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Photoelectron Spectroscopic Study of the Ground States of CH_2Cl^+, $CHCl_2^+$, and $CHFCl^+$

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Abstract: Reactions of chloromethanes with fluorine atoms produced the CH_2Cl, $CHCl_2$, and CHFCl free radicals for observation of structured first photoelectron bands. These bands at 8.87, 8.54, and 9.16 ± 0.01 eV vertical ionization energies, respectively, exhibited 1040 ± 30, 860 ± 30, and 920 ± 40 cm^{-1} vibronic intervals that are due to symmetric C–Cl stretching fundamentals in the ground states of the CH_2Cl^+, $CHCl_2^+$, and $CHFCl^+$ cations. The observed fundamentals are substantially higher than corresponding values for the ground electronic states of the neutral radicals, which indicates a substantial increase in net C–Cl bonding in the cations as compared to the free radicals.

Introduction

Photoelectron spectroscopy has been generally employed to study stable molecules and low-lying electronic states of the corresponding cations.[1,2] Although free radicals require special methods for preparation, these species are interesting subjects for photoelectron spectroscopic investigation since the cations formed on ionization may have different bonding and structure from the neutral free radicals. Hydrogen atom abstraction by fluorine atoms from suitable precursors has proven to be an effective method for preparing free radicals for photoelectron spectroscopic study.[3-5] This paper reports such a study of the ground states of CH_2Cl^+, $CHCl_2^+$, and $CHFCl^+$ produced by ionization of the corresponding free radicals; preliminary photoelectron spectra of the CH_2Cl free radical have been communicated in an earlier letter.[6]

Only a few direct observations of chloromethyl free radicals have been reported, although these radicals have been proposed as reaction intermediates.[7-9] The infrared spectrum of CH_2Cl in solid argon provided evidence for a planar radical with some $(C_{2p}-Cl_{3p})\pi$ bonding,[10,11] a point confirmed by a more recent ESR study of CH_2Cl in glassy matrices.[12] The electron impact ionization energy (8.80 ± 0.05 eV)[13] for CH_2Cl suggests a substantial electronic effect for the chlorine substituent compared to CH_3 (9.84 ± 0.01 eV vertical ionization energy).[14] This effect is enhanced in $CHCl_2$, again based on the electron impact ionization energy (8.45 ± 0.05 eV).[13] Subsequent ESR studies of CH_2Cl and $CHCl_2$ in single crystals[15-17] and glassy matrices[12] at low temperature have found no major deviation from planarity for these radicals although the corresponding fluoromethyl radicals are slightly nonplanar.[18]

Experimental Section

He(I) photoelectron spectra were recorded on a new multichannel detector photoelectron spectrometer equipped with a concentric tube flow reactor for producing free radicals by fluorine atom reactions.[25,26] The usual experimental resolution was 25–30 meV as measured for argon (full width at half-maximum). The helium dc discharge lamp employed here emits primarily He I_α (21.22 eV) radiation, with about 2% He I_β (23.09 eV) and about 0.2% He I_γ (23.74 eV) subsidiary lines. One experiment used a neon discharge source which gives mainly the Ne I_α (16.85 eV) line with a small amount of the Ne I_α (16.67 eV) line. Fluorine atoms, produced by microwave discharge of 5% F_2 diluted by helium (B.O.C. Special Gases) in an alumina tube, were mixed with reagent molecules 0.5–9.0 cm above the ionizing radiation. Methyl chloride (BDH Chemicals Ltd.), methylene chloride (May and Baker, Ltd.), CD_2Cl_2 (Aldrich, 99.6% D), chlorofluoromethane (Allied Chemical Corp.), chloroform, and ethyl chloride (BDH Chemicals, Ltd.) reagents were used as received. Photoelectron spectra of the reaction products were studied as a function of each reagent concentration and mixing distance above the He(I) photon beam. Spectra were calibrated in situ against CH_3I added to the sample chamber,[28] and reported ionization energies are accurate to within ±0.01 eV except where otherwise noted. In this paper PES bands are conveniently referred to by their vertical ionization energies in electron volts.

Results

The results from fluorine atom reactions with a number of chloroalkane precursors will be described in turn.

CH_3Cl. A large number of F + CH_3Cl experiments were performed using a variety of reaction conditions. The initial studies employed sufficiently high F atom partial pressures to react 10–50% of the CH_3Cl reagent and almost all of the atomic fluorine at short mixing distances (0.6 cm). This gave a new structured band in the 8.7–9.2 eV ionization energy region. The intensity of this new band was approximately 70% of the CH_3Cl first band ionized by He I_β radiation (at 9.43 eV apparent ionization energy). The new product band was substantially stronger than the CH_3Cl

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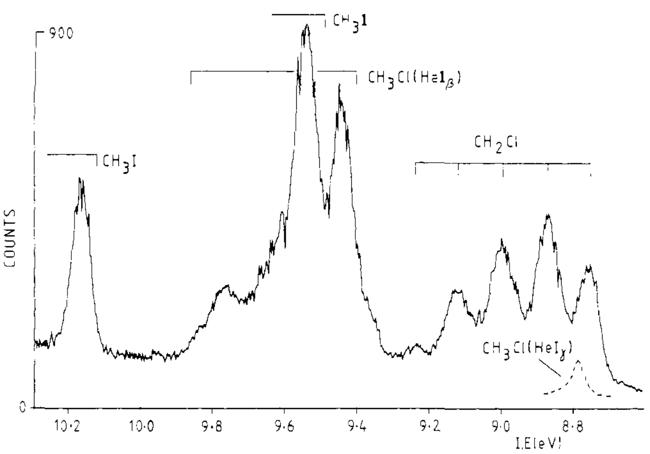

Figure 1. He I photoelectron spectrum in the 8.5–10.4-eV ionization energy region for the primary product of the fluorine atom–methyl chloride reaction using 0.6 cm reagent mixing distance above the photon beam. The spectrum, composed of 2500 added scans, also illustrates CH_3I added to the sample chamber for calibration purposes, and the contribution from the first precursor band ionized with He I_γ radiation.

first band ionized with He I_γ radiation (at 8.78 eV apparent ionization energy). These photoelectron bands and the two strong CH_3I calibrant signals are shown in Figure 1, which is a minicomputer plot of 2500 added scans of the 8.6–10.2 eV ionization energy region. Virtually identical spectra were recorded 10 times in a 1-h period. The structured product band exhibited 8.75 and 8.87 ± 0.01 eV adiabatic and vertical ionization energies, respectively. The separations between the five vibronic peaks were measured as 970, 1020, 1000, and 990 ± 30 cm^{-1}, respectively, from lower to higher ionization energy. Since the weak band at 8.78 eV apparent ionization energy from He I_γ ionization of CH_3Cl contributes to the 8.75 eV vibrational component profile, a more accurate $v' = 0–1$ band separation can be deduced by extrapolation from the higher intervals. This procedure gives a 1040 ± 30 cm^{-1} value for the $v' = 0–1$ separation. The harmonic vibrational constant derived from these separations is 1060 ± 30 cm^{-1}, and the anharmonic constant is 10 ± 5 cm^{-1}. The spectrum recorded with Ne I_α ionizing radiation exhibited a 1040 ± 30 cm^{-1} $v' = 0–1$ vibrational spacing in support of the above analysis of the structured product band.

A survey spectrum from 8.0 to 18.0 eV showing the structured 8.8-eV product band, the very strong CH_3Cl band from He I_α ionization at 11.30 ± 0.01 eV, and weaker signals due to the reaction products HCl (12.75, 12.83 eV),[2] Cl atom (12.97, 14.41 eV),[29] HF (16.06 and 16.41 eV),[30] and unreacted F atoms (17.42 eV),[29] has been reported in the earlier letter.[6] A similar spectrum of the reaction mixture recorded with the discharge off revealed CH_3Cl and F_2 bands without HF, HCl, Cl, and the structured product band in the 8.5–9.2-eV region; this demonstrates that the latter signals arise from the F + CH_3Cl reaction.

The effect of reagent mixing distance on the product band intensities was studied in three separate experiments with slightly different F/CH_3Cl partial pressure ratios in the initial low F/high CH_3Cl range as described above. In all of these experiments, increasing the mixing distance from 0.6 to 3.0 cm reduced the CH_3Cl first band intensity by 10–30%, depleted the F atom band, and doubled the HF signal. The structured 8.87-eV band and Cl atom signal intensities were approximately halved while the HCl signal tripled. In addition, a weak band with resolved 10.00 and 10.18-eV components and a strong band with intense vertical ionization at 10.62 eV and a weaker vibrational component at 10.88 eV appeared in the spectrum; these bands are in very good agreement with known photoelectron spectra of vinyl chloride and chloroacetylene, respectively.[31,32] Increasing the mixing distance to 6.0 cm had little effect on the CH_3Cl and HF bands and markedly decreased the structured 8.87-eV and Cl atom bands. It also revealed a weak sharp new signal at 9.12 ± 0.02 eV and slightly increased the vinyl chloride, chloroacetylene, and HCl signals. At 6.0 cm mixing distance, increasing the F atom partial pressure by 20% reduced the CH_3Cl band intensity by 30% and increased all of the above product bands. However, the structured band at 8.87 eV was not observed. A final increase to 9.0 cm mixing distance halved the CH_3Cl intensity and slightly decreased the band at 9.12 eV. The vinyl chloride and Cl atom signals slightly decreased and the HCl and HCCCl bands slightly increased. New sharp bands were observed at 9.55 and 9.76 eV. The latter bands are two of the strongest vibronic components of the CF radical.[33] Returning to 6.0 cm mixing distance, reducing the CH_3Cl partial pressure with increased F atom partial pressure gave a clean, resolved CF radical first band at 9.11 eV adiabatic and 9.55 eV vertical ionization energies, a weak CH_3Cl first band at 11.30 eV, and strong HCl and Cl atom signals.

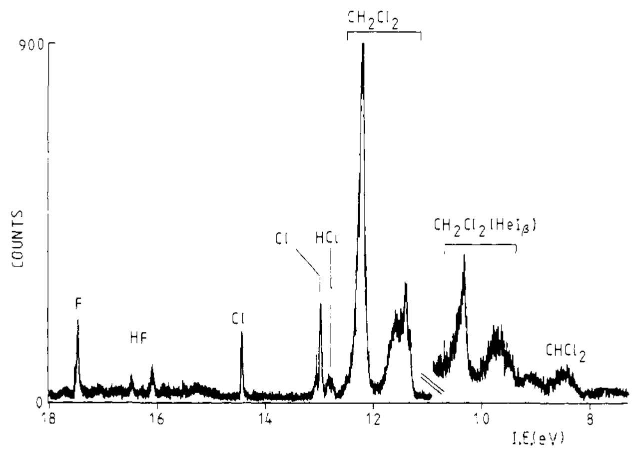

Figure 2. He I survey photoelectron spectrum of the 8–18-eV ionization energy region for fluorine atom–methylene chloride reaction products using 1.5 cm mixing distance. The voltage to the channel plates was reduced at 11.1 eV to prevent overloading of the strong precursor signals.

CH_2Cl_2. The F + CH_2Cl_2 reaction was also explored under a variety of reaction conditions. Since the rate constant for this reaction is about 40% of the rate constant for the F + CH_3Cl reaction at room temperature,[8] slightly longer mixing distances were required to give comparable yields of HF. Figure 2 shows a survey spectrum for the F + CH_2Cl_2 reaction using low F/high CH_2Cl_2 partial pressures and 1.5 cm mixing distance. The He I_α bands of CH_2Cl_2 at 11.41 and 12.20 eV are in agreement with published spectra;[1,2] the spectrum shows weaker 9.69- and 10.33-eV apparent ionization energy bands due to He I_β ionization and the weak 9.04-eV apparent ionization energy band due to He I_γ ionization of CH_2Cl_2. A new structured band in the 8.2–9.0 eV ionization energy region, strong Cl atom, and weak HCl signals appeared as products of the F + CH_2Cl_2 reaction. On increasing the F atom partial pressure from zero, the new structured band quickly went through an intensity maximum and then decreased while Cl atom and HCl signals and a new broad band with a 9.14 ± 0.02 eV maximum increased. A similar effect was found on increasing the reagent mixing distance from 0 to 9 cm. Unlike the structured product band in the F + CH_3Cl reaction, 20% of the structured product band in the F + CH_2Cl_2 reaction survived at 6 cm mixing distance. Also, the 9.14-eV band intensity was approximately double the 8.54-eV band intensity at 6 cm, and increasing the F atom/CH_2Cl_2 ratio virtually eliminated CH_2Cl_2 and increased the 9.14-eV band intensity at the expense of the structured product band. In contrast to the short mixing distance used for the spectrum shown in Figure 2, the HCl signal dominated over the Cl atom signal at long mixing distances.

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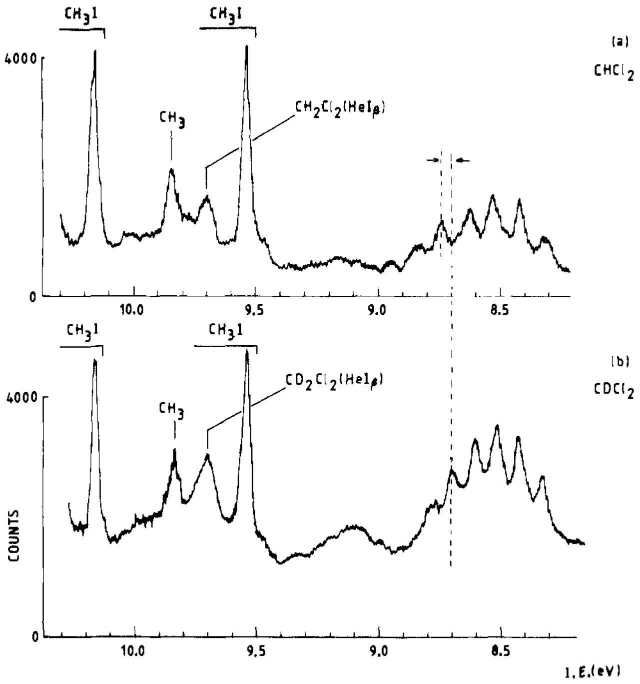

Figure 3. He I photoelectron spectra in the 8.2–10.4-eV ionization energy region for the primary product of the fluorine atom–methylene chloride reaction at 1.5 cm mixing distance: (a) F + CH_2Cl_2; (b) F + CD_2Cl_2. The broad 9.0–9.2-eV band contains contributions from the first precursor band ionized with He I_γ radiation and a secondary reaction product species. The dashed lines show the isotopic shift in the fifth vibronic bands for each product.

The F + CH_2Cl_2 reaction was further examined in 98 spectra run under optimum conditions for yield and resolution of the vibronic structure of the primary reaction product band using the signal averaging capability of the multidetector instrument. Figure 3a illustrates the spectrum in the 8.2–10.4-eV I.P. region resulting from the addition of four sets of 1000 scans each recorded in a total time of 60 s showing the structured product band and CH_3I calibrant bands.

Equivalent spectra were produced from the addition of other sets of 1000 and 1500 scans recorded on two successive days. The adiabatic ionization energy (8.32 ± 0.01 eV), vertical ionization energy (8.54 ± 0.01 eV), and $v' = 0$–1 ionic vibrational spacing (860 ± 30 cm^{-1}) were measured by use of the methyl iodide calibrant bands. The separations for each vibronic component in the structured band yielded the harmonic vibrational constant 890 ± 30 cm^{-1} and a 15 ± 5 cm^{-1} value for the anharmonic constant.

Deuterated methylene chloride was used as the reagent in four separate runs. This reaction revealed the first band of DF at 16.07 ± 0.01 eV with a vibrational component at 16.33 ± 0.01 eV,[30] Cl and HCl bands and a slightly different structured band, which is illustrated in Figure 3b obtained from four added sets of 2500 scans. Similar spectra to that shown in Figure 3b were obtained from other sets of 1500 and 2500 scans. The deuterated product spectrum revealed adiabatic (8.33 ± 0.01 eV) and vertical (8.52 ± 0.01 eV) ionization energies and $v' = 0$–1 ionic vibrational spacing (790 ± 30 cm^{-1}). As expected, the isotopic shift for the product becomes larger at higher vibrational levels as can be seen for the fifth components at 8.74 ± 0.01 eV in Figure 3a and 8.70 ± 0.01 eV in Figure 3b. The vibrational intervals in the latter band give harmonic and anharmonic vibrational constants of 820 ± 30 cm^{-1} and 15 ± 5 cm^{-1}, respectively. Similar variations of F atom partial pressure and mixing distance were performed for the CD_2Cl_2 reaction with identical results as described for the CH_2Cl_2 reaction including a new broad band at 9.12 ± 0.02 eV that increased with increasing mixing distance.

CH_2FCl. The F + CH_2FCl reaction was examined in four runs involving a total of 93 spectra. Precursor spectra are in good agreement with those reported earlier;[34] the first vertical ionization energy of CH_2FCl was measured here as 11.71 ± 0.01 eV relative to CH_3I. Spectra recorded for medium F atom/high CH_2FCl partial pressure conditions using a 2.0 cm mixing distance revealed substantial HCl, Cl, and HF signals and a weak 8.8–9.5 eV ionization energy product band with partially resolved structure. Figure 4 illustrates a spectrum composed of 2500 scans in the 8.4–10.4 eV ionization energy region showing the CH_2FCl band from He I_β ionization at 9.84 ± 0.01 eV apparent ionization energy and the new structured band at 8.81 and 9.16 ± 0.02 eV adiabatic and vertical ionization energies, respectively, with a 920 ± 40 cm^{-1} average vibrational separation. The contribution from He I_γ ionization of CH_2FCl to the observed band is indicated by the dashed inset spectrum recorded with the discharge off and scaled to the He I_β band of CH_2FCl in the reaction product spectrum. This contribution from CH_2FCl slightly affects the apparent $v' = 3$–4 vibrational separation in the new product band, but the $v' = 0$–1 and 1–2 separations are not altered. Increasing the mixing distance to 3.5, 5.5, and 7.5 cm increased HCl, Cl atom, and HF band intensities and decreased the CH_2FCl, F atom, and the structured product band intensities with about 40% of the maximum structured product intensity being observed at the longest mixing distance employed.

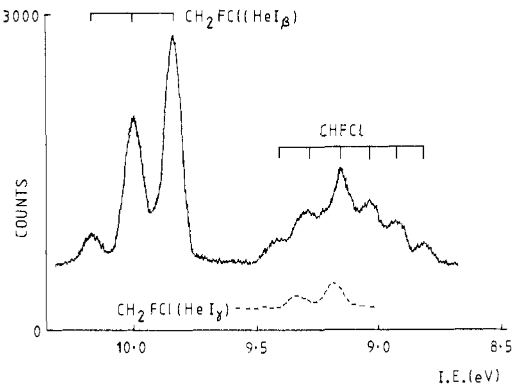

Figure 4. He I photoelectron spectrum in the 8.6–10.4-eV ionization energy region for the primary product of the fluorine atom–chlorofluoromethane reaction using a 2.0 cm mixing distance. The dashed spectrum shows the contribution from the first precursor band ionized with the He I_γ radiation.

$CHCl_3$. The F + $CHCl_3$ reaction was studied with several reagent partial pressures and mixing distances. The yield of HF was low compared to the other reactions studied here owing to the much smaller reaction rate.[8] Sharp Cl atom signals were observed at mixing distances of 1–2 cm and HF and Cl signals increased with mixing distance, but no other product band was observed. Particular attention was given to the 8.0–8.5 eV ionization energy region[13] using signal averaging, but no product band could be detected in this region.

C_2H_5Cl. Ethyl chloride was reacted with fluorine atoms in one experiment. At short mixing distances (0.5 cm) the yield of HF was more than in a comparable CH_3Cl experiment. A weak, structureless product band at 8.10 ± 0.05 eV vertical ionization energy (calibrated with the C_2H_5Cl first band at 11.06 eV and the second band of Cl atoms at 14.41 eV),[2,29] and weak HCl and strong Cl atom bands were also observed. At increased mixing distances, the C_2H_5Cl bands and the band at 8.10 eV decreased while HCl, Cl, and HF bands increased.

Computational Details

The CH_2Cl radical has the electronic ground-state configuration: $(7a_1)^2(2b_2)^2(3b_1)^2(3b_2)^1\ X^2B_2$, where the outermost molecular orbital, the $3b_2$ level, is an antibonding π orbital composed mainly of a carbon 2p atomic orbital with a small contribution from a Cl 3p atomic orbital.

Vertical ionization potentials have been predicted by performing SCF calculations for the CH_2Cl X^2B_2 state and the CH_2Cl^+ states

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Table I. Calculated Vertical Ionization Potentials (eV) of $CH_2Cl(X^2B_2)$[a]

orbital ionized	ionic state	ΔSCF vert I.P.	ΔSCF value plus correl cor	exptl vert I.P., this work
$3b_2$	$^1A_1$	8.72	9.52	8.87
$3b_1$	$^3A_2$	11.02	12.18	-
$3b_1$	$^1A_2$	11.15	12.31	-
$2b_2$	$^3A_1$	11.54	12.81	-
$2b_2$	$^1A_1$	11.71	12.99	-
$7a_1$	$^3B_2$	14.41	15.83	-
$7a_1$	$^1B_2$	15.14	16.56	-

[a] The electronic configuration of $CH_2Cl(X^2B_2)$ is $\cdots(7a_1)^2(2b_2)^2(3b_1)^2(3b_2)^1$; all calculations performed at the geometry of ref 11.

$^1A_1$, $^{3,1}A_1$, and $^{3,1}B_2$ arising from the $(3b_2)^{-1}$, $(3b_1)^{-1}$, $(2b_2)^{-1}$, and $(7a_1)^{-1}$ ionizations using the ATMOL3 suite of programs.[35] All calculations were performed at the planar equilibrium geometry suggested by Andrews and Smith.[11] The basis set used in these ab initio calculations was an STO double-ζ basis taken from those of Clementi[36] with added polarization functions (the exponents used were C(3d, 2.27), H(2p, 1.08) Cl(4s, 1.00; 4p, 1.00; 3d, 1.45). The method of Liu and Verhaegen[37] was used to estimate the correlation energy difference between $CH_2Cl(X^2B_2)$ and the ionic state under consideration. The results of these calculations are summarized in Table I.

Similar calculations have also been performed for $CHCl_2(X^2B_2)$ using a planar geometry and the same bond lengths used for the above CH_2Cl calculations. Only the first vertical ionization energy for the process $CHCl_2^+(X^1A_1) \leftarrow CHCl_2(X^2B_2)$ has been computed giving a ΔSCF value of 8.53 eV, which becomes 8.99 eV after allowance for the correlation energy correction.

Discussion

The structured product bands will be assigned to primary free-radical reaction products, reaction mechanisms will be given for each system, and finally vibrational spectroscopy and bonding in ground state carbocations will be considered.

CH_3Cl. The structured band at 8.87 eV vertical ionization energy behaves as a primary reaction product transient species when reagent partial pressures and mixing distance are altered; the 8.87-eV band intensity is favored at low F/high CH_3Cl partial pressures and short mixing distances. Accordingly, this band is assigned to ionization of the CH_2Cl free radical[6] product of (1).

$$F + CH_3Cl \rightarrow HF + CH_2Cl \qquad (1)$$

Reaction 1 is relatively fast, with a rate constant at room temperature of approximately 40% of that for the F + CH_4 reaction which is known to be a source of methyl radicals for PES studies.[8,38] Support for this assignment is provided by the direct electron impact determination of the first adiabatic ionization energy of CH_2Cl, 8.80 ± 0.05 eV,[13] which lies between the 8.75- and 8.87-eV PES adiabatic and vertical ionization energy values. The carbon bearing transients CHCl and CCl can be ruled out on mechanistic and spectroscopic grounds. The first adiabatic ionization energy of $CHCl(X^1A')$ is predicted to be (10.0 ± 0.2) eV on the basis of the known first adiabatic ionization energies of $CH_2(a^1A_1)$ at 10.0 ± 0.2 eV and $CCl_2(X^1A_1)$ at 9.8 ± 0.1 eV.[39,40] Also, the first adiabatic ionization energy of CCl is deduced to be 8.98 ± 0.02 eV from the first adiabatic ionization energy of CF (9.11 ± 0.01 eV)[33] and the difference between the CCl and CF first adiabatic ionizations (0.13 ± 0.01 eV).[41] Furthermore, the $v' = 0\text{–}1 = 1165\ \text{cm}^{-1}$ vibrational spacing of CCl^+ from optical emission studies[42] is incompatible with the 1040 ± 30-cm^{-1} spacing for the new transient species identified here as CH_2Cl^+.

As can be seen from Table I, the computed ΔSCF first V.I.P. of CH_2Cl is slightly lower than the experimental value, whereas approximate allowance for the correlation correction on ionization leads to a value higher than experiment. This is common for SCF ab initio calculations of this type using basis sets of the double-ζ plus polarization quality. A number of higher bands of CH_2Cl are predicted in Table I, but these were not observed presumably due to overlapping band problems.

Increasing the mixing distance at low F atom/high CH_3Cl partial pressures gave a weak band system with components at 10.00 and 10.18 eV appropriate for vinyl chloride, which is probably produced by the radical recombination reaction 2.

$$CH_2Cl + CH_2Cl \rightarrow [CH_2Cl\text{–}CH_2Cl]^\dagger \rightarrow CH_2{=}CHCl + HCl \qquad (2)$$

Increasing the F atom/CH_3Cl partial pressure ratio and the mixing distance favored the products of the secondary reactions 3–5.

$$F + CH_2Cl \rightarrow HCl + CHF \qquad (3)$$

$$\rightarrow HF + CHCl \qquad (4)$$

$$\rightarrow Cl + CH_2F \qquad (5)$$

Reaction 3 appears to be the dominant secondary reaction in the present PES studies; this is in accord with the observation of only CHF emission from infrared laser multiphoton dissociation studies of CH_2FCl.[43] The CHF and CH_2F transient products of (3) and (5) were not detected here, but strong HCl and Cl atom signals were observed. Although CHCl was not directly observed, evidence for its presence is found in the production of chloroacetylene via reaction 6. The weak feature at 9.12 eV, which appeared on the side of the CH_3Cl He(I_β) band using medium mixing distances, could be due to the first vertical ionization of CCl produced by (7), but more evidence is required for a definitive assignment.

$$CHCl + CHCl \rightarrow [CHCl{=}CHCl]^\dagger \rightarrow HC{\equiv}CCl + HCl \qquad (6)$$

$$F + CHCl \rightarrow HF + CCl \qquad (7)$$

Finally, continuation of the reaction at long mixing distances and increased F atom partial pressures gives the CF radical via reaction 8 for observation of its strong first photoelectron band.[33]

$$F + CHF \rightarrow HF + CF \qquad (8)$$

Under these conditions, F atom reactions with CH_3F, CH_3Cl, and CH_3Br give the same CF radical final product.[44,45] It is perhaps noteworthy that the F + CH_2Cl_2 reactions, to be discussed next, did not produce CF radical spectra.

CH_2Cl_2. Reaction conditions of low F atom partial pressure and short mixing distances favor the structured 8.54-eV vertical ionization energy band which suggests its assignment to the $CHCl_2$ free-radical product of reaction 9. This reaction is slightly slower than (1), in accord with a rate constant approximately 15% of the F + CH_4 value.[8] Assignment of the PES band at 8.54 eV

$$F + CH_2Cl_2 \rightarrow HF + CHCl_2 \qquad (9)$$

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to $CHCl_2$ is supported by the electron impact ionization energy measured directly for $CHCl_2$ at 8.45 ± 0.05 eV[13] and the small isotopic shift observed in the $CDCl_2$ PES band. The major secondary reaction 10 clearly produces Cl atoms and a new un-

$$F + CHCl_2 \rightarrow Cl + CHFCl \tag{10}$$

structured band with a vertical ionization energy of 9.14 eV. Atom-switching reactions of this type have been proposed by earlier workers.[9] Another possible secondary reaction product species, CCl_2, with a first ionization energy of 9.8 ± 0.1 eV measured directly by electron impact,[40] could not be observed due to overlap with the high ionization energy side of the first band of CH_2Cl_2 recorded with He I_β radiation. The unstructured secondary product band in the CH_2Cl_2 experiments is probably due to the CHFCl radical, which has been observed with greater yield as the primary reaction product in F + CH_2FCl experiments where structure was partially resolved.

CH_2FCl. The new primary reaction product transient species observed at 9.16 eV is assigned to the CHFCl free-radical product of (11) by analogy with (1) and (9). Furthermore, the 920 ± 40

$$F + CH_2FCl \rightarrow HF + CHFCl \tag{11}$$

cm^{-1} vibrational spacings are reasonable for the $CHFCl^+$ cation, as will be discussed in a later section. The major secondary reaction 12 produces Cl atoms and the CHF_2 free radical, which

$$F + CHFCl \rightarrow Cl + CHF_2 \tag{12}$$

is too reactive to be observed under these conditions.[44]

C_2H_5Cl. The rapid F + C_2H_5Cl reaction 13 gave a primary

$$F + C_2H_5Cl \rightarrow HF + C_2H_4Cl \tag{13}$$

product band at 8.10 ± 0.05 eV. Since β-H abstraction is probably favored over α-H abstraction, the product radical is likely to be CH_2CH_2Cl. This chlorine-substituted ethyl radical has an ionization energy which is intermediate between the ethyl (8.51 eV) and isopropyl (7.62 eV) radicals.[46]

Vibrational Spectra of Carbocations. This PES study of the ground electronic states of CH_2Cl^+, $CHCl_2^+$, and $CHFCl^+$ provides vibrational fundamentals to compare with infrared spectra of these and related cations in solid argon. Antisymmetric C–Cl stretching fundamentals have been observed in solid argon for CCl_3^+, $CHCl_2^+$, and $CFCl_2^+$ at 1037, 1045, and 1142 cm^{-1}, respectively,[21-23,47] and the symmetric C–Cl fundamental has only been observed for $CHCl_2^+$ at 845 cm^{-1}.[23] The 1040 ± 30 cm^{-1} fundamental for CH_2Cl^+ is a reasonable value for a single C–Cl stretching mode in view of the matrix observations, and the 860 ± 30 cm^{-1} symmetric C–Cl stretching fundamental for $CHCl_2^+$ agrees with the matrix value within experimental error. Deuterium substitution displaced this mode to 790 ± 30 cm^{-1} for $CDCl_2^+$ owing to interaction with the C–D stretching mode. Matrix infrared studies[24] of $CHFCl^+$ revealed the antisymmetric predominantly C–F stretching mode at 1436 cm^{-1} and the 920 ± 40 cm^{-1} vibronic structure in the PES band is assigned to the symmetric predominantly C–Cl stretching mode. Internal coordinate mixing in $CHFCl^+$ causes this mode to fall between the symmetric C–Cl stretching modes in $CHCl_2^+$ and CH_2Cl^+.

Although precise structural data are not available for the free radicals studied here, the observation of only symmetric C–Cl stretching mode progressions in their first PES bands is consistent with ionization of essentially planar radicals to give planar cations.

Bonding in Carbocations. The carbon–halogen stretching fundamentals in carbocations measured from vibronic photoelectron and matrix infrared spectra are substantially higher than values for the corresponding free radicals. This comparison is straightforward for the CH_2Cl species where the C–Cl stretching fundamental increased from 826 cm^{-1} for the radical to 1040 ± 30 cm^{-1} for the cation, and it indicates a substantial increase in net $(C_{2p}-Cl_{3p})\pi$ bonding in the cation as compared to the radical. Ab initio calculations performed as a part of this study show that the electron removed in the first ionization process comes essentially from the $(C_{2p}-Cl_{3p})$ antibonding $(3b_2)\pi$ molecular orbital. Hence an increase in the (C–Cl) fundamental is expected in the cation. Also, the electron density differences between the ground state CH_2Cl radical and cation computed from SCF wave functions (C, 0.382; H, 0.123; Cl, 0.372) show a substantial amount of delocalization of positive charge in the cation. Like calculations for $CHCl_2$ radical and cation reveal similar electron density differences (C, 0.269; H, 0.104; Cl, 0.314). It appears that charge delocalization in the cations contributes to the increase in the net C–Cl bond strength for CH_2Cl^+ and $CHCl_2^+$.

A final comparison for the CH_2X species is of interest. The cation/radical C–X stretching fundamental ratio is 1.28, 1.26, and 1.24, respectively, for X = F, Cl, and Br.[44,45] This suggests that the cation enhancement of C–X bonding is more effective for fluorine than the larger halogens.

Conclusions

Flow reactions of fluorine atoms with chloromethanes provides CH_2Cl, $CHCl_2$, and CHFCl free radicals for observation of structured first photoelectron bands. The $v' = 0$–1 vibronic intervals 1040 ± 30, 860 ± 30, and 920 ± 40 cm^{-1} are appropriate for symmetric C–Cl stretching fundamentals in the ground electronic states of CH_2Cl^+, $CHCl_2^+$, and $CHFCl^+$, and are complementary to matrix infrared studies on these and similar carbocations. It is noteworthy that the symmetric $C-Cl_2$ stretching fundamental for $CHCl_2^+$ from photoelectron and matrix infrared spectra are in agreement within experimental error. Finally, carbon–halogen fundamentals are substantially higher in carbocations than the corresponding free radicals. This suggests a substantial increase in net C–Cl bonding involving charge delocalization between halogen lone pairs and the carbocation center as compared to the free radicals.

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Registry No. $CH_2Cl\cdot$, 6806-86-6; $CHCl_2\cdot$, 3474-12-2; $CHFCl\cdot$, 33272-71-8; CH_2Cl^+, 59000-00-9; $CHCl_2^+$, 56932-33-3; $CHFCl^+$, 40640-66-2; CH_3Cl, 74-87-3; CH_2Cl_2, 75-09-2; CH_2FCl, 593-70-4; F, 14762-94-8; H_2, 1333-74-0.

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