr and the reaction time was 0.8 ms. $[H] = 6 \times 10^{13}$. Both HCN and HNC emission are thought to result from the $N + CH_2I$ reaction.

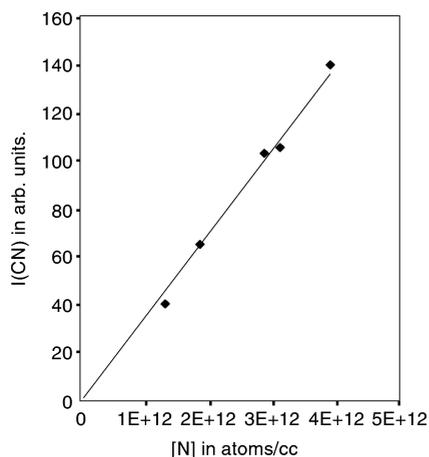


Fig. 6 The CN(A → X) emission intensity from the F + CH₃Cl + N reaction system as a function of [N]. The [N] was determined by titration with NO by observation of the N₂(B-A) emission intensity to determine the end point. [F] = 2 × 10¹² and [CH₃Cl] = 3 × 10¹³ molecules cm⁻³; the reaction time was 5 ms.

intensities were measured with a 0.5 m monochromator fitted with a cooled S-1 photomultiplier tube. The experiments were done with CH₃Cl and CH₄ concentrations of $\sim 3 \times 10^{13}$ molecules cm⁻³ with [F] = 3 × 10¹² and [N] = 0.5–5 × 10¹² atoms cm⁻³. For a fixed [N] concentration, the CN emission intensity increased linearly with [F] for fixed [CH₃Cl] and with [CH₃Cl] 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 [CH₃Cl] = 4 × 10¹³ and [F] = 2 × 10¹² molecule cm⁻³. The results, shown in Fig. 6, demonstrate apparent first-order kinetics for [N] = 1–5 × 10¹² atoms cm⁻³.

IV. Discussion

IV.1 The H + CH₂ClI and CH₂FI reactions

The H + CH₂ClI reaction at room temperature has several surprising aspects. Foremost was the HCl(*v* > 0) product channel with a rate constant of $5 \pm 2 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 300 K, which is much larger than that for H + CH₃Cl or CH₂Cl₂. A second surprise was the observation of both HCl and DCl formation from D + CH₂ClI. Finally the HCl(*v*) distribution was rather flat with strong emission from HCl(*v* ≤ 4) and weak emission from *v* = 5, which indicates a low *D*(Cl–CH₂I) as already discussed. All of these aspects are consistent only with addition of the H atom to the iodine atom 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.^{17–19} Attack at the iodine atom serves as a way of circumventing the energy barrier for direct abstraction. The HCl(*v*) distribution gives $\langle f_v(\text{HCl}) \rangle = 0.48$, which is much larger than most 3- or 4-centred unimolecular elimination reactions. The linear vibrational surprisal and the large $\langle f_v \rangle$ 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 CH₂ClI, F with CH₂BrCl and Cl with CH₃I 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–I–Cl structures of CH₃I and CH₂ClI with weak I–Cl bonds (55 kJ mol⁻¹).^{12,15} 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 Cl 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 $\angle\text{HIC}$ is not linear, as theoretically found for $\angle\text{ClIC}$, 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 H atoms originally bound to I and C interchange positions by a rearrangement pathway. Recently, Holmes and coworkers have identified such an unusual 1,2-FCl rearrangement pathway in CF₂ClCF₂CH₃, which facilitates 4-centered HCl elimination through CF₃CFCICH₃.⁵⁶

Is the HI formation, (R1), process always direct or can it be an exit channel from the adduct? Certainly the O atom addition mechanism seems to be fairly general for alkyl iodides.^{13,14} The HCl(*v*) and DCl(*v*) intensities reported in Table 2 offer some important clues. Intensities of both HCl(*v*) and DCl(*v*) increase on N atom addition to the D + CH₂ClI reaction system. If DI formation occurs through direct abstraction only, then one would expect the HCl(*v*) intensity alone to increase by the contribution from N + CH₂ClI, with no change in DCl(*v*). 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 DCl(*v*) (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(⁴S) atom and CH₂X radicals is association to give the CH₂XN triplet ground-state nitrene radical. The nitrene 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,^{57–59} but dissociation of a carbon–halogen bond might be possible. The (R4) (or (R8)) step requires intersystem crossing to the singlet nitrene potential surface,^{20,57} 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(*v*) distribution appears similar to that of the H + CH₂ClI 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 nitrene 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.⁵⁷ 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.

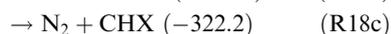
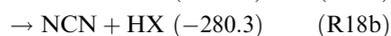
Secondary reactions must be responsible for the CN chemiluminescence because N + CH₃ does not provide sufficient energy to give CN(A) + HX + H. Since the radical species from the primary steps seem reasonably well established and since

the thermochemistry can be estimated, a discussion of the mechanism responsible for the chemiluminescence in the $N + CH_2X$ reaction seems worthwhile. Since the $CN(X, v)$ and $CN(A, v)$ states are rapidly interconverted^{60–62} 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 exoergicity to give $CN(A, v' = 8)$. As a consequence of early work on the subject^{33–38} several excitation steps have been discussed. These include: (i) the $N(^4S) + CX(X^2A)$ 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 $N + NCN$. Dorthé and coworkers⁶³ 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 argument⁶⁴ 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. Except for 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.³⁷ Benson and coworkers⁵⁵ have suggested the following sequence to explain the CN emission from the $N + CHCl_3$ reaction system:



The $N + ClCN$ 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 $CCl(X^2\Pi)$ or $CH(X^2\Pi)$ 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 (CH_2N or $CHXN$) from the $N + CH_2X$ 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 $\Delta_f H^\circ(CH_2N)^{66} = 238.5$ and $\Delta_f H^\circ(NCN)^{67} = 456.1$ kJ mol⁻¹.



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. Steif and coworkers²³ 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 $N + CH_2N$ seems unlikely. The isomerization of CH_2N to $HCNH$ or CNH_2 have calculated barriers⁵⁷ of 188.3 and 288.7 kJ mol⁻¹ and they are unlikely candidates. Since the CH_2N 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 coworkers⁶⁸ observed CN formation when monitoring the products from the $N + CF_3$ reaction by mass spectrometric detection. Most spectroscopic studies of NCN radicals have used the $N_2/CF_4/He$ microwave discharge as the source for NCN,^{69–71} 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 $HCl(v > 0)$ formation from the $H + CH_2ClI$ reaction with a rate constant of $5 \pm 2 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at room temperature. The $D + CH_2ClI$ reaction gives both HCl and DCl products, which strongly suggests a mechanism in which H/D exchange occurs in an adduct. The $HCl(v)$ distribution has a linear surprisal with $\langle f_v \rangle = 0.48$, which suggests an analogy to the dynamics for the addition–migration channel of the $H + ICl$ reaction. From the highest observed $HCl(v = 5)$ level, $D(Cl-CH_2I)$ is estimated to be ≤ 301.2 kJ mol⁻¹ compared to a theoretical estimate of 326.4 kJ mol⁻¹. The $H + CH_2FI$ reaction is similar to the $H + CH_2ClI$ and the highest observed $HF(v = 3)$ level from the $H + CH_2FI$ reaction implies that the C–F bond energy is ≤ 460.2 kJ mol⁻¹. The lower $D(C-Cl)$, relative to that of CH_3Cl , is consistent with the bond energies of other CH_2XCl molecules. In contrast, multiple halogen substitution does not seem to affect the $D(C-F)$ values very much. The I atom in the CH_2XI molecules provides a reaction pathway to access the Cl or F atoms with a lower energy barrier compared to direct X abstraction. The H/D exchange was identified by the inference of CH_2Cl and $CHDCl$ product as well, which suggests that the HI formation channel also arises *via* the adduct.

The addition of N atoms to the reactor containing CH_2Cl radicals gave additional $HCl(v)$ emission plus weak HCN and HNC emission. These observations identify a singlet exit channel from the $N + CH_2Cl$ reaction, although the spin-conserving triplet channel giving $Cl + CH_2N$ products is probably the dominant one. Fast secondary reactions starting with $N + CH_2N$ reaction must lead to CN formation, in part, as identified by the $CN(A)$ chemiluminescence from several $F/CH_3X/N$ and $H/CH_2XI/N$ reaction systems. One possibility for the $CN(A)$ forming step is $N + NCN$. However, the products from the $N + CH_2N$ reaction need to be identified before this possibility could be confirmed.

Acknowledgements

RV acknowledges the support of the National Science Foundation under a REU grant CHE-9732103 to KSU. EA thanks the Director, IISc and IISc-ISRO Space Technology Cell for partial support. We thank G. C. Manke II for communicating unpublished results on $H + Cl_2$ rate constant measurements.

References

- 1 E. Arunan, S. J. Wategaonkar and D. W. Setser, *J. Phys. Chem.*, 1991, **95**, 1539.
- 2 E. Arunan, R. Rengarajan and D. W. Setser, *Can J. Chem.*, 1994, **72**, 568.
- 3 A. Srivatsava, E. Arunan, G. Manke, D. W. Setser and R. Sumathi, *J. Phys. Chem. A*, 1998, **102**, 6412.
- 4 N. I. Butkovskaya and D. W. Setser, *J. Chem. Phys.*, 1996, **105**, 5064.
- 5 R. A. Morris, K. Donohue and D. L. McFadden, *J. Phys. Chem.*, 1989, **93**, 1358.
- 6 P. Marshall, A. Misra and R. J. Berry, *Chem. Phys. Lett.*, 1997, **265**, 48.
- 7 J. Yuan, L. Wells and P. Marshall, *J. Phys. Chem. A*, 1997, **101**, 3542.
- 8 R. Vogt, R. Sander, R. Von Glasow and P. J. Crutzen, *J. Atmos. Chem.*, 1999, **32**, 375.

- 9 O. V. Rattigan, D. E. Shallcross and R. A. Cox, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 2839.
- 10 C. M. Roehl, J. B. Burkholder, G. K. Moortgat, A. R. Ravishankara and P. J. Crutzen, *J. Geophys. Res. [Atmos.]*, 1997, **102**, 12819.
- 11 M. Bilde, J. Sehested, O. J. Nielsen, T. J. Wallington, R. J. Meagher, M. E. McIntosh, C. A. Piety, J. M. Nicovich and P. H. Wine, *J. Phys. Chem. A*, 1997, **101**, 8035.
- 12 K. G. Kambanis, D. Y. Argyris, Y. G. Lazarou and P. Papiannakopoulos, *J. Phys. Chem. A*, 1999, **103**, 3210. (The experimental value for the CH₂I enthalpy of formation has been quoted in this paper from W. B. DeMore, S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb and M. J. Molina, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, JPL Publication 97-4, 1997.
- 13 X. Gao, J. Essex-Lopresti, S. Munro, M. P. Hall, D. J. Smith and R. Grice, *J. Phys. Chem. A*, 1998, **102**, 1912.
- 14 R. A. Loomis, J. J. Klaassen, J. Linder, P. G. Christopher and S. R. Leone, *J. Chem. Phys.*, 1997, **106**, 3934.
- 15 Y. V. Ayhens, J. M. Nicovich, M. L. McKee and P. H. Wine, *J. Phys. Chem. A*, 1997, **101**, 9382.
- 16 M. Bilde, J. Sehested, O. J. Nielsen and T. J. Wallington, *J. Phys. Chem. A*, 1997, **101**, 5477.
- 17 K. Tamagake and D. W. Setser, *J. Phys. Chem.*, 1979, **83**, 1000.
- 18 D. Brandt and J. C. Polanyi, *Chem. Phys.*, 1980, **45**, 65.
- 19 J. C. Polanyi, J. L. Schreiber and W. J. Skrlac, *Faraday Discuss Chem. Soc.*, 1979, **67**, 66.
- 20 R. G. Sadygov and D. R. Yarkony, *J. Chem. Phys.*, 1997, **107**, 4994.
- 21 L. J. Steif, G. Marston, D. F. Nava, W. A. Payne and F. L. Nesbitt, *Chem. Phys. Lett.*, 1988, **147**, 570.
- 22 G. Marston, F. L. Nesbitt, D. F. Nava, W. A. Payne and L. J. Steif, *J. Phys. Chem.*, 1989, **93**, 5769.
- 23 G. Marston, F. L. Nesbitt and L. J. Steif, *J. Chem. Phys.*, 1989, **91**, 3483.
- 24 D. F. Davidson and R. K. Hanson, in *Proceedings of the 23rd Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 1990, p. 267.
- 25 Y. L. Yung, M. Allen and J. P. Pinto, *Astrophys. J. Suppl.*, 1984, **55**, 465.
- 26 E. Arunan and Setser, *J. Phys. Chem.*, 1991, **95**, 4190.
- 27 E. Arunan, G. Manke II and D. W. Setser, *Chem. Phys. Lett.*, 1993, **207**, 81.
- 28 (a) L. R. Copeland, F. Mohammad, M. Zahedi, D. H. Volman and W. M. Jackson, *J. Chem. Phys.*, 1992, **96**, 5897; (b) L. R. Copeland, F. Mohammad, M. Zahedi, D. H. Volman and W. M. Jackson, *J. Chem. Phys.*, 1992, **97**, 3878.
- 29 M. S. Gordon and T. N. Truong, *Chem. Phys. Lett.*, 1987, **142**, 110.
- 30 W. G. Clark, D. W. Setser and K. Dees, *J. Am. Chem. Soc.*, 1971, **93**, 5328.
- 31 K. Dees and D. W. Setser, *J. Chem. Phys.*, 1968, **49**, 1193.
- 32 C. F. Rodriguez, D. K. Bohme and A. C. Hopkinson, *J. Phys. Chem.*, 1996, **100**, 2942 and references cited therein.
- 33 T. Iwai, M. I. Savadatti and H. P. Broida, *J. Chem. Phys.*, 1967, **47**, 3861.
- 34 D. W. Setser and B. A. Thrush, *Proc. R. Soc. London, Ser. A.*, 1965, **288**, 256 and 275.
- 35 J. C. Boden and B. A. Thrush, *Proc. R. Soc. London, Ser. A.*, 1968, **305**, 93 and 107.
- 36 K. D. Bayes, *Can. J. Chem.*, 1961, **39**, 1074.
- 37 M. R. Gorbali and M. I. Savadatti, *Chem. Rev.*, 1982, **82**, 527.
- 38 C. A. Arrington Jr., O. O. Bernardini and G. A. Kistiakowsky, *Proc. R. Soc. London, Ser. A.*, 1969, **310**, 161.
- 39 R. N. Haszeldine, *J. Chem. Soc.*, 1952, 4259.
- 40 E. Arunan, D. W. Setser and J. F. Ogilvie, *J. Chem. Phys.*, 1992, **97**, 1734.
- 41 P. Botschwina, *Chem. Phys.*, 1983, **81**, 73.
- 42 J. D. Rogers and J. J. Hillman, *J. Chem. Phys.*, 1982, **77**, 3615.
- 43 K. B. Hewett, G. Manke II, D. W. Setser and G. Breewood, *J. Phys. Chem. A*, 2000, **104**, 539.
- 44 B. E. Holmes and D. W. Setser, in *Physical Chemistry of Fast Reactions*, ed. I. W. M. Smith, Plenum Press, New York, 1980.
- 45 M. W. Chase, Jr., C. A. Davies, J. R. Downey Jr., D. J. Frurip, R. A. McDonald and A. N. Syverud, *J. Phys. Chem. Ref. Data.*, 1985, **14**, (Suppl. No 1).
- 46 A. K. Chandra and T. Uchimaru, *J. Phys. Chem. A*, 2000, **104**, 9244.
- 47 D. Kita and D. H. Stedman, *J. Chem. Soc., Faraday Trans. 2*, 1982, **78**, 1249.
- 48 P. P. Bemard and M. A. A. Clyne, *J. Chem. Soc., Faraday Trans. 2*, 1977, **73**, 394. (A recent measurement by O. Dobis and S.W. Benson suggests a rate constant that is 1/2 of the value given by refs. 47 and 48, *J. Phys. Chem. A*, 2000, **104**, 777. However, unpublished results by G. C. Manke II and M. C. Heaven support the earlier results.)
- 49 P. B. Roussel, P. D. Lightfoot, F. Caralp, V. Catoire, R. Lesclaux and W. Forst, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 2367.
- 50 A. A. Zavitsos, *J. Phys. Chem.*, 1987, **91**, 5573.
- 51 D. F. McMillen and D. M. Golden, *Annu. Rev. Phys. Chem.*, 1982, **33**, 493.
- 52 E. Arunan, C. P. Liu, D. W. Setser, J. V. Gilbert and R. D. Coombe, *J. Phys. Chem.*, 1994, **98**, 494.
- 53 R. Rengarajan, D. W. Setser and D. D. DesMariseau, *J. Phys. Chem.*, 1994, **98**, 10568.
- 54 Atom-radical reactions are usually fast. For example the H + CF₃ reaction has a rate constant of 8.9×10^{-11} cm³ molecule⁻¹ s⁻¹; K. R. Ryan and I. C. Plumb, *Plasma Chem. Plasma Process.*, 1984, **1**, 141.
- 55 S. C. Jeoung, K. Y. Choo and S. W. Benson, *J. Phys. Chem.*, 1991, **95**, 7282.
- 56 M. O. Burgin, G. L. Heard, J. M. Martell and B. E. Holmes, *J. Phys. Chem. A*, 2001, **105**, 1615.
- 57 M. T. Nguyen, D. Sengupta and T.-K. Ha, *J. Phys. Chem.*, 1996, **100**, 6499.
- 58 B. S. Jursic, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 2355.
- 59 P. Felder, J. A. Harrison and J. R. Huber, *J. Phys. Chem.*, 1991, **95**, 1945.
- 60 (a) G. Jihua, A. Ali and P. J. Dajdigian, *J. Chem. Phys.*, 1986, **85**, 7098; (b) G. Jihua, A. Ali and P. J. Dajdigian, *J. Chem. Phys.*, 1987, **87**, 2045.
- 61 N. Furio, A. Ali and P. J. Dajdigian, *J. Chem. Phys.*, 1986, **85**, 3860.
- 62 M. de Moor, Ch. Ottinger, A. F. Vilesov and D. D. Xu, *J. Chem. Phys.*, 1994, **101**, 9506.
- 63 N. Daugey, A. Bergeat, J.-C. Loison, A. Schuck, P. Caubet and G. Dorthe, *Chem. Phys. Lett.*, 2000, **324**, 1.
- 64 D. W. Setser and B. Thrush, *Nature*, 1963, **200**, 864.
- 65 M. T. Rayez, Ph. Halvick, J. C. Rayez, Ph. Millie and B. Levy, *Chem. Phys.*, 1994, **188**, 161.
- 66 (a) R. Sumathi and M. T. Nguyen, *J. Phys. Chem. A*, 1998, **102**, 8013; (b) D. C. Cowels, M. J. Travers, J. L. Freuh and G. B. Ellison, *J. Chem. Phys.*, 1991, **94**, 3517; (c) D. C. Cowels, M. J. Travers, J. L. Freuh and G. B. Ellison, *J. Chem. Phys.*, 1991, **95**, 3864 report 213 ± 21 kJ mol⁻¹.
- 67 L. V. Moskaleva and M. C. Lin, *J. Phys. Chem. A*, 2001, **105**, 4156.
- 68 C.-P. Tsai, S. M. Belanger, J. T. Kim, J. R. Lord and D. L. McFadden, *J. Phys. Chem.*, 1989, **93**, 1916.
- 69 R. T. Bise, H. Choi and D. M. Neumark, *J. Chem. Phys.*, 1999, **111**, 4923.
- 70 G. P. Smith, R. A. Copeland and D. R. Crosley, *J. Chem. Phys.*, 1989, **91**, 1987.
- 71 K. D. Hensel and J. M. Brown, *J. Mol. Spectrosc.*, 1996, **180**, 170.