

ALKOXYFLUOROALKYL RADICALS: STRUCTURE AND CONFORMATIONS FROM SOLID STATE ESR SPECTRA

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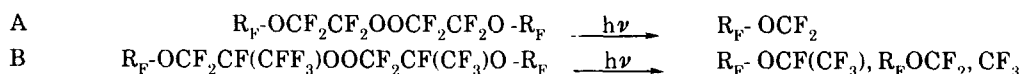
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Abstract: The anisotropic components of the α and β Fluorine h.f. tensors of alkoxyfluoroalkyl radicals ROCF_2 and $\text{ROCF}(\text{CF}_3)$ were experimentally determined and basic informations pertaining the geometry of the radical centres and the mechanism of magnetic interactions were obtained.

The structure of alkoxyfluoroalkyl radicals is not yet known in detail: the only informations so far available come from few isotropic ESR spectra reported in the literature¹⁻³ which consistently show larger isotropic α -F couplings as compared to the analogous perfluoroalkyls; this property is considered diagnostic of a greater departure from planarity of the radical centres imputed to a destabilizing π conjugative interaction of half filled orbitals with lone pairs on adjacent oxygen atoms¹. In this work the detailed structures and conformations of the model alkoxyfluoroalkyl radicals $\text{R}_\text{F}\text{OCF}_2$ (I), $\text{R}_\text{F}\text{OCF}(\text{CF}_3)$ were obtained by analysis of both the isotropic and anisotropic components of α and β fluorine h.f. tensor, based on computer simulation of solid state ESR spectra. The results are aimed to contribute to a better understanding of the structure-reactivity relationships for this class of important intermediates in fluorine free radical chemistry. Radicals I and II were obtained by photolysis at 77 K under vacuum of peroxydic perfluoropolyethers A, B, respectively, prepared according to reference 4



Radicals I and II were previously identified from their well resolved isotropic ESR spectra obtained by photolysis in the liquid state under stationary conditions². The solid state X band ESR spectra were recorded on a Varian E-109 spectrometer and analyzed by computer simulation following the procedure outlined by Thuomas and Lund (5) which employ the Hamiltonian

$$H = \beta \cdot H \cdot g \cdot S + \sum_{i=1}^n \{ S \cdot A_i \cdot I_i - \beta_N \cdot g_i \cdot H \cdot I_i \}$$

under the approximation of a dominant Zeeman interaction. The experimental results are summarized in Fig. 1, 2 and in Table 1

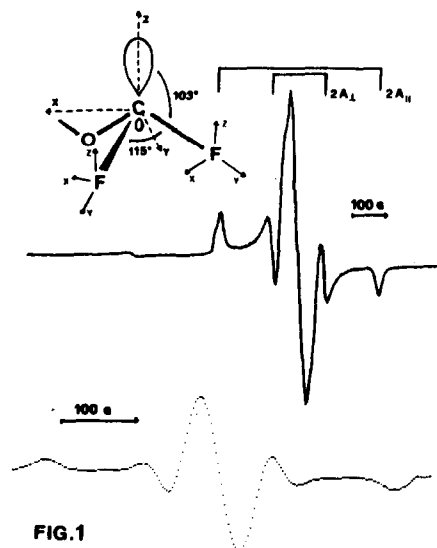


FIG. 1

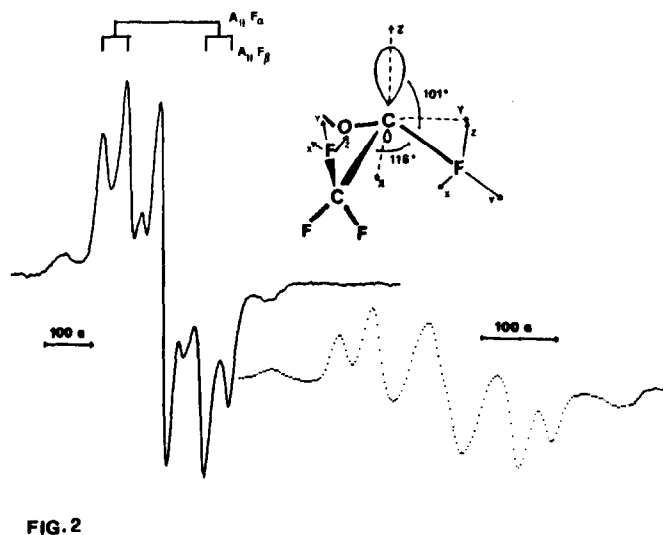


FIG. 2

Table 1: h.f. coupling tensors for radicals $-R_F\dot{O}CF(CF_3)$ AND $-R_F\dot{O}CF_2$

Radical	A_{190}	A_{\perp}	A_{\parallel}	T_{\perp}	T_{\parallel}	Direction cosines		
						a	b	c
$R_F\dot{O}CF(CF_3)$								
$F(\alpha)$	88.3	20.0	225.0	-68.3	136.7	1.000	0.000	0.000
						0.000	0.980	-0.190
						0.000	0.190	0.980
$F(\beta_1)$	26.7	5.0	70.0	-21.7	43.3	-0.500	-0.866	0.000
						0.439	-0.253	0.861
						-0.746	0.431	0.507
$F(\beta_2)$	7.3	1.0	20.0	-6.3	12.7	0.393	0.350	0.850
						0.614	0.588	-0.526
						-0.685	0.728	0.016
$F(\beta_3)$	7.3	1.0	20.0	-6.3	12.7	0.393	0.350	0.850
						0.614	0.588	-0.526
						-0.684	0.728	0.016
$R_F\dot{O}CF_2$								
$F(\alpha_1)$	126.2	68.0	242.7	-58.2	116.5	0.537	0.843	0.000
						-0.821	0.523	-0.227
						-0.191	0.122	0.974
$F(\alpha_2)$	126.2	68.0	242.7	-58.2	116.5	0.537	-0.843	0.000
						0.821	0.523	-0.227
						0.191	0.122	-0.974

The experimental polycrystalline spectrum of $R_p\text{OCF}_2$ (Fig. 1) is diagnostic of the interaction of two equivalent α -fluorine atoms with axially symmetric h.f. tensors. A satisfactory matching with the computed pattern was obtained by assuming the h.f. tensors and direction cosines shown in Table 1 together with a strongly pyramidal structure of the radical centre with a degree of deviation from planarity of 13° , close to tetrahedral. Calculations with planar or significantly less bent structures, always led to an excessive flattening of the outer peaks as compared to the central one. As expected, the maximum, minimum and intermediate principal values are oriented along the symmetry axis of the p_z fluorine orbital, along the C-F bond and perpendicular to it. A significant detail is represented by the orientation of the A_{zz} components which had to be held at the eclipsed position in respect to the symmetry axis of the u.s. orbital on the adjacent carbon in order to get satisfactory results in the simulations. This may be considered direct evidence for the transfer of unpaired spin density from the carbon radical centre to the α -fluorine atoms via $sp^3(\text{C})-p_z(\text{F})$ orbital overlap.

The polycrystalline spectrum obtained from peroxide B (Fig. 2) is simulated by assuming 70% of radicals II and 30% of radical I and by employing the h.f. tensors and direction cosines reported in table 1. The $A_{//}$ features of II show a doublet splitting of ~ 70 G corresponding to the $A_{//}$ value of a single $F\beta$ atom in CF_3 group. As β -fluorine couplings follow the $\cos^2\theta$ rule⁶, the lack of observation of the other β -F couplings and the magnitude of the observed one implies that, at 77 K, the CF_3 group is locked to a conformation such that one C-F bond is eclipsed in respect to the symmetry axis of the u. electron orbital on the adjacent carbon. This conformation together with a degree of deviation from planarity of 11° leads to the reproduction of the experimental spectrum as shown in fig. 2. The direction cosines are consistent with the $A_{//}$ values for both α and β fluorines being oriented along the symmetry axis of the $F-P_z$ orbitals, whilst the A_{\perp} values are alligned along and perpendicular to C-F bonds. As in the case of species I, the $A_{//}$ principal directions are eclipsed in respect to the Carbon hybrid orbital, thus stressing the importance of orbital overlaps for the transmission of spin density to fluorine from the radical centre. The presence of both isotropic and anisotropic components in the h.f. tensors of I and II indicated that the electron is partly in an s and partly in a p state; accordingly from the relationships⁷

$$T_{//} = \pm 2B_0C_F^2(2p)$$

$$T_{\perp} = \pm B_0C_F^2(2p)$$

$$A_{\text{iso}} = \pm A_0C_F^2(2s)$$

The following LCAO coefficients are derived for the $R_p\text{OCF}_2$ radical: $C_F(2s) = 0.086$, 6% 2s character; $C_F(2p) = 0.34$, 94% 2p character. Similar calculations, applied to the $R_p\text{OCF}(\text{CF}_3)$ specie yield: $C_F(2s) = 0.072$, 4% 2s character; $C_F(2p) = 0.35$, 96% 2p character. For β -Fluorine both s and p contributions are controlled by the $\cos^2\theta$ rule, so that at the eclipsed position; the following coefficients are derived: $C_F(2s) = 0.039$; 3.6% 2s character; $C_F(2p) = 0.20$, 96.4% 2p character.

Table 2 shows the results of INDO calculations⁸ of isotropic and anisotropic components of the α -F h.f. tensors in the radical I ROCF_2 , performed as a function of the structure of the radical centre (degree of bending θ defined as in Fig. 1, 2); for the sake of comparison, also the L.C.A.O. coefficients of the highest occupied α -spin orbital (which roughly corresponds to the half filled orbital in the close shell approximation) are reported. The anisotropic components T_{xx} , T_{yy} , T_{zz} were obtained from the unpaired spin densities ρ on fluorine $2p_x$, $2p_y$, $2p_z$ orbitals following the methods described in reference 9. According to the data of Table 2, both the isotropic and anisotropic components of the h.f. tensor are predicted to rapidly increase with increasing the deviation from planarity and a 'satisfactory' agreement (considering the approximation of the method) with the experimental results is obtained with $\theta > 95^\circ$. The major mechanism responsible for this effect is shown by the M.O. method to be enhancement of the

delocalization of the u.s. onto the F-2p_z orbital (parallel increase of C_F²(2p_z) and ρ_F(2p_z)) followed by partial transfer of unpaired spin density from F-2p_z to F-2s orbital by spin polarization. This is inferred from the parallel increase of C_F²(2p_z) ≈ ρ_F(2p_z), ρ_F(2s), whilst C_F²(2s) (direct delocalization of unpaired electron to the F-2s orbital) never acquires enough magnitude to contribute for more than 25% to the overall A_{iso} splitting.

Table 2 - Radical ROCF₂: INDO calculation of α-F Hyperfine Tensor

θ	90.0°	93.5°	97.5°	101.5°	101.5°	109.5°	112.0°
C _F ² (2p)	0.0000	0.0000	0.002	0.0027	0.0024	0.0019	0.0018
C _F ² (2p)	0.0880	0.0940	0.1060	0.1160	0.1240	0.1300	0.1220
ρ(2p _x)	0.0002	-0.0030	-0.0180	-0.0184	-0.0140	-0.0160	-0.0020
ρ(2p _y)	-0.0283	-0.0236	-0.0010	0.0034	-0.0130	-0.0128	-0.0112
ρ(2p _z)	0.0596	0.0642	0.0780	0.0890	0.0978	0.1038	0.1030
A _{iso}	59.5	87.2	166.5	188.1	172.7	141.3	127.0
T _{xx}	-16.8	-25.6	-61.3	-70.0	-61.8	-51.1	-51.7
T _{yy}	-63.1	-58.7	-33.6	-34.6	-59.0	-69.3	-67.8
T _{zz}	79.6	84.3	94.9	104.6	120.8	120.4	119.5

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