Electron Paramagnetic Resonance Study of X-Irradiated Perfluoroneopentane

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Abstract: Perfluoromethyl, perfluoro-*tert*-butyl, perfluoroneopentyl, and perfluro-*tert*-pentyl radicals were observed via EPR in x-irradiated perfluoroneopentane and their equilibrium geometries and/or conformations suggested. The hfsc's of the observed perfluoroalkyl radicals were compared with their hydrocarbon counterparts and the size of the fluorine hfsc's explained in terms of the effect of fluorine substitution on hyperconjugation.

I. Introduction

The controversy over the planarity of the *tert*-butyl radical as deduced by EPR studies[1-7] has presumably been settled in favor of a nonplanar geometry by the recent photoelectron spectroscopy results of Koenig et al.[8] EPR studies of the β-halo-*tert*-butyl radicals indicate that they are also nonplanar.[9]

Because the fluorination of methyl radical apparently causes a change from a planar to a pyramidal geometry, we became interested in the effect of extensive fluorine substitution on the geometry of the *tert*-butyl radical. The EPR spectrum of the perfluoro-*tert*-butyl radical is known;[6,10] however, an extensive study of the temperature dependence of the ^{19}F hfsc's has not yet been reported. Since the bond strength of C–F is stronger than that of C–C, x irradiation of neat perfluoroneopentane should generate both perfluoro-*tert*-butyl and perfluoromethyl radicals. Furthermore radicals generated in a perfluoroneopentane matrix would be expected to exhibit isotropic EPR spectra over a large temperature range similar to that observed for an adamantane matrix.[4,5]

This paper is a report of the geometries and conformations of the radicals detected in x-irradiated perfluoroneopentane and the reaction steps involving these radicals in the matrix monitored through the changes in EPR spectra. This is part of a continued effort to elucidate the effects of fluorine on the molecular orbitals of free radicals compared to their hydrocarbon counterparts. Previous studies in this series include fluorinated benzene anion radicals[11] and fluorinated cyclohexadienyl radicals.[12]

II. Experimental Section

Perfluoroneopentane[13] purified by GC and checked by mass spectroscopy was kindly supplied by Dr. N. J. Maraschin and Professor R. J. Lagow of Massachusetts Institute of Technology.

The sample was transferred through a high vacuum line to a Spectrasil sample tube equipped with a vacuum stopcock and degassed vigorously by the freeze–pump–thaw method. The sample tube was x irradiated directly in a liquid nitrogen styrofoam dewar for 30 min with a Machlett AEG 50T x-ray tube operated at 50 kV and 30 mA. The EPR spectra were recorded using a Varian Associates V-4502 spectrometer with a 12-in. magnet and Fieldial Mark II field regulation. The microwave frequency was measured with a Hewlett-Packard X 532B wavemeter. Second derivative presentation was obtained by phase detection of a 500 Hz second modulation frequency with a PAR HR-8. The hfsc's of perfluoro-*tert*-butyl radical were measured between the two central lines from the first derivative presentation. To increase the accuracy of the measurement, a Hewlett-Packard Model 3440A digital voltmeter was used for obtaining the line positions and directly compared with Fremy's salt (A_N = 13.09 ± 0.004 G; g = 2.005 50 ±0.000 05) in a Varian Associates TE$_{104}$ dual cavity.

III. Results and Discussion

(1) Annealing Observations. At 110 K, CF_3 radical[14] (A) could be easily detected although the outer lines were broadened ($M_I^F = \pm 3/2$). In the central part of the spectrum between the sharper central lines of CF_3 ($M_I^F = \pm 1/2$), six broad lines (radical B) could be observed. In addition, there was one extra line (radical C) located at higher field than the center of the lines belonging to B. When the two central lines of B were compared with one another, the lower field line was more intense and broader than the other, suggesting overlap with another line belonging to radical C.

The EPR spectrum obtained at 121 K (Figure 1) shows well-resolved lines from CF_3 radical (A) with close to the expected intensity ratios. The six lines from radical B become sharper at this temperature and three more outer lines become obvious. The pattern from radical B at this point was clearly a result of nine equivalent $I = 1/2$ nuclei with the low-field line obscured by one of the CF_3 lines ($M_I^F = +1/2$). In addition to the two previously observed lines from radical C, two broad lines symmetrical with them appeared just outside of the CF_3 lines ($M_I^F = \pm 1/2$) with increased gain, modulation, and power. When the sample was warmed above 121 K, lines belonging to C increased while those of CF_3 (A) appeared to weaken.

At 153 K, the intensity of the CF_3 (A) lines decreased to about half compared with that at 110 K while another set of lines (radical D) appeared between those of radical B. As the intensity of CF_3 (A) continued to decrease, two more lines from radical C, originally overlapped with CF_3 lines ($M_I^F = \pm 1/2$), became resolved. The lines from radical B become very sharp and intense at this temperature and all ten lines were resolved.

Warming the sample to 203 K did not change the intensity of the lines from C very much but they did become broader. However, the lines from radical D became sharper and more intense. Meanwhile, the lines from CF_3 (A) had completely disappeared at 180 K (Figure 2). The second derivative EPR spectrum obtained at 203 K is shown in Figure 3. The lines from radical C show some partially resolved structure at this temperature. After warming the sample to 203 K it was recooled to 153 K. While the radical C shows sharper lines than those at 203 K, the intensity of these lines is less than the *original* 153 K spectrum. This kind of process, warm and recool between 203 and 153 K, causes a continuous decrease in the intensity of C. A noticeable increase of intensity of D could be observed during this process.

At 220 K radical C had completely disappeared while B and D became weaker. At 243 K radical D had decreased in intensity to ~1/6 of that at 180 K. On the basis of these annealing experiments we judge that D is more stable than B.

(2) Identification of Radical B. The radical species B (Figure 2) can be easily identified as perfluoro-*tert*-butyl radical on the basis of both its ten-line spectrum (Table I) and the mechanistic point of view. A C–C bond of perfluoroneopentane would be expected to be cleaved and CF_3 (A) and $C(CF_3)_3$ (B) formed. The temperature dependence of the isotropic hfsc and the g value of perfluoro-*tert*-butyl radical have been measured between 119 and 220 K (Table II and Figure 4). The fluorine

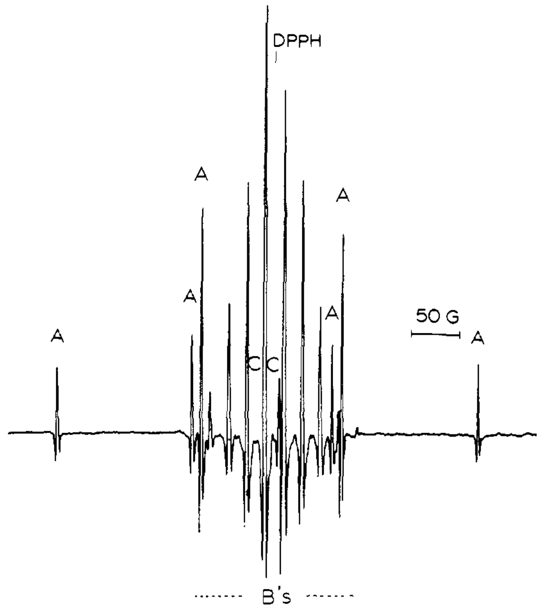


Figure 1. Second derivative EPR spectrum from perfluoroneopentane x irradiated at 77 K and observed at 121 K.

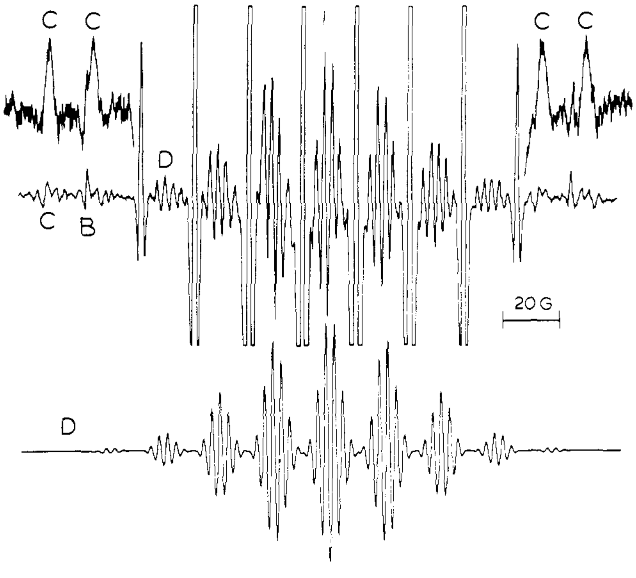


Figure 3. Second derivative EPR spectrum from perfluoroneopentane x irradiated at 77 K and observed at 203 K compared with computer simulation for radical species (D) (lower). A partial spectrum with high gain observed at 158 K by recooling from 204 K is also shown.

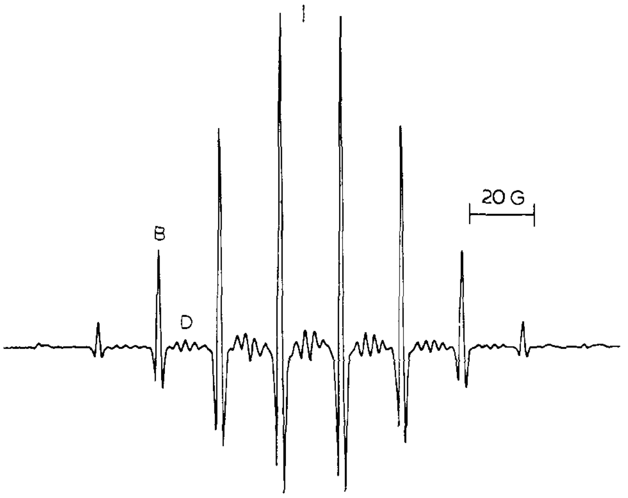


Figure 2. Second derivative EPR spectrum from perfluoroneopentane x irradiated at 77 K and observed at 180 K.

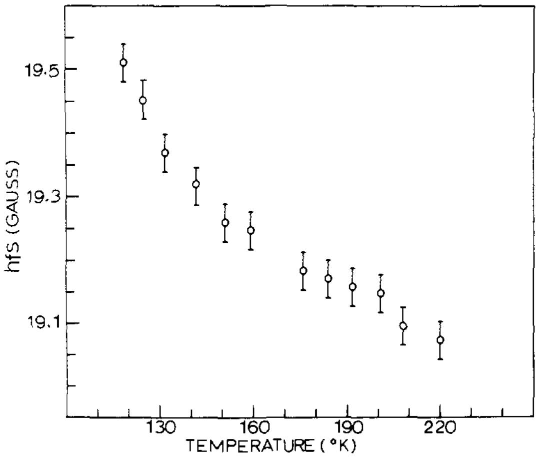


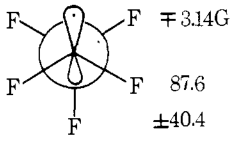
Figure 4. Temperature dependence of isotropic hfsc's of perfluoro-*tert*-butyl radical (B).

hfsc and the *g* value both show a negative temperature dependence which indicates a planar equilibrium geometry of the radical. Out of plane deformation of the perfluoro-*tert*-butyl radical from its INDO[16] optimized geometry has been performed and tabulated in Table III. The INDO optimized geometry for this radical (C–C = 1.4683 Å, C–F = 1.3487 Å) is planar and shows a negative dependence on A_F^β when the geometry is forced to be nonplanar.

Krusic and Meakin[6] generated $C(CF_3)_3$ by photolysis of dilute solutions of $(CF_3)_3$-COF in CF_2Cl_2/perfluoro-1,2-dimethylcyclobutane and obtained A_F^β = 18.69 at 26 °C. Lloyd and Rogers[10] prepared this radical by photolysis of perfluoro-*tert*-butyl iodide in di-*tert*-butyl peroxide to give A_F^β = 17.6 G at −60 °C. It is not clear why the A_F^β of this radical should be reported with such diverse values, even though the solvents and temperatures were different from one another.

(3) **Identification of Radical C.** The two lines which were badly overlapping with the broad lines of $C(CF_3)_3$ at 110 K and the four lines resolved a 153 K (Figure 3) have the same *g* value. At the higher temperature (i.e., 153 K) the intensity of $C(CF_3)_3$ lines is so strong that the observation of the two center lines first observed at 110 K is quite difficult. However, we conclude that the spectrum of radical C is a large triplet of small doublets. The hfsc's obtained for this radical are $A_F(2)$ = 87.80, $A_F(1)$ = 15.31 G, and g = 2.0041 at 167 K. Some of the fluorinated alkyl radicals previously reported are tabulated in Table I with our results.

The 87.80 G is a typical fluorine hfsc for α fluorine of a primary perfluoroalkyl radical. The 15.31 G hfsc of one I = ½ nucleus is harder to assign. There are two possibilities: (1) one β-fluorine atom and other groups which do not give resolved hfsc's; (2) no β-fluorine but with one γ fluorine which has an efficient overlap with the unpaired electron orbital. The most probable model for case 1 is $CF_2CF(CF_3)_2$. Meakin and Krusic[17] have reported a temperature-dependent study of perfluoroethyl and perfluoropropyl radicals and demonstrated that equilibrium geometries are as shown below. By analogy,



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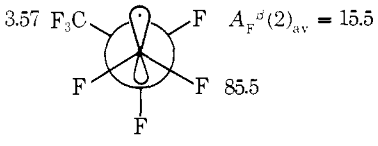


II

Table I. EPR Parameters of Some Fluorinated Alkyl Radicals

Radicals	T, K	A_{F^α}, G	A_{F^β}, G	A_{F^γ}, G	g	Ref
CF_3 (A)		142.4			2.0031	14
CF_2CH_3	195	94.01	13.99 (CH_3)		2.00361	15
CF_2CF_3	213	84.9	11.2		2.0054	10
	189	87.26	11.36		2.00386	15
$CF_2CF_2CF_3$	213	86.2	15.09 (CF_2)	3.61	2.0039	15
	213	93.	15.	4		10
$CF(CF_3)_2$	213	67.4	19.2		2.0033	10
$C(CF_3)_3$ (B)	184		19.17		2.00205	This work
	213		17.9		2.0015	10
	299		18.69			6
$CF_2C(CF_3)_3$ (C)	167	87.80		15.31[a]	2.0041	This work
$(CF_3)_2CCF_2(CF_3)$ (D)	203		21.31 (CF_2) 18.69 (CF_3)	3.00	2.0024	This work

[a] Only one of the γ fluorines.

Table II. Temperature Dependence of Isotropic Hyperfine Splitting Constant and g Value of Perfluoro-*tert*-butyl Radical

Temp, K	Hfsc, G	g
119	19.51[a]	2.002 23[b]
125	19.45	2.002 23
132	19.37	2.002 23
142	19.32	2.002 19
151	19.26	2.002 16
159	19.25	2.002 09
176	19.18	2.002 07
184	19.17	2.002 05
192	19.16	2.002 04
201	19.15	2.002 02
208	19.09	2.002 01
220	19.07	2.002 00

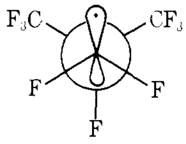
[a] Error is ±0.03 G relative to Fremy's salt A_N = 13.09 G. [b] Error is ±0.000 02 relative to Fremy's salt g = 2.005 50.

Table III. Out of Plane Deformation of Perfluoro-*tert*-butyl Radical from INDO Optimized Geometry[a]

Out of plane, deg	Energy, kcal/mol	Hfsc, G
0	−166 565.6119	65.7495
5	−166 564.6810	63.7571
10	−166 561.5655	59.7723
15	−166 555.6833	52.3007
20	−166 545.8335	43.3349
25	−166 528.5300	34.8672
30	−166 490.3390	25.9013
35	−166 380.1371	15.9393

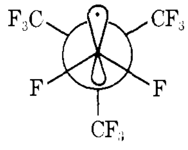
[a] C–C bond length, 1.4683 Å. C–F bond length, 1.3487 Å.

the equilibrium geometry of $CF_2CF(CF_3)_2$ is shown below.



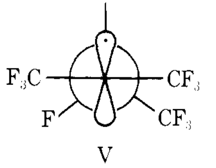
III

The conformation III will necessarily give A_{F^β} = ~40 G, which does not agree with our result. The radical C, therefore, is probably $CF_2C(CF_3)_3$. The three β-CF_3 groups would be locked in the equilibrium geometry IV and would give only one fluorine of one CF_3 group preferentially overlapped with the unpaired electron orbital. Fessenden and Schuler[18] studied neopentyl radical and observed that the γ protons are not exactly equivalent at −13 °C. Lin and Williams[19] found that only one of the methyl groups in neopentyl radical gives significant hfsc's. Our result of a locked geometry of perfluoroneopentyl radical agrees well with the expectation that this radical will be crowded more than neopentyl radical which is probably planar at the unpaired electron site.

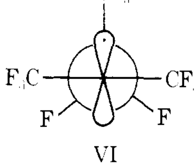


IV

(4) Identification of Radical D. The EPR spectrum of radical D at 203 K is shown in Figure 3 compared with its computer simulation based on the parameters of Table I. The radical with these parameters can be assigned as perfluoro-*tert*-pentyl with $A_{F^\beta}(CF_3)$ = 18.69, $A_{F^\beta}(CF_2)$ = 21.31, $A_{F^\gamma}(CF_3)$ = 3.00 G, and g = 2.0024. The total width of the perfluoro-*tert*-pentyl radical spectrum appears to decrease as the temperature is raised. However, we could not measure it quantitatively because of overlapping of the intense signal from $C(CF_3)_3$. If a planar geometry is assumed, conformation V, rather than VI, must be the equilibrium geometry since the observed β coupling of CF_2 is closer to 23.36 than 9.34 G (assuming that $A_{F^\beta} = B(\cos^2\theta)$ holds with $\frac{1}{2}B = A^\beta(CF_3)$ = 18.69 G). It is quite interesting that this is the opposite of the eclipsed conformation preferred by the protonated *tert*-pentyl radical.[18,20]



V



VI

(5) Radical Reactions in the Matrix. The radicals obtained in this experiment can be qualitatively summarized in terms of the following reaction steps.

$$C(CF_3)_4 \xrightarrow[77\ K]{x\ ray} CF_3\ (A) + C(CF_3)_3\ (B) \quad (1)$$

$$CF_3\ (A) + C(CF_3)_4 \longrightarrow (CF_3)_3CCF_2\ (C) + CF_4 \quad (2)$$

$$(CF_3)_3CCF_2\ (C) \longrightarrow (CF_3)_2CCF_2CF_3\ (D) \quad (3)$$

The CF_3 radicals have apparently started to react with the matrix at 110 K, the lowest temperature employed to take EPR spectra. Step 3 is achieved via the usual 1,2 shift. This scheme is consistent with the experimental observations noted before.

(6) Fluorine Hfsc's. Comparing the β-fluorine hfsc's of $C(CF_3)_3$ with its hydrocarbon counterpart, $C(CH_3)_3$ ($A_H{}^\beta$ = 22.93 at −113 °C), we find that $A_F{}^\beta$ is smaller than $A_H{}^\beta$. This is in spite of the fact that their respective equilibrium geometries favor a larger $A_F{}^\beta$. The same trend is observed for perfluoro-*tert*-pentyl radicals: $A_F{}^\beta(CF_3) = 18.6$ and $A_H{}^\beta(CH_3) = 22.77$.

It is generally accepted that β atoms obtain spin density mostly via hyperconjugation. The fact that $A_F{}^\beta < A_H{}^\beta$ can thus be explained by the relative energies of CF_3 and CH_3 group orbitals to the unpaired electron orbital. The CF_3 group orbital of π symmetry which interacts with the unpaired electron orbital will be lowered in energy by replacement of fluorine for hydrogen and the hyperconjugation will therefore be less effective. This kind of phenomena was also noticed in the dramatic reduction of $A_H{}^\beta$ in the methylene group of hexafluorocyclohexadienyl radical[12] and was explained in the same way. Stock and Wasieluski[21] have also pointed out this reduction of β-proton hfsc's in β-fluorinated radicals. A closely related argument has been forwarded to explain the difference in magnitude of the $A_F{}^\beta$ between hexafluoroacetone anion and bis(trifluoromethyl) nitroxide.[22,23]

Chen et al.[15] observed that B_F and B_H for the β interaction ($A_\beta = A + B\cos^2\theta$) are not constant for the fluorinated ethyl radicals and decrease with the extent of β-fluorine substitution for hydrogen, such as in Chart I. This reduction would be expected qualitatively on the basis of the above arguments. The reduction in hyperconjugation with the CF_3 group filled orbitals as a result of their lowering will reduce the charge density on the trigonal carbon compared to the CH_3 analogue. This in turn should result in a more carbonium-ion like structure and therefore a more planar one for the perfluoro-*tert*-butyl radical. This result together with the σ^*-π^* crossover phenomena observed in fluorinated benzene anions[11] shows that fluorine substitution for hydrogen affects energy levels dramatically and is an important factor in explaining fluorine hfsc's in general.

Chart I

	CH_3CH_2	CH_2FCH_2	CF_2HCH_2	CF_3CH_2
B_H, G	51	46	41	
B_F, G		106	92	59

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Single Crystal EPR, Zero-Field ODMR, and Phosphorescence Studies of the T_1 State of Coumarin

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Abstract: Single-crystal EPR, zero-field ODMR, phosphorescence excitation, and emission studies of the T_1 state of coumarin were made using durene and 1,4-dibromobenzene (DBB) host. It was shown that $D = 0.0984\ cm^{-1}$ and $|E| = 0.0414\ cm^{-1}$ in durene host when the out-of-plane axis is taken as the z axis. Hyperfine splittings observed in the x, y, and z axis spectra in durene host indicate about 0.5 spin density on the -C═C- group of the pyrone moiety. The phosphorescence excitation spectrum shows that the $^3n\pi^*$ state is far above the T_1 ($^3\pi\pi^*$) state and the location of the $^1n\pi^*$ state is likely to be close to that of the lowest $^1\pi\pi^*$ state. It was found that $k_x > k_y \gg k_z$ as in other $^3\pi\pi^*$ aromatic carbonyls, but $k_x{}^r$ and $k_y{}^r$ are strongly dependent on the vibrational bands. At 0–0 and 0–1628 cm^{-1} bands, $k_y{}^r > k_x{}^r$ indicating the importance of the $^1\sigma\pi^*$ ($^1\pi\sigma^*$) state mixing in the radiative process contrary to the cases of many other $^3\pi\pi^*$ aromatic carbonyls. Vibronic band dependence of $(k_x{}^r - k_y{}^r)$ was studied by means of the rapid passage microwave modulated phosphorescence spectrum and the microwave induced delayed phosphorescence technique. Observed results are discussed in terms of the possible mechanisms of radiative and nonradiative decay. The external heavy-atom effect in DBB host is briefly described.

I. Introduction

The photochemical and photobiological behavior of coumarin have attracted considerable attention in recent years.[1-8] It is considered that the lowest excited triplet state plays an important role in these processes. In particular, dimerization and addition at the ethylenic double bond in the pyron moiety appear to be related to the large spin densities there.[5] Cou-