Radiation Chemical Formation of Radical Cations of Halogenoalkanes and their Electron Spin Resonance Spectra and Structure

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Exposure of dilute solutions of chloro-, bromo- and iodo-alkanes in trichlorofluoromethane to ^{60}Co γ-rays at 77 K gave the corresponding cations. However, for RCl^+ and RBr^+ the hole is shared with one chlorine atom of a solvent molecule *via* the formation of a σ bond, as in $[RCl\dot{-}ClCFCl_2]^+$. For alkyl chlorides the hyperfine coupling constants of the two chlorine nuclei are nearly equal. The $(RBr)^+$ adduct shows e.s.r. spectra consisting of dominant quartet splittings from bromine and additional quartet splittings from chlorine. For the iodo-cations, no clear evidence for such bonding is obtained, and there are very large shifts in the *g*-values resulting from marked spin–orbit coupling. For more concentrated solutions, the e.s.r. spectra show septet hyperfine patterns arising from coupling to two equivalent halogen nuclei, which indicates the formation of dimer radical cations, $(RX)_2{}^+$, again having the unpaired electron in a σ^* orbital. In the particular case of t-butyl chloride, neither the parent cation, nor its complex with a solvent molecule were detected. Instead, a multiline spectrum was obtained which we assign to $(Me_2C{=}CH_2)^+$ cations weakly complexed with HCl. Theoretical calculations on the parent cations, their dimers, and adducts with $CFCl_3$ support these assignments.

It is well established that exposure of dilute solutions of a solute (S) in solvents such as trichlorofluoromethane ($CFCl_3$) to ionizing radiation at 77 K gives the cations $(S\cdot)^+$ or some breakdown products thereof, provided the ionization potential of S is less than that for the solvent.[1–4] The cations are formed by positive-charge transfer from solvent cations to the solute molecules (S).[1–4] For solution in CCl_4, however, it is possible to detect trapped solvent cations, $(CCl_4)^+$, even in the presence of S, and to follow the reaction with S thermally.[5] The radical cation $(CFCl_3)^+$ has not yet been detected, but weak complexes between S^+ and $CFCl_3$ have.[6–8] We have previously suggested that an extra, unexpected doublet splitting observed on all e.s.r. features for the cation $(C_2F_4)^+$ might be due to ^{19}F coupling from a $CFCl_3$ molecule.[6] This was unexpected because charge-transfer from $CFCl_3$ is expected to involve chlorine more strongly than fluorine. However, this expectation is fulfilled for acetaldehyde [7,8] and methyl formate cations.[7,9]

In the unrelaxed forms, $(RX)^+$ cations are orbitally degenerate, or nearly so, the SOMO (semi-occupied molecular orbital) being largely confined to the p_π orbitals on halogen. We therefore expected to detect some form of Jahn–Teller distortion. However, for the chloro- and bromo-derivatives this distortion is achieved inter- rather than intra-molecularly, *via* the formation of a weak σ-bonded complex with a single $CFCl_3$ molecule.

When pure alkyl halides are exposed to ionizing radiation the parent radical cations are not detected, but dimer cations, $(Rhal\dot{-}halR)_2{}^+$ constitute a major product at 77 K.[10]

Experimental

A range of alkyl chlorides, bromides, and iodides has been studied. These were the best available commercial samples. $[^2H_5]$Ethyl chloride and bromide were prepared by halogenation of $[^2H_5]$ethyl $[^2H]$alcohol (Merck) with phosphorus trichloride and phosphorus tribromide, respectively, and purified by repeated distillations. Solutions of trichlorofluoromethane or tetrachloromethane containing these alkyl halides in a range of concentrations were frozen as small beads or in quartz e.s.r. capillary tubes and irradiated with ^{60}Co γ-rays at 77 K to doses of *ca.* 1 Mrad. E.s.r. spectra were measured on JEOL JES-FE3X (Hiroshima) and Varian E-109 (Leicester) spectrometers. Samples were cooled between *ca.* 4 K and 70 K using an Oxford Instruments liquid helium cryostat.

Results and Discussion

Alkyl Bromides.—Exposure of a solid solution containing C_2H_5Br of less than 5 mol % in $CFCl_3$ to γ-rays at 77 K gave a poorly defined, highly asymmetric e.s.r. spectrum. Similar experiments with C_2D_5Br resulted in the well defined spectrum shown in Figure 1. This shows that the linewidth is greatly reduced by deuterium substitution. The spectrum shows resolved features for ^{81}Br and ^{79}Br (each have *I* 3/2 and are almost equally abundant), with an extra quartet splitting assigned to coupling to a single chlorine nucleus. The possibility that this secondary coupling is also due to bromine was ruled out since similar spectra were obtained even for extremely dilute samples of C_2D_5Br in $FCCl_3$. The form of the spectrum is typical of those for similar halogeno-radicals.[10,11] As shown in Figure 2, an excellent fit was obtained between the observed spectrum and the stick diagrams calculated by a matrix diagonalization using *g*-tensors and hyperfine and quadrupole interaction parameters listed in Table 1. Since orbital degeneracy is not completely quenched as shown by the *g* anisotropy, equations (1)—(4), which have been used for trapped

$$A_{\parallel} = \tfrac{4}{5}p[1 - \tfrac{1}{4}(\Delta g_{\parallel} + 3\Delta g_{\perp})] - p\mathrm{K}(1 + \Delta g_{\parallel}) \qquad (1)$$

$$A_{\perp} = -\tfrac{2}{5}p[1 - \tfrac{1}{4}(13\Delta g_{\perp} - 9\Delta g_{\parallel})] - p\mathrm{K}(1 + \tfrac{1}{2}\Delta g_{\parallel}) \qquad (2)$$

$$\tfrac{2}{5}p = \tfrac{2}{5}\, g_n\beta_n g_e\beta_e <r^{-3}> = B \qquad (3)$$

$$-p\mathrm{K} = \tfrac{8}{3}\,\pi g_n\beta_n g_e\beta_e|\psi^2(0)| = A \qquad (4)$$

$$\Delta g_{\parallel} = g_{\parallel} - 2 \text{ and } \Delta g_{\perp} = g_{\perp} - 2 \qquad (5)$$

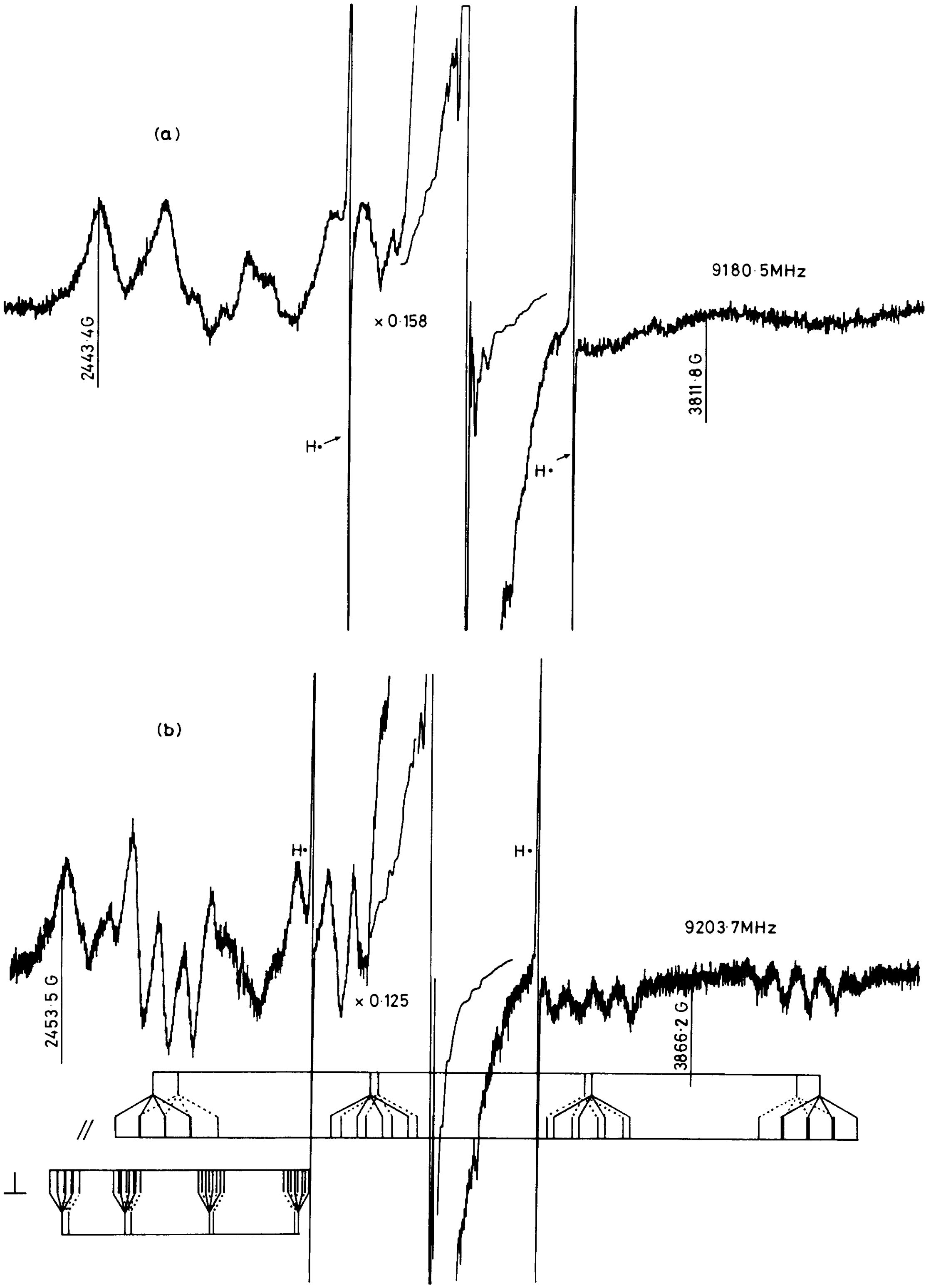


Figure 1. First-derivative *X*-band e.s.r. spectra of solutions containing (a) 2.1 mol% C_2H_5Br and (b) 1.4 mol% C_2D_5Br in Freon ($CFCl_3$) after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $[C_2H_5Br\dot{-}ClCFCl_2]^+$ radical cations. Stick diagrams in (b) were obtained from a calculation using e.s.r. parameters listed in Table 1

iodine 'atoms'[12] and trapped bromine 'atoms,'[13] have been used for estimation of the anisotropic term *B* and isotropic term *A* of the hyperfine coupling of Br from the observed $A_{\parallel}$ and $A_{\perp}$ values. As a result of these calculations, 230 and 782 MHz were obtained as the *A* and *B* values, respectively, for ^{81}Br. It is of interest to compare these values with 86 and 790 MHz reported for the corresponding values of the bromine 'atom' species.[13] The *B* values of these radicals are very close, but our species has

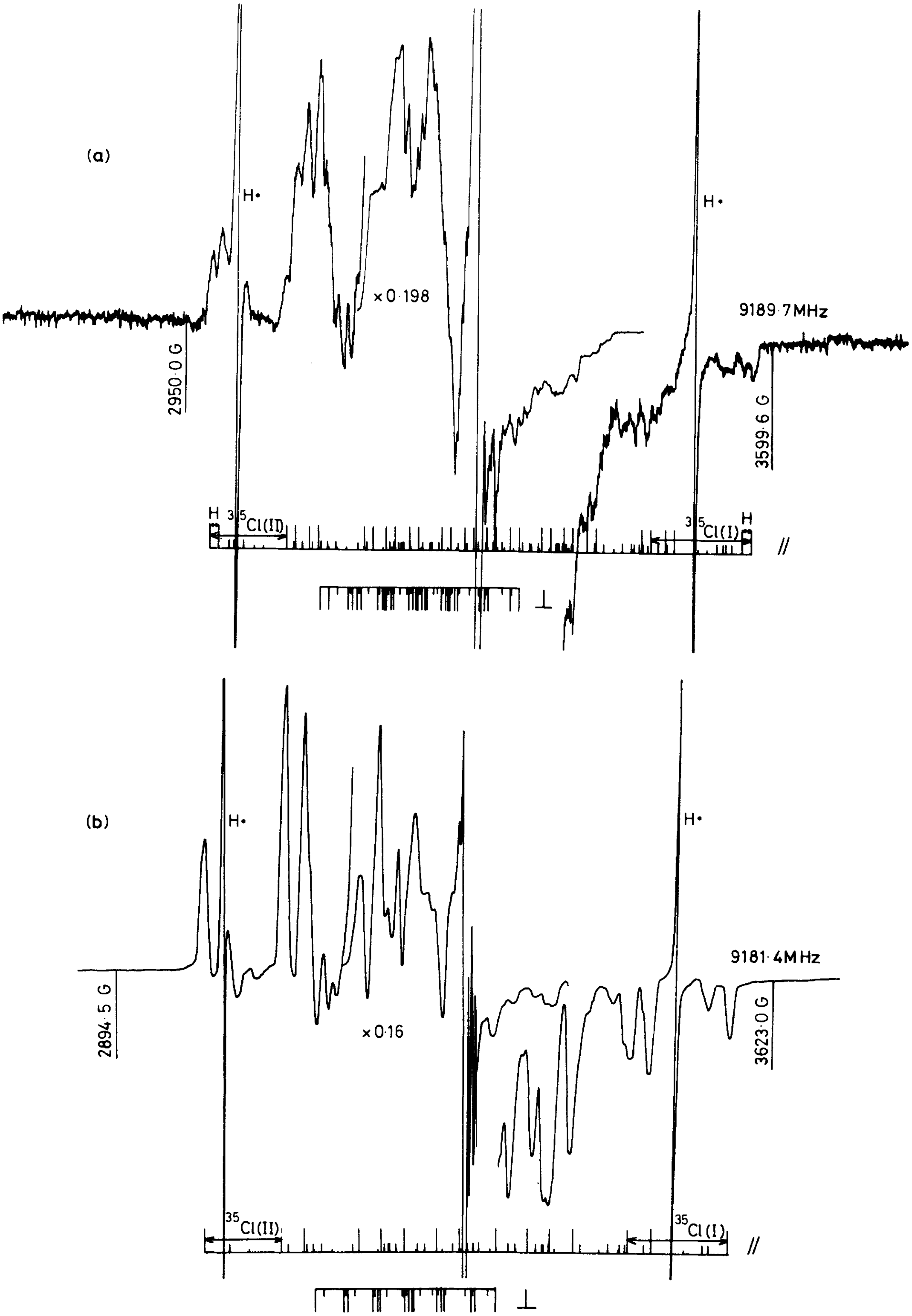


Figure 2. First-derivative X-band e.s.r. spectra of solutions containing (a) 0.13 mol% C_2H_5Cl and (b) 0.68 mol% C_2D_5Cl in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $[C_2H_5\ Cl\overset{\cdot}{-}ClCFCl_2]^+$ radical-cations. Stick diagrams in (b) were obtained for hyperfine structure due to two different Cl nuclei, and those in (a) were obtained for that due to the two Cl nuclei and an additional H nucleus

an appreciably larger isotropic coupling. If one electron-atomic parameters for ^{81}Br calculated by Morton and Preston[14] are used (A_0 3 458 and B_0 881 MHz), we obtain ρ_{4s} 0.07 and ρ_{4p} 0.89 for the orbital populations on bromine. Similar calculations for the extra splittings of the chlorine nuclei gave ρ_{3s} 0.015 and ρ_{3p} 0.212. Thus, one can see that the unpaired electron is largely confined to the $4p_z(Br)-3p_z(Cl)$ σ^* orbital and that the $4p_z(Br)$ orbital has a much larger contribution than

Table 1. E.s.r. parameters assigned to alkyl halide cation adducts and dimers

Host	Matrix	Radical	*g*-values		Hyperfine couplings[a]			
			g	$g_{\perp}$	Nucleus	$A_{\parallel}$	$A_{\perp}$	eq$Q$[b]
C_2D_5Br	$CFCl_3$	$[C_2D_5Br\overset{\cdot}{-}ClCFCl_2]^+$	1.922	2.392	^{79}Br	464	159	500
					^{81}Br	500	171	420
					^{35}Cl	57	*ca.* 17[c]	
C_2H_5Br	$CFCl_3$	$[C_2H_5Br]_2^+$	1.988	*ca.* 2.0[c]	^{79}Br	421	*ca.* 120	
					^{81}Br	454	*ca.* 130	
C_2H_5Br	CCl_4	$[C_2H_5Br\overset{\cdot}{-}ClCCl_3]^+$	1.955	2.329	^{79}Br	480	119	500
					^{81}Br	517	129	420
					^{35}Cl	68	*ca.* 17	
C_2H_5Cl	$CFCl_3$	$[C_2H_5Cl\overset{\cdot}{-}ClCFCl_2]^+$	2.002	*ca.* 2.0	$^{35}Cl(I)$	110	*ca.* 35	
					$^{35}Cl(II)$	85	*ca.* 35	
					$^{37}Cl(I)$	92	*ca.* 30	
					$^{37}Cl(II)$	71	*ca.* 30	
					^{1}H	10	10	
C_2H_5Cl	$CFCl_3$	$[C_2H_5Cl]_2^+$	2.006	*ca.* 2.0	^{35}Cl	99	*ca.* 35	
					^{37}Cl	82	*ca.* 30	
C_2H_5Cl[d]	CCl_4	$[C_2H_5Cl\overset{\cdot}{-}ClCCl_3]^+$	2.003	*ca.* 2.0	$^{35}Cl(I)$	105	*ca.* 35	
					$^{35}Cl(II)$	88	*ca.* 35	
					$^{37}Cl(I)$	87	*ca.* 30	
					$^{37}Cl(II)$	73	*ca.* 30	
					^{1}H	7	7	
C_2H_5I	$CFCl_3$	$[C_2H_5I]_2^+$	1.877	*ca.* 2.1	^{127}I	460	*ca.* 120	

[a] In G (1 G = 1 × 10^{-4} T). [b] In MHz. [c] Parameters for perpendicular components were estimated roughly. [d] Observed at 96 K, where CCl_4^+ was lost (others were observed at 77 K).

the $3p_z$(Cl) in the σ* orbital. These results indicate that the radical cation $C_2H_5Br^+$ forms an adduct with a solvent $CFCl_3$ molecule *via* the formation of a σ bond to one chlorine ligand, after the capture of a positive hole, as suggested by MO calculations (see below). The SOMO is the σ* orbital which is largely confined to the $4p_z$(Br) orbital.

The quadrupole term eQq was estimated to be 420 MHz for ^{81}Br and 500 MHz for ^{79}Br. These values are smaller than the corresponding values of 560 and 670 MHz reported for the trapped bromine 'atom' centre.[13] There is no question of identification in the present study. The evidence shows clearly that the species are the primary radical cations weakly adducted to a solvent molecule, and are not bromine 'atoms' in any sense. On the other hand, the centre identified as a 'trapped bromine atom' in irradiated crystals of *N*-bromosuccinimide[13] is thought to be formed from the cation *via* N–Br bond scission. A similar radical observed in irradiated *N*-chlorosuccinimide crystals was identified as the corresponding chlorine 'atom.' However, this showed a nitrogen coupling which suggests that the N–Cl bond did not rupture completely.[13,14] We suggest that these radicals are the parent cations rather than being atoms. In order to check this, we irradiated solutions of *N*-bromosuccinimide and *N*-chlorosuccinimide in $CFCl_3$. Unfortunately, the solubility of these reagents in $CFCl_3$ proved to be too low to produce radical cations in detectable yields.

When solutions of $CFCl_3$ containing C_2H_5Br in concentrations higher than *ca.* 10 mol% were exposed to γ-rays at 77 K, a species with seven major hyperfine components was detected (Figure 3). The seven lines are similar to those assigned to σ* dimer-radical-cations previously identified in various irradiated pure alkyl halides.[15] This result nicely supports our original identification,[10] and once again shows the marked propensity for the formation of σ*-dimer centres.

Very similar spectra to those of the dimer-radical-cations of ethyl bromide have been observed in pure solids of alkyl bromides[15–17] and 1,1-dibromo-1,1-difluoroethane.[18] These were assigned to Br_2^-. However, the present study shows that the radicals formed in these organic bromides are not Br_2^- but radical-cations. (For 1,1-dibromo-1,1-difluoroethane it may be a monomer radical-cation with intramolecular interaction between two bromine atoms.)

These σ* dimer radical cations $(RX)_2^+$ are analogous to those formed by alkyl derivatives of neighbouring elements in the Periodic Table such as $Me_2S\overset{\cdot}{-}SMe_2^+$, $Me_2Se\overset{\cdot}{-}SeMe_2^+$,[19–21] and $Me_6P_2^+$.[22,23] (The cations $Me_3Si{\cdot}SiMe_3^+$, $Me_6Si_2^+$, and $Me_3Ge{\cdot}GeMe_3^+$ [24,25] are σ rather than σ* species.) The present $(Rhal\overset{\cdot}{-}halR)^+$ cations are structurally similar to the V_K^- centres, (hal$\overset{\cdot}{-}$hal) formed in irradiation alkali halides.[26,27] Furthermore, the adducts $(RBr\overset{\cdot}{-}ClCFCl_2)^+$ are structurally related to the anion-radical $(Br\overset{\cdot}{-}Cl)^-$.[28,29] The $BrCl^-$ anion formed in an irradiated KCl crystal doped with LiBr gave the e.s.r. parameters: g_1 1.9977, g_2 2.061, and g_3 2.066; A_1 512, A_2 130, and A_3 148 G for ^{81}Br, and $A_1$103, $A_2$10, and A_3 10 G for ^{35}Cl.[28] These results are indeed quite similar to those obtained for $[C_2D_5Br–ClCFCl_2]^+$ listed in Table 1.

When pure C_2H_5Br is irradiated, adducts of ethyl radicals and bromine anions[29] were detected in addition to the dimer-radical-cations.[10] However, when $CFCl_3$ is dissolved in C_2H_5Br, no signals of the adducts were observed, showing that the adducts are formed by dissociative electron-capture which is suppressed by the Freon.

When CCl_4 was used as a matrix, well defined radical-cation spectra were observed. For C_2H_5Br the spectrum is very similar to that for C_2D_5Br in $CFCl_3$ shown in Figure 1. Thus, any splitting from the fluorine nucleus in $CFCl_3$ interacting with the unpaired electron must be less than the linewidth (*cf.* Figure 1). The cation $C_2H_5Br^+$ interacts with only one chlorine atom of a CCl_4 molecule. Therefore, electron loss is again strongly confined to one chlorine rather than being delocalised within the CCl_4 molecule.

Irradiated solid solutions containing dilute n-C_3H_7Br gave spectra similar to those for dilute solutions of C_2H_5Br in $CFCl_3$.

Alkyl Chlorides.—A species characterised by seven features was formed in irradiated solids of $CFCl_3$ containing C_2H_5Cl of

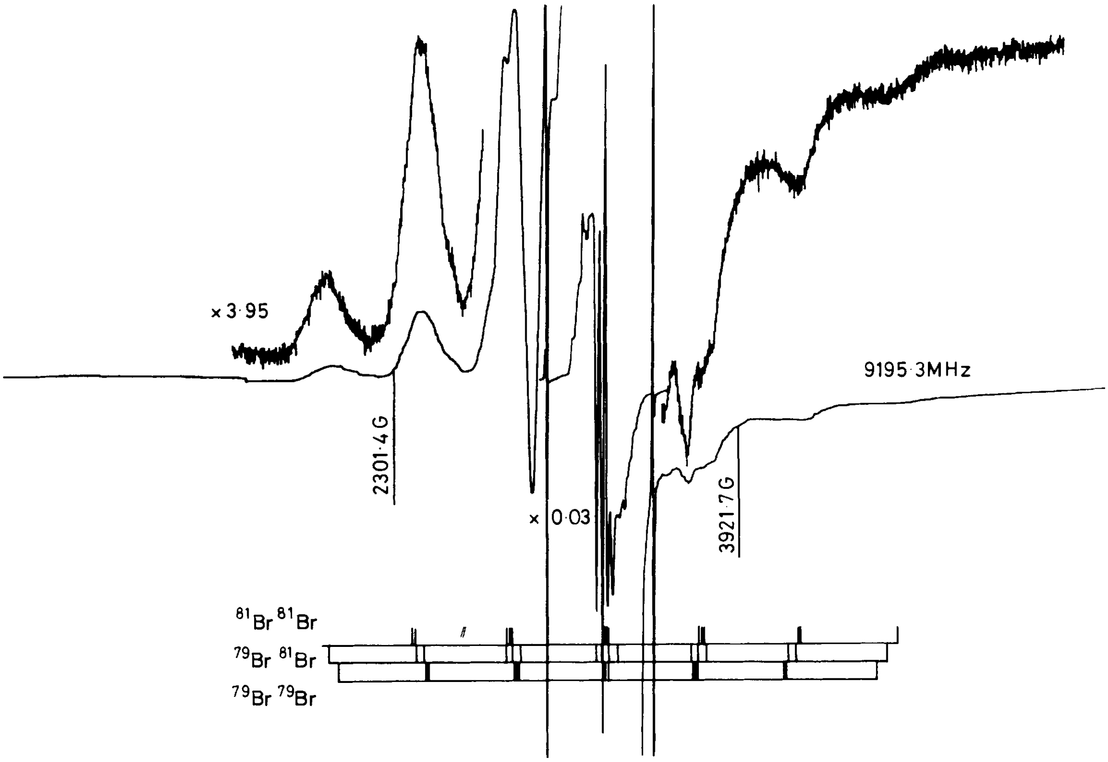
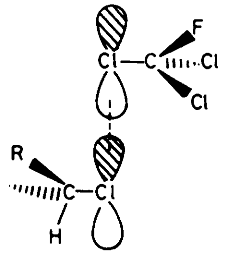


Figure 3. First-derivative X-band e.s.r. spectrum of a solution containing 35 mol% C_2H_5Br in $CFCl_3$ after exposure to γ-rays at 77 K, showing features assigned to $[C_2H_5Br]_2^+$ dimer-radical-cations.

more than *ca.* 9 mol%. The seven lines can be interpreted in terms of two equivalent chlorine nuclei, including features from ^{35}Cl-^{35}Cl, ^{35}Cl-^{37}Cl, and ^{37}Cl-^{37}Cl. Perpendicular features could not be extracted unequivocally, but approximate values were estimated and are included in Table 1. Thus, as with the alkyl bromide solutions, dimer-radical-cations readily form in $CFCl_3$ solid solutions.

When the concentration of C_2H_5Cl was reduced to less than *ca.* 1 mol%, the spectra became more complicated, as shown in Figure 2(a). These features could not be interpreted in terms of two equivalent chlorine nuclei, but were satisfactorily analysed in terms of two inequivalent chlorine nuclei, each feature being split into doublets. These doublets were still observed when CCl_4 was used in place of $CFCl_3$ as a matrix, so this splitting must stem from a single hydrogen of the alkyl group. In order to confirm this, a spectrum of C_2D_5Cl in $CFCl_3$ was measured after irradiation [Figure 2(b)] and was compared with the spectrum of C_2H_5Cl in $CFCl_3$. The well defined doublet splitting was lost on deuteriation, thus confirming our assignment. The coupling constant of 10 G for this hydrogen is substantial, and thus strongly supports our conclusion that the radical is a molecular radical-cation interacting with the $CFCl_3$ molecule. Coupling to only a single proton shows that there must be a strongly preferred conformation such as (I).



(I)

This is an indication of the expected Jahn–Teller effect for the uncomplexed cation. Of the two chlorine couplings, the larger is assigned to $(C_2H_5Cl)^+$ and the smaller coupling to the $CFCl_3$ molecule. It is perhaps surprising that the spin-density distribution for the RCl adduct is so uniform when the ionization potential difference is *ca.* 0.9 eV. However, we stress that the e.s.r. results show that electron loss is strongly confined to one chlorine rather than being delocalised with the $CFCl_3$ molecule.

E.s.r. parameters for perpendicular components could not be determined accurately, but approximate values were obtained and are listed in Table 1. It is interesting to note that the $A_{\parallel}$ value of a chlorine nucleus for the dimer radical cation $(\mathrm{RCl}\dot{-}\mathrm{ClR})^+$ is almost equal to the average value of the $A_{\parallel}$ values for two different chlorine nuclei of the $[\mathrm{RCl}\dot{-}\mathrm{ClCFCl_2}]^+$.

Alkyl Iodides.—The chlorine coupling from the solvent molecules is greatly reduced for $[\mathrm{RBr}\dot{-}\mathrm{ClCFCl_2}]^+$, as expected, because of its lower ionization potential of RBr molecules. Delocalisation onto $CFCl_3$ should be still further reduced for RI-adducts, partly because of the low ionization potentials for alkyl iodides (*ca.* 9.3 eV) and partly because of the poor matching in orbital size. Solid solutions of different concentration of C_2H_5I in $CFCl_3$ were irradiated at 77 K. For concentrations > 1.5 mol%, eleven lines appeared in the e.s.r. spectra. These lines were interpreted in terms of two equivalent iodine nuclei, indicating the formation of dimer radical cations (Figure 4). However, on reducing the concentration of the iodide, no new features were detected at 77 K. Similar results were obtained when CCl_4 was used as the matrix. On annealing above 77 K, no improvement was obtained. However, on cooling to *ca.* 4 K after irradiation at 77 K definite features spread over a very wide field range were obtained.

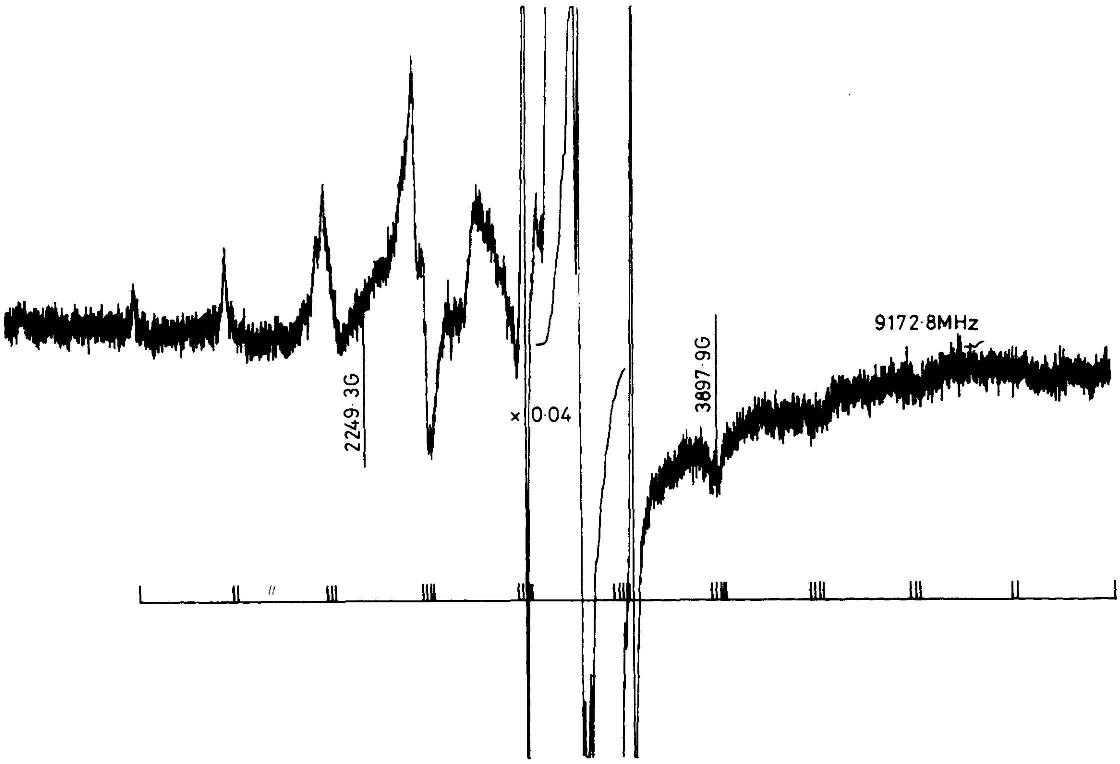


Figure 4. First-derivative X-band e.s.r. spectrum of solutions containing 1.6 mol% C_2H_5I in $CFCl_3$ after exposure to γ-rays at 77 K, showing features assigned to $[C_2H_5I]_2^+$

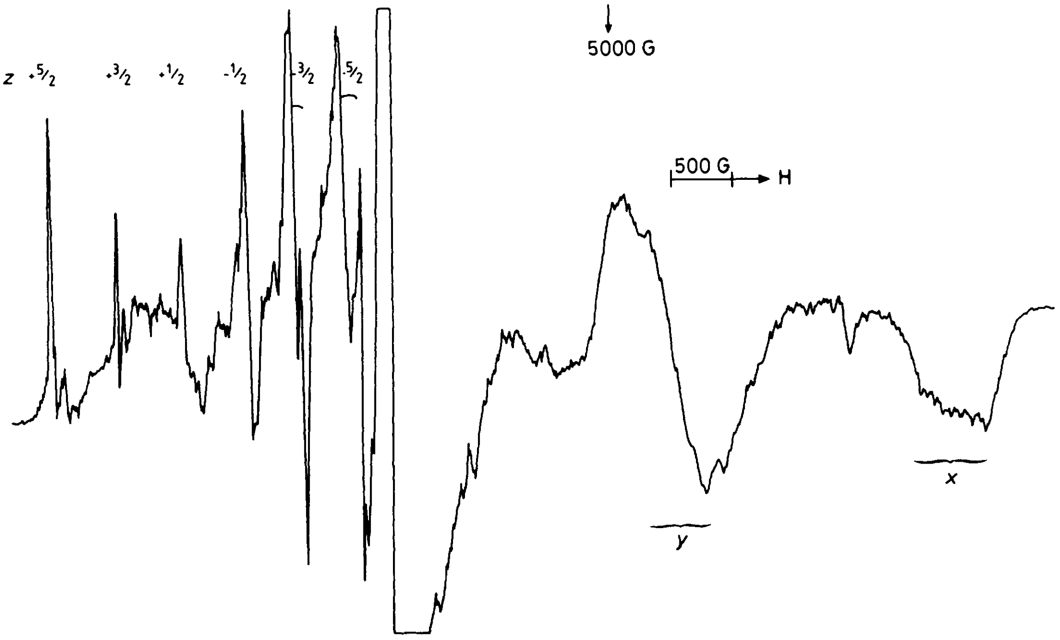


Figure 5. First-derivative X-band e.s.r. spectrum for methyl iodide in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K and cooling to *ca.* 4 K for measurement, showing features assigned to $Me{-}I^{\bullet+}$ radical cations

The e.s.r. features obtained for methyl iodide solutions at 4 K are shown in Figure 5. They are remarkable in the very large span of g-values (*ca.* 3.61, 1.2, and 0.85) and the clear splitting of the z (3.61) feature into six components, as expected for a single ^{127}I nucleus (I 5/2) (A_z = 550 G). This establishes the presence of only one iodine atom. There is incipient resolution into six components for the x and y features, from which we conclude that the hyperfine coupling is *ca.* 100 G for both A_x and A_y. The lines are too broad to reveal any extra splitting from hydrogen or chlorine.

These results are qualitatively what we expect for almost free $RI^{\bullet+}$ cations, since the g-values are quite close to the limiting

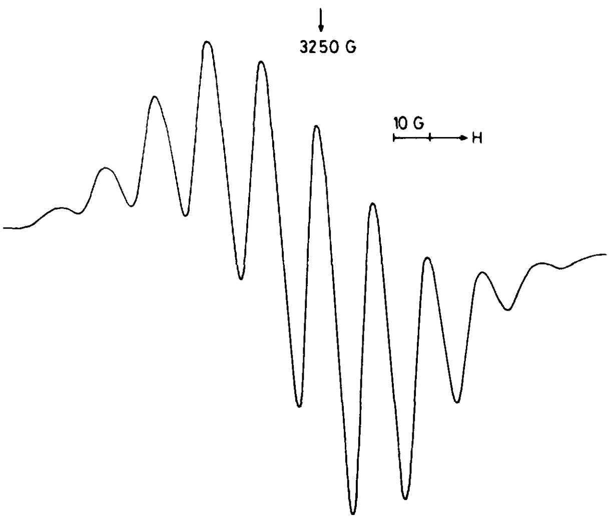


Figure 6. First-derivative *X*-band e.s.r. spectrum for t-butyl chloride in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $(Me_2C{=}CH_2)^+$ cations weakly complexed to HCl

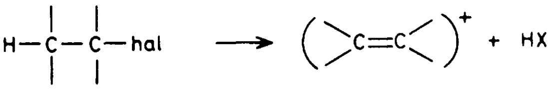
values of 4, 0, and 0. The perturbation responsible for distortion from axial symmetry is evidently unable to quench the orbital angular momentum because of the large spin–orbit coupling for iodine. This perturbation is presumably along the y-axis, and is either due to incipient bonding to chlorine as is found for the alkyl chloride and bromide cations or is due to the expected Jahn–Teller distortion. Such bonding or distortion is clearly unable to overcome the orbital angular momentum around z.

We stress that the apparent g_z value of 3.61 is not the true value since, for such large shifts and hyperfine splittings, a full quantum mechanical treatment is required in order to obtain the correct value. However, there can be no doubt that the true value is in the region of 3.6, and in view of our inability to assign good values of A_x and A_y, it is not worth attempting to obtain a more precise value of g_z. We also note that the $M_{I(z)}$ $-3/2$ and $-5/2$ components appear as doublets. We think that this may be due to a small site-splitting giving rise to two slightly different species.

t-Butyl Chloride and Bromide.—This gave e.s.r. spectra characteristic of organic radicals with no evidence for the parent cations or their adducts with $CFCl_3$ (Figure 6). We suggest that reaction (1) giving $(Me_2C{=}CH_2)^+$ cations is responsible for these features, but we need to explain the presence of an extra doublet splitting of *ca.* 14 G giving ten lines rather than nine. Since all structure was lost for $(CD_3)_3C$ derivatives this extra splitting must be due to an extra hydrogen with a splitting fortuitously close to those of the alkene cation. This must surely be the H-hal proton remaining in close proximity to the radical-cation. We are unable to discover any alternative explanation.

Some evidence for the formation of $(CH_3)CH{=}CH_2^+$ cations was obtained when systems containing $(CH_3)_2CHhal\cdot^+$ adducts were annealed, although the major reaction was dimerisation to give $(\mathrm{Rhal}\dot{-}\mathrm{halR})^+$ cations.

Calculation of the values of ΔH° for the gas-phase reaction (1) using experimental ΔH_f° values[30,31] suggest that for C_2–C_4 alkyl groups, such elimination of HX is thermodynamically possible for the chlorides, but is not expected for the methyl and ethyl derivatives or for the bromides or iodides. Also, halogen atom loss as in (2) is predicted[30–32] for the t-butyl halides.


(1)

$$RX \longrightarrow R^+ + X \qquad (2)$$

We stress that, for both modes of dissociation, the calculations refer to gas-phase species, no account being taken of changes consequent upon change of phase from gas to frozen solution, or of activation energies. Subject to minor energy changes in inert matrices both Bu^sBr and Bu^tBr could possibly undergo HBr loss upon ionization.

Calculations

It is of interest to compare these results with calculations at the MNDO and INDO level for the cations and their adducts. All our calculations of molecular geometries and energies were made using MNDO,[33] employing UHF wavefunctions for open-shell species: geometries were fully optimised, without constraints, unless specifically stated otherwise. Hyperfine couplings in the $Me_2C{=}CH_2^+$ cation were calculated by the INDO method.[34]

Calculated Spin Densities for Isolated RX^+.—The calculated values of the spin density at hydrogen are given in Table 2. The cation $MeCl^+$ is subject to a strong first-order Jahn–Teller distortion from the C_{3v} symmetry of the neutral parents, resulting in the lowering of the overall symmetry to C_s: the spin densities quoted in Table 2 for this cation are appropriate to a static Jahn–Teller distortion. In the case of a dynamic distortion, the calculated mean spin density for the methyl hydrogens is 0.032.

For any plausible value of the MNDO scale factor relating calculated spin density at hydrogen with hyperfine coupling, in the range 800—1 100, [35] the expected hyperfine couplings for the α-hydrogens of unbranched RCl^+ are in the range 35—53 G. For Pr^iCl^+ the expected range of the α-hyperfine coupling, for the isolated cation-radical is 155—215 G, assuming the same range for the scale-factor. Unfortunately, we have not been able to prepare the free cations and so are unable to check these interesting predictions.

Dimer Cations $(RX)_2^+$.—In this work, two species were studied, $(MeCl)_2^+$ and $(Bu^tCl)_2^+$. Both dimer cations were calculated to be stable with respect to dissociation, having ΔH_f° values of +804.0 and +674.8 kJ mol^{-1}, respectively. $(MeCl)_2^+$ is calculated to be more stable than ($MeCl + MeCl^+$) by 164.7 kJ mol^{-1}, and $(Bu^tCl)_2^+$ is calculated to be more stable than ($Bu^tCl + Me_3C^+ + Cl$) by 101.8 kJ mol^{-1}. At equilibrium, the calculated Cl ••• Cl distances are 2.238 and 2.213 Å, respectively, and the CCl ••• ClC fragments are *trans*-planar.

In each cation the SOMO is antibonding in Cl ••• Cl, and bonding in both Cl–C and C–C/H; this is exactly the pattern of the SOMO found in both $Me_4S_2^+$ and $Me_6P_2^+$, but differs from that in $Me_6Si_2^+$, where the SOMO is bonding in Si ••• Si and in Si–C, but antibonding in C–H. As in the sulphur, selenium, and phosphorus cations, but differing sharply from the silicon and germanium species, there is a marked decrease in the calculated hydrogen spin density upon formation of $(MeCl)_2^+$ from $MeCl^+$, from 0.0317 to 0.0048. In this respect those species $(Me_nM_2)^+$ (M = P, S, Se, Cl) having a SOMO which is σ*(M ••• M) differ sharply from those (M = Si, Ge) where the SOMO is σ(M ••• M).

Table 2. Calculated spin densities at hydrogen for various alkyl chloride cations and their adducts

R	ρ(H) in RCl$^+$	SOMO in RCl$^+$	ρ(H) in (RCl $\cdots$ ClCFCl$_2$)$^+$	
			A	*B*
Me	+0.0478 (×2) −0.0004 (×1)	π^*(C–Cl), A′	+0.0165 (×1) 0.0003 (×2)	
Et	+0.0461 (α, ×2)	pπ(Cl), A″	+0.0163 (α, ×1) −0.0010 (α, ×1)	−0.0006 (α, ×2)
	~0 (β, ×3)		~0 (β, ×3)	+0.0017 (β, ×3)
Pr^n	+0.0437 (α, ×2)	π^*(C$_\alpha$–C$_\beta$), A″	+0.0164 (α, ×1) −0.0010 (α, ×1)	−0.0006 (α, ×2)
	+0.0017 (β, ×2)		~0 (β, ×2)	−0.0007 (β, ×2)
	~0 (γ, ×3)		~0 (γ, ×3)	~0 (γ, ×3)
Pr^i	+0.1961 (α, ×1)	*a*	+0.0158 (α, ×1)	−0.0012 (α, ×1)
	+0.0081 (β, ×6)		0.0003 (β, ×6)	+0.029 (β, ×3)[c] ~0 (β, ×3)[d]
Bu^t	*b*			0.0015 (β, ×9)

A Conformer having a single α-hydrogen in R *transoid* to CCl $\cdots$ Cl fragment. *B* Conformer having β-carbon in R *transoid* to CCl $\cdots$ Cl. [a] SOMO in Pr^{i}Cl$^+$ spans C$_2$HCCl; A′ symmetry. [b] Calculation for Bu^{t}Cl$^+$ indicates dissociation to Bu^{t+} and Cl. [c] Methyl group with carbon in CCl $\cdots$ ClC plane. [d] Methyl group with carbon out of CCl $\cdots$ ClC plane.

Adduct Formation with CCl$_3$F.—For RCl$^+$ having R = Me, Pr^n, Pr^i, and Bu^t, the adducts (RCl $\cdots$ ClCFCl$_2$)$^+$ are all calculated to have stable minima (Table 2); each has a Cl $\cdots$ Cl distance of *ca.* 2.22 Å and a SOMO which is σ^*(Cl $\cdots$ Cl), analogous to the dimer cations (RCl)$_2^+$ discussed above. Since the calculated $\Delta H_f^\ominus$ value for CCl$_3$F is −267.5 kJ mol^{-1} (*cf.* the experimental value, −268.3 kJ mol^{-1} [31]) formation of these adducts from RCl$^+$ and CCl$_3$F is endothermic by *ca.* 100 kJ mol^{-1}. It is noteworthy that although Bu^{t}Cl$^+$ is unstable in isolation, it is nevertheless predicted to form a stable adduct with CCl$_3$F. There is essentially no barrier to rotation about the C–Cl bond in the RCl portion of the adduct, but for rotation about the corresponding bond in the Cl–CFCl$_2$ part, the conformer having the fluorine atom in the plane CC $\cdots$ ClC is generally *ca.* 10 kJ mol^{-1} higher in energy than conformers having one terminal chlorine atom in this plane.

Spin densities at hydrogen are recorded in Table 2 for two conformations of the RCl$^+$ portion: conformer *A* has a single α-hydrogen of R in the CCl $\cdots$ ClC plane, while conformer *B* has a β-carbon of R in this plane.

Conformer *B* always has very low spin-densities calculated for all the hydrogen atoms (Table 2), while conformer *A* always has a single α-hydrogen (except for R = Bu^t) for which the spin density is appreciably different from zero. This density is nevertheless smaller than that calculated for the corresponding hydrogens in uncomplexed RCl$^+$, and is calculated to be more than an order of magnitude smaller in the case of R = Pr^i.

These results are in remarkably good agreement with experiment (Table 1). This gives us confidence in our interpretations, and underlines the power of the MNDO and INDO techniques for calculations of this type.

Possible Products from t-Butyl Chloride Cations.—As mentioned above, we suggest that the organic radical product from t-butyl chloride in Freon is (Me$_2$C=CH$_2$)$^+$. However, there is an extra doublet splitting which we tentatively assign to the proton of the ejected H–Cl molecule. Our INDO calculations predict, for freely rotating methyl groups, ρ(H) values of −0.027 for the two CH$_2$ protons and +0.031 for the six methyl protons, giving *A*(H) values of −14.7 and +16.9 G, respectively, which are close to the mean experimental value of ±14.1 G. However, since the spectra comprise a set of 10 lines, requiring the coincidence of an extra 14 G splitting from the HCl proton, we wondered if there might be an alternative explanation in which the t-butyl group remained intact, thereby giving rise to the 10-line spectrum.

For the Me$_3$C· radical, the observed hyperfine coupling of 22.7 G corresponds to a calculated spin-density on hydrogen of 0.022. To accommodate the observed splitting of *ca.* 14 G, we need to find a species with a calculated hydrogen spin density of *ca.* 0.014.

Although free optimisation of the structure of Bu^{t}Cl$^+$ as an isolated species led to chlorine atom loss, it was thought possible that, in a frozen solution, cage effects might stabilise a perturbed cation perhaps having a long C–Cl bond. In a series of optimisations for fixed values of the C–Cl distance in the range 1.80—3.0 Å, the calculated ρ(H) never rose above 0.003, indicative at all points along the reaction pathway of loss of a chlorine atom, leaving a residual Me$_3$C$^+$ cation. In a second series of calculations on the isolated, but non-planar, Me$_3$C· radical the required value of ρ(H) was achieved when the angle CCC is *ca.* 105° (free optimisation predicts a planar skeleton): this configuration of the Me$_3$C· radical is over 100 kJ mol^{-1} higher in energy than the equilibrium planar form, and it is not easy to see what the source for such a large magnitude perturbation might be.

In the radical Me$_3$CCl$_2$, which is a possible product resulting from addition of chlorine atoms to Me$_3$CCl, the calculated ρ(H) value is 0.001, far too low to explain the observed spectrum; the isomeric radical Cl–Me$_3$C–Cl is calculated to dissociate back into Me$_3$CCl and chlorine atoms. Both the anion Me$_3$CCl$^-$ and the triplet state T_1 of Me$_3$Cl are calculated to dissociate, as isolated species, giving Me$_3$C· radicals, and chloride ions or chlorine atoms respectively.

Comparison with Halogenobenzene Cations.—It is of interest to compare the present results with the results obtained for halogenobenzenes in CFCl$_3$.[36,37] In contrast to the present results, dilute samples gave isolated radical cations of halogenobenzene, which show no splitting due to chlorine nuclei of CFCl$_3$. The $A_\parallel$ value, for example, of Br for C$_6$H$_5$Br$^+$ is 185 G and the calculated spin-density on this nucleus is only *ca.* 0.30. Extensive delocalisation of the unpaired electron onto the benzene ring must oppose the formation of a σ^* bond with CFCl$_3$, which tends to localise the SOMO to the σ^* orbital. However, for more concentrated solutions dimer radical cations were detected, which is similar to the result of the present study.

We suggest that interaction between two benzene rings helps the formation of these dimer-radical-cations.

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