Electron Spin Resonance of RCHCOR' Radicals in X-Irradiated Ketone-Urea Inclusion Compounds

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Single crystals of six inclusion compounds formed between aliphatic ketones and urea were x irradiated at room temperature, and the free radicals produced were investigated by electron spin resonance. The six ketones investigated were 2-nonanone, 6-undecanone, 3-tetradecanone, 2-undecanone, 2-dodecanone, and 3-undecanone. The long-lived free radicals observed in all of these compounds (RCHCOR') are formed by the removal of one a proton from the parent ketone. The unpaired spin density in the 2y orbital adjacent to the carbonyl group is 0.81±0.08. A contour plot of the spin density as a function of the molecular orbital parameters is given. In qualitative agreement with the ESR results, the molecular orbital methods predict the position of maximum spin density to be adjacent to the carbonyl group.

INTRODUCTION

Three free radicals produced in a series of x-irradiated aliphatic ester-urea inclusion compounds have recently been investigated by electron spin resonance (ESR).1 The use of an inclusion compound has the distinct advantage over a low-temperature glass or powder in that all of the guest molecules of the compound are magnetically equivalent at one or more crystalline directions. Only one ester radical (RCHCOR') and no urea radicals were detected after x irradiation. The ester-urea single crystals were investigated as a function of temperature and of orientation in the magnetic field, and information regarding the structure and motion of the ester radical was obtained. It is of interest to investigate other aliphatic molecules by this method. In particular, the aliphatic ketone molecules are of interest because of the presence of only one oxygen atom. This simplification in structure makes possible a more quantitative investigation of the x-ray-produced ketone radicals. In this paper the radicals in a series of x-irradiated ketone-urea inclusion compounds are identified, the coupling constants are given, and the experimental and theoretical positions of maximum spin density are determined.2

EXPERIMENTAL

Single crystals of the inclusion compounds formed between urea and the aliphatic straight-chain ketones were grown from a methanol solution by either slow evaporation or by slow cooling. In all cases ketones were chosen which gave the best quality of urea inclusion crystals and, therefore, the lengths of the ketone molecules studied are somewhat arbitrary. The crystals obtained were either hexagonal needles or flat hexagonal plates and were stable for several months in air at room temperature. The axis of the Cartesian crystalline coordinate system is defined to lie along the needle axis of the urea compound, and therefore the z axis is parallel to the six faces of the hexagonal prism. The x and y axes are not specified other than that they lie in a plane perpendicular to the needle axis of the crystal. The morphology of the ketone-urea crystals is typical of the morphology of crystals formed between urea and a variety of long straight-chain molecules.3 The ketone molecules are therefore expected to exist in an extended zigzag conformation in the hollow (hexagonal) cavities formed by the urea molecules.4 We assume this to be the case throughout the following discussion, although no crystallographic data have been reported for the ketone-urea compounds studied in this paper.

The x-ray apparatus, X-band ESR spectrometer, modulation amplitude, and calibration standards were the same as employed in I. A conventional small Dewar connected by means of a transfer tube to a liquid helium Dewar was used to cool the crystals below room temperature. The rate of cold helium gas flow was controlled by varying the power dissipated in a resistor located inside the liquid helium Dewar. A heated nitrogen gas flow system was used to obtain temperatures above room temperature. Crystals of the 6-undecanone-urea compound were heated to ~325°K for a few minutes prior to recording the final ESR spectra. For any given inclusion compound, the major lines of the ESR spectra were resolved to allow identification of the radicals. The other x-irradiated ketone-urea inclusion compounds listed in Table I were not heated before obtaining the ESR spectra. For any given inclusion compound, the major lines of the ESR spectra were independent of the ratio of the ketone to urea in the methanol solution and to the length of time the crystals were x irradiated.

Table I. Proton hyperfine coupling constants of ketone radicals.\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Radical\textsuperscript{c}</th>
<th>(T) (K)</th>
<th>(\alpha^a)</th>
<th>(\alpha^b)</th>
<th>(\alpha^c)</th>
<th>(\alpha^d)</th>
<th>(\alpha^e)</th>
<th>(\alpha^f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)CH(_2)C(_6)H(_5)CH(_3)</td>
<td>298</td>
<td>76</td>
<td>71</td>
<td>47</td>
<td>5.4</td>
<td>38</td>
<td>68</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)C(_2)H(_5)C(_6)H(_5)CH(_3)</td>
<td>298</td>
<td>76</td>
<td>66</td>
<td>48</td>
<td>9.1</td>
<td>39</td>
<td>63</td>
</tr>
<tr>
<td>CH(_3)C(_2)H(_5)CoC(_6)H(_5)CH(_3)</td>
<td>310</td>
<td>~75</td>
<td>64</td>
<td>64</td>
<td>9.0</td>
<td>39</td>
<td>58</td>
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<tr>
<td>O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)C(_2)H(_5)C(_6)H(_5)CH(_3)</td>
<td>313</td>
<td>77</td>
<td>71</td>
<td>53</td>
<td>5.0</td>
<td>39</td>
<td>68</td>
</tr>
<tr>
<td>O</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)C(_2)H(_5)C(_6)H(_5)CH(_3)</td>
<td>322</td>
<td>75</td>
<td>70</td>
<td>52</td>
<td>3.5</td>
<td>38</td>
<td>60</td>
</tr>
<tr>
<td>CH(_3)C(_2)H(_5)CoC(_6)H(_5)CH(_3)</td>
<td>298</td>
<td>~75</td>
<td>65</td>
<td>65</td>
<td>9.5</td>
<td>38</td>
<td>57</td>
</tr>
</tbody>
</table>

\textsuperscript{a} \(\alpha^a\), \(\alpha^b\), and \(\alpha^c\) are the coupling constants for three \(\alpha\) protons, \(\beta\) proton, and the \(\gamma\) proton, respectively, and \(\alpha^d\) and \(\alpha^e\) denote the spins of adjacent to the magnetic field in the crystalline \(\alpha\) and \(\alpha\) directions. All coupling constants are reported in megacycles per second and are accurate to within \(\pm 2\) Mc/sec.

\textsuperscript{b} All reported coupling constants are accurate to within \(\pm 0.7\) Mc/sec unless otherwise stated.

\textsuperscript{c} From the crystalline \(\alpha\) axis. The reconstructed spectrum is that of the CH\(_3\)CH\(_2\)COCH(CH\(_2\))\(_9\)CH\(_3\) radical and the remaining (major) lines are apparently due to the CH\(_3\)CH\(_2\)COCH(CH\(_2\))\(_9\)CH\(_3\) radical.

\textsuperscript{d} The small \(g\) values should be accurate to within \(\pm 2\) Mc/sec.

\textsuperscript{e} The values are indicated to be within \(\pm 2\) Mc/sec.

\textsuperscript{f} The values of all six radicals were measured at room temperature and were found to be the same within experimental error. The average \(g\) values and the estimated error with the magnetic field paralleled and perpendicular to the \(\alpha\) axis, respectively, are \(g\) (\(\alpha\)) = 2.0040 \(\pm 0.0003\) and \(g\) (\(\perp\alpha\)) = 2.0041 \(\pm 0.0003\). As may be seen from Fig. 3, the ESR spectra of the x-irradiated 3-tetradecanone-urea compound are complicated by the presence of one or more additional radicals. All radicals present have roughly the same thermal stability, and it was not possible to greatly change the relative concentrations of the radicals by either heating the crystal or subjecting the crystal to ultraviolet light. However, the outermost unidentified doublet is split by two small and approximately equivalent coupling constants. From further considerations of the magnitude of the various splittings it appears that all major unidentified lines can be assigned to the radical CH\(_3\)CH\(_2\)COCH(CH\(_2\))\(_9\)CH\(_3\). An analogous situation occurs in the case of the x-irradiated 3-tetradecanone-urea compound. We will not be concerned further with these additional radicals since a well resolved example of a nearly identical radical is present in the 6-undecanone-urea crystal.

All of the above radicals were remarkably stable. The radical concentrations remained approximately constant during the several hours of room temperature experimentation. However, the concentrations of the radicals decreased slowly as the crystals were heated and the ESR signals disappeared at temperatures well below the melting points of the crystals.

EXPERIMENTAL DETERMINATION OF THE SPIN DENSITY \(g\)

It is apparent from the data of Table I that the ketone radicals are very similar to the previously reported carboxylic acid\textsuperscript{6} and ester\textsuperscript{1} radicals. That is, there is a large spin density associated with Carbon Atom 2, a small spin density associated with Carbon Atom 1, and presumably a small spin density associated with the oxygen atom. These are evidently \(\alpha\)-electron spin densities and are referred to as \(\alpha^a\), \(\alpha^b\), and \(\alpha^c\), respectively.

This is also the case for the methyl group of the 3-
undecanone radical, and for these two radicals the 
usual expression relating the spin density to the \( \beta \)-proton coupling constants reduces to \( \alpha_0/(2B_a^2/\gamma_a) \), where \( \alpha_0 \) is the isotropic component of the \( \beta \)-proton coupling constant and \( B_a \) is a proportionality constant. The experimental constant \( B_a \) is determined by an anisotropic compo-
iment as well as the isotropic component and these two 
contributions must be separated before this equation 
can be used to obtain \( \alpha_0 \). Fortunately, the anisotropic 
component is small and, therefore, the method employed 
to extract \( \alpha_0 \) is not critical.

Heller24 has observed that, for the CH(\text{CH})CH(\text{CO}) radicals, the anisotropic components of the \( \beta \)-proton hyperfine coupling constants are adequately described by the Hamiltonian

\[ H = -\frac{e}{\hbar} g_N p_N \mathbf{h} \cdot \mathbf{S} + \sum_{i=1}^{5} \frac{\mu_i}{2} \left( I_i^x \mathbf{S} - \frac{a_i}{\hbar} \mathbf{S} \right) + \sum_{i=1}^{5} \frac{1}{2} \mu_i \left( I_i^x \mathbf{S} - \frac{a_i}{\hbar} \mathbf{S} \right) \]

In Eq. (5) \( a^x \) is the angle between the magnetic field 
and the \( C_2=\text{CH} \) carbon-bond, \( H \) and \( H_0 \) are the 
components of \( \beta \) and \( p \) along \( H \) and \( H_0 \), 
respectively, and \( g_N \) is the nuclear gyromagnetic ratio 
for the \( \beta \)-proton. In this model the \( \beta \)-proton hyperfine 
coupling constants characteristic of a rotating methyl group. For the ethyl radical the \( \alpha_0 \) constant was 
used to obtain \( \alpha_0 \) from experimental values of \( \beta_\text{C2}^\text{H} \) and \( \beta_\text{C2}^\text{C} \). This value was used as an average of the \( \alpha_0 \) for the four radicals studied. In obtaining Eq. (5), the \( \alpha_0 \) tensor elements were assumed to be averaged by molecular motion. This averaging can be accom-
plished by various types of motion. The tensor elements are obviously averaged by rapid rotation of the radicals 
about the crystalline \( z \) axis. They are approximately 
averaged if the amplitude of the radical motion in the 
\( xy \) plane is greater than \( \sim 80^\circ \) and all bond positions in 
this range are equally probable (the residual few 
positions are obviously averaged by rapid rotation of the radicals 
than for radicals rapidly tumbling in solution 
or rigidly held in a crystal lattice, because molecular 
motion in the urea inclusion compounds averages a 
portion, but not all, of the anisotropic proton-electron 
broadening of the ESR lines). The tensor averaging would 
be achieved if the amplitude of the radical 
motion in the \( xy \) plane is greater than \( \sim 80^\circ \) and all bond positions in 
this range are equally probable (the residual few 
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motion in the urea inclusion compounds averages a 
portion, but not all, of the anisotropic proton-electron
zy and z crystalline directions as ay and a spectra, respectively.) Well resolved ay and a spectra were also recorded for the 6-undecanone and 2-undecanone radicals at approximately 335°K. The a-proton coupling constants derived from these data are the same as those of Table I within the estimated experimental error of ±0.2 Mc/sec. At these temperatures the spectra record the a electron in the xy plane, and spectra for all orientations of the magnetic field were symmetrical.

The a-irradiated 6-undecanone-urea crystals were cooled from room temperature to 30°K. Both the ay and a spectra changed gradually with temperature, and the ay spectra began showing signs of asymmetry below 270°K. At 77°K the ay spectra were anisotropic with respect to rotations of the magnetic field in the xy plane. The features of these anisotropic spectra were repeated at intervals of 60° in the xy plane, and at no other orientations of the magnetic field. As with the other radicals, this observation supports the assumption that the carbonyl group was in the z direction, and that the a direction lay along the crystallographic c axis. Although no coupling-constant data were obtained from the symmetric-ay ESR spectra, approximate coupling constants were measured from the symmetric-6-undecanone radical ay spectra for temperatures down to 190°K. Over this range, a in temperature within an estimated experimental error of ±0.2 Mc/sec, which suggests that a is temperature independent (over this temperature range). Below 190°K the ay spectra were sufficiently broadened and unresolved to prevent measurement of the coupling constants. There was, however, no indication of any major changes in the magnitude of ay from 190° to 30°K. Below 190°K, there was little change in the general features of the spectra obtained with the magnetic field either parallel or perpendicular to the xy plane. This follows from the fact that the “walls” of the tubular cavities restrict the possible orientations of the long-cylindrical molecules. Smith has found using x-ray crystallographic techniques that the included a-hydrogen atom is time averaged extended alicyclic conformation (this would place the C6-H bond of the corresponding BCH radical in the xy plane). In this work we have observed that the C6-H bond of the carboxylic acid radicals are approximately in the xy plane by comparing the a in these radicals with the known principal elements of the a-proton tensor. Extending these arguments to the ketone radicals, the ratio of a to a (ketone)/a (acid or ester) is 0.93 and the ratio of a to a (ketone)/a (acid or ester) is 0.92. These two ratios are the same within experimental error which implies a similar averaging of the tensor elements in both of these systems. The one-electron wave functions are obtained by the usual variational procedure and the spin densities are given by the squares of the coefficients of the filled-molecular orbital. The spin densities are, of course, a function of the two parameters k and A. In order to obtain the best over-all view of the method, the range of k and A values used here is much larger than the usual range employed in Hückel calculations.

The results for a are summarized by the solid lines of Fig. 4. It is interesting to note that the spin density is quite insensitive to variations in k and A and it is very sensitive to changes in A. Even though only one spin-density site is being considered (and hence a unique pair of k and A is not obtained), this insensitivity to k makes possible an estimation of A. If A is constrained to the liberal range of 0.7 ≤ A ≤ 2.0 then k ≈ 0.96 ± 0.03.

This value compares favorably with k = 0.96 reported by Vincow and Frankel for a series of semiquinone anion radicals. Both of these values, however, are somewhat higher than the range 0.5 ≤ A ≤ 1.4 most frequently employed in the determination of properties.

Molecular orbital calculations of spin density

The spin densities were calculated using the Hückel theory and the method of McLachlan for these molecular orbital calculations. The molecular orbital framework of the ketone radical is represented by the structure

\[
\begin{align*}
\sigma_{\mathrm{C}} &\quad \sigma_{\mathrm{O}} \\
\pi_{\mathrm{C}} &\quad \pi_{\mathrm{O}} \\
\sigma_{\mathrm{C}} &\quad \sigma_{\mathrm{O}}
\end{align*}
\]

McLachlan has obtained approximate spin-density formulas from considerations of the perturbed self-consistent field theory. In the simplest form of McLachlan’s approximate method the spin density is given by

\[
\rho(r) = C\overline{\rho}_r(r) \quad (9)
\]

where \(\rho_r\) and \(\overline{\rho}_r\) are the atom-atom polarizabilities and spin densities, respectively, calculated from the Hückel theory, and \(\rho(r)\) is a semicircular constant which we will take equal to 1.0. The values of \(\rho_r\) obtained by this method are given by the broken lines of Fig. 4. Equation (9) has the pronounced effect of shifting \(\rho_r\) to lower values of \(r\). A unique pair of \(k\) and \(A\) values cannot, of course, be obtained from the single experimental quantity \(\rho_r\).

The ketone radical can be considered as an allyl radical in which the electron distribution is polarized by replacing one terminal carbon atom of the core by an oxygen atom. For the allyl radical, \(k = 0.5 = 1\) and the Hückel and McLachlan values of \(\rho_r\) are 0.50 and 0.60, respectively. In the ketone radical the \(\rho_r\) electron density on the oxygen atom increases with \(k\) and therefore \(\rho_r\) decreases. For example, the Hückel charge densities of the ketone radical are 0.30, 0.17, and 0.07 for C6, C5, and the oxygen atom, respectively (assuming \(k = 1.0\) and \(k = 2.0\)). The Hückel spin densities for these choices of parameters are 0.76, 0.03, and 0.18 for C6, C5, and the oxygen atom, respectively. 

The Hückel charge densities on all three carbon atoms of the allyl radical are zero, and the Hückel spin densities are 0.50, 0.00, and 0.50 for the three carbon atoms, taken consecutively. The effect of oxygen is so strong that the ketone radical is probably better described as an allyle group weakly interacting with the adjacent \(\pi\)-electron system. Further considerations of the electronic structure of this radical are of interest, and self-consistent field and configuration-interaction calculations are currently in progress.

Acknowledgment

We are especially indebted to Professor Harland M. McConnell for enlightening discussions and for the use of his laboratory facilities.

(8) For the allyl radicals, the McLachlan C6, C5, and oxygen spin densities for the ketone are 0.49, 0.08, 0.08, and 0.19, respectively. The McLachlan spin densities are +0.97, -0.194, and +0.097 for the three allyl carbon atoms, taken consecutively.

