Chlorofluoroalkyl Radical Rearrangements mediated by Electron Donors. An E.S.R. Study in Freon Matrices

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E.s.r. studies reveal that the $CF_2Cl\dot{C}FCl$ radical ordinarily produced in γ-irradiated $CF_2ClCFCl_2$ solid solutions can rearrange to $CF_3\dot{C}Cl_2$ in the presence of amines with low ionization potentials, suggesting that this unexpected radical isomerization proceeds through chlorofluoroalkyl carbanionic species formed reversibly by electron transfer.

The rearrangement of perhalogenated alkyl radicals by a 1,2-fluorine shift appears to be unprecedented. Here, we demonstrate that this shift can occur in the presence of strong reducing agents.

It is now well established that γ-irradiation of a dilute solution of a substrate in a Freon matrix at 77 K results in the formation of the substrate radical cation[1,2] *via* the sequence of reactions (1)—(4), (RCl represents the Freon and S denotes the substrate). The dissociative electron-capture reaction (2)[3] produces chlorofluoroalkyl radicals which usually give rise to broad e.s.r. features in the solid state. However, the spectra of these radicals can often be characterized at elevated temperatures, as exemplified by the observation of $CF_3\dot{C}Cl_2$ in CF_3CCl_3 above 145 K.[4]

$$RCl \rightarrow RCl^{+\cdot} + e^- \qquad (1)$$

$$e^- + RCl \rightarrow RCl^{-\cdot} \rightarrow R^{\cdot} + Cl^- \qquad (2)$$

$$RCl^{+\cdot} + RCl \rightarrow RCl + RCl^{+\cdot} \qquad (3)$$

$$RCl^{+\cdot} + S \rightarrow RCl + S^{+\cdot} \qquad (4)$$

Using $CF_2ClCFCl_2$ as a matrix to study localized forms of C···C ring-opened oxirane radical cations, a well-defined doublet e.s.r. spectrum with a 69 G splitting was observed above 125 K.[5] Although no additional hyperfine structure was resolved, the 69 G doublet splitting is characteristic of an α-fluorine substituent, and accordingly the radical can be assigned to $CF_2Cl\dot{C}FCl$ formed from the dissociation of $CF_2ClCFCl_2^{-\cdot}$, as in reaction (2). We have also observed this broad doublet at 125 K in the e.s.r. spectra of other γ-irradiated $CF_2ClCFCl_2$ solutions, including samples prepared from pure (>99%) material.

In the course of studying radicals derived from tetrahydrofuran (THF), we were therefore very surprised to detect the unusually well-resolved features of $CF_3\dot{C}Cl_2$[4] in $CF_2ClCFCl_2$ solutions at 125 K. Since this radical cannot be produced directly from the dissociation of $CF_2ClCFCl_2^{-\cdot}$, some type of rearrangement must clearly be involved in its formation. The experiments were carried out by exposure of 1 mol.% of the substrate (THF) in $CF_2ClCFCl_2$ to γ-rays for a dose of 0.3

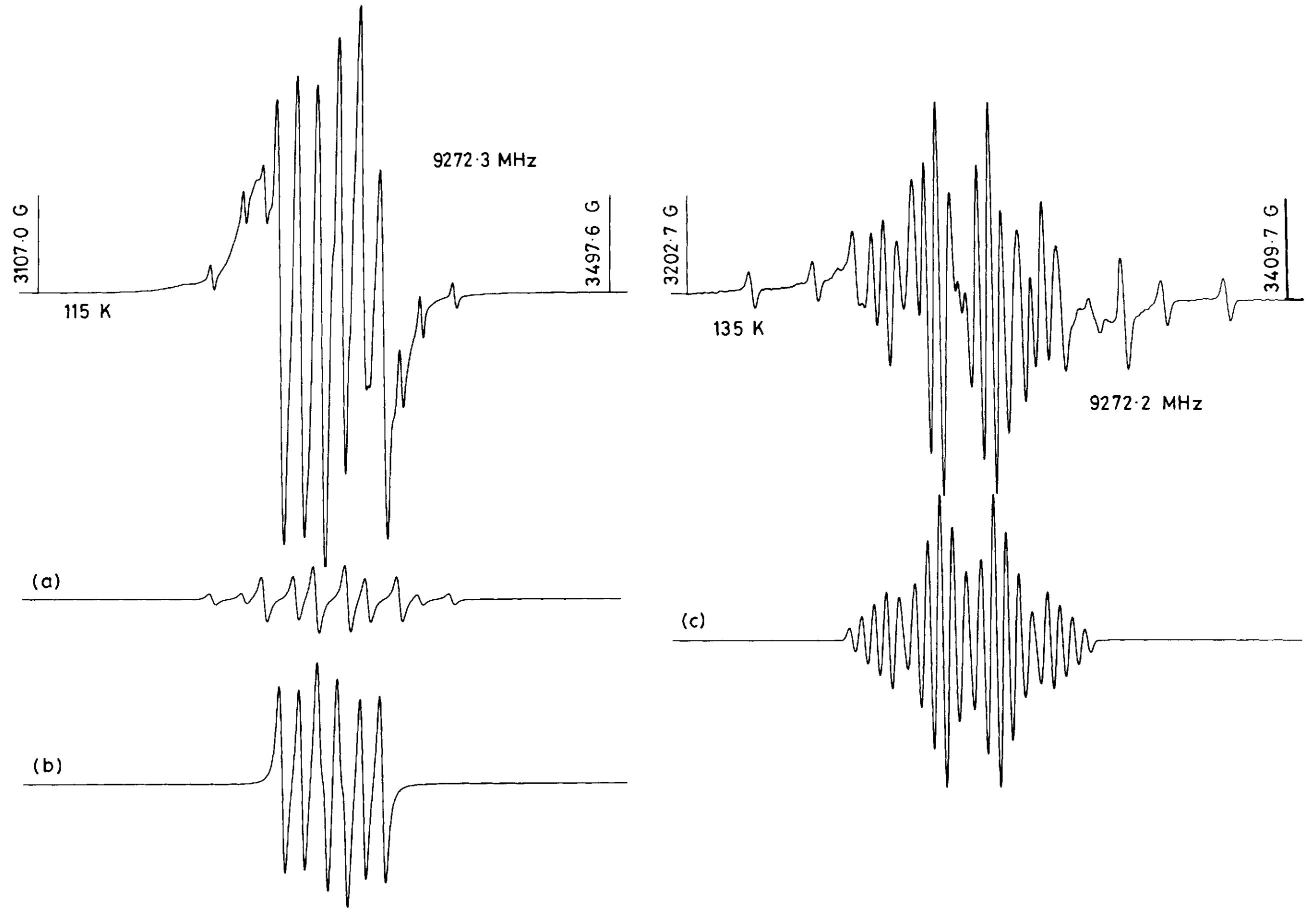

Figure 1. First-derivative e.s.r. spectra of radicals present in a γ-irradiated solution of tetrahydrofuran (THF) in $CF_2ClCFCl_2$ at 115 and 125 K. The simulated spectra (a), (b), and (c) are those of the THF-3-yl, THF-2-yl, and $CF_3\dot{C}Cl_2$ radicals, respectively, and were computed using the parameters in Table 1, the linewidths being 3.5 G (Lorentzian) for (a) and (b), and 3.2 G (Gaussian) for (c) ($G = 10^{-4}$ T).

Mrad at 77 K. After irradiation, the THF radical cation[6] was present initially at 80 K, and it underwent ion–molecule reactions to produce two neutral radicals at 100 K. As shown in Figure 1, the dominant radical is the tetrahydrofuran-2-yl radical (Table 1 and simulation b), while the minor radical is the tetrahydrofuran-3-yl radical (Table 1 and simulation a). On annealing to above 125 K, the major radical decayed while signals from $CF_3\dot{C}Cl_2$ grew in as illustrated by the spectrum at 135 K and simulation c, the e.s.r. parameters being the same as those previously reported (Table 1).

Similar experiments were carried out with trimethylamine as the substrate. The $Me_3N^{+\cdot}$ cation formed initially at low temperatures (Figure 2a and Table 1) decayed on annealing to 115 K but in this case, the neutral $\cdot CH_2NMe_2$ radical could not be detected. At 120 K, the broad doublet belonging to the $CF_2Cl\dot{C}FCl$ radical was clearly observed as shown in Figure 2b. Comparison of this spectrum with that in Figure 1 at 115 K strongly suggests that this doublet also accounts for the underlying broad humps in the latter, thereby confirming the initial presence of the $CF_2Cl\dot{C}FCl$ radical in the THF sample. On warming the sample containing Me_3N above 125 K, the features from $CF_2Cl\dot{C}FCl$ disappeared gradually while the sharp lines from $CF_3\dot{C}Cl_2$ grew at the same time, as seen in Figure 2.

From these experiments it appears that $CF_2\dot{C}FCl$ can rearrange to $CF_3\dot{C}Cl_2$ under certain conditions. The possibility that $CF_3\dot{C}Cl_2$ may arise from impurities in the solvent can easily be ruled out by the fact that γ-irradiated neat $CF_2ClCFCl_2$ (both gold label and HPLC grade from Aldrich) does not give any signals from $CF_3\dot{C}Cl_2$ between 115 and 140 K. Although the addition of 2 mol.% of CF_3CCl_3 into $CF_2ClCFCl_2$ followed by γ-irradiation does give $CF_3\dot{C}Cl_2$, the spectrum appeared at 115 K, 10 K lower than that mentioned in the previous cases. Also, the spectrum of $CF_3\dot{C}Cl_2$ in $CF_2ClCFCl_2$ has only been observed in relatively few cases, most noticeably when dimethylamino compounds were present. Also, it should be emphasized that $CF_2Cl\dot{C}FCl$ does not rearrange spontaneously under these conditions, as demonstrated by the fact that $CF_2Cl\dot{C}FCl$ persists in neat $CFCl_2CF_2Cl$ up to 145 K without changing to $CF_3\dot{C}Cl_2$.

Clearly, the mechanism cannot involve a sequence of unimolecular 1,2-shifts of fluorine and chlorine. On the contrary, the rearrangement seems to be promoted by certain substrates, or conceivably by the radicals derived from them. The results for trimethylamine are particularly significant in this regard since they indicate that solute-derived radicals play no role in the process. Also, the low ionization potential of Me_3N (8.44 eV)[7] suggests that it acts as an electron donor. Therefore, we propose the mechanism in equations (5)—(7).

$$Me_3N + CF_2Cl\dot{C}FCl \rightleftharpoons Me_3N^{+\cdot} + CF_2Cl\bar{C}FCl \quad (5)$$

$$CF_2Cl\bar{C}FCl \rightleftharpoons \bar{C}F_2CFCl_2 \rightleftharpoons CF_3\bar{C}Cl_2 \quad (6)$$

$$CF_3\bar{C}Cl_2 + Me_3N^{+\cdot} \rightleftharpoons CF_3\dot{C}Cl_2 + Me_3N \quad (7)$$

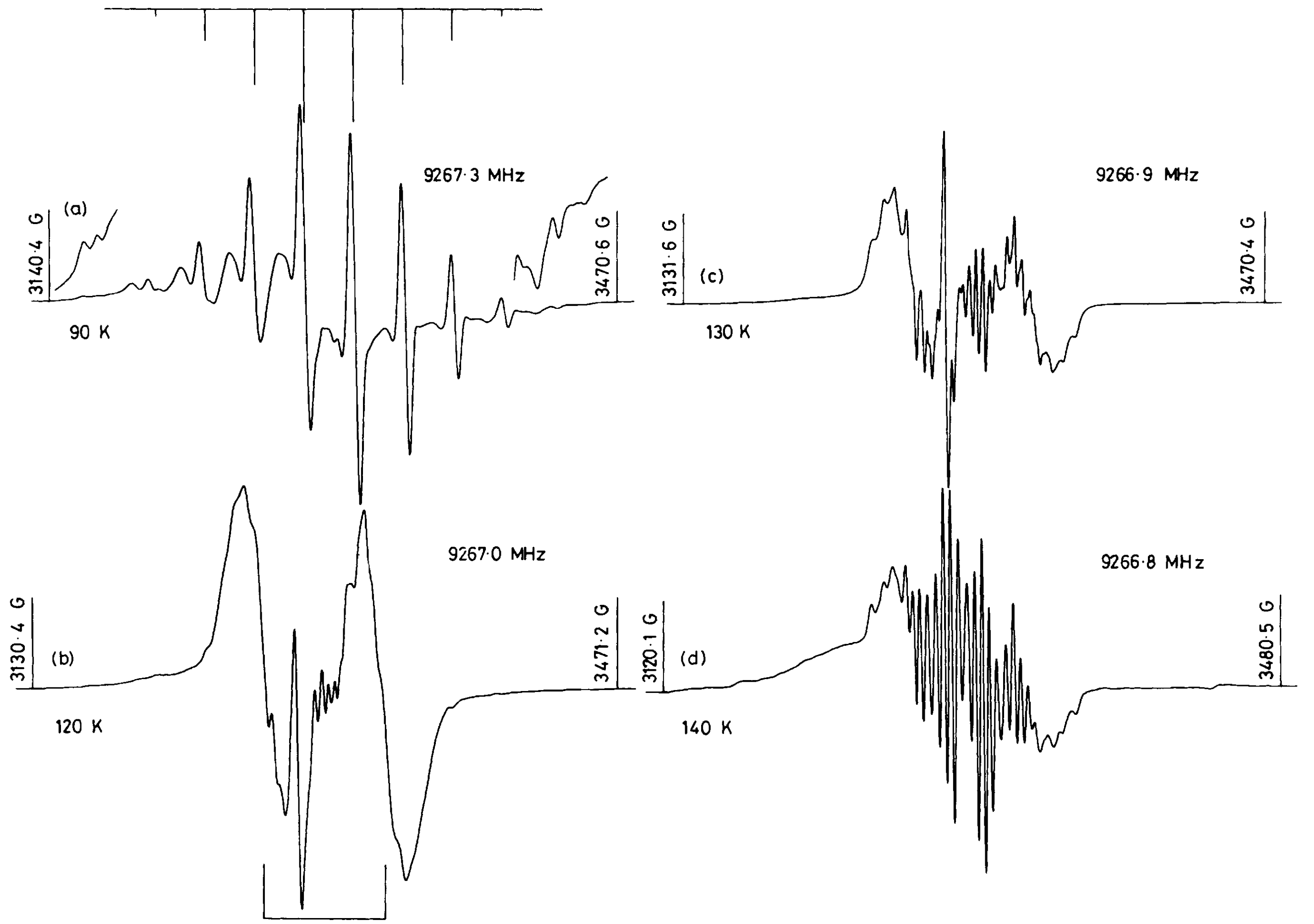

Figure 2. First-derivative e.s.r. spectra of radicals present on annealing a γ-irradiated solution of trimethylamine in $CF_2ClCFCl_2$ between 90 and 140 K. Spectra (a) and (b) are attributable mainly to the trimethylamine radical cation and the $CF_2Cl\dot{C}FCl$ radical, respectively, while spectra (c) and (d) show the growth of the $CF_3\dot{C}Cl_2$ radical accompanied by the decay of $CF_2Cl\dot{C}FCl$. The stick (diagram above spectrum (a) refers only to the ten $M_I(^{14}N) = 0$ components of $Me_3N^{+\cdot}$. The diagram below spectrum (b) shows the two broad components $[M_I(^{19}F) = \pm 1/2]$ of $CF_2Cl\dot{C}FCl$.

Table 1. E.s.r. parameters for radicals generated in Freon matrices.

Radical cation or radical	Solvent	T/K	Hyperfine couplings /G	g_{iso}	Reference
$\overline{\mathrm{OCH_2CH_2CH_2C}}\mathrm{H}\cdot$	$CFCl_2CF_2Cl$	115	$a(H_{\beta 1}) = 29.6, a(H_{\beta 2}) = 25.8, a(H_\alpha) = 13.3$	2.0029	This work
	H_2O-THF	281	$a(2H_\beta) = 28.57, a(H_\alpha) = 12.29, a(2H_{\gamma 1}) = 0.82, a(2H_{\gamma 2}) = 1.64$	—	[a]
	H_2O-THF	room temp.	$a(2H_\beta) = 28.3, a(H_\alpha) = 12.3, a(2H_{\gamma 1}) = 0.8, a(2H_{\gamma 2}) = 1.6$	2.0032	[b]
$\overline{\mathrm{CH_2OCH_2CH_2C}}\mathrm{H}\cdot$	$CFCl_2CF_2Cl$	115	$a(4H_\beta) = 35.4, a(H_\alpha) = 21.5$	2.0025	This work
	H_2O-THF	281	$a(4H_\beta) = 35.5, a(H_\alpha) = 21.2$	—	[a]
	H_2O-THF	room temp.	$a(4H_\beta) = 35.0, a(H_\alpha) = 21.2$	2.0027	[b]
$Me_3N^{+\cdot}$	$CFCl_2CF_2Cl$	90	$A_{iso}(9H) = 28.6$	2.0038	This work
	$CFCl_3$	77	$A_{iso}(9H) = 28.2, A_\parallel(^{14}N) = 47, A_\perp(^{14}N) = 0 \pm 4$	—	[c]
	$CFCl_3$	77	$A_{iso}(9H) = 28.6, A_\parallel(^{14}N) = 47, A_\perp(^{14}N) = \leqslant 4$	2.0040	[d]
$CF_3\dot{C}Cl_2$	$CFCl_2CF_2Cl$[e]	125	$a(2^{35}Cl) = 4.2, a(3^{19}F) = 18.5$	2.0078	This work
	CF_3CCl_3	145	$a(2^{35}Cl) = 4.2, a(3^{19}F) = 18.5, a(^{13}C_\alpha) = 67.3$	2.0077	[4]
$CF_2Cl\dot{C}Cl_2$	CF_2ClCCl_3	163	$a(2^{35}Cl_\alpha) = 4.6, a(^{35}Cl_\beta) = 4.6, a(2F_\beta) = 9.8$	2.0081	This work[f]
	$CFCl_2CFCl_2$[g]	155	$a(2^{35}Cl_\alpha) = 4.6, a(^{35}Cl_\beta) = 4.6, a(2F_\beta) = 9.8, a(^{13}C_\alpha) = 60.3$	2.0080	This work

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The rearrangement of the $CF_2Cl\bar{C}FCl$ carbanion to the thermodynamically more stable $CF_3\bar{C}Cl_2$ anion can be understood by the equilibria (8) and (9).[8]

$$CF_2Cl\bar{C}FCl \rightleftarrows CF_2 = CFCl + Cl^- \rightleftarrows \bar{C}F_2CFCl_2 \tag{8}$$

$$\bar{C}F_2CFCl_2 \rightleftarrows CF_2 = CCl_2 + F^- \rightleftarrows CF_3\bar{C}Cl_2 \tag{9}$$

This general mechanism has obvious similarities to that for electron-transfer quenching of excited states by tertiary amines.[9] In each case a strong electron acceptor[†] is involved and the energy of the anionic species is lowered before back electron transfer.

Finally, in the course of similar studies in the $CFCl_2CFCl_2$ matrix using various dimethylamino compounds as substrates, we have observed exceptionally strong e.s.r. signals from the $CF_2Cl\dot{C}Cl_2$ radical whereas the initial radical expected by reaction (2) in this matrix should be $CFCl_2\dot{C}FCl$. In fact, the signals were sufficiently intense to detect the ^{13}C satellite lines of $CF_2Cl\dot{C}Cl_2$ (Table 1) in natural abundance. It appears, therefore, that chlorofluoroalkyl radical rearrangements in the presence of amines are of rather general occurrence under the conditions of these Freon matrix experiments.

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[†] Recently, stable perfluoroalkyl radicals[10] have been found to be excellent electron acceptors in the formation of charge-transfer complexes with azoalkanes.[11]

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