Electron Spin Resonance Study of Some Perfluoroalkyl Radicals[1]

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Abstract: Some simple perfluoroalkyl radicals have been prepared by uv photolysis of the corresponding iodides and have been characterized by esr spectra. The α-fluorine hyperfine interaction decreases, and the β-fluorine interaction increases, as the fluorine atoms of $\cdot CF_3$ are progressively replaced by CF_3 groups in the series $\cdot CF_2CF_3$, $\cdot CF_3(CF_3)_2$, and $\cdot C(CF_3)_3$. This behavior is consistent with the hypothesis that the radicals deviate increasingly from planarity with increasing number of α-fluorine substituents. The fact that the α-fluorine hyperfine interaction is little changed in going from radicals $\cdot CF_nH_{3-n}$ to $\cdot CF_n(CF_3)_{3-n}$ indicates that the geometry is primarily determined by the number of α-fluorine substituents and is not much affected by replacement of hydrogens by CF_3 groups. This conclusion is supported by INDO calculations of the geometry of some fluorinated ethyl radicals and perfluoroalkyl radicals.

Fluorocarbon radicals have been less extensively studied than the parent hydrocarbon radicals, and the only perfluoroalkyl radical for which detailed esr results are available is the trifluoromethyl radical itself, which has been observed in irradiated liquid tetrafluoromethane and hexafluoroethane,[2] irradiated solid trifluoroacetamide,[3] and rare gas matrices.[4] The increase in both carbon and fluorine isotropic hyperfine interactions with increasing fluorine substitution in the series $\cdot CH_nF_{3-n}$ indicates that the radicals are deviating more from planarity, with methyl planar and $\cdot CF_3$ essentially tetrahedral;[2] the proton hyperfine splittings also increase in this series from $a_H = -23$ G in methyl to $a_H = +22$ G in difluoromethyl radical.[2,5] It has similarly been noted that increasing fluorine substitution in the series $\cdot CCl_nF_{3-n}$[6] and SiH_nF_{3-n}[7] leads to increased bending. These observations, and others,[8] suggest that fluorine hyperfine interactions are a fairly sensitive indicator of geometry in simple aliphatic radicals. There is a recent review of fluorine hyperfine interactions in organic radicals.[9]

It would be of particular interest to know the effect of perfluoromethyl groups, and also the relative influence of α- and β-fluorine substituents, on the structure of simple carbon-centered radicals. We have therefore prepared the perfluoroethyl, perfluoropropyl, perfluoroisopropyl, and perfluoro-*tert*-butyl radicals by uv photolysis in di-*tert*-butyl peroxide (DTBP) of the corresponding iodides. Photolysis in DTBP has been used previously for the production of radicals from aliphatic hydrocarbons,[10,11] as well as for the production of various classes of radicals from organic bromides and chlorides,[12,13] although, generally, substrates with available protons have been used. The solution esr parameters of these new perfluoroalkyl radicals have been obtained and their structures discussed.

Experimental Section

Perfluoroethyl iodide (Columbia Organic Chemicals, Inc., Columbia, S. C.) and perfluoro-*n*-propyl iodide (PCR Inc., Gainesville, Fla.) were commercial samples. Perfluoroisopropyl iodide and perfluoro-*tert*-butyl iodide were a gift from W. A. Sheppard and D. England, Du Pont, Wilmington, Del.

Samples were prepared by dissolving the appropriate iodide in di-*tert*-butyl peroxide (DTBP) (Wallace and Tiernan, Inc., Buffalo, N. Y.), used as received, in a Suprasil tube, to make an approximately 10% solution. The solution was then degassed by the freeze–pump–thaw technique and the tube sealed off under vacuum. It was found in this work that the solutions were unusually difficult to degas and that two cycles were insufficient.

The iodide solutions were continuously irradiated in the cavity of a Varian E-4 ESR spectrometer with a Hanovia 1000-W mercury–xenon arc lamp. The temperature was held at −60° by use of a Varian variable-temperature accessory.

Solid perfluoro-*tert*-butyl iodide was also γ-irradiated in a ^{60}Co source at 77°K and examined using a Varian V-4503 Q-band esr spectrometer equipped with a Varian V-4540 variable-temperature accessory.

Results

A single, intense line with a first-derivative peak-to-peak line width ΔH_{pp} of ~2 G and $g = 2.014 \pm 0.001$ appeared immediately after irradiation of most of the samples was begun. Over the first 10–15 min this line gradually decreased in intensity and was replaced by a spectrum which could easily be interpreted as resulting from the radical formed by the removal of the iodine atom from the particular perfluoroiodide present in the solution. After the initial induction period, the intensity of the second spectrum remained roughly constant for the next several hours at −60°. At the end of the experiment the previously clear solutions were noticeably pink in color. The measured hyperfine splittings are given in Table I.

Radical from Iodopentafluoroethane (Perfluoroethyl Iodide). The spectrum obtained from perfluoroethyl

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[1] This work was supported through a contract with the Atomic Energy Commission and this is AEC Document COO-1385-44.

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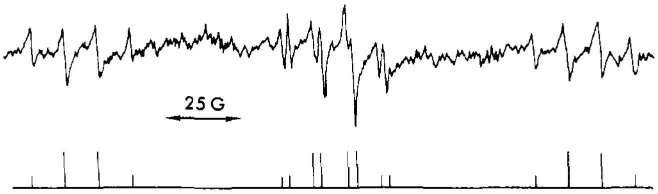

Figure 1. First-derivative esr spectrum of the perfluoroethyl radical in DTBP; a "stick" diagram based on the parameters of Table I is shown below.

Table I. Esr Parameters of Fluorinated Alkyl Radicals

Radical	Hyperfine splittings, G a_F^α	a_F^β	a_H^α	g
$\cdot CH_3$[a]			23.0	2.0026
$\cdot CFH_2$[a]	64.3		21.1	2.0045
$\cdot CF_2H$[a]	84.2		22.2	2.0081
$\cdot CF_3$[a]	142.4			2.0031
$\cdot CF_2CF_3$	84.9	11.2		2.0054
$\cdot CF(CF_3)_2$	67.4	19.2		2.0033
$\cdot C(CF_3)_3$		17.9		2.0015
$\cdot CF_2CF_2CF_3$	93	15	4 (F_γ)	
$\cdot CCl_2F$[b]	84.6		10.5 (Cl)	
$\cdot CClF_2$[b]	109.8		16.1 (Cl)	

[a] Reference 2. [b] Reference 6.

iodide (Figure 1) consists of a triplet of quartets with the lines of the central multiplet further split into doublets. We assign this spectrum to the perfluoroethyl radical, $CF_3\dot{C}F_2$, the triplet splitting arising from the two α-fluorine atoms, the quartet splitting from the three β-fluorine atoms, and the doubling of the central lines from a second-order effect. The additional structure may be accounted for by calculating the energy levels to second order in the hyperfine splittings using perturbation theory. The extra lines are usually resolved only when the hyperfine splittings are large and a general solution to the problem has been given;[14] for the ethyl radical multiplets are observed with spacings a_1^2/H_0 and $3a_2^2/H_0$, where a_1 and a_2 are the methylene and methyl proton hyperfine interactions, respectively, and H_0 is the external magnetic field.[12] For the perfluoroethyl radical, these splittings are calculated to be $a_{CF_2}^2/H_0 = 2.20$ G and $a_{CF_3}^2/H_0 = 0.12$ G, using the parameters of Table I. The latter correction is negligible compared with the line width, and the splitting of 2.3 ± 0.1 G observed for each line of the central quartet is in good agreement with the theoretical prediction including only the larger correction factor.

The intensities of the lines within each quartet are not in the expected 1:3:3:1 ratios, the central pair of lines being observed to be considerably broader than the outer pair, with peak-to-peak widths $\Delta H_{pp} \simeq 1.5$ G (inner) and $\Delta H_{pp} \simeq 1.0$ G (outer). This is most easily seen in the outer two quartets (Figure 1). If the lines were Lorentzian in shape, the areas would be proportional to[15] (first-derivative height $\times \Delta H_{pp}^2$); using this relationship we obtain from our spectrum areas in the ratios 1:2.5:2.5:1, reasonably close to the expected values. A similar broadening of the central lines of the CF_3 quartet in the spectrum of $CF_3\dot{C}(OH)OSi(C_2H_5)_3$ has been noted and was attributed to restricted rotation of the trifluoromethyl group about the C–C bond.[13]

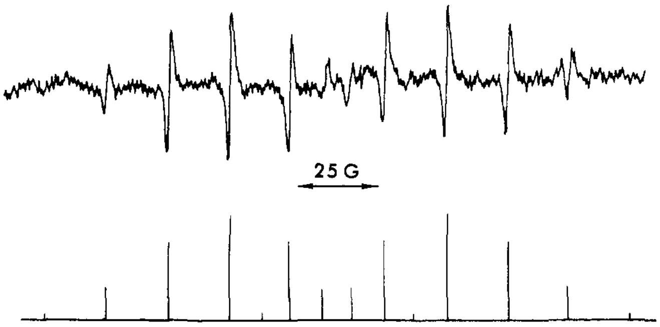

Figure 2. First-derivative esr spectrum of the perfluoroisopropyl radical in DTBP; a "stick" diagram based on the parameters of Table I is shown below.

Since the radical tentatively identified[2] as $CF_3\dot{C}F_2$ in irradiated C_2F_6 showed a 1:2:1 triplet with $a_F^\alpha \simeq 87$ G, in reasonable agreement with the value we observe in irradiated CF_3CF_2I, it probably was the perfluoroethyl radical.

Radical from Iodoheptofluoropropane (Perfluoropropyl Iodide). The spectrum had a much lower signal-to-noise ratio than that from any of the other iodides and there was a broad interfering line in the center of the spectrum. The remainder consisted of a triplet of triplets with each line of the outer triplets further split into a 1:3:3:1 quartet and each line of the center triplet split to give a complex poorly resolved central pattern. We attribute this spectrum to the perfluoropropyl radical $CF_3CF_2CF_2\cdot$ with the larger triplet spacing arising from hyperfine interaction with the two α-fluorine atoms, the smaller triplet spacing from the two β-fluorine atoms, and the quartet from the three γ-fluorines.

Radical from 2-Iodoheptafluoropropane (Perfluoroisopropyl Iodide). This compound gave a spectrum (Figure 2) consisting of a doublet of septets, each with the binomial intensity distribution expected for six equivalent spin one-half nuclei, which we attribute to the perfluoroisopropyl radical $CF_3\dot{C}FCF_3$.

Radical from Tris(trifluoromethyl)iodomethane (Perfluoro-*tert*-butyl Iodide). This compound gave a readily interpretable spectrum (Figure 3) with ten lines of binomial intensity distribution appropriate for nine spin one-half nuclei; we assign it to the perfluoro-*tert*-butyl radical $\cdot C(CF_3)_3$ with $a_F = 17.9$ G. The solid iodide examined at −130° also gave a ten-line spectrum, but with $a_F = 13.60$ G. This spectrum began to disappear, and lines of another spectrum began to appear, at temperatures above −110°.

When the iodide was dissolved in pentane in the absence of DTBP and photolyzed within the temperature range −100 to −80°, a weak 1:2:1 triplet with spacing about 72 G was observed. We attribute this to the radical $\cdot CF_2CI(CF_3)_2$, formed by removal of a fluorine atom, and the measured hyperfine splitting is quite reasonable for α-fluorine atoms in such a radical.[16] In the absence of the DTBP, the perfluoro-*tert*-butyl radical obviously was not formed, but it is not known whether, in other cases, the peroxide is necessary.

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Table II. Hyperfine Splittings for Some Substituted Ethyl Radicals (Gauss)

Radical	a_F^{β}	a_F^{α}	a_H^{α}	a_H^{β}	Ref
$CH_3CH_2\cdot$			26.87	22.38	14
$CFH_2CH_2\cdot$	48.5		27.4	22.5	*a*
$CF_2HCH_2\cdot$	49.5		12.3	23.4	9
$CF_3CH_2\cdot$	29.9			23.9	*a*
$CF_3CHCl\cdot$	23.4			22.2	*a*
$CF_3CH(OH)\cdot$	31.8			18.1	*b*
$(CF_3)_2\dot{C}O^-$	34.7				*c*
$CO_2^-CF_2\dot{C}FCO_2^-$	~39	~75			20
$CF_3\dot{C}FCONH_2$	22.3	74			*d*
$-CF_2\dot{C}FCF_2$ (Teflon)	~34	90			*e*
$-CF_2\dot{C}(CF_3)CF_2-$ (polymer)	~33 (CF_2) ~23 (CF_3)				*f*
$-CF_2CF_2\cdot$ (Teflon)	~15	86			*e, g*
$CF_3CF_2CF_2\cdot$	15	93			This work
$CF_3CF_2\cdot$	11.2	84.92			This work

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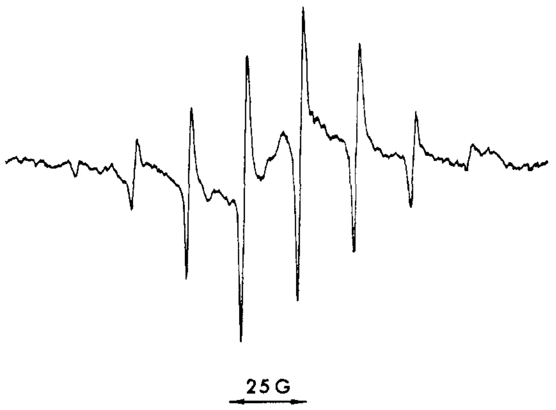

Figure 3. First-derivative esr spectrum of the perfluoro-*tert*-butyl radical in DTBP.

Discussion

Primary Radicals. The g value of the single, featureless line observed initially is similar to those (2.0155–2.0148) previously found for broad single lines in irradiated hydrocarbons containing dissolved oxygen, which have been ascribed to alkylperoxy radicals,[17,18] $\cdot O_2R$. In the present case, the line is probably from the *tert*-butylperoxy radical formed by reaction of the initially produced *tert*-butoxy radicals with dissolved oxygen. The induction period we observe would then be the time required for the solution to be scavenged of oxygen, which shows that the reaction of the *tert*-butoxy radicals with oxygen is more rapid than their reaction with the fluoroiodides. In several samples that were very thoroughly degassed, the initial line was not observed.

In the reaction of DTBP with hydrocarbons, primary radicals cannot be observed,[11] and in our work the spectra of the primary radicals were less intense than the others.

Fluorine Hyperfine Interactions. The values of a_F^{α} found in the perfluoroethyl and perfluoroisopropyl radicals are almost exactly the same as the values in the fluoromethyl radicals with the same number of α-fluorine atoms, $\cdot CHF_2$ and $\cdot CH_2F$, respectively (Table I). The similarity is especially remarkable since the fluoromethyl radicals were studied in rare-gas matrices at $-188°$. We believe that this very close agreement indicates that the geometries about the central carbon atoms are the same in the corresponding radicals so that, as far as radical geometry is concerned, the substitution of a trifluoromethyl group for a hydrogen does not make much difference. Pauling's suggestion[19] that substitution of more electronegative groups should increase the bending seems to hold in the series $\cdot CH_nF_{3-n}$ and $\cdot CCl_nF_{3-n}$ but not here, since CF_3 is much more electronegative than hydrogen. It may be that the effect of electronegativity is just cancelled here by a steric effect, with the larger size of the CF_3 group tending to decrease the bending.

To the extent that the β-fluorine hyperfine interaction arises from hyperconjugation, it would be expected to decrease as the radical deviates increasingly from planarity. Such a decrease in a_H^{β} with increased bending has been noted in halogen-substituted carbon- and silicon-centered radicals.[20] Unfortunately, no good estimates of the geometry of any radicals showing β-fluorine splittings, such as might come from $a(^{13}C)$ observations, are available. However, Pauling[19] has suggested that radicals of the type $\cdot CX_3$ will become more pyramidal as X becomes more electronegative and we have therefore listed the radicals in Table II in order of increasing electronegativity of substituents and so, presumably, of increasing deviation from planarity. It is known that a_F^{β} shows a dependence of the form $a_F^{\beta} = B_0 + B_2\rho_{\pi} \cos^2 \phi$ on the dihedral angle ϕ between the odd electron orbital and the C–F bond.[21] The radicals studied here have been observed only over a narrow temperature range, presumably near the "free-rotation" limit, so only an average value of a_F^{β} for the chemically equivalent fluorines is observed in each case. We have no data concerning the temperature dependence of the fluoroethyl radicals, so we have calculated approximate average values of $B_2\rho_{\pi}/2$ from the values of a_F^{β} of Table

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(18) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

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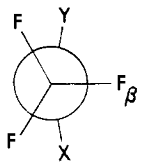
(21) See, for example, L. D. Kispert and M. T. Rogers, *J. Chem. Phys.*, **54**, 3326 (1971).

II, assuming B_0 zero.[22] There is no way to obtain ρ_π and B_2 separately at present.

It may be seen from Table II that there is a marked tendency for a_F^β (and so $\rho_\pi B_2$) to decrease with increased bending. There are some deviations from a monotonic decrease but these may arise, at least partly, from the fact that ρ_π and B_2 are changing in different ways with radical structure. The increase in a_F^α values in going down the table is consistent also with increasing bending and, by analogy with α-fluorine interactions in radicals where $a(^{13}C)$ values are also known,[8] we estimate the deviation from planarity θ to be about 8° in $CF_3CF_2\cdot$ and in $\cdot CF(CF_3)_2$ (θ is the angle between the plane perpendicular to the axis of the odd electron orbital and the C–C or C–F_α bond). The a_F^α and a_F^β values for $\cdot CF(CF_3)_2$ and $(CF_3)_3C\cdot$ then indicate that these are nonplanar with $\theta \sim 5°$.

INDO Calculations. We have calculated by means of the INDO approximation[23,24] the minimum-energy geometries and the esr parameters for these geometries for the $CF_3\dot{C}H_2$, $CF_3\dot{C}HF$, and $CF_3\dot{C}F_2$ radicals. In the calculations, the CF_3 group geometry was required to be tetrahedral with all C–F_β bond lengths the same; the other parameters were allowed to vary at will. The general structure is shown below, where X and Y are either H or F, and the results of the minimization are listed in Table III. Our calculation for the $CF_3\dot{C}F_2$ radical is in agreement with that of Pople and Beveridge,[25] who state that the α carbon is much less planar in $CF_3\dot{C}F_2$ than in $CH_3\dot{C}H_2$. Comparison of the experimental esr parameters for $CF_3\dot{C}H_2$ (Table II) and $CF_3\dot{C}F_2$ (Table I) with the calculated values (Table III) shows that the INDO calculations give fairly good quantitative results for a_F^α and a_H^α but that those for a_F^β are only qualitatively correct, that is, they decrease with increased pyramidal character. In separate INDO calculations on the $(CF_3)_2\dot{C}F$ and $(CF_3)_3\dot{C}$ radicals, in which only the amount of bending was varied, we again found that a_F^β decreased with increased bending, although it was again quantitatively much too large. Beveridge, Dobosh, and Pople[26] previously used the INDO approximation to calculate the equilibrium geometries of the fluoromethyl radicals and also concluded that those radicals became increasingly nonplanar with increasing fluorine substitution. Overall, then, the perfluoro radicals were found by INDO to be increasingly pyramidal in the order $(CF_3)_3\dot{C} < (CF_3)_2\dot{C}F < CF_3\dot{C}F_2$, which is, of course, the same order as the experimental decrease in a_F^β and increase in a_F^α.



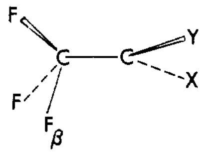


Table III. Esr and Structural Parameters from INDO Calculations of Some Fluorinated Ethyl Radicals

	$CF_3CH_2\cdot$	$CF_3CHF\cdot$	$CF_3CF_2\cdot$
$r(C–F_\alpha)$		1.33	1.33
$r(C–F_\beta)$	1.35	1.35	1.35
$r(C–C)$	1.45	1.46	1.47
$r(C–H)$	1.11	1.11	
$\angle CCF_\alpha$		117.2°	118.8°
$\angle CCH$	121.9°	126.4°	
$\angle C_\beta F_\beta–C_\alpha X$	85.0°	84.0°	68.5°
$\angle C_\beta F_\beta–C_\alpha Y$	89.4°	76.0°	68.5°
$a(F_\alpha)$, G		90.7	90.4
$a(F_\beta)$	106.5	93.2	67.9
$a(H_\alpha)$	−21.8	−17.9	
$a(^{13}C_\alpha)$	41.2	48.1	96.3

In view of the apparent similarities in geometry between the fluoromethyl radicals and the perfluoroalkyl radicals discussed above, one might expect the g values to be similar. However, they actually behave in opposite ways; in the former radicals (and also in the fluorosilyl radicals[7] $\cdot SiF_nH_{3-n}$), the g values decrease with increasing number of α-fluorine atoms, or increasing pyramidal character, while in the latter radicals the g values increase (see Table I). Thus, it appears that interaction of the unpaired electron with the β-trifluoromethyl groups is important in determining the g values. The decrease as trifluoromethyl groups are added suggests that the important unpaired electron excitations involve unfilled orbitals on the β-fluorine atoms. Also, the increasing planarity would make the overlap between the half-filled orbital on carbon and the fluorine p orbitals more favorable for interaction.

Acknowledgment. We wish to thank Dr. David E. Wood and Mr. John B. Lisle for their assistance with the INDO calculations, Dr. David England and Dr. Willam A. Sheppard of E. I. du Pont de Nemours and Co. for the gift of perfluoroiodides, and Dr. P. J. Krusic (Du Pont) for helpful comments on the manuscript.

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(22) P. J. Krusic (private communication) has observed a temperature dependence of a_F^β in $\cdot CH_2CHF_2$ and $\cdot CH_2CH_2F$ showing that there is a barrier to free rotation in these radicals.

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