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Perfluoropolyethers with Acid End Groups: An ESR Study of Decarboxylation

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An ESR study was performed on photodecarboxylation of perfluoropolyether acids, perfluoropoly(alkene oxide) terminated with carboxylic acid end groups. Three commercially available perfluoropolyethers (Fomblin Z, Krytox, and Demnum) with carboxylic ends were examined. ESR spectra of radicals expected from decarboxylation (e.g., $R-O-CF_2-CF_2^{\bullet}$) were readily observed from each sample exposed to 254 nm radiation at 77 K. The observed, ostensible patterns are shown to be intricate manifestations of large anisotropy of α- and β-fluorine hyperfine coupling tensors and the differing orientations of their principal axes. The principal hyperfine coupling tensors of the relevant F nuclei were determined by an iterative simulation process. The structures and conformations of the radicals thus revealed are in good accord with those given by molecular orbital calculations (MNDO). A possible significance of the decarboxylation process in actual material application is discussed.

Introduction

Perflouropolyethers are currently the lubricant of choice for magnetic recording media[1] and are also in use as lubricants in such severe environments as aerospace engines and satellite instruments.[2] Excellent lubricity aside, a wide liquid-phase temperature range, low vapor pressure, small temperature dependence of viscosity, high thermal stability, and low chemical reactivity are the attributes that have led to these high performance applications. The most-often cited, commercially available perfluoropolyethers are Fomblin Z, Fomblin Y, Krytox, and Demnum. Representative structural formulae of these materials are shown in Figure 1. Fomblin Z and Y are prepared by photooxidation of tetrafluoroethylene and hexafluoropropylene, respectively, and are random copolymers of indicated units.[3] Krytox and Demnum are synthesized via base-catalyzed polymerization of perfluoropropylene oxide[4] and trimethylene oxide,[5] respectively. In this report the notations Z-, Y-, K-, and D-lubes shall be used to indicate the respective perfluoropolyethers.

These perfluoropolyethers are completely transparent in the UV−visible range (200−800 nm) and are hence photostable. Recently Saperstein and Lin[6] reported that improved surface adhesion was achieved between a perfluoropolyether film and the substrate (amorphous carbon) upon exposure of the lubricated surface to far-UV radiation ($\lambda = 185$ *nm*). More recently Vurens et al.[7] showed that the enhanced adhesion observed above was due to radicals generated by dissociative capture (by perfluoropolyethers) of photoelectrons released from the substrate. The work function of carbon film is ~5 eV. Enhanced adhesion was not observed when the lubricated surface was exposed to 254 nm (4.9 eV) radiation.

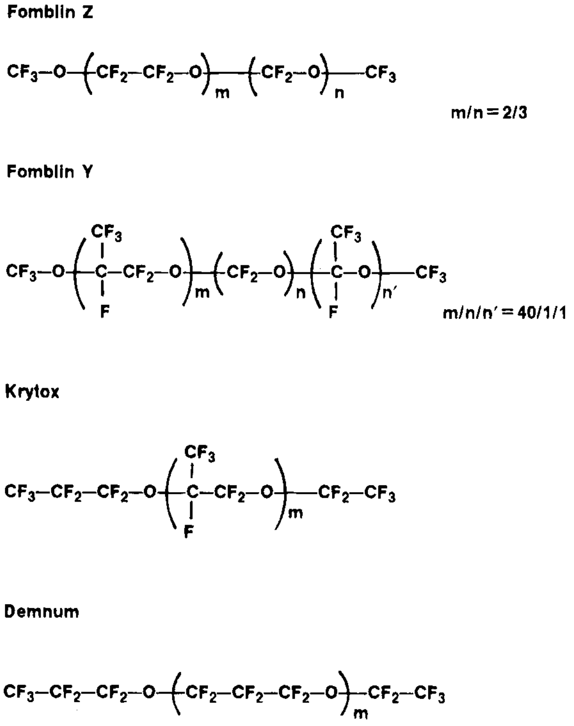

Figure 1. Formulas of commercial perfluoropolyethers, Fomblin Z., Fomblin Y. Krytox, and Demnum.

Z-, K-, and D-lubes are also available in the acid-functionalized form, perfluoropolyethers terminated with carboxylic acid end groups. We shall use notations Z-COOH, K-COOH, and D-COOH to indicate these materials. Z-COOH has the carboxylic group $-O-CF_2-COOH$, at both ends. K-COOH and D-COOH have the respective carboxylic groups, $-O-CF(CF_3)-COOH$ and

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$-O-CF_2-CF_2-COOH$, only at the terminating end of the chain. In the base-catalyzed polymerization, the polymerization cycle is terminated by acylfluoride formation, e.g.

$$R-O-CF_2-CF_2-CF_2-O^- \rightarrow R-O-CF_2-CF_2-COF + F^-$$

The carboxylic acid end group is formed from the acyl fluoride end group.[4,5]

It is well-known that the decarboxylation of carboxylic acids R−COOH can be effected by 254 nm radiation.[8] The process involves the biradical state $R^\bullet\ {}^\bullet H$ after CO_2 removal. As hydrogen atoms could readily diffuse, irradiation of perfluoropolyether acids with 254 nm light should lead to generation of perfluoropolyethers terminated with radical ends, e.g., $-O-CF_2-CF_2^\bullet$. Their chemistry should differ significantly from that of intrachain radicals generated by dissociative electron capture, e.g.

$$R-CF_2-R + e^- \rightarrow R-\dot{C}F-R + F^-$$

We thence examined, by ESR, (1) whether radicals could be formed from perfluoropolyethers with acid end groups by 254 nm radiation, and (2) the identity and structure of the resulting radicals, if formed. The result of that study is presented in this report.

Faucitano et al. have studied extensively the radicals generated from Z and Y lubes of peroxidic form (perfluoropolyethers containing ~1% peroxy linkage) by γ and UV irradiation.[9-11] The radicals principally observed were $R-O-CF_2^\bullet$ in Z-lube, and $R-O-\dot{C}F(CF_3)$ in Y-lube. They concluded that these radicals were formed by homolysis of the peroxy link, followed by a β scission.

No ESR signals were observed when Z-COOH, K-COOH, and D-COOH were irradiated with 254-nm light at room temperature. Strong ESR signals were observed when they were frozen and exposed to 254 nm radiation at 77 K. The observed spectra were indeed due to radicals expected from the decarboxylation process, $R-O-CF_2^\bullet$, $R-O-\dot{C}F(CF_3)$, and $R-O-CF_2-CF_2^\bullet$. The spectra are complicated by large anisotropies of the ^{19}F hfc (hyperfine coupling) tensors and the differing orientations of their principal axes. Careful analyses of the spectra revealed the structure and conformation of the radical sectors in good agreement with those predicted by molecular orbital calculations (MNDO).[12]

Experimental Section

Perfluoropolyether acids Z-COOH, K-COOH, and D-COOH were obtained from Montefluos, duPont Co., and Daikin Ind., respectively. Analyses by ^{19}F NMR confirmed that Z-COOH molecular chains were functionalized at both ends, while K-COOH and D-COOH chains were functionalized at the terminating ends only, as described above. The ^{19}F NMR analyses also yielded the number average molecular weights of ~2000 for Z-COOH, ~5000 for K-COOH, and ~3000 for D-COOH.

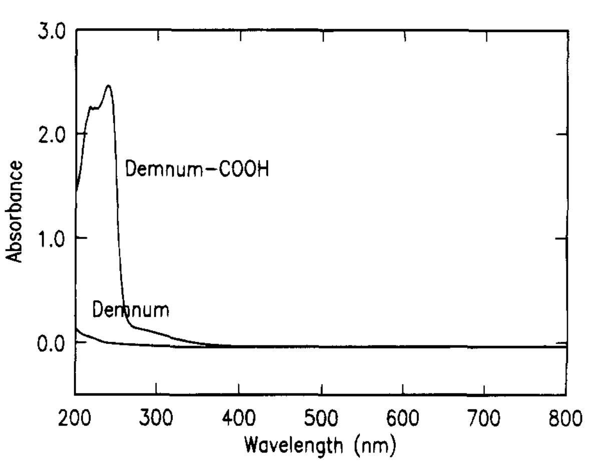

Figure 2. UV−visible spectra of Demnum and Demnum-COOH.

The ESR spectrometer used was an ER100D (IBM Instruments) X-band system. Typically a sample tube (4 mm o.d. quartz) containing a given perfluoropolyether acid was placed in a liquid nitrogen filled quartz "finger" Dewar, and was irradiated with UV (254 nm) for 20 min through the transparent finger section. For and during irradiation, a low-pressure mercury lamp ("ozone free" 254 nm lamp of Jelight Co., 10 W) was placed in contact with the finger section of the Dewar.

After irradiation, the sample tube was quickly transferred into the second liquid nitrogen filled Dewar placed into the ESR cavity. The transfer to the second Dewar was done in order to avoid ESR signals due to radiation damage accumulated in the outermost wall of the Dewar used for irradiation. The frequency of the ESR spectrometer locked to the sample cavity was 9.26 GHz.

ESR Spectra and Analyses

As stated earlier, no ESR signals were observed when any of the samples, Z-COOH, K-COOH, and D-COOH, were irradiated with UV (254 nm) at room temperature. Strong ESR signals were observed when the samples were irradiated and maintained at 77 K. The signals disappeared completely when the irradiated samples were warmed to room temperature and quenched back to 77 K. Only weak, ill-defined signals were observed when Z-, K-, and D-lubes of the standard, nonfunctionalized form were similarly irradiated at 77 K.

The strong ESR signals observed from perfluoropolyether acids were hence attributed to radicals resulting from decarboxylation at the carboxylic ends of the molecular chains. Figure 2 shows the UV−visible spectra of the standard D-lube and that of D-COOH. The absorption band due to the carboxylic sector with $\lambda_{max} = 240$ nm is clearly revealed.

The ESR spectra thus observed from Z-COOH, K-COOH, and D-COOH are shown and analyzed below individually. In each case, the ostensible ESR pattern proved to be a complex manifestation of the anisotropies of ^{19}F hfc tensors and the differing orientations of their principal axes. The assignment was made via an iterative simulation process and was facilitated greatly by the structure and the SOMO (semifilled molecular orbital) predicted by the MNDO molecular orbital method.[12]

Z-COOH. Figure 3a shows the ESR spectrum observed, at 77 K, from Z-COOH after it had been exposed to 254 nm radiation for 20 min. The signals did not

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(8) See, for example: Horspool, W. M. *Aspects of Organic Photochemistry*; Academic Press: London, 1976; p 251.

(9) Faucitano, A.; Buttafava, A.; Martinotti, F. F.; Caporiccio, G.; Corti, C.; Maini, S.; Viola, G. T. *Fluorine Chem.* **1980**, *16*, 649.

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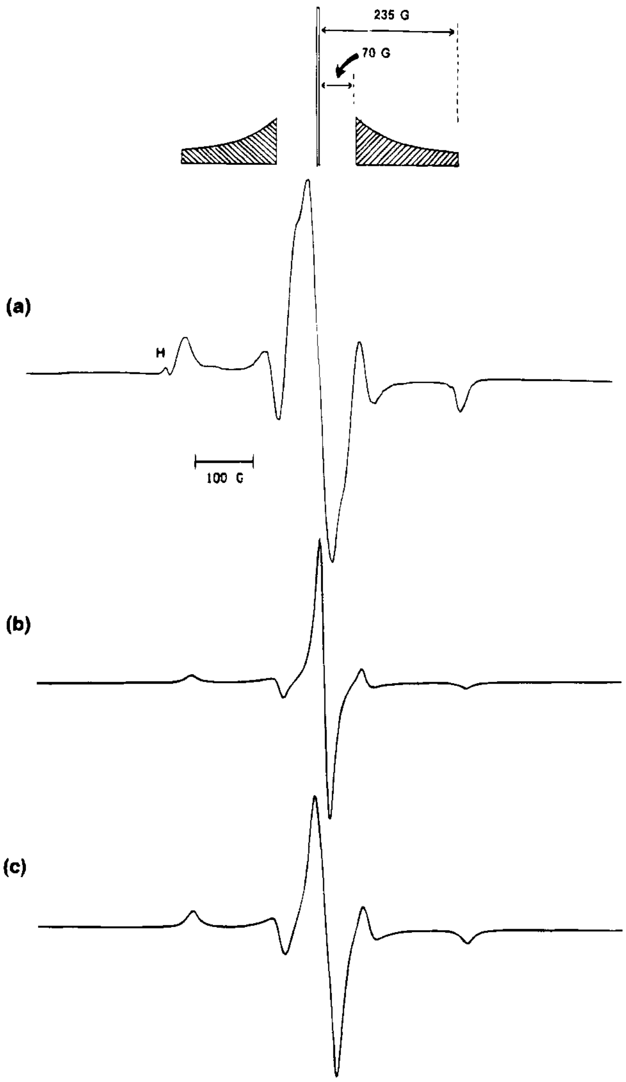

Figure 3. (a) ESR spectrum observed from Z-COOH after exposure to 254 nm radiation at 77 K. The spectrum is assigned to R$-$O$-$CF$_2^{\bullet}$. The pattern is ascribed to the hfc interactions (of extreme uniaxial asymmetry) with the two α F nuclei, as indicated. "H" indicates the lower field component of the hydrogen atom doublet. (b) Simulated spectrum based on the two F hfc tensors obtained by identifying the observed splittings with $A_{\parallel}$ and $A_{\perp}$. (c) Simulated spectrum based on the **g** tensor, the two α F hfc tensors and their orientations given in Table 1.

decay when the sample was maintained at 77 K and increased further with further irradiation. The overall pattern is readily recognized as that resulting from hfc interactions of extreme uniaxial asymmetry ($A_{\parallel} \gg A_{\perp}$) with two ^{19}F nuclei ($I = {}^1/_2$) as indicated.[13] The spectrum is hence assigned to radicals R$-$O$-$CF$_2^{\bullet}$ expected from decarboxylation of Z-COOH. Figure 3b shows the simulated spectrum based on the hfc tensors of the two α F nuclei obtained by identifying the indicated spacings, 235 and 70 G, with the principal elements $A_{\parallel}$ and $A_{\perp}$, respectively. The simulated spectrum is at discord with the observed spectrum overemphasizing the prominence of the central component.

As stated earlier, Faucitano et al. have examined the ESR spectrum of radicals R$-$O$-$CF$_2^{\bullet}$ generated from peroxidic Z-lube. They determined from the spectrum obtained by photothermolysis of a fluid sample at elevated temperature (100$-$250 C), the isotropic hfc constant of 126.5 G for the two α F nuclei.[11] They also reported, based on the spectrum observed from samples γ irradiated at 77 K, the hfc tensor of $A_{\parallel}$ = 225 G and $A_{\perp}$ = 63 G for the two F nuclei of the same radical.[9] The spectrum for the latter case was not shown. Faucitano et al. also concluded, based on INDO molecular orbital calculations, that radical R$-$O$-$CF$_2^{\bullet}$ has a pyramidal shape at the radical center.[11]

The hfc interaction of a particular magnetic nucleus is determined essentially by the distribution of the unpaired electron in the immediate vicinity of the nucleus. Thus, analyzed in terms of the SOMO given in the LCAO form, the hfc tensor of a ^{19}F nucleus of a fluorocarbon radical is determined by the F(2s) and F(2p) atomic orbitals of the particular fluorine involved in the SOMO. The hfc tensor would hence be axially symmetric about the symmetry axis of the F(2p) orbital, and should assume the following form:[14]

$$A_{\parallel} = A_{\text{iso}} + 2A_{\text{dip}}$$

$$A_{\perp} = A_{\text{iso}} - A_{\text{dip}} \qquad (1)$$

where A_{iso} and A_{dip} are the isotropic and dipolar components of the hfc tensor resulting from the spin densities in the F(2s) and F(2p) orbitals, respectively. It follows immediately that, if radical R$-$O$-$CF$_2^{\bullet}$ is pyramidal at the α carbon, the symmetry axes of the hfc tensors of the two α F nuclei would not be parallel to each other.

We examined the structure of a model system CF$_3$$-O-CF_2^{\bullet}$ using the geometry optimized MNDO molecular orbital method in the MOPAC package.[15] In agreement with Faucitano et al.,[11] the MNDO calculation also predicted a pyramidal shape for the radical. The calculation also placed the unpaired electron density of ~0.7 at the α carbon and ~0.1 each at the peripheral O and two F atoms. Pertinent features of the calculated structure are shown in Figure 4. Here the radical is oriented so that the peripheral O and two α F atoms lie in the $x$$-$$y$ plane, and the $y$$-$$z$ plane bisects the F$-$C$-$F angle. The z coordinate of the α carbon (given in the figure) is thus a measure of the departure from the planar geometry, and the unpaired electron is localized (~70%) in a sp$_z$ orbital of the α carbon.

From the geometry and the SOMO thus given by the MNDO method, a reasonable estimate can be made for the magnitude and orientation of each α F hfc tensors. The direction of the F(2p) component of a particular fluorine in the SOMO, hence the direction of the symmetry axis of its hfc tensor, relative to the z axis may be given by two angles of rotations, ϕ about the z axis, and θ about the x axis, as indicated.

The assumption that the hfc tensor of magnetic nucleus is determined by the atomic orbitals of the particular atom in the SOMO does not rigorously hold if there is a large spin density in orbitals of the adjacent atom as in the present case. The anisotropic hf interaction between an unpaired electron and a magnetic nucleus is biven by eq 2, where r is the distance between

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[13] For analyses of ESR powder patterns, see, for example: Atkins, P. W.; Symons, M. C. R. *The Structure of Inorganic Radicals*; Elsevier: Ameterdam, 1067; pp 268$-$272.

[14] Smith, W. V.; Sorokin, P. P.; Gelles, I. L.; Lasher, G. J. *Phys. Rev.* **1959**, *115*, 1546.

[15] MOPAC (V.5) by J. P. Stewart of Frank J. Seiler Research Laboratory, U. S. Air Force Academy, Colorado Springs, CO.

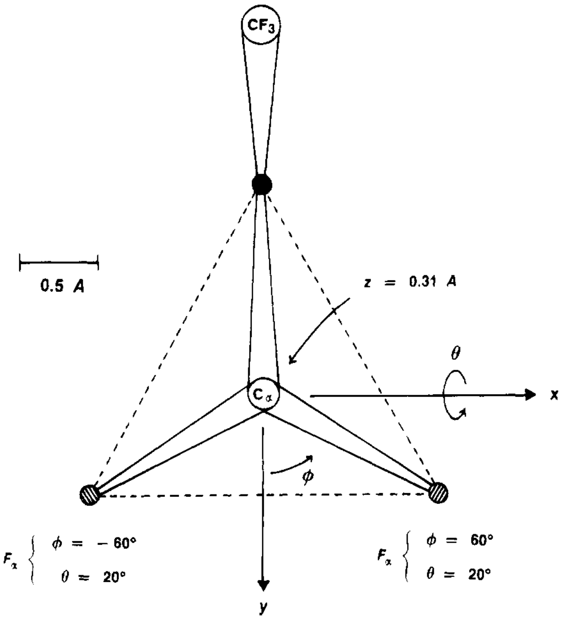

Figure 4. Conformation of $\mathrm{R{-}O{-}CF_2^{\bullet}}$ given by the MNDO theory. The O and two α F atoms are in the x−y plane. Two angles of rotations, ϕ and θ, define the direction of the symmetry axis of each F hfc tensor given by its F(2p) orbital in the SOMO.

$$A_{ij}(=x,y,z) = g_e\beta_e g_n\beta_n \left\langle \Phi \left| \frac{3ij - \delta_{ij} r^2}{r^5} \right| \Phi \right\rangle \qquad (2)$$

the unpaired electron and the nucleus. We estimated the contribution of the spin density at the α carbon to the α F hfc tensor by numerical evaluation of eq 2 using the Slater orbitals of carbon. The result showed that it would be ~0 G along the z axis (using the coordinates of Figure 3), ~+8 G along the C−F bond, and ~−8 G along the direction perpendicular to the C−F bond in the x−y plane.

A computer program that would simulate the ESR powder pattern of radicals possessing an anisotropic **g** tensor and a multiple number of sets of anisotropic hfc tensors of differing orientations has been described earlier.[16] Starting with an initial set of the **g** tensor, the hfc tensors, and their orientations estimated from the observed spacings, the structure, and the SOMO given by MNDO, the ESR powder pattern was simulated iteratively for the best overall fit with the observed spectrum. Some orthorhombicity of the hfc tensor expected from the spin density on the α carbon was also considered. The **g** tensor, the α F hfc tensors, and their orientations so determined are given in Table 1. Figure 3c shows the simulated spectrum based on these parameters.

The central component of the observed spectrum (Figure 3a) has shoulders on each side giving it an appearance of a triplet. However, the intensity of these shoulders (relative to the central signal) increased with increased duration of irradiation. The shoulders are hence attributed to a second species. As noted earlier, Z-lube is a random copolymer of methylene oxide units, $\mathrm{-O{-}CF_2{-}O-}$, and ethylene oxide units, $\mathrm{-O{-}CF_2{-}CF_2{-}O-}$. The radicals generated here, $\mathrm{R{-}O{-}CF_2^{\bullet}}$, may have slightly different hfc tensors and/or orientations depending on the monomer unit to which the radical sector is attached. The spectrum of Figure 3a can be simulated accurately (including shoulders), for example, if one assumes the presence of equal amounts of two types of radicals having the **g** tensor and the α F hgc tensors exactly the same as those given above, but with slightly different orientations of the hfc tensors, (i.e., $\phi/\theta = \pm 60°/6°$ for one type, and $\phi/\theta = \pm 60°/14°$ for the other).

Table 1. g Tensors and ^{19}F hfc Tensors of Radicals Generated from Perfluoropolyether Acids by Photodecarboxylation at 77 K

	z	x	y	ϕ/θ^a
$\mathrm{R{-}O{-}CF_2^{\bullet}}$				
g	2.0023	2.0065	2.0065	
$A(\alpha\mathrm{F})$	236.5	60.0	76.0	±60°/8°
$\mathrm{R{-}O{-}\dot{C}F(CF_3)}$				
g	2.0023	2.0065	2.0065	
$A(\alpha\mathrm{F})$	230.0	37.0	47.0	55°/10°
$A(\beta\mathrm{F})$	90.0	20.0	20.0	180°/44°
$\mathrm{R{-}O{-}CF_2{-}CF_2^{\bullet}}$				
g	2.0023	2.0023	2.0023	
$A(\alpha\mathrm{F})$	207.0	34.0	50.0	±60°/10°
$A(\beta\mathrm{F})$	35.0	15.0	15.0	160°/−30°

[a] ϕ and θ define the direction of the symmetry axis of the hfc tensor relative to the z axis of the **g** tensor (see Figures 4, 6, and 8).

K-COOH. Figure 5a shows the ESR spectrum observed, at 77 K, from K-COOH that had been irradiated with 254 nm light for 20 min. The overall pattern was recognized as a doublet of doublet, the major doublet having a large uniaxial asymmetry as indicated. The spacings of the major doublet, ~240 and ~40 G, are close to those found for the α fluorine nuclei of $\mathrm{R{-}O{-}CF_2^{\bullet}}$. The spectrum was hence assigned to $\mathrm{R{-}O{-}\dot{C}F(CF_3)}$. The second doublet with the ostensible spacings of 52 and 72 G is attributed to the hfc interaction with one of the β fluorine nuclei. Figure 5b shows the simulated spectrum based on two fluorine hfc tensors obtained by identifying the observed spacings with the respective $A_{\parallel}$'s and $A_{\perp}$'s and neglecting the effect of differing orientations. The simulated spectrum failed grossly to reproduce the relative intensities of individial components.

For fluorine hfc tensors of fluorocarbon radicals, it has been consistently seen that $A_{\parallel} \gg A_{\perp}$.[17] As the F(2s) orbital is much more stable than other valence orbitals, it mixes little into the SOMO. Thus for the hfc tensor given by eq 1, $A_{\mathrm{iso}} \approx A_{\mathrm{dip}}$, and consequently $A_{\parallel} \gg A_{\perp}$. When the angle between the magnetic field and the symmetry axis of an axially symmetric hfc tensor is η, the hf splitting constant is given by $[A_{\parallel}^2 \cos^2 \eta + A_{\perp}^2 \sin^2 \eta]^{1/2}$. It follows that, if $A_{\parallel} \gg A_{\perp}$, the splitting constant is given approximately by $A_{\parallel} \cos \eta$ unless η is equal or close to $\pi/2$. Let us assume that $A_{\parallel} \gg A_{\perp}$ for the β F responsible for the minor doublet of Figure 4a. As the overall pattern of the spectrum is dictated by the large anisotropy of the α F hfc tensor, the observed minor splittings, 52 and 72 G, must be the hfc interaction of the β F nucleus manifested along the principal axes of the α F hfc tensor. We may thus advance the following assignments:

$$A_{\parallel}(\mathrm{F}_{\beta}) \cos \eta \cong 52\ G$$

$$A_{\parallel}(\mathrm{F}_{\beta}) \sin \eta \cong 72\ G$$

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(16) Kasai, P. H. *J. Am. Chem. Soc.* **1972**, *94*, 5950.

(17) See, for example: Iwasaki, M. *Fluorine Chemistry Review*; Tarrant, P., Ed.; Marcell Dekker: New York, 1971; Vol. 5.

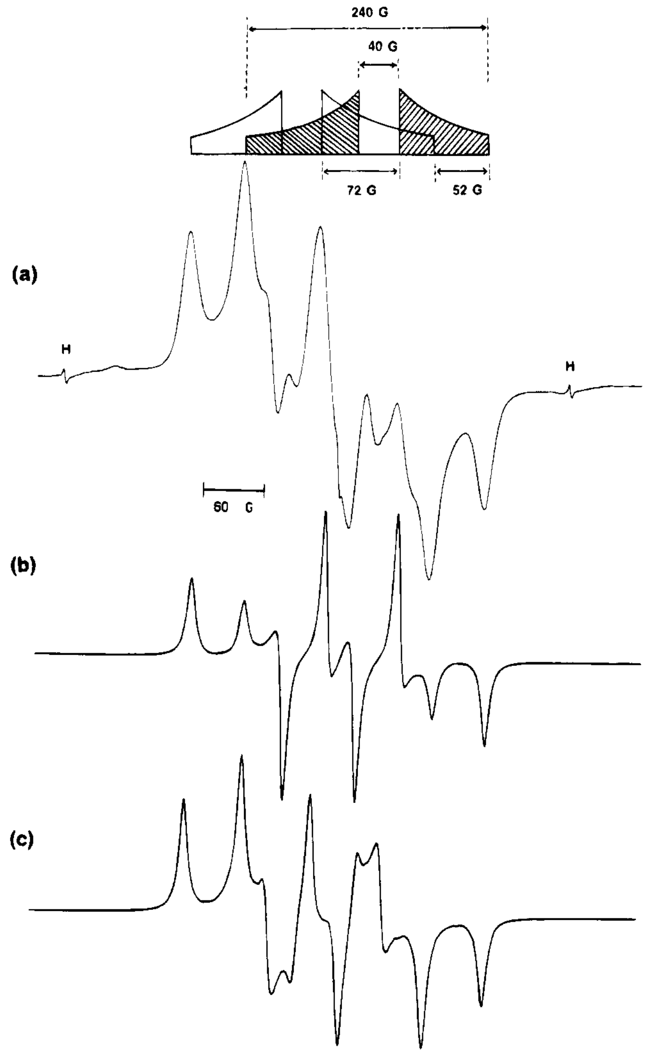

Figure 5. (a) ESR spectrum observed from K-COOH after exposure to 254 nm radiation at 77 K. The spectrum is assigned to $\mathrm{R{-}O{-}\dot{C}F(CF_3)}$. The observed pattern is recognized as a doublet of doublet, the major doublet having a large uniaxial asymmetry as indicated. "H" indicates the signals due to hydrogen atoms. (b) Simulated spectrum based on the two F hfc tensors obtained by identifying the observed splittings with the respective $A_{\parallel}$'s and $A_{\perp}$'s. (c) Simulated spectrum based on the **g** tensor, the α and β F hfc tensors, and their orientations given in Table 1.

where η is now the angle between the symmetry axes of the two hfc tensors. These relation then yield $A_{\parallel}(\mathrm{F}_\beta) = 89\ G$ and $\eta = 54°$.

We examined the structure and the SOMO of a model system $\mathrm{CF_3{-}O{-}\dot{C}F(CF_3)}$ by the MNDO method. Pertinent features of the calculated structure are shown in Figure 6. In the figure the radical is oriented so that the peripheral O, β C, and α F atoms are in the $x{-}y$ plane, and the $y{-}z$ plane bisects the $\mathrm{O{-}C_\alpha{-}F_\alpha}$ angle. The calculation predicted the following: (1) The β $\mathrm{CF_3}$ group is locked as shown. (2) The unpaired electron is mostly localized at the α carbon (78%), but 9% each are at the O and α F atoms, and 4% at the β F atom located trans to the unpaired spin orbital of the α carbon. (3) The directions of the symmetry axes of the α F and β F hfc tensors (relative to the z axis) are as shown in the figure. Again starting with an initial set of the g-tensor, the hfc tensors and their orientations deducted above, the ESR powder pattern was simulated iteratively for the best fit with the observed spectrum. The **g** tensor, the α and β F hfc tensors, and their orientations so determined are given in Table 1. Figure 5c shows the simulated spectrum based on these parameters.

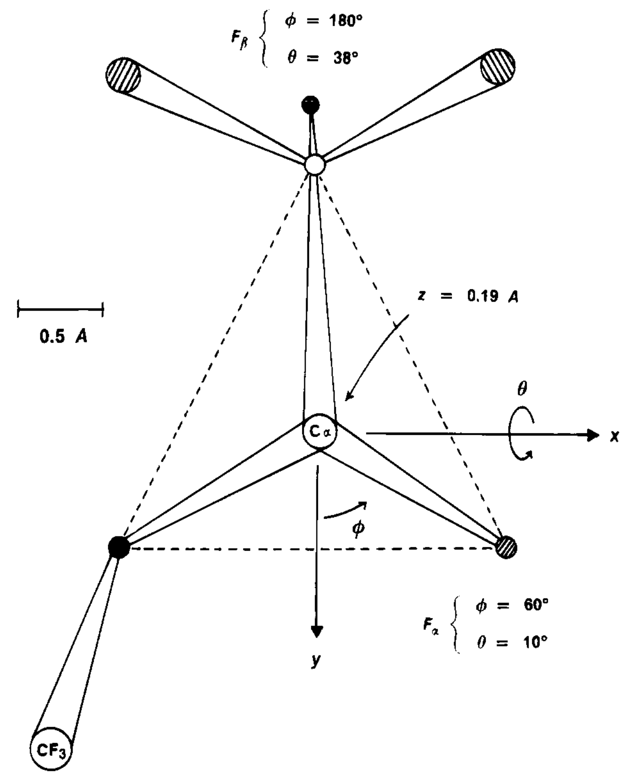

Figure 6. Conformation of $\mathrm{R{-}O{-}\dot{C}F(CF_3)}$ given by the MNDO method. The O, β C, and α F atoms are in the $x{-}y$ plane. Two angles of rotations, ϕ and θ, define the direction of the symmetry axis of each F hfc tensor given by its F(2p) orbital in the SOMO.

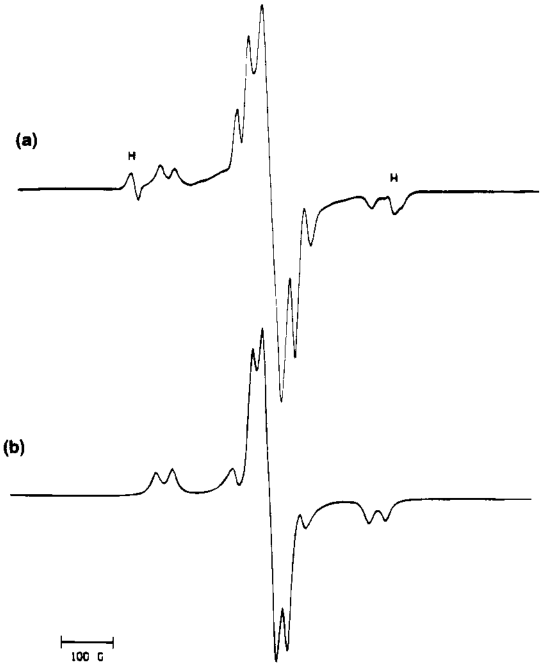

Figure 7. (a) ESR spectrum observed from D-COOH after exposure to 254 nm radiation at 77 K. The spectrum is assigned to $\mathrm{R{-}O{-}CF_2{-}CF_2^{\bullet}}$. The overall pattern is similar to that of $\mathrm{R{-}O{-}CF_2^{\bullet}}$ (Figure 3); the additional small splitting is due to one of the β F nuclei. "H" indicates the signals due to hydrogen atoms. (b) Simulated spectrum based on the **g** tensor, the two α F hfc tensors, one β F hfc tensor, and their orientations given in Table 1.

D-COOH. Figure 7a shows the ESR spectrum observed, at 77 K, from D-COOH that had been irradiated

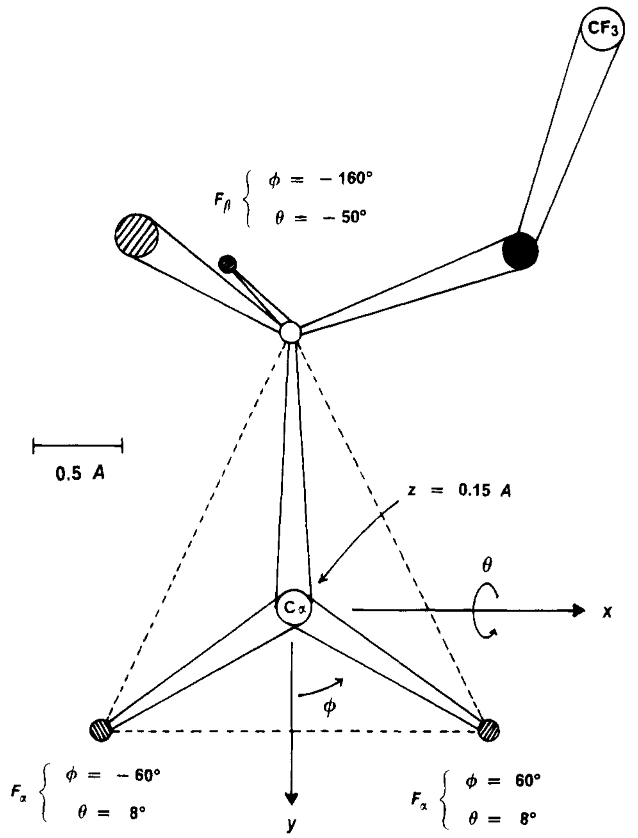

Figure 8. Conformation of $R-O-CF_2-CF_2^\bullet$ given by the MNDO theory. The β C and two α F atoms are in the $x-y$ plane. Two angles of rotations, φ and θ, define the direction of the symmetry axis of each F hfc tensor given by its F(2p) orbital in the SOMO.

with 254 nm light for 20 min. The overall pattern is similar to that of $R-O-CF_2^\bullet$ observed earlier. The spectrum is hence assigned to radicals $R-O-CF_2-CF_2^\bullet$ expected from decarboxylation of D-COOH. The additional splittings of 30 G resolved on the outermost components is attributed to one of the β F nuclei. Pertinent structural features of a model system $CF_3-O-CF_2-CF_2^\bullet$ calculated by the MNDO method are shown in Figure 8. In the figure the radical is oriented so that the peripheral α F and β C atoms are in the $x-y$ plane, and the $y-z$ plane bisects the $F_\alpha-C_\alpha-F_\alpha$ angle. The calculation predicted the following: (1) The β alkyl group is locked as shown. (2) The unpaired electron is mostly localized at the α carbon (76%), but 10% each are at the two α F atoms, and finally 2% each at the β C atom and the β F atom located trans to the unpaired electron orbital at the α C carbon. (3) The directions of the symmetry axes of the α F and β F hfc tensors are as shown in the figure. Again starging with an initial set of the **g** tensor, the hfc tensors and their orientations deducted above, the ESR powder pattern was simulated iteratively for the best fit. The **g** tensor and the hfc tensors thus determined are given in Table 1. Figure 7b shows the simulated spectrum based on these parameters.

Summary and Remarks

The present study confirmed that perfluoropolyether chains terminated with radical ends are readily generated on exposure of perfluoropolyether acids, Z-COOH, K-COOH, and D-COOH, to 254 nm radiation.

Analysis of the α F hfc tensor of $R-O-CF_2^\bullet$ (Table 1) according to eq 1 yields

$$A_{\mathrm{iso}} = 124.2\ G \quad \text{hence} \quad \varrho(2s) = 0.007$$

$$A_{\mathrm{dip}} = 56.2\ G \quad \text{hence} \quad \varrho(2p) = 0.089$$

Here the spin densities, $\varrho(2s)$ and $\varrho(2p)$, were obtained by comparison with the atomic values, A_{iso} and A_{dip} expected from a unit density in the F(2s) and F(2p) orbitals, respectively.[18] The MNDO calculation predicted $\varrho(2s) = 0.001$ and $\varrho(2p) = 0.099$. The INDO method[19] gave, for the same geometry, $\varrho(2s) = 0.004$ and $\varrho(2p) = 0.080$. These calculated values are considered in reasonable agreements with the values deducted above from the observed hfc tensors.

The isotropic α F coupling constant of $R-O-CF_2^\bullet$ determined presently is in close agreement with the splitting constant (126.5 G) determined earlier for the same radical generated by thermophotolysis of peroxidic Z-lube in the fluid state.[11] Similar analyses of the α and β F hfc tensors of $R-O-\dot{C}F(CF_3)$ in Table 1 yield $A_{\mathrm{iso}}(\alpha F) = 105\ G$ and $A_{\mathrm{iso}}(\beta F) = 43\ G$. These values differ significantly from those determined for $R-O-{}^\bullet CF(CF_3)$ generated by photothermolysis of peroxidic Y-lube, $A_{\mathrm{iso}}(\alpha F) = 89\ G$ and, for the rotating β CF_3 group, $A_{\mathrm{iso}}(\beta F) = 12\ G$.[11] The discrepancy may be ascribed to structural alteration that occurs when the β CF_3 group freely rotates.

Recently it has been demonstrated that perfluoropolyethers have propensity to undergo the intramolecular disproportionation process of the following scheme:[20]

$$R-CF_2-O-CF_2-R \rightarrow R-C(F){=}O + CF_3-R$$

The process is catalyzed by Lewis acids (metal oxides or halides). For perfluoropolyethers having an odd number of backbone carbons between successive ether oxygens, e.g., Z- and D-lubes, the reaction occurs at any such ether linkage. For perfluoropolyethers having an even number of backbone carbons between successive ether oxygens, e.g., K-lube or perfluoropoly(ethylene oxide), the process is limited to the terminal ether oxygen. Here the fluorine transfer is always from the end unit to the internal unit, and the fluorocarbonyl group is formed in the leaving monomer unit.

Thus an immediate "physical consequence" of the catalytic degradation is shortening of the chain length. The drop in the average chain length associated with the process would be precipitous for perfluoropolyethers of the "odd number carbon" type. In contrast, for perfluoropolyethers of the "even number carbon" type, the chain length decrement is by one monomer unit per each reaction.

The "chemical consequence" of the catalytic degradation is that, for perfluoropolyethers such as Z- and D-lubes, even when one starts our with the normal, nonfunctionalized form, perfluoropolyether chains with carboxylic end groups will be generated. Deleterious effect may result either from its acidity or from the decarboxylation process under radiation. If based on these issues only, perfluoropolyethers of choice would clearly be those with even number of backbone carbons in each building monomer units.

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[18] Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577.

[19] See, for example: Pople, J. A.; Beveridge, D. L. *Approximate Molecular Orbital* Theory; McGraw-Hill: New York, 1970.

[20] Kasai, P. H. *Macromolecules* **1992**, *25*, 6791.