

Electron Spin Resonance and Electronic Structure of the RĊHOR' Ether Radicals*

O. HAYES GRIFFITH

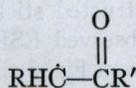
Gates and Crellin Laboratories of Chemistry,† California Institute of Technology, Pasadena, California

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Single crystals of inclusion compounds formed between urea and a series of aliphatic ethers were x irradiated and studied by electron spin resonance. The stable, x-ray-produced free radicals were all of the general type RĊHOR'. The approximate value for the spin density on the carbon atom is 0.70 ± 0.10 . The unpaired spin distribution is discussed in terms of the Hückel and approximate configuration interaction π -electron molecular orbital models and the valence bond method. The theoretical spin distributions are found to be in qualitative agreement with the experimental spin distribution.

INTRODUCTION

IN the preceding paper,¹ the radical



was investigated by electron spin resonance (ESR). This ketone radical is of special interest because it is one of the simplest heteroatom radicals in which each atom contributes one electron to the π system. Radicals in which one atom contributes two electrons to the π system are also of interest, and one of the simplest examples of this type of radical is RĊ-OR'. Here the spin density is primarily localized on only two atoms: the oxygen atom and an adjacent carbon atom. In this paper a positive identification of the radical RĊHOR' is reported in a series of ether-urea inclusion compounds.² Approximate values of the carbon and oxygen spin densities are determined from the coupling-constant data and the spin distribution is discussed in terms of the π -electron molecular orbital and valence bond methods.

EXPERIMENTAL

To prepare single crystals of each inclusion compound investigated, the ether was added slowly to a urea-saturated methanol solution until the inclusion com-

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¹ O. H. Griffith, *J. Chem. Phys.* **42**, 2644 (1965) (referred to as II).

² We are unaware of any previous investigation of this type of aliphatic ether radical in an oriented matrix. Radicals of the type ROĊHCO₂H and ROĊHCO₂⁻ have been reported previously [A. Horsfield and J. R. Morton, *Trans. Faraday Soc.* **58**, 470 (1962), and references quoted therein]. However, it is difficult to estimate the effect of the carboxyl group on both the formation and the unpaired spin distribution of the ether radical (the removal of an α proton adjacent to a carboxyl group by x irradiation is well known). An ESR investigation of the alcohol radical reported by Dixon and Norman³ is closely related to our work and we have occasion to compare the results obtained for the two systems.

³ W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, **1963**, 3119.

pound began to precipitate out of solution. The precipitate was then redissolved by the addition of a slight excess of methanol, and the solution was cooled slowly from 298° to 273°K over a period of from 36 to 48 h. The resulting crystals were long hexagonal needles. The z axis of each crystal is defined as lying along the needle axis, and the plane perpendicular to the needle axis is referred to as the xy plane. Apparently no crystallographic data has been reported for these ether-urea crystals. The general hexagonal structure of urea inclusion compounds has, however, been shown to be independent of the exact nature of the linear host molecule.⁴ We may safely assume, therefore, that the ether-urea crystals have the tubular structure characteristic of organic urea inclusion compounds.⁵

The ether-urea inclusion compounds are relatively unstable, decomposing in 1-3 h in air at room temperature. To avoid this problem, the crystals were x irradiated at liquid-nitrogen temperatures and the majority of the ESR spectra were taken with the sample at $\sim 273^\circ\text{K}$, rather than at room temperature. Below 273°K the crystals were stable for at least one or two days. A few crystals, x irradiated at 273°, had 273°K ESR spectra identical to those obtained from crystals x-irradiated at 77°K. It appears, therefore, that the 273°K ESR spectra are independent of the temperature at which the crystals were x irradiated. The other experimental details, including the x-ray tube, X-band ESR spectrometer, and cooling apparatus were the same as employed in II.

RADICAL IDENTIFICATION

To obtain a positive identification of the x-ray produced free radicals it was necessary to investigate more than one aliphatic ether. The walls of the tubular cavities hinder intermolecular radical reactions but do not prevent intramolecular radical rearrangements and therefore there are several possible structures for the final radicals produced. Furthermore, the relative magnitudes of the ζ - and γ -proton coupling constants were

⁴ W. Schlenk, Jr., *Ann. Chem.* **565**, 204 (1949).

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

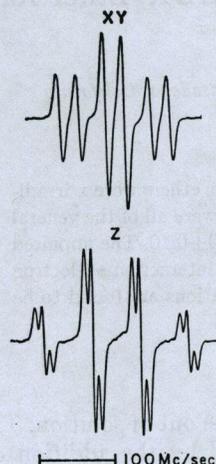
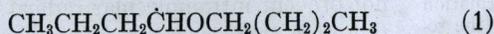


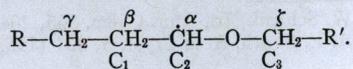
FIG. 1. The 273°K ESR spectra of an x-irradiated dibutyl ether-urea crystal with the magnetic field in the xy plane and parallel to the z axis, respectively.

not known.⁶ However, it sufficed to investigate examples of two types of ether molecules; RCH_2OCH_2R and RCH_2OCH_3 . As examples of the first type, several of the symmetrical ethers were investigated briefly. Single crystals of the inclusion compounds formed between urea and dibutyl ether (di- n -butyl ether), di- n -pentyl ether, di- n -hexyl ether, di- n -octyl ether, or di- n -decyl ether were prepared and x irradiated. The ESR spectra were qualitatively the same for all five systems. The spectra of dibutyl ether, however, was much more nearly symmetric (suggesting the presence of only one radical), therefore this compound was chosen for further study. The spectra obtained with the magnetic field along the needle axis and perpendicular to the needle axis of the dibutyl ether-urea crystal are given in Fig. 1.

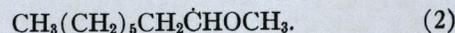
The methyl octyl ether (methyl n -octyl ether) urea inclusion compound was chosen as an example of a long-chain methyl ether, RCH_2OCH_3 . The spectra obtained from these crystals at $\sim 273^\circ\text{K}$ are shown in Fig. 2. These spectra result from one anisotropic coupling constant, two equal and nearly isotropic coupling constants, and three small coupling constants. The small splittings are only resolved when the angle between the magnetic-field vector and the z axis is less than $\sim 75^\circ$. The dibutyl ether-urea spectra, on the other hand, result from one anisotropic proton coupling constant, two equal and nearly isotropic coupling constants, and two much smaller coupling constants. Again the two small coupling constants are not resolved when the magnetic-field vector is within 15° of the xy plane. From the consideration of both sets of data it is easily seen that the radicals produced from dibutyl ether and methyl octyl ether are, respectively,



⁶ The convention for the labeling of protons (α , β , γ , ζ) and Carbon Atoms (C_1 , C_2 , C_3) used here is

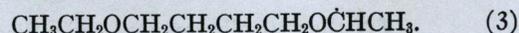


and

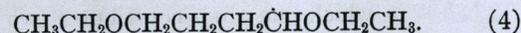


The anisotropic proton coupling constant and the large isotropic coupling constants are the familiar α - and β -proton coupling constants, a^α and a^β , respectively. The small coupling constants are associated with the ζ protons rather than the γ protons since the spectra of Radicals (1) and (2) exhibit small triplet and quartet splittings, respectively.

In addition to the above inclusion compounds, one other compound, 1,4-diethoxybutane-urea, was investigated in order to obtain the value of a^β for a rotating group. The radical of interest for this purpose is



The reconstructed stick spectra for this radical, along with the observed ESR spectra, are shown in Fig. 3. It is clear from Fig. 3 that Radical (3) and at least one other radical are present in the x-irradiated 1,4-diethoxybutane-urea compound. From the magnitude of the splittings of the z -orientation spectrum, the second radical is *evidently*



No further investigation of Radical (4) was undertaken because, for our purposes, it is essentially equivalent to Radical (2).

The 273°K ESR spectra for all of the above ether radicals are isotropic with respect to rotations of the magnetic field in the xy plane and are anisotropic with respect to other rotations of the magnetic field (this is characteristic of included radicals). The g value is also very nearly isotropic. The g values measured with the magnetic field parallel and perpendicular to the z axis of Radicals (1)–(3) are 2.0040 ± 0.0004 and 2.0030 ± 0.0003 , respectively. All of the radicals observed were stable for several hours at 273°K. If the crystals were allowed to warm up to room temperature, however, the ESR signal disappeared in 15 to 30 min.

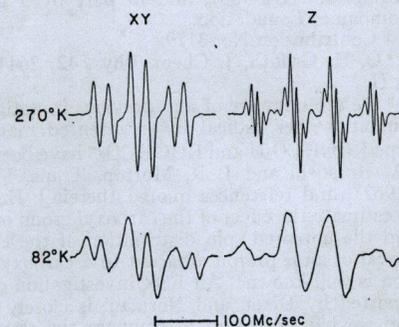


FIG. 2. The ESR spectra of an x-irradiated methyl octyl ether-urea crystal.

TABLE I. Proton hyperfine coupling constants.^{a-c}

Ether	Radical	a_z^α	a_z^β	a_z^ζ	a_{xy}^α	a_{xy}^β
Dibutyl ether	$\text{CH}_3(\text{CH}_2)_3\text{O}\dot{\text{C}}\text{H}(\text{CH}_2)_2\text{CH}_3$	64	63	8.2	23.6	60.4
Methyl octyl ether	$\text{CH}_3(\text{CH}_2)_6\dot{\text{C}}\text{HOCH}_3$	63	63	8.5	24.3	60.4
1,4-diethoxybutane	$\text{CH}_3\text{CH}_2\text{O}(\text{CH}_2)_4\text{O}\dot{\text{C}}\text{HCH}_3$	63	62	8.5	24.3	56.6

^a a^α , a^β , and a^ζ are the α , β , and ζ proton coupling constants, respectively, and xy and z denote the spectra recorded with the magnetic field in the crystalline xy and z directions. The two β protons of the dibutyl ether radical or the methyl octyl ether radical are magnetically equivalent and the three β protons of the 1,4-diethoxybutane radical are magnetically equivalent.

^b The coupling constants reported here are the average values obtained from a minimum of three groups of four spectra, each group being obtained from a different crystal. All values are in units of megacycles per second. The limits of experimental error varied with the orientations of the crystal in the magnetic field and the accuracy was greatest in the xy orientation (where the differences

between the a^α and a^β are the largest). The estimated errors in a_{xy}^α and a_{xy}^β for the first two radicals are ± 1.5 Mc/sec. a_{xy}^α and a_{xy}^β of the 1,4-diethoxybutane radical are accurate to ± 2.0 Mc/sec and the a_z^α and a_z^β for all three radicals are accurate to within ± 2.5 Mc/sec. The accuracy of the small ζ proton coupling constants are estimated to be ± 0.8 Mc/sec.

^c The temperature of the inclusion crystals was maintained at approximately 273°K, while obtaining the data reported in Table I. However, the spectra are relatively insensitive to changes in temperature and variations as great as $\pm 15^\circ\text{K}$ produced no measurable change in the coupling constants.

The coupling-constant data for Radicals (1)–(3) are summarized in Table I.

In addition to the ESR data obtained at 270°K, the methyl octyl ether–urea crystals were investigated over the temperature range from 290° to 40°K. There were no changes in either the line widths or the splittings over the range 290° to 240°K. Around 240°K the spectra began to show signs of broadening and the 82°K ESR lines are significantly broadened (Fig. 2). Below 80°K the spectral lines appeared to broaden slightly as the temperature was lowered, but the effect was not as pronounced. The over-all width of the 40°K ESR spectra increased $\sim 10\%$ over the 270°K value; this is consistent with a decrease in the amplitude of motion about the $\text{C}_2\text{--C}_1$ bonds as the temperature was lowered from 240° to 40°K. There were no rapid changes in the ESR spectra as the temperature was lowered (such as might be caused by a reorientation of the ether radicals) and all temperature effects were reversible.

EXPERIMENTAL SPIN-DENSITY DISTRIBUTION

a. From α -Proton Coupling-Constant Data

It is immediately apparent from Table I that the values of the α -proton coupling constants for all three radicals are the same. Therefore, in addition to identifying the radicals produced, some general conclusions may be reached regarding the unpaired spin distribution of this class of aliphatic ether radicals. Equation (4) of II will be useful in obtaining the isotropic component, a_0^α , from the experimental values of a_{xy}^α and a_z^α . First, however, the effect of the dipolar interaction between the α proton and the spin density on the oxygen atom must be estimated. To accomplish this the unpaired spin density on Carbon Atom 2, ρC^π , and the unpaired spin density on the oxygen atom, ρO^π , are assumed to

be associated with the $2p$ orbitals of the carbon and oxygen atoms, respectively. The α proton is sp^2 hybridized and the oxygen atom, Carbon Atoms 1 and 2, and the α proton are coplanar. All of the dipolar matrix elements obtained using the above assumptions may be evaluated according to the method of McConnell and Strathdee.⁷ In the present work, only the α -proton– ρO^π interaction was estimated by this method and the α -proton– ρC^π dipolar tensor elements were taken from the experimental data on the malonic acid radical ($\rho\text{C}^\pi \approx 0.90$) obtained at zero magnetic field.⁸

For the numerical calculations, the $\dot{\text{C}}\text{--H}$ and the $\dot{\text{C}}\text{--O}$ bond distances were assumed to be 1.08 and 1.35 Å, respectively. The oxygen $2p$ orbital was approximated by a Slater orbital with $z=4.55$ and the nondiagonal elements of the spin density matrix were neglected

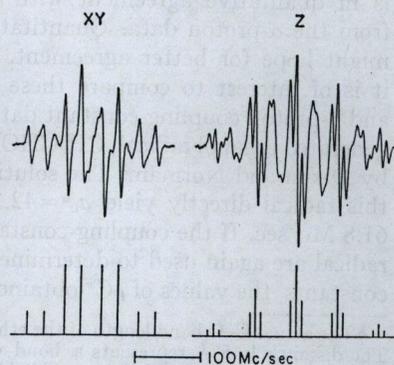


FIG. 3. The 273°K ESR spectra of an x-irradiated 1,4-diethoxybutane-urea crystal with the magnetic field along the xy and z crystalline directions, respectively. Below the observed spectra are the reconstructed stick spectra for the xy and z orientations of the radical $\text{CH}_3\text{CH}_2\text{O}(\text{CH}_2)_4\text{O}\dot{\text{C}}\text{HCH}_3$.

⁷ H. M. McConnell and J. Strathdee, *Mol. Phys.* **2**, 129 (1959).

⁸ T. Cole, T. Kushida, and H. C. Heller, *J. Chem. Phys.* **38**, 2915 (1963).

(so that $\rho O^\pi + \rho C^\pi = 1.0$).⁹ Using these approximations, the α -proton- ρO^π dipolar tensor elements were calculated, the tensor was transformed to the usual α -proton- ρC^π coordinate system, and the total contributions to a^α were calculated by standard methods.¹² The value of a_z^α and a_{xy}^α were obtained by assuming motional averaging in the xy plane and integrating over the angular variables in the general expression for a^α . The resulting equations are not given here because they are space consuming and are not of use in later discussions. Values of ρC^π ranging from 0.5 to 0.9 were substituted into these equations, and in each case the estimate of a_0^α , obtained using Eq. (4) of II and the computed a_{xy}^α and a_z^α , was compared with a_0^α obtained directly from the initial ρC^π . The net result is that the difference between the value of a_0^α obtained from Eq. (4) of II and the correct value of a_0^α is quite small for the large ρC^π encountered in the ether radicals. For example, from the data obtained from Radicals (1)–(3) and using Eq. (4) of II, $a_0 = 37.2$ Mc/sec. If the proportionality constant relating a_0^α and ρC^π is assumed to be the same for the ether radicals and the ethyl radical (CH_3CH_2 , $\rho C^\pi \approx 1.0$, $a_0^\alpha = 62.7$ Mc/sec),¹³ then $\rho C^\pi(\text{ether}) = 37.2/62.7 \approx 0.60$. The correction for the α -proton- ρO^π dipolar interaction lowers this value negligibly, 0.7%. Therefore, the value predicted for ρC^π from the above simple model is ~ 0.60 .

b. From β -Proton Coupling Constant Data

The isotropic component of the β -proton coupling constant estimated from Eq. (8) of II and the data of the 1,4-diethoxybutane Radical (3) is 58.4 Mc/sec. The value of $R/2$ for the ethyl radical is 75.4 Mc/sec, and if Radical (3) is assumed to have this same $R/2$, then $\rho C^\pi(\text{ether}) = 58.4/75.4 = 0.77$. This value of ρC^π is in qualitative agreement with the value obtained from the α -proton data. Quantitatively, however, one might hope for better agreement. In this connection, it is of interest to compare these results with the α - and β -proton coupling-constant data for the chemically generated ethanol radical, $\text{CH}_3\dot{\text{C}}\text{HOH}$, recently reported by Dixon and Norman.³ The solution ESR spectra for this radical directly yield $a_0^\alpha = 42.1$ Mc/sec and $a_0^\beta = 61.8$ Mc/sec. If the coupling-constant data of the ethyl radical are again used to determine the proportionality constants, the values of ρC^π obtained from a_0^α and from

⁹ The actual $\dot{\text{C}}\text{--O}$ bond length of the ether radical is not known. The distance 1.35 Å represents a bond with two-thirds single-, and one-third double-bond character. (This, for example, is a reasonable length for a three-electron bond¹⁰ between a carbon and an oxygen atom.) The double and single bond lengths were obtained using the formula of Schomaker and Stevenson.¹⁰ The effective nuclear charge of oxygen and of carbon were obtained from Slater's rules.¹¹ These values of Z_O , Z_C , and the internuclear distance R_{CO} , were employed in all calculations of this paper.

¹⁰ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960).

¹¹ C. A. Coulson, *Valence* (Clarendon Press, Oxford, England, 1952) p. 41.

¹² H. M. McConnell, C. Heller, T. Cole, and R. W. Fessenden, *J. Am. Chem. Soc.* **82**, 766 (1960).

¹³ R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.* **39**, 2147 (1963).

a_0^β are 0.67 and 0.81, respectively. These values are in good agreement with the corresponding ether radical values of 0.61 and 0.77. The discrepancy between the values obtained from the α - and β -proton coupling-constant data is apparently caused by a poor choice of the proportionality constants. In other words, the difference in the σ bonds of the two radicals apparently is reflected in the values of the proportionality constants. However, we tentatively assign the approximate values of 0.70 ± 0.10 and 0.30 ± 0.10 for the experimental spin densities on the ether carbon and oxygen atoms, respectively. These values and the estimated errors may be subject to change as better values of the proportionality constants become available.¹⁴

To what extent this spin distribution is effected by molecular motion is difficult to determine quantitatively because of the broadened lines of the low-temperature spectra (Fig. 2). It is clear that there are no major changes in the width of the spectra over a wide temperature range. As the temperature is lowered the small changes that do occur are in a direction consistent with a decrease in β -proton motion and inconsistent with an increase in the contribution of the structure $\text{RH}\dot{\text{C}}\text{--}\dot{\text{O}}\text{R}'$ (see valence bond section). That is, the small temperature dependence of the splittings is readily explained in terms of the β -proton motion, but is much more difficult to explain in terms of a temperature-dependent spin distribution. This does not provide a complete answer to the question of motion about the $\dot{\text{C}}\text{--O}$ bond, but does strongly suggest that the spin distribution measured is a meaningful approximation to the maximum π -overlap spin distribution.

THEORETICAL SPIN-DENSITY DISTRIBUTION

a. Hückel MO Method

In view of the experimental results, the natural starting point for a discussion of the $\text{R}\dot{\text{C}}\text{HOR}'$ radical is the π -electron approximation. The two π molecular

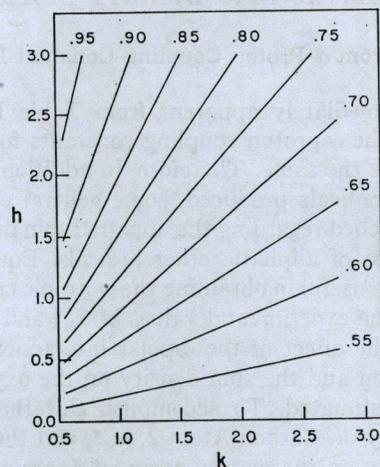


FIG. 4. The electron spin density on Carbon Atom 2 as a function of the two Hückel molecular orbital parameters, h and k .

¹⁴ Preliminary data from x-irradiated sulfide-urea inclusion compounds suggest that a similar problem may exist for the RHCSR' radicals.

orbitals are approximated as linear combinations of the $2p_x$ atomic orbitals of Carbon Atom 2 (χ_C) and the Oxygen Atom (χ_O). The three σ MO's of Carbon Atom 2 are taken to be sp^2 hybrids and the oxygen atom is assumed to be unhybridized.¹⁵ Therefore, of the eight oxygen electrons, four are associated with the oxygen $1s$ and $2s$ AO's, one with a $2P_y\sigma$ MO, another with a $2P_z\sigma$ MO, and the remaining two with the π -electron system. The σ (or σ and n) electrons are not considered explicitly. With these assumptions the ether radical becomes a three-electron problem. In this respect the ether radical is formally similar (except for symmetry) to the ethylene negative ion. The ether radical is first considered in the framework of the Hückel MO approximation and then as a configuration interaction (CI) problem. Finally the CI results are interpreted in terms of the valence bond formalism in order to obtain a better physical description of the unpaired spin distribution.

The single configuration wavefunction appropriate for the ether radical in the Hückel approximation is

$$\psi = (6)^{-\frac{1}{2}} \sum_P (-1)^P P \phi_{1\alpha} \phi_{1\beta} \phi_{2\alpha}, \quad (5)$$

where

$$\phi_i = C_{i1}\chi_C + C_{i2}\chi_O, \quad (6)$$

and P is the π -electron permutation operator. The C_{ij} 's are determined by the variational method using a one-electron Hamiltonian and the usual Hückel approximations¹⁸ for the matrix elements of the 2×2 secular determinant. The spin densities are the squares of the AO coefficients of ϕ_2 and are a function of the two parameters h and k . A partial contour plot of ρC^π is given in Fig. 4 (and ρO^π is just $1 - \rho C^\pi$). The Hückel spin densities are in qualitative agreement with the experimental spin densities. That is, the range of generally accepted values of h and k ($1 \leq h \leq 2$ and $0.8 \leq k \leq 1.6$)¹⁴ predict a large spin density on the carbon atom and a much smaller spin density on the oxygen atom. It is obvious from Fig. 4 that the problem is overdetermined. A given spin density may be obtained using any value of h , provided the proper k is chosen. In other words, the spin density is determined

¹⁵ These assumptions do not enter into the Hückel calculation explicitly, but they do, of course, affect the magnitudes of the core integrals in the configuration-interaction calculation. The oxygen atom is undoubtedly hybridized to some extent and Sidman¹⁶ has discussed this question for the case of formaldehyde. However, the ionization potential, Coulomb integrals, and neutral penetration integral apparently do not depend critically on the degree of core hybridization.^{16,17} Hybridization of the carbon atom may be more troublesome. In the contributing structure RHC-ÖR' (see valence bond section), there is an unshared electron pair on the carbon atom and this is reminiscent of the non-planar ammonia molecule. If the carbon atom has a tendency to hybridize in a similar fashion, then the a_{xy}^2 , a_x^2 and a^2 coupling constants might well appear anomalous. Nevertheless, a large nonplanarity of the carbon core would greatly increase the magnitude of the proton-coupling constants and this is not observed.

¹⁶ J. W. Sidman, *J. Chem. Phys.* **27**, 429 (1957).

¹⁷ R. D. Brown and M. L. Heffernan, *Trans. Faraday Soc.* **54**, 757 (1958).

¹⁸ A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists* (John Wiley & Sons, Inc., New York, 1961).

only by the ratio h/k and not by the individual h and k values. The ratio of h and k corresponding to $\rho C^\pi = 0.70 \pm 0.10$ is 0.9 ± 0.5 and this overlaps well with the generally accepted range, $0.6 \leq h/k \leq 2.5$.

The ether charge densities may also be obtained from Fig. 4. In the Hückel theory the carbon-atom charge density of the ether radical is $\rho C^\pi - 1$ and the oxygen charge density is equal to the oxygen spin density (ρC^π and ρO^π are chosen to be positive). If the ratio h/k is positive then $-0.5 < (\rho C^\pi - 1) < 0.0$ and $0.0 < \rho O^\pi < +0.5$ (Fig. 4). For $\rho C^\pi = 0.70 \pm 0.10$, the π -electron carbon and oxygen charge densities are -0.30 ± 0.10 and $+0.30 \pm 0.10$, respectively. This rather large polarization of the π -electron distribution corresponds to a π -electron dipole moment of 1.9 ± 0.6 D.

b. Configuration Interaction

The ether radical represents one of the simplest possible heteronuclear configuration interaction (CI) problems since there are only two π -electron configurations. The two configuration wavefunctions and the two configurations are

$$\psi_1 = (6)^{-\frac{1}{2}} \sum_P (-1)^P P \phi_{1\alpha} \phi_{1\beta} \phi_{2\alpha} \quad \begin{array}{c} \uparrow \\ \phi_2 \\ \uparrow \downarrow \\ \phi_1 \end{array} \quad (7)$$

and

$$\psi_2 = (6)^{-\frac{1}{2}} \sum_P (-1)^P P \phi_{1\alpha} \phi_{2\alpha} \phi_{2\beta} \quad \begin{array}{c} \uparrow \downarrow \\ \phi_2 \\ \uparrow \\ \phi_1 \end{array} \quad (8)$$

ψ_1 is similar to Eq. (5) except that in the CI case the wavefunctions ϕ_1 and ϕ_2 are taken to have the full ethylenic symmetry.¹⁹ That is

$$\phi_1 = (2)^{-\frac{1}{2}} (1+S)^{-\frac{1}{2}} (\chi_C + \chi_O) \quad (9)$$

and

$$\phi_2 = (2)^{-\frac{1}{2}} (1-S)^{-\frac{1}{2}} (\chi_C - \chi_O), \quad (10)$$

where S is the atomic orbital overlap integral. The functions ψ_1 and ψ_2 are normalized and are rigorously orthogonal. The CI wavefunction Ψ_{MO} and Hamiltonian \mathcal{H}_π in this approximation are

$$\Psi_{MO} = C_1 \psi_1 + C_2 \psi_2 \quad (11)$$

and

$$\mathcal{H}_\pi = \mathcal{H}_{\text{core}(1)} + \mathcal{H}_{\text{core}(2)} + \mathcal{H}_{\text{core}(3)} + (r_{12})^{-1} + (r_{13})^{-1} + (r_{23})^{-1}. \quad (12)$$

Using McConnell's definition of the spin-density operator,²⁰ the elements of the atomic orbital spin-density matrix may be determined from Ψ . In terms of

¹⁹ R. G. Parr, *Quantum Theory of Molecular Electronic Structure* (W. A. Benjamin, Inc., New York, 1963).

²⁰ H. M. McConnell, *J. Chem. Phys.* **28**, 1188 (1958).

the coefficients C_1 and C_2 these elements are

$$\rho C^\pi = \frac{1}{2} C_2^2 (1-S)^{-1} + \frac{1}{2} C_1^2 (1-S)^{-1} + C_1 C_2 (1-S^2)^{-\frac{1}{2}}, \quad (13)$$

$$\rho O^\pi = \frac{1}{2} C_2^2 (1+S)^{-1} + \frac{1}{2} C_1^2 (1-S)^{-1} - C_1 C_2 (1-S^2)^{-\frac{1}{2}}, \quad (14)$$

$$\rho C O^\pi = \rho O C^\pi = \frac{1}{2} C_2^2 (1+S)^{-1} - \frac{1}{2} C_1^2 (1-S)^{-1}, \quad (15)$$

and the spin-density function $\rho^\pi(x, y, z)$ is

$$\rho^\pi(x, y, z) = \rho C^\pi | \chi_C |^2 + \rho C O^\pi (\chi_C^* \chi_O + \chi_O^* \chi_C) + \rho O^\pi | \chi_O |^2. \quad (16)$$

The coefficients C_1 and C_2 are determined by the usual variational procedure. The matrix elements of the resulting 2×2 secular determinant may be expanded in terms of the AO's in much the same way as for ethylene.¹⁹ The estimation of the core integrals of the ether radical deserves some elaboration. The core Hamiltonian is

$$\mathcal{H}_{\text{core}(i)} = -\frac{1}{2} \nabla_{(i)}^2 + U_{C_2(i)}^+ + U_{O(i)}^{++} + U_{C_1(i)}^0 + U_{C_3(i)}^0 + H_{H\alpha(i)}^0, \quad (17)$$

where U^+ (or U^{++}) and U^0 denote the potentials due to charged and neutral atoms of the core. The approximate eigenvalue equation²¹

$$\left[-\frac{1}{2} \nabla_{(i)}^2 + U_{O(i)}^+ \right] \chi_{O(i)} = U_{OO} \chi_{O(i)}, \quad (18)$$

can be used to eliminate the kinetic integral providing one assumes that²²

$$U_{O(i)}^{++} = U_{O(i)}^+ - \int \chi_{O(i)}^2 \frac{1}{r_{ij} dV_j}. \quad (19)$$

In Eq. (18) U_{OO} is the usual valence-state orbital energy. There is, of course, a similar eigenvalue equation involving χ_C and U_{CC} . In other aspects, the treatment of the ether core parallels that of the ethylene molecule. The expressions obtained for the oxygen core integral $\alpha_{O^{\text{core}}}$ and the carbon core integral $\alpha_{C^{\text{core}}}$ are

$$\alpha_{O^{\text{core}}} = U_{OO} - (CC | OO) - (OO | OO) - (C_2 : OO) - (C_3 : OO), \quad (20)$$

$$\alpha_{C^{\text{core}}} = U_{CC} - (CC | OO) - (O : C_2 C_2) - (C_1 : C_2 C_2) - (H_\alpha : C_2 C_2), \quad (21)$$

²¹ M. Goepfert-Mayer and A. L. Sklar, J. Chem. Phys. 6, 645 (1938).

²² Alternatively, one may consider an eigenvalue equation involving the second ionization potential of oxygen. The spin-density distribution obtained by the two approaches is essentially the same if the appropriate valence-state ionization potentials are employed.

and the parameter, β , introduced by Pariser and Parr²³ is

$$\beta = \frac{\beta^{\text{core}} - (S/2)(\alpha_{C^{\text{core}}} + \alpha_{O^{\text{core}}})}{(1-S^2)}. \quad (22)$$

Fortunately the spin-density distribution depends only on the difference between $\alpha_{O^{\text{core}}}$ and $\alpha_{C^{\text{core}}}$ and not on the individual core integrals. This tends to reduce the errors involved in the values of U_{OO} and U_{CC} and renders the method of evaluating the Coulomb and neutral-penetration integrals less critical. Initially, we take the orbital energies to be the negative of the valence-state ionization potentials; $U_{OO} = -I_O = -17.3$ eV and $U_{CC} = -I_C = -11.4$ eV.^{16,24} The Coulomb integrals obtained by the method of Pariser and Parr with $Z_C = 3.25$, $Z_O = 4.55$, and $R_{CO} = 1.35$ Å, are $(CC | CC) = 10.8$ eV, $(OO | OO) = 14.7$ eV, and $(CC | OO) = 8.2$ eV.¹⁶ The neutral penetration integrals ($p : qq$) were calculated by standard methods^{21,25} using Slater orbitals. The contributions of these penetration integrals to $\alpha_{O^{\text{core}}}$ and $\alpha_{C^{\text{core}}}$ were found to be the same within ~ 0.3 eV,²⁶ and therefore they were not included in the spin-density calculations. If differential overlap is neglected, these are all of the quantities (other than β) entering into the expressions for the spin-density matrix elements. The appropriate value of β for this radical is not available, but the values -1.5 , -2.5 , and -3.5 eV span what might be considered a reasonable range. From Eqs. (13), (14), and (15), $(\rho C^\pi, \rho C O^\pi, \rho O^\pi)$ are (0.97, 0.16, 0.03), (0.93, 0.25, 0.07), and (0.89, 0.32, 0.11) for $\beta = -1.5$, -2.5 , and -3.5 eV, respectively.

The calculated values for ρC^π are somewhat larger than the experimental value. This is due, in part, to the neglect of the effect of bonding on U_{OO} and U_{CC} . For example, in benzene and other hydrocarbons Hush and Pople²⁷ found that the value of U_{CC} is ~ -9.5 eV, which is significantly less negative than the valence-state value -11.4 eV. The effect of bonding of the hydrocarbon σ electrons is apparently to decrease the stability of the π electrons.¹⁶ For the ether radical the large dipole moments present an added complication. The π -electron dipole moment is apparently $\sim 1.9 \pm 0.5$ D and is in the direction $C^- - O^+$. There is also present a large σ -electron moment. In ether molecules this moment is $1-2$ D^{28,29} and is almost certainly in

²³ R. Pariser and R. G. Parr, J. Chem. Phys. 21, 466 (1953); 21, 767 (1963).

²⁴ J. Parks and R. G. Parr, J. Chem. Phys. 32, 1657 (1960).

²⁵ K. Ruedenberg, J. Chem. Phys. 34, 1861 (1961).

²⁶ To obtain the penetration integrals the $C-H_\alpha$ was taken to be 1.08 Å. The C_1-C_2 and C_3-O bonds were assumed to have normal single-bond lengths; 1.54 and 1.42 Å, respectively. Equally complete cancellation of the penetration integrals occurs if a Slater Z value of 4.90 is used.

²⁷ N. S. Hush and J. A. Pople, Trans. Faraday Soc. 51, 600 (1955).

²⁸ C. P. Smyth, Dielectric Behavior and Structure (McGraw-Hill Book Company, Inc., New York, 1955).

²⁹ L. G. Wesson, Tables of Electric Dipole Moments (The Technology Press, Cambridge, Massachusetts, 1948).

the direction C⁺-O⁻. The π and σ dipole moments therefore have opposite polarity. The π -electron moment of the ether radical increases the electronegativity of the oxygen atom and this should increase the σ -dipole moment over the value obtained for the ether molecule. The sum of the σ and π contributions may therefore be a moment in the direction C⁺-O⁻, and this would increase the stability of the electrons on carbon while decreasing the stability of the electrons on oxygen (through changes in electron repulsion). If this is the case, the net effect is a suppression of the quantity $U_{OO} - U_{CC}$ below the valence state value of -5.9 eV. An arbitrary, but not unreasonable, choice of $U_{OO} - U_{CC}$ is -2.5 eV. For this choice (ρ_{C^π} , ρ_{CO^π} , ρ_{O^π}) become (0.93, 0.25, 0.07), (0.86, 0.34, 0.14), and (0.79, 0.40, 0.21) for $\beta = -1.5$, -2.5 , and -3.5 eV, respectively. These spin densities are in much better agreement with the experimental values. (The agreement could be further improved if the differences between the coulomb integrals were also suppressed.)

The approximations employed to obtain these spin distributions are obviously not free from criticism. Nevertheless, the simplified CI theory does predict the correct order of magnitude for the unpaired spin densities (for either choice of $U_{OO} - U_{CC}$). Furthermore, if overlap is retained and the Mulliken approximation¹⁹ $pq = \frac{1}{2}S(pp + qq)$ is employed, then the calculated spin densities are not significantly altered from the above values. No major change occurs because the overlap integral is small ($S = 0.165$) and because all terms appearing in C_1 and C_2 which depend linearly on S , vanish.

c. Valence Bond Model

The two valence bond or spin wavefunctions and corresponding structures are

$$\psi_{ne} = 6^{-\frac{1}{2}}(1 - S^2)^{-\frac{1}{2}} \sum_P (-1)^P P \chi_C \alpha \chi_O \alpha \chi_O \beta \quad \text{RH}\overset{\ominus}{\text{C}}-\overset{\oplus}{\text{O}}\text{R}' \quad (23)$$

$$\psi_{ch} = 6^{-\frac{1}{2}}(1 - S^2)^{-\frac{1}{2}} \sum_P (-1)^P P \chi_C \alpha \chi_C \beta \chi_O \alpha \quad \text{RH}\overset{\oplus}{\text{C}}-\overset{\ominus}{\text{O}}\text{R}' \quad (24)$$

where ψ_{ne} and ψ_{ch} designate the functions corresponding to the neutral structure and the structure with charge separation, respectively. The appropriate linear combination of these two functions, Ψ_{VB} , would normally be obtained from the Hamiltonian \mathcal{H}_π by the variational method. However, in this case Ψ_{VB} is entirely equivalent to Ψ_{MO} . By expanding ψ_1 and ψ_2 in terms of ψ_{ne} and ψ_{ch} , Ψ_{MO} becomes

$$\Psi_{MO} = \left[\frac{C_1}{[2(1+S)]^{\frac{1}{2}}} + \frac{C_2}{[2(1-S)]^{\frac{1}{2}}} \right] \psi_{ne} + \left[\frac{C_2}{[2(1-S)]^{\frac{1}{2}}} - \frac{C_1}{[2(1+S)]^{\frac{1}{2}}} \right] \psi_{ch} \quad (25)$$

If overlap is neglected, ρ_{C^π} is just the square of the coefficient of ψ_{ne} and this is identical to Eq. (13). In other words, ρ_{C^π} is a measure of the contribution of the valence bond structure RH[⊖]C-[⊕]OR' to the total wavefunction. The CI theory predicts the contribution of this structure to be 95%-80%, which compares favorably with the experimental value of 70±10%. Similarly, the π -electron charge density is directly related to the contribution of the structure RH[⊕]C-[⊖]OR'. By comparing Eq. (25) with Eqs. (13) and (14), the charge densities associated with oxygen and carbon are $|\rho_{O^\pi}|$ and $1 - |\rho_{C^\pi}|$, respectively (which are of the same form as the Hückel MO results). The CI (or VB) theory predicts a π -electron polarization of C^{δ-}-O^{δ+} where $0.05 < \delta < 0.2$. The valence bond method is perhaps the easiest to visualize; one readily predicts that the neutral structure (23) contributes to a larger extent than does the polar structure (24). However, the simple Hückel, CI, and VB predictions are all in agreement with the experimental results.

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