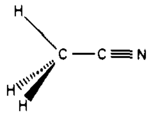

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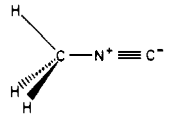
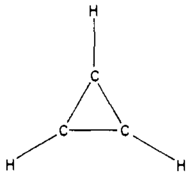


10

If the framework group has a center of symmetry, the latter may be replaced by a dot to relate its position to that of other nuclei in the linear subspaces. For example, the two D_{3h} structures **11** and **12** for C_3H_3 both belong to the A_3B_3 framework group



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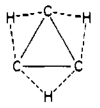

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$D_{3h}[{}^3C_2(\mathrm{AB})]$ but may be distinguished as $D_{3h}[3C_2(.\mathrm{CH})]$ for **11** and $D_{3h}[{}^3C_2(\mathrm{C.H})]$ for **12**.

Conclusion

The principal purpose of this paper has been to propose a complete classification of the nuclear symmetries of molecules in terms of framework groups, together with an associated notation. The clearest advantages that would follow from adoption of such a scheme are provision of (1) a simple method of distinguishing molecular structures which belong to the same point group but really have different symmetry properties, (2) a classification of molecular structures by framework groups, such that all nuclear arrangements belonging to the same framework group have identical symmetry properties, and (3) an ordered enumeration of all possible framework groups for a molecule of given composition.

Acknowledgments. This work was supported by the National Science Foundation under Grant CHE-79-01061. It parallels unpublished work by Professor Kurt Mislow and collaborators at Princeton University. I am indebted to Professor Mislow for some valuable correspondence. I also wish to thank Dr. D. J. DeFrees for valuable suggestions about the manuscript.

Interpretation of Temperature-Dependent ESR Spectra of Peroxy Polyethylene Radicals in Urea-Polyethylene Complex

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Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received December 10, 1979*

Abstract: Temperature-dependent ESR spectra of peroxy polyethylene radicals in urea-polyethylene complexes are successfully simulated by the modified Bloch equations in terms of g anisotropy averaging of *one* radical. The motional model that averages the **g** tensor corresponds to 180° rotational jumps of the O-O fragment around the C-O bond. An activation energy of 16.6 kJ/mol is derived for this motion. A comparison of peroxy with nitroxide spin probes in polyethylene shows that the peroxy probe is more sensitive to the particular motional model that controls the dynamics.

Introduction

Formation of peroxy radicals by high-energy irradiation of polymers in the presence of oxygen has been extensively studied by electron spin resonance (ESR).[1] In most cases the spectra show g anisotropy, and the interpretation of the results is facilitated by the usually constant principal values of the **g** tensor for peroxy-polymer radicals. These values are typically 2.038 (g_1), 2.008 (g_2), and 2.002 (g_3) at low temperatures. The highest principal value is along the oxygen-oxygen bond. In many instances it has been found that the principal values of the **g** tensor vary with temperature and molecular motions are usually invoked to account for these changes.

Peroxy radicals in γ-irradiated polyethylene are less stable than in other polymers[2] and are also less stable than the alkyl or allyl radicals formed exclusively in the absence of oxygen. By a combination of favorable microwave power saturation properties and temperature, however, the temperature dependence of ESR spectra of peroxy radicals in polyethylene[3] (PE) and in urea-polyethylene complexes[4] (UPEC) has recently been published. Results for UPEC are shown in Figure 1. Basically it is seen that the lowest principal value of the **g** tensor, g_3, remains constant and at the highest temperature g_2 and g_1 are averaged. At intermediate temperatures it is hard to interpret the spectra visually. Similar results are obtained in PE. In both cases[3,4] the ESR spectra were interpreted as a superposition of two chemically identical radicals, A and B, both being peroxy polyethylene radicals, trapped however at different locations and with different motional freedom. Rotation about the polymer chain axis was assumed, parallel to the direction of g_3. In radicals of type B the motion around the chain axis is postulated to be more rapid than for radicals of type A and therefore more effective in averaging g_2 and g_1. In order to simulate the spectra, a different ratio of A/B at each temperature was assumed and this ratio changed significantly, between 0.12 and 1.5 in PE and between 0.085 and 1.0 in UPEC.

We have recently reported a study of g anisotropy from the triphenylmethyl peroxy radical in γ-irradiated triphenylacetic acid as a function of temperature.[5] In the limits of low and high temperatures, the spectra are relatively easy to interpret by assuming respectively rhombic and axial **g** tensors. In the intermediate temperature range the spectrum is very complex, containing extra features over the entire range of g values. These experimental spectra were simulated successfully by the formalism of the modified Bloch equations, assuming 120° jumps of the O-O group around the C-O bond. This model is quite reasonable if we remember that the C-O bond has a threefold axis of symmetry for the three phenyl groups in the molecule. This method has also been applied to a mobile peroxide $(CO_2\text{-}O_2)^-$ on a MgO surface.[6] We have stressed the important fact that extra lines in a g an-

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(2) Y. Hori, S. Shimada, and H. Kashiwabara, *Polymer*, **18**, 151 (1977).
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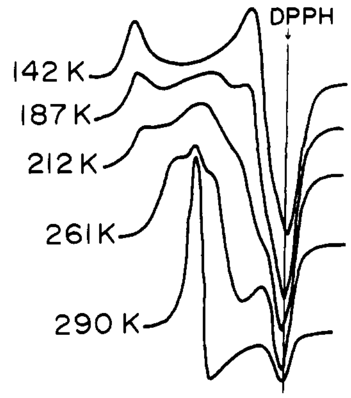

Figure 1. ESR spectra of peroxy radicals in UPEC observed at the indicated temperature (from ref 4).

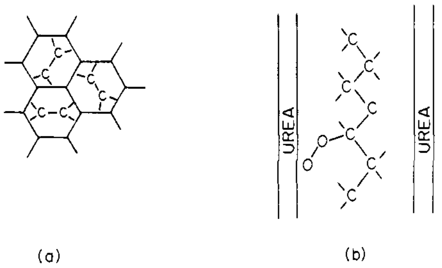

Figure 2. Structure of peroxy radicals in UPEC: (a) view of the urea-polyethylene structure along the *c* axis; (b) projection of structure along the *b* axis. The COO group is in a plane perpendicular to the chain axis.

isotropic powder spectrum are not always due to a different radical. In many cases it was found that these lines are due to exchange narrowing of radicals so oriented that the motional process does not change their resonant field appreciably.[5-7]

Here we apply the same formalism to the peroxy radicals in PE and UPEC. Previous studies suggested two radicals in different, but unspecified, sites. We show that all spectra can be interpreted in terms of one radical.

In the PE case,[3] the allylic radicals are much more stable than the peroxy radicals, and therefore the temperature dependent spectra of the peroxy radicals were obtained by subtracting the allylic radical spectra from the superimposed spectra at each temperature. In the case of UPEC,[4] no allyl radicals are formed and all alkyl radicals are converted to peroxy radicals when oxygen is introduced into the system. In addition, the peroxy radicals in UPEC are stable even at room temperature, resulting in considerable improvement in the quality of the ESR spectra. For this reason and also because the line width is less in UPEC than in PE, we will focus our attention on this case. Many of the conclusions are, however, applicable to peroxy radicals in PE and possibly, as will be shown below, to other cases as well.

Simulations

As seen in Figure 1, at the lowest temperature given, 142 K, the spectrum can be interpreted by assuming a rhombic **g** tensor with principal values $g_1 = 2.0366$, $g_2 = 2.0081$, and $g_3 = 2.0022$. At the highest temperature, 290 K, the **g** tensor becomes axial with $g_{\parallel} = g_3$ and $g_{\perp}$ equal to the average of g_2 and g_1.

Figure 2 illustrates the structure of UPEC[8,9] and the peroxy radicals in UPEC.[4] The COO fragment is considered to be perpendicular to the chain axis, and therefore g_3 is parallel to the chain axis. Hori et al.[3,4] excluded both the possibility of complete *g* averaging by three-dimensional tumbling *and* rotation about the C–O bond. Instead they invoked two radical sites with various degrees of rotation about the chain axis to explain their spectra.

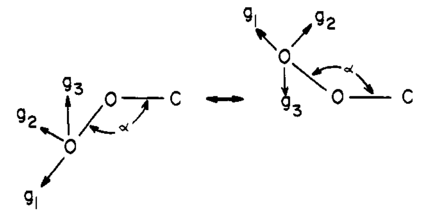

Figure 3. Motional model of the O–O group about the C–O axis. 180° jumps leave g_3 unchanged while g_2 and g_1 are averaged at high-frequency jumps if the rotation axis is at 135° to the O–O bond.

We disagree with this interpretation because the ratio of the two radical concentrations [A]/[B] varies in an irregular way as a function of temperature.

We propose to explain the experimental results in terms of one radical, jumping between equivalent sites. Two rotational models are assumed: (1) Hindered rotation about the chain axis. Jumping angles of 90 and 60 or 120° are considered. This motion leaves g_3 unchanged. (2) Hindered rotation about the C–O bond 90 and 180° jumps are considered. As seen in Figure 3, 180° jumps leave g_3 unchanged, and for a COO bond angle of 135°, g_2 and g_3 are averaged in the limit of rapid jumps, as experimentally observed.

The evolution of the spectrum as a function of the jumping rate τ is calculated by using the formalism of the modified Bloch equations.[5,10-12] These equations are obtained by adding to the Block equations kinetic terms that express the changes in magnetization due to the interconversions among N equally populated sites.

The total complex transverse magnetization is the sum over all sites:

$$M = \sum_{x=1}^{N} M_x \qquad (1)$$

The imaginary part of M in (1) gives the absorption line shape.

A general solution for M was obtained for a system with N sites when all interconversion rates between sites are equally probable.[12] The imaginary part of the transverse magnetization is

$$G = \frac{i\gamma H_1 M_0 \tau \sum_{x=1}^{N} f_x}{N(1 - \sum_{x=1}^{N} f_x)} \qquad (2)$$

with

$$f_x = (N + \alpha_x \tau)^{-1} \qquad (3)$$

and

$$\alpha_x = \frac{1}{T_{2x}} - i(\omega_x - \omega) \qquad (4)$$

Here γ is the gyromagnetic ratio, H_1 is the microwave field, τ is the mean lifetime of any species in the system, and ω_x is the resonant frequency of species x. In (2) M_0 is used instead of M_z, in absence of saturation and for relatively long spin–lattice relaxation time T_1.

Equation 2 is easily applicable to the 2-jump and 3-jump situations assumed here.

For 90° jump angles about the CO bond a restricted 4-jump model is assumed[12,13]

$$\begin{tikzcd} A \arrow[r, leftrightarrow] \arrow[d, leftrightarrow] & B \arrow[d, leftrightarrow] \\ D \arrow[r, leftrightarrow] & C \end{tikzcd}$$

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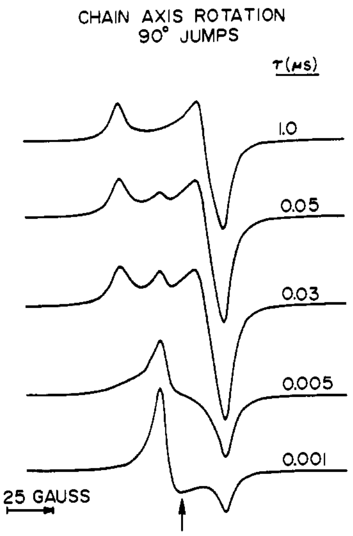

Figure 4. Simulated ESR powder spectra assuming 90° jumps about the chain axis, as a function of τ, the mean lifetime between jumps. The principal values of the g tensor in the rigid lattice limit are 2.0366, 2.0081, and 2.0022. T_2^{-1} in the absence of intramolecular motion is 13 MHz. The arrow represents H_0, the magnetic field corresponding to g_{average}.

in which transitions A ↔ C and B ↔ D are not allowed.

The expression for G is

$$G = -i\omega_0 M_0 \tau \times \left\{\frac{(\sigma_A + \sigma_C)(\sigma_B + \sigma_D + 2) + (\sigma_B + \sigma_D)(\sigma_A + \sigma_C + 2)}{4 - (\sigma_A + \sigma_C)(\sigma_B + \sigma_D)}\right\} \quad (5)$$

with

$$\sigma_x = f_x(1 - 3f_x)^{-1} \quad (6)$$

The rate of interconversion between sites, τ^{-1}, is of the order of the frequency spread of the spectrum which is ~80 G or ~200 MHz. Spectral changes are expected to occur for $\tau \simeq 10^{-8}$ s.

The other parameter that is needed for calculation is the line width in the absence of site interconversion. Values of 11–15 MHz for T_2^{-1} were used, on the basis of a comparison of calculated and experimental spectra in the limit of high and low temperature. In the intermediate temperature range the line shape was not very sensitive to variation of the line width within the limits defined above.

Spectra were calculated for a 3-jump process with jump angles of 120 or 60° about the chain axis and for a 2-jump process with a jump angle of 90° about the chain axis and of 180° about the CO bond. Equations 2, 4, and 5 were used, with $N = 3$ and $N = 2$, respectively. In addition, the restricted 4-jump model was used for 90° jumps about the CO bond, by using eq 3–6.[14] In all cases the diagonal **g** tensor of site 1 denoted by $g(1)$ in a coordinate axis system x, y, z is used to calculate the **g** tensor for the other sites.

The **g** tensor for site 2, $g(2)$, is given by

$$g(2) = Lg(1)\mathbf{L}^{-1} \quad (7)$$

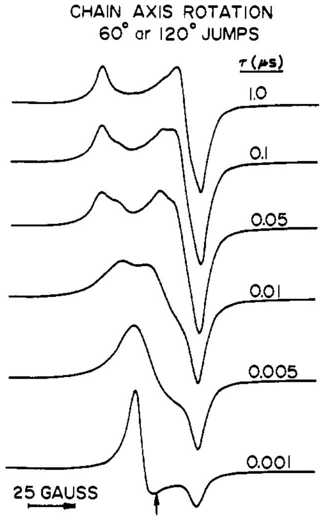

Figure 5. Simulated ESR powder spectra assuming 120 or 60° jumps about the chain axis, as a function of τ, the mean lifetime between jumps. T_2^{-1} in the absence of intramolecular motion is 13 MHz. The arrow represents H_0, the magnetic field corresponding to g_{average}.

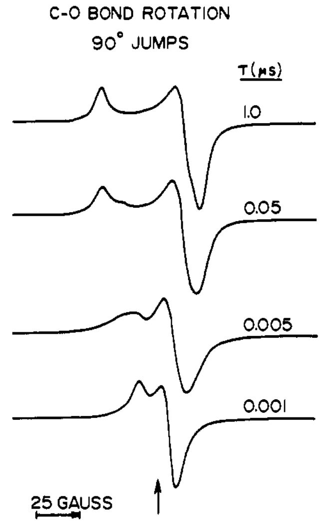

Figure 6. Simulated ESR powder spectra assuming 90° jumps about the CO bond, as a function of τ, the mean lifetime betwen jumps. The COO bond angle is 135° and T_2^{-1}, in the absence of intramolecular motion, is 13 MHz. The arrow represents H_0, the magnetic field corresponding to g_{average}.

where the matrix **L** relates the molecular coordinate axis system of site 1 and site 2:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}_{(\text{site } 2)} = \mathbf{L}\begin{pmatrix} x \\ y \\ z \end{pmatrix}_{(\text{site } 1)} \quad (8)$$

The elements of **L** are expressed in terms of angles β, which is the jump angle about the rotation axis and $\gamma = \alpha - 90°$. We obtain[5] eq 9. For simulations of the powder spectrum, we calculate for each site orientation with respect to the magnetic field the resonance frequency and then apply the modified Bloch equations.

Spectral simulations for hindered rotations about the chain axis as a function of τ are given in Figures 4 and 5, for jump angles of 90 and 120° (or 60°), respectively. In both cases the calculated spectra are identical in the limits of long τ (~1.0 μs) and short τ (0.001 μs) but quite different in their evolution as a function of τ. For 90° jumps one prominent feature appears between g_1 and g_2, which grows in intensity and finally becomes $g_\perp$ as τ becomes shorter. For 120° (60°) jumps two such features appear between g_1 and g_2 which merge and become $g_\perp$ as τ becomes shorter. Simulations with 90° jumps about the chain axis re-

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(13) A. Carrington, *Mol. Phys.*, **5**, 425 (1962).

(14) When the **g** tensor is rotated about an axis parallel to the direction of one principal value, the same tensor is obtained after a 180° rotation. For the case of 90° jumps about the chain which is parallel to g_3, a 2-jump formalism has therefore been used. This is also the reason for the fact that 60° jumps about the chain axis are identical with 120° jumps and can be treated by a 3-jump formalism. For **g** tensor rotations about an arbitrary axis, however, a rotation of 360° is necessary to obtain the original tensor. For 90° jumps about the CO bond, a restricted 4-jump formalism had to be used. We are indebted to Dr. Z. Luz for pointing out to us this subtle difference.

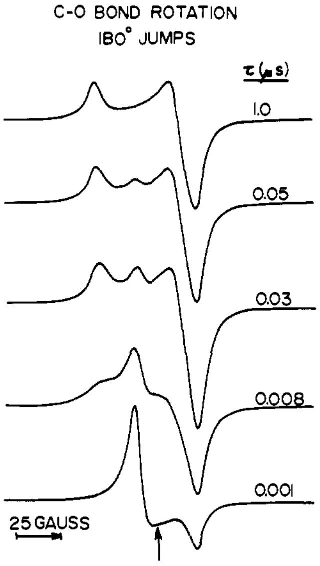

Figure 7. Simulated ESR powder spectra assuming a jump angle of 180° about the C–O bond as a function of τ, the mean lifetime between jumps. The COO angle is 135° and T_2^{-1}, in the absence of intramolecular motion, is 13 MHz for $\tau = 0.001$ μs and 15 MHz for the other simulations. The arrow represents H_0, the magnetic field corresponding to g_{average}.

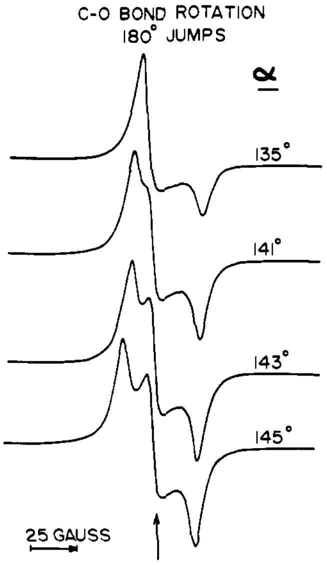

Figure 8. Simulated ESR powder spectra assuming 180° jumps about the C–O bond, as a function of α, the COO angle, for $\tau = 0.001$ μs. T_2^{-1}, in the absence of molecular motion, is 13 MHz. The arrow represents H_0, the magnetic field corresponding to g_{average}.

$$\mathbf{L} = \begin{pmatrix} \cos^2\gamma\cos\beta + \sin^2\gamma & \sin\gamma\cos\beta\cos\gamma - \cos\gamma\sin\gamma & -\sin\beta\cos\gamma \\ \cos\gamma\sin\gamma\cos\beta - \sin\gamma\cos\gamma & \sin^2\gamma\cos\beta + \cos^2\gamma & -\sin\beta\sin\alpha \\ \cos\gamma\sin\beta & \sin\gamma\sin\beta & \cos\beta \end{pmatrix} \qquad (9)$$

produce well the experimental results in the entire temperature range.

Figure 6 illustrates spectra calculated by using 90° jumps about the CO bond. The restricted 4-jump model is used, and the COO bond angle is taken as 135°. These spectra show a change in g_3 as a function of τ and a highly reduced g anisotropy at short values of τ. Neither of these features was observed experimentally.

Figure 7 shows spectral simulations as a function of τ for 180° jumps around the C–O bond. The COO bond angle is taken as 135°. These simulations reproduce the salient features of the experimental results over the entire temperature range, with τ between 0.001 and 1.0 μs. For instance spectra are simulated well at 142 K with $\tau = 1.0$ μs, at 187 K with $\tau = 0.03$ μs, at 212 K with $\tau = 0.08$ μs, and at 290 K with $\tau = 0.001$ μs.

The value chosen for the COO angle, α, is an important parameter in the simulations. The rotation axis is parallel to the CO bond, in the plane of the principal values g_2 and g_1. g_1 is along the O–O bond. For a rotation of 180° around the CO bond g_3 is unchanged. The angle between the rotation axes and the directions of g_2 and g_1 greatly affect the averaging of these values. If the rotation axis is parallel to the direction of either g_2 or g_1, no averaging of the g in the plane of g_2, g_1, and the rotation axis occurs. Complete averaging of g_2 and g_1 occurs when the rotation axis is equally inclined to the directions of g_2 and g_1 or 45 and 135° to the O–O bond. In between these situations of complete averaging and no averaging, various amounts of averaging occur. This effect is shown in Figure 8 which illustrates spectra obtained for $\tau = 0.001$ μs, as a function of the COO angle, α, between 135 and 145°. From these simulations it can be concluded that the limits on α are about 135 ± 4° in order to agree with the experimental line shape. By comparison, a value of 127° for the COO angle was used to simulate ESR spectra of the triphenylmethyl peroxy radical,[5] while a value of 130° was calculated for $(CO_2\text{–}O_2)^-$[15] and used to simulate the ESR results.[6] A value of ~135 ± 4° for the COO angle in peroxy PE is thus acceptable. The slightly larger value might be more stable in this system in order to avoid steric hindrance with the polymeric chain.

Figure 9 shows an Arrhenius plot of τ^{-1} vs. T^{-1} for 180° jumps about the CO bond. The plot is linear and corresponds to an activation energy of 16.6 kJ/mol and a frequency factor of 1.2×10^{12} s^{-1}.

Discussion

It has been shown before that extra lines appear in ESR spectra exhibiting g anisotropy when the temperature is varied. The position, intensity, and shape of these lines can be simulated by a suitable motional model.[5-7]

Of the numerous possible motional models, one has to choose those that are logical and take into account chemical realities. In addition the theoretical formulation should be sensitive to the various models possible so that the best model can be singled out.

The motional model for peroxy PE is a very difficult problem because of the complexity of a polymeric chain. As a simplification, three main types of motion can be imagined as effective for g value averaging: (1) three-dimensional reorientation of polymer chains, (2) cooperative segmental motion around the polymer chain axis, and (3) localized processes such as segmental

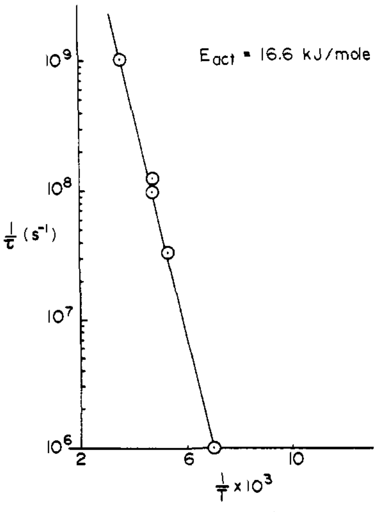

Figure 9. Arrhenius plot of the jump rate τ^{-1} as a function of absolute temperature for 180° jumps about the CO bond direction.

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[15] Y. Ben Taarit, J. C. Vedrine, C. Naccache, Ph. de Montgolfier, and P. Meriaudeau, *J. Chem. Phys.*, **67**, 2880 (1977).

motion or internal motion of the O–O fragment about the C–O bond.

These three motional models roughly parallel the α, β, and γ relaxation processes in PE which have been studied by ESR[16] and by dielectric relaxation.[17] These processes have activation energies of >100, 65–100, and 45–60 kJ/mol, respectively. No activation energies are known for PE–urea complexes. The lower activation energy for a segmental motion has been studied for polystyrene solutions by nitroxide spin labeling and found to have an activation energy of 18 kJ/mol.[18] The activation energy for an internal rotation such as rotation of O–O about the CO bond should have an activation energy lower than that for the segmental motion value of 45–60 kJ/mol.

Hori et al.[3,4] excluded both the three-dimensional reorientation *and* the C–O bond rotation. They rejected the first because of its expected high activation energy and the second because they thought that such a motion was incompatible with the ESR results. The reorientation around the chain axis was chosen because by such a motion g_3 remains constant while g_2 and g_1 are averaged. It has been shown here, however, that spectra calculated by using 90° jumps about the chain axis and 180° jumps about the CO bond reproduce equally well the experimental results and therefore the CO bond rotation need not be rejected. The choice between these two possibilities could be attempted by inspection of the dynamics of a polymeric chain.

It is hard to imagine chain axis rotation in UPEC for the following reasons. It is known that for small paraffin chains of 4–20 carbon atoms, all C–H bonds are ruptured with the same probability[19,20] at low temperatures to form alkyl radicals. It is generally believed that allyl radicals are formed after irradiation at 77 K by migration of alkyl radicals via H atom abstraction to groups adjacent to a double bond. The implication is that the radical site is next to the chain end.[21] Now it is easy to imagine rotation around the chain axis of a carbon atom that is near a chain end. When PE is γ irradiated at 291 K, the presence of allyl radicals has been observed.[3,22] In γ-irradiated UPEC however, allyl radicals are not detected[4] by ESR. We interpret this difference to mean that the initial alkyl radicals formed do not migrate to chain ends and therefore the rotation about the chain axis is not very probable. This suggestion, together with the improbability of a three-dimensional reorientation, leaves C–O bond rotation as the most logical possibility. This motion requires a minimum amount of activation energy and explains the experimental ESR results. The activation energy of 16.6 kJ/mol obtained by simulation with 180° jumps around the CO bond is similar to that found for the triphenylmethyl peroxy radical and less than for segmental motion in PE.[17]

Finally, we can compare information that has been obtained from peroxy-PE with ESR spectra of nitroxide spin-labeled PE.[16] The rotational correlation time τ has been obtained from N–O spin-labeled PE as a function of temperature, but not many details of the motion could be derived. In the temperature range 77–294 K ESR spectra of N–O labeled PE do not show much change in line shape while dramatic line shape changes occur in peroxy PE in this temperature range. The nitroxide spin probe is more sensitive to the temperature in the range 323–389 K,[16] and it is possible that the peroxy label might complement the data obtained with the nitroxide probe. The peroxy group is very easily formed in polymers, and the study of its g anisotropy with temperature might provide motional details in many polymeric systems. An interesting example is a study of the g anisotropy from peroxy polyfluoroethylene.[23,24] In this case different spectra have been obtained in the temperature range 77–293 K for the peroxy end radical $-CF_2-CF_2-OO\cdot$ and for the peroxy chain radical $-CF_2-CF(OO\cdot)-CF_2-$. We believe these results can be interpreted in terms of molecular motion as outlined above. The temperature variation for the chain radical has been only qualitatively interpreted by assuming a rotation about the chain axis. For the present study however, it seems clear that a model assuming 180° jumps about the CO bond offers an alternative explanation.

Acknowledgments. This work was supported by the Army Research Office.

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