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Electron Spin Resonance of Oriented $R\dot{C}HSR'$ Sulfide Radicals*

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Single crystals of the di-*n*-hexyl sulfide–urea and diethyl sulfide–urea inclusion compounds were x irradiated at 77°K and the long-lived free radicals produced were investigated by electron spin resonance. The free radicals observed in both crystals were of the type $R\dot{C}HSR'$. The value for the spin density on the carbon atom is 0.74 ± 0.07. The unpaired spin distribution is discussed in terms of simple molecular-orbital models.

I. INTRODUCTION

In previous work[1,2] we have investigated a number of oxygen-containing free radicals by x irradiating the corresponding urea inclusion compounds. Urea readily forms large hexagonal crystals with a variety of linear hydrocarbon derivatives.[3] These hydrocarbon derivatives are in an extended zigzag conformation and are enclosed in tubular cavities formed by spirals of hydrogen-bonded urea molecules.[4] The resulting crystals are convenient for ESR studies because all guest molecules are magnetically equivalent and no urea free radicals are observed. In this paper we wish to report the first use of this technique to study radicals derived from linear sulfides.[5] The identification of the x-ray-produced free radicals is discussed below and the experimental unpaired spin distribution is discussed in terms of simple molecular-orbital theories.

II. EXPERIMENTAL

Single crystals of the sulfide inclusion compounds were prepared as follows: di-*n*-hexyl sulfide (Aldrich, used without further purification) was added to urea-saturated methanol until a precipitate formed; the mixture was heated until the precipitate dissolved, and the solution was then cooled slowly to 273°K over a period of two days. Diethyl sulfide–urea crystals were obtained in a similar manner using Eastman diethyl sulfide. In each case, the crystalline z axis was defined to be the needle axis of the long hexagonal crystals, and the xy plane to be perpendicular to the z axis. Molecular motion about the z axis causes the hyperfine tensors and g tensors to be isotropic in the xy plane. This feature of the ESR spectra suggests that these hexagonal crystals have the typical tubular structure of organic urea inclusion compounds.[1,4]

The crystals were x irradiated at 77°K in the same manner as in III; irradiation time was 2 h for di-*n*-hexyl sulfide and 4 h for diethyl sulfide. The ESR spectra were obtained with a Varian V-4500 spectrometer operating at 9.5 GHz and modulated at 100 kc/sec. Temperature control was effected through the use of a Varian V-4557 variable-temperature accessory. Except for resolution, no apparent changes in any of the spectra were observed over the temperature range investigated, i.e., 253° to 293°K. The temperatures quoted in Figs. 1 and 2 represent the upper limits beyond which the crystals decompose rapidly. These experimental spectra were substantiated by other experiments, using several different crystals of each compound, and the coupling constants extracted from each agreed to within experimental error.

The coupling constants of Table I are quoted directly from the computer-simulated spectra. To obtain these values, the experimental spectra were analyzed for trial coupling constants, and these values were used as parameters in a computer program which generates and plots Gaussian spectra. The input coupling constants were then adjusted to give the best fit to the experimental spectrum. The simulations were carried out on an IBM 360 computer using a Calcomp digital incremental plotter. All spectra, both experimental and computer simulated, are shown as taken, and were not retraced.

The g values were measured relative to DPPH ($g=2.0036$)[6] using a Varian V-4532 dual cavity, and peroxylamine disulfonate ($a=13.0$ G)[7] was used for a scan calibration for all spectra.

III. RADICAL IDENTIFICATION

The ESR spectra obtained for the x irradiated di-*n*-hexyl sulfide and diethyl sulfide–urea inclusion com-

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[1] O. H. Griffith, J. Chem. Phys. **41**, 1093 (1964); **42**, 2644 (1965). (These papers have previously been referred to as I and II.)

[2] O. H. Griffith, J. Chem. Phys. **42**, 2651 (1965), referred to as III.

[3] See, for example, O. Redlich, C. M. Gable, A. K. Dunlop, and R. W. Millar, J. Am. Chem. Soc. **72**, 4153 (1950); K. A. Kobe and W. G. Domask. Petrol. Refiner **31**, 106 (1952); W. Schlenk, Jr., Ann. Chem. **565**, 204 (1949).

[4] A. E. Smith, Acta Cryst. **5**, 224 (1952).

[5] We are unaware of any previous investigation of these sulfide radicals in an oriented matrix. Similar radicals have undoubtedly been studied in randomly oriented samples where even the identification of the radicals is at best uncertain.

[6] R. T. Weidner and C. A. Whitmer, Phys. Rev. **91**, 1279 (1953).

[7] J. J. Windle and A. K. Wiersema, J. Chem. Phys. **39**, 1139 (1963).

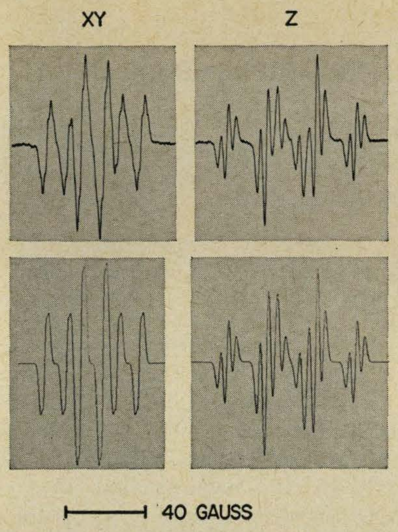


FIG. 1. The 273°K ESR spectra of an x-irradiated single crystal of di-*n*-hexyl sulfide with the magnetic field in the *xy* plane and parallel to the *z* axis, respectively. Computer-simulated spectra are shown below each of the two experimental curves.

pounds are given in Figs. 1 and 2. The ESR hyperfine pattern of the di-*n*-hexyl sulfide–urea crystal results from one large anisotropic proton coupling constant and two large equivalent but nearly isotropic coupling constants. The lines are further split by two small coupling constants which are resolved only with the magnetic field near the *z* axis of the crystal. The ESR spectra obtained for the diethyl sulfide–urea crystal are similar except that in this case there are three large equivalent but nearly isotropic proton coupling constants. Therefore, the logical choices for the free radicals produced in the di-*n*-hexyl sulfide and diethyl sulfide–urea inclusion compounds are, respectively,

$$\mathrm{CH_3(CH_2)_3\overset{\beta}{C}H_2\overset{\alpha}{\dot{C}}HS\overset{\zeta}{C}H_2(CH_2)_4CH_3} \qquad (1)$$

and

$$\mathrm{\overset{\beta}{C}H_3\overset{\alpha}{\dot{C}}HS\overset{\zeta}{C}H_2CH_3}, \qquad (2)$$

in which the protons are labeled α, β, or ζ as shown. The magnitudes and assignments of the proton coupling constants are given in Table I. The spectra reconstructed using these coupling constants are given below the original spectra in Figs. 1 and 2. The reconstructed spectra, with one minor exception, are in excellent agreement with the corresponding experimental spectra. The exception occurs with the magnetic field in the *xy* plane of the di-*n*-hexyl sulfide–urea crystal. In this orientation there appear to be partially resolved splittings not visible in the spectra reconstructed by the computer (Fig. 1). There are several possible explanations for these additional splittings including a slight nonequivalence of the β-proton coupling constants or partial resolution of the ζ-proton splittings. Since this effect was not observed in the other spectra and does not affect the discussion of the spin-density distribution, it is not considered further.

The free radicals 1 and 2 can be thought of as being formed by the removal of one hydrogen atom from the α position of the sulfide molecule. Thus, the sulfide free radicals bear the same relationship to the parent molecules as do the radicals observed in the ester, ketone, and ether inclusion compounds.[1,2]

IV. EXPERIMENTAL SPIN-DENSITY DISTRIBUTION

A. From α-Proton Coupling-Constant Data

It can be seen from the data of Table I that the α-proton coupling constants are highly anisotropic. This anisotropy and the magnitude of the α-proton coupling constant are characteristic of π-electron radicals. To obtain the π-electron spin density on Carbon Atom 2 the isotropic component of the α-proton coupling constant, a_0^α, is needed. This would be measured directly if the radicals were rapidly tumbling in solution or would equal one-third of the trace of the hyperfine tensor if the radicals were present in a *rigid* crystal. In urea inclusion crystals the situation is slightly more complex because molecular motion averages only a part of the hyperfine anisotropy. To a good approximation, however, a_0^α may be obtained from the relation[1,2]

$$a_0^\alpha = \tfrac{1}{3}(2a_{xy}^\alpha + a_z^\alpha). \qquad (3)$$

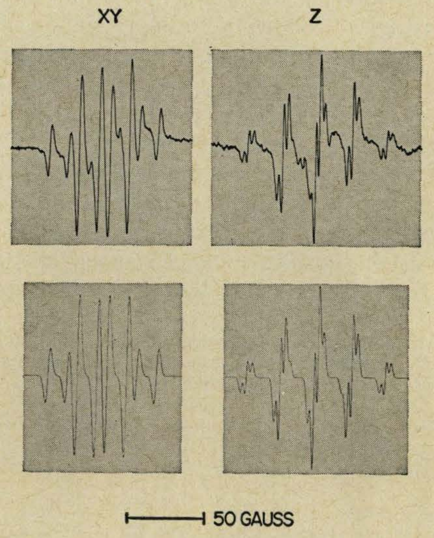


FIG. 2. The 253°K ESR spectra of x-irradiated single crystals of diethyl sulfide (above) and the computer-simulated spectra (below) for each orientation. In order to gain sufficient signal intensity for this measurement, six crystals were aligned parallel on the crystal mount.

TABLE I. Proton hyperfine coupling constants and *g* values.[a]

Radical	a_z^α	a_z^β	a_z^ζ	a_{xy}^α	a_{xy}^β	g_{xy}	g_z
(1) $\mathrm{CH_3(CH_2)_4\dot{C}HS(CH_2)_5CH_3}$	25.4	20.3	3.7	11.5	18.9	2.0037	2.0059
(2) $\mathrm{CH_3\dot{C}HSCH_2CH_3}$	24.6	21.8	2.8	12.8	19.4	2.0036	2.0059

[a] a^α, a^β, and a^ζ are the coupling constants (in gauss) of the α, β, and ζ protons, respectively, as used in the computer-simulated spectra of Figs. 1 and 2. *xy* and *z* specify the orientation of the magnetic field with respect to the crystalline axes.

The limits of accuracy differed among the various spectra; in the case of a^α and a^β in the *z* orientation, the coupling constants are believed to be correct within ±0.3 G. a_{xy}^α and a_{xy}^β are correct to ±0.5 G for Radical (1) and ±0.4 G in the case of Radical (2). The ζ-proton coupling constants are accurate to ±0.1 G, and the *g* values are correct to within ±0.0002.

Once a_0^α is known the π-electron spin density on Carbon Atom 2, ρ_C, is obtained from the familiar relation $a_0^\alpha = Q\rho_C$, where Q is a proportionality constant.[8] The value of Q varies slightly from radical to radical but a good choice is 22.4 G. This number is the value of a_0^α reported by Fessenden and Schuler[9] for the $\mathrm{CH_3\dot{C}H_2}$ radical which has a spin density of approximately one. Taking Q to be 22.4 G, ρ_C is 0.72 for the di-*n*-hexyl radical and 0.75 for the diethyl sulfide radical. These two values are the same within experimental error.

B. From β-Proton Coupling-Constant Data

A value of ρ_C can also be obtained from the β-proton coupling constants, providing the β protons are part of a rapidly rotating methyl group (e.g., Radical 2). The procedure is the same as in the α-proton case. The first step is to calculate a_0^β from the relation

$$a_0^\beta = \tfrac{1}{3}(2a_{xy}^\beta + a_z^\beta).$$

The spin density ρ_C can then be obtained from the relation $a_0^\beta = (\tfrac{1}{2}B)\rho_C$ where $\tfrac{1}{2}B$ is a proportionality constant equal to 26.9 G for the ethyl radical.[1,9] The resulting value of ρ_C for Radical 2 is 0.75. This number is in excellent agreement with the values obtained from the α-proton coupling-constant data, and we conclude that an average of the values, 0.74, is a reliable estimate of the spin density. Assigning a limit of error to this number is more difficult, but a realistic (if somewhat arbitrary) estimate of the accuracy is ±10%. The final value is therefore $\rho_C = 0.74 \pm 0.07$.

V. THEORETICAL SPIN-DENSITY DISTRIBUTION

A. Hückel MO Method

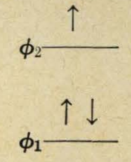
It is clear from the experimental results that this is a two-center problem involving a delocalization of unpaired spin density over one carbon atom and one sulfur atom. Formally, in the simple Hückel approximation, the problem is the same as in the previously investigated ether radical $\mathrm{RH\dot{C}OR'}$ except that the π orbital of the heteroatom is a $3p$ rather than a $2p$ orbital. The Hückel calculation has already been performed for this general type of radical and the plot of ρ_C vs the two parameters h and k is given in III. The spin-density contour of 0.74 ± 0.07 corresponds to $h = (1.1 \pm 0.4)k$. That is, only the relation between the two Hückel parameters, and not their individual values, are specified for this radical.

It is of interest to compare the spin-density distribution of the sulfide radical with that of the corresponding ether radical. The ESR spectra and spin-density distributions of the two radicals are surprisingly similar. The spin density on the carbon atom of the ether radical was found to be 0.70 ± 0.10 and the corresponding relation between h and k is $h = (0.9 \pm 0.5)k$.[2] It is gratifying to note that the variation in ρ_C obtained from the α- and β-proton coupling constants of the sulfide radical is much less than in the corresponding ether radical. The errors are apparently introduced in the choices of Q and R rather than in the measurement of the coupling constants. However, very few radicals have been reported for which two values of the spin density on one site can be obtained from α- and β-proton coupling-constant data, and it is not yet possible to draw general conclusions regarding the best choice of proportionality constants.

B. Configuration Interaction

The configuration-interaction (CI) treatment of the sulfide spin distribution is formally the same as for the ether radical providing only the $3p$ orbital of sulfur is considered explicitly. The two-configuration wavefunctions and the two configurations are[2]

$$\psi_1 = (6)^{-1/2} \sum_P (-1)^P P\phi_1\alpha\phi_1\beta\phi_2\alpha$$



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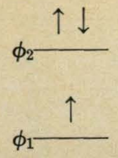
[8] H. M. McConnell and D. B. Chesut, J. Chem. Phys. **28**, 107 (1958).

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

and

$$\psi_2=(6)^{-1/2}\sum_P(-1)^P P\phi_1\alpha\phi_2\alpha\phi_2\beta,$$



where ϕ_1 and ϕ_2, the two π molecular orbitals, are linear combinations of the $2p_x$ atomic orbital on Carbon Atom 2 (χ_C) and the $3p_x$ orbital of the sulfur atom (χ_S):

$$\phi_1=(2)^{-1/2}(1+S)^{-1/2}(\chi_C+\chi_S),$$

$$\phi_2=(2)^{-1/2}(1-S)^{-1/2}(\chi_C-\chi_S).$$

The expressions for the core integrals and spin-density function are given in III and the atomic integrals may be assigned semiempirical values according to the method of Pariser and Parr.[10] It would be appropriate at this point to calculate the spin-density distribution as a function of the parameter β and the Coulomb integrals and to compare the results with calculations for other hydrocarbon radicals containing sulfur. Unfortunately, there are not sufficient published data to warrant this approach. One can, however, use semiempirical parameters obtained from optical data to calculate the spin density. The optical data of thiophene have been satisfactorily reproduced by several authors using semiempirical calculations.[11] The sulfur atom of thiophene, like that of the sulfide radicals 1 and 2, contributes two electrons to the π system and thiophene appears to be the best model compound currently available. For thiophene, Solony, Birss, and Greenshields (SBG)[11] employ $I_c=11.5$ eV, $I_s(2)=22.9$ eV, $\langle SS \mid SS\rangle=11.9$ eV, $\langle SS \mid CC\rangle=6.9$ eV, $\langle CC \mid CC\rangle=11.0$ eV, $\beta=-0.9$ eV, and neglect overlap integrals and neutral penetration integrals. The quantity $I_s(2)$ is the appropriate valence-state *second* ionization potential of sulfur and the other symbols follow the usual convention for ionization potentials and Coulomb integrals. Using these values we find $\rho_C=0.98$. Thus, the parameters of SBG correctly predict a large spin density on carbon. Quantitatively, however, the agreement is not satisfactory and even if the magnitude of β is increased to -3.0 eV, ρ_C is reduced only to 0.88. One may also develop the spin density in terms of the first ionization potential of the heteroatom as was done in III. Again, however, the value of ρ_C is too large unless $\beta\approx-3$ eV, and this would seem to be an unreasonably low value of β. It is tempting to suggest that unpaired spin density is also associated with sulfur orbitals of higher energy, such as the *3d* orbitals. The net effect could be to increase the spin density on sulfur and thereby decrease the spin density on carbon below the value predicted when only the *3p* orbital of sulfur is considered explicitly. This may in fact be the case. However, as pointed out by Sidman,[12] the effective orbital energies may differ significantly from the valence-state ionization potentials and this introduces another source of uncertainty in heteroatom systems. It is, therefore, unrealistic to conclude that the difference between the calculated and experimental values of ρ_C is quantitatively related to the participation of sulfur *3d* orbitals. In any case it is clear that the existing semiempirical approach will yield results in qualitative agreement with the experimental values.

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[10] R. Pariser and R. G. Parr, J. Chem. Phys. **21**, 466 (1953); **21**, 767 (1953).

[11] N. Solony, F. W. Birss, and J. B. Greenshields, Can. J. Chem. **43**, 1569 (1965); and references quoted therein.

[12] J. W. Sidman, J. Chem. Phys. **27**, 429 (1957).