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ELECTRON SPIN RESONANCE STUDIES OF RADICALS IN IRRADIATED CRYSTALS*

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MASTER

Introduction

The electronic and molecular structures of free radicals may be conveniently studied by ESR spectroscopy when the radicals are trapped in single crystals of a diamagnetic material. In the present work irradiation of organic compounds with 1 m.e.v. electrons has been used to produce the radicals and ESR spectra have been obtained at 77°K and at 300°K. Sodium acetate trihydrate yields the methyl radical at 77°K but only the CH_2COO^- radical at 300°K. Trifluoroacetamide gives rise to the trifluoromethyl radical at 77°K and to the CF_2CONH_2 radical at 300°K. Irradiated crystals of $\text{CClF}_2\text{-COONa}\cdot 2\text{H}_2\text{O}$ give only the radical CF_2COO^- but these are in several different types of environment in the crystal lattice.

The Walsh rules predict that CH_3 and CF_3 will be bent since the 25th electron goes into a molecular orbital which becomes more stable on going from a planar to a pyramidal configuration. It is, therefore, of particular interest to obtain the ^{13}C hyperfine splittings for the central carbon atoms of the various radicals since this quantity permits an estimate of the deviation from planarity of the radicals. Our results, along with data in the literature, indicate that aliphatic radicals of the type CXYZ are planar if one of the substituents is hydrogen and nonplanar if two or three of the substituents are fluorine.

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Experimental

Crystals of trifluoroacetamide were grown from aqueous solution at 3°C and are monoclinic¹, elongated along c and have (100), (010) faces developed. Sodium chlorodifluoroacetate was recrystallized from aqueous solution and X-ray investigation showed that the crystals were monoclinic with four molecules of $\text{CClF}_2\text{COONa} \cdot 2\text{H}_2\text{O}$ per unit cell, space group C_c . Single crystals of $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$, $\text{CH}_3\text{COONa} \cdot 3\text{D}_2\text{O}$ and $^{13}\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ were all grown from aqueous (or D_2O) solution; they are monoclinic with space group $C_{2/m}$ and eight molecules per unit cell.

Trapped radicals were produced by irradiation with the 1 m.e.v. electron beam of a G. E. Resonant Transformer. The crystals were cooled with liquid air during irradiation and transferred to the ESR cavity without permitting their temperature to rise.

ESR spectra were taken with a Varian V-4200-10A spectrometer and details of operation have been given².

Results

The ESR spectra of the irradiated crystals have been presented³. In each case rotations were made at 10° intervals about three orthogonal axes (a,b,c* or a*,b,c) and the plots of splitting versus orientation for each hyperfine splitting were made. An undiagonalized tensor was constructed in the usual manner using a least squares fit to the curves and then diagonalized by means of a computer program. The results are summarized in Table I.

Discussion

Methyl Radical:

Because the methyl radical has not previously been reported in irradiated single crystals and because there is some possibility of species such as $\text{CH}_3\text{-COO}$ also giving four-line patterns with spacing ≈ 23 G we have studied also the irradiated $^{13}\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ and $\text{CH}_3^{13}\text{COONa} \cdot 3\text{H}_2\text{O}$ crystals. The former gives the well-known lines

for the $^{13}\text{CH}_3$ radical⁴ while the latter gives only the expected quartet of CH_3 so it seems likely that it is actually the methyl radical which we observe. Also the isotropic proton and ^{13}C hyperfine splittings (22.3 and 37.76) are close to the values reported⁵ for CH_3 in the liquid phase in a krypton matrix, or adsorbed on a surface. The anisotropy of the proton hyperfine splitting is very small as would be expected for rapid reorientation of CH_3 about its threefold axis while the value of $(A_{zz} - A_{iso}) = 2B$ found, 45 G, is close to the average of several pi-electron radicals (42 G) which are of the type CXYZ.

Each line of the quartet is accompanied by satellite lines which are spaced 11.2 G (or 22.4 G) apart corresponding to the NMR frequency at this magnetic field. These are then attributed to spin-flip transitions⁶ involving neighboring protons of the molecules of water of crystallization.

Trifluoromethyl radical:

The trifluoromethyl radical has been identified⁷ in the products of pulse radiolysis of liquid C_2F_6 ; the other simple radicals CF_2H and CFH_2 were also found by pulse radiolysis studies and their ESR spectra analyzed⁷. The isotropic fluorine and ^{13}C hyperfine splittings found here for CF_3 in the solid (144.6 and 271 G) are similar to those reported for the radical in the liquid phase. The very large value of the ^{13}C splitting indicates that the odd electron is an orbital nearly sp^3 in character and the radical is pyramidal with $\angle\text{FCF} \approx 110^\circ$.

CF_2CONH_2 Radical:

This radical was reported¹ in CF_3CONH_2 irradiated at 300°K and we find it also in the material irradiated at 77°K. However, the hyperfine splitting constants are larger at 77° and show a strong temperature dependence. The large values of the isotropic splittings, $A^F = 77.3$ and $A^{13}\text{C} = 147.5$, for the 77° radical suggest that it is nonplanar with a deviation from planarity $\theta \approx 8^\circ$ (here θ is the angle between the CF bond and the plane normal to the axis of the odd electron orbital).

The NH_2CO Radical:

Our data do not permit a structure to be assigned unambiguously to this radical. The isotropic splittings ($a_N = 16.6$, $a_{H_1} = 21$, $a_{H_2} = 19$) and the anisotropic splitting for nitrogen ($2B(N) = 15.8$) correspond roughly to the values⁸ for NH_2SO_3 and it is therefore possible that the radical is NH_2CO .

CF_2COO^- Radicals:

Irradiated crystals of $\text{CF}_2\text{ClCOONa} \cdot 2\text{H}_2\text{O}$ contain three sets of CF_2COO^- radicals which differ in local environment. The hyperfine splittings are rather similar for all three and the isotropic fluorine splittings (70 G) are large enough to suggest that they are not quite planar. No complete analysis of the ^{13}C lines could be made but the values of $A_{zz}^{13}\text{C}$ are rather large and suggest values of 70-90 G for the isotropic ^{13}C splitting which again would correspond to some deviation from planarity.

The most unusual feature is the triplet structure for the lines of one radical which appears to be a superhyperfine splitting from two protons (or fluorine atoms) of neighboring diamagnetic molecules. This superhyperfine structure is anisotropic and the tensor is traceless so it could be a simple dipole-dipole interaction but the distance ($r = 2\overset{\circ}{\text{A}}$) computed on this basis is so short as to correspond to a weak bond.

The spin populations in the various molecular orbitals may be estimated by combining a set of estimated values which accounts for the observed fluorine hyperfine splittings. The observed tensor is not cylindrically symmetrical which suggests some odd electron density in the C-F bonding orbital. In Table II a set of values applicable to CF_2COO^- or CF_2CONH_2 radicals is shown.

Reactions of the Radicals:

The CF_2COO^- radical reacts rapidly with oxygen to give a new radical with only a single ESR line. This is believed to be a peroxy radical such as $\text{OOCF}_2\text{COO}^-$ since the g_{zz} value is large. Hydrogen reacts with CF_2COO^- to give a diamagnetic species but does not react with the peroxide radical.

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TABLE I. Principal values of the hyperfine coupling tensors for various radicals.

Crystal	Radical	A	A_z^{13C}	g
$CH_3COONa \cdot 3H_2O$	CH_3	$A_{zz}^H = -21.8$	+82.7	
77°K		$A_{xx}^H = -22.5$	+15.5	
		$A_{yy}^H = -22.5$	+15.0	
CF_3CONH_2	CF_3	253	318	2.0024
77°K		92	238	2.0046
		88	258	2.0038
CF_3CONH_2	$\cdot CF_2CONH_2$	180	130	2.0024
		23.5	68.6	2.0045
300°		14	66.1	2.0045
$CF_2ClCOONa \cdot 2H_2O$	$\cdot CF_2COO^-$	185.7	135.0	2.0034
300°K		20.6		2.0050
(singlet)		14.3		2.0045
$CF_2ClCOONa \cdot 2H_2O$	$\cdot CF_2COO^-$	182.8	124.0	2.0026
300°K		10.5		2.0055
triplet shf		15.7		2.0048
$CF_2ClCOONa \cdot 2H_2O$	$OO CF_2 COO^-$	---	---	2.0356
300°K	(peroxide)			2.0102
				2.0090

TABLE II. Breakdown of the α -Fluorine Hyperfine Splitting Tensor^a

Radical	Direction	Spin Popula- tion	to Radi- cal	C-F	C-F
CF ₂ CONH ₂ or CF ₂ COO ⁻	1) orbital c2p _π	0.82 ^b	-0.4	4.6	-4.1
	2) F 2p _σ	-0.011	6 ^c	-12	+6
	3) F 2p _π	+0.094	102	-51	-51
	4) F 2s	+0.004	72.4	72.4	72.4
	5) Total		180	14	23.3
	Observed for [•] CF ₂ CONH ₂		180	14	23.5

^aAssumes all signs are positive for the α -F hyperfine splitting tensor.

^bBy difference.

^cCalculated to fit the observed splittings for [•]CF₂CONH₂ but only a slight variation in value is needed for [•]CF₂COO⁻.