Electron Spin Resonance Spectrum of Oxygen-17 Enriched *t*-Alkylperoxy Radicals

K. Adamic, K. U. Ingold, and J. R. Morton

Contribution No. 11197 from the Division of Chemistry, National Research Council, Ottawa, Canada. *Received June 16, 1969*

Abstract: Esr spectra of ROO radicals (R = *t*-butyl, cumyl) containing oxygen enriched in the isotope ^{17}O, have been detected at $-100°$. The ^{17}O hyperfine constants were 21.8 ± 0.1 G and 16.4 ± 0.1 G. From the variation in the line widths across the ^{17}O manifolds it was possible to assign these two hyperfine constants to the terminal and inner oxygen nuclei, respectively, and to conclude that the spin density on the terminal oxygen was approximately twice that on the inner.

Recent interest in the structure and chemistry of peroxyradicals prompted us to attempt to measure the ^{17}O hyperfine interactions in $(CH_3)_3COO$ and $C_6H_5(CH_3)_2COO$, both of which have been studied by esr in our laboratories.[1] Although ^{17}O hyperfine interactions have been reported for the fluoroperoxy radicals FOO[2,3] and CF_3OOO,[4] the only existing data on alkyl peroxides are those of Fessenden and Schuler.[2] Unfortunately, however, they were unable to identify the species involved.

Experimental Section

The above peroxy radicals were prepared by uv photolysis of 10^{-2} *M* solutions of azoisobutane and azocumene in oxygen-saturated CF_2Cl_2. The oxygen, which contained 47.0% ^{17}O and 5.2% ^{18}O, had been obtained from Yeda Inc., Israel. The spectra were recorded on a Varian E-3 spectrometer at temperatures between -140 and $-90°$. It was found that the resolution and intensity of the spectra varied with temperature and with the concentration of oxygen in the solution, the optimum spectra being obtained at -110 to $-100°$. In such a spectrum (Figure 1) maximum slope line widths of the $R^{16}O^{16}O$ resonances were 2.95 G, and their *g* values were, in both cases, 2.0146.

Results and Discussion

Species Containing One ^{17}O Nucleus. Examination of Figure 1 reveals that the spectra were slightly asymmetric with respect to the width and the position of the hyperfine satellites. Asymmetry in the position of hyperfine satellites is due to second-order and/or quadrupole effects. The resolution in our spectra was not sufficiently good to warrant a detailed analysis, so the ^{17}O hyperfine interactions were measured as 0.2 times the field increment between the $M_I = \pm 5/2$ resonances. Our results, together with those for other peroxy radicals, are listed in Table I.

Table I. ^{17}O Hyperfine Constants for Peroxy Radicals

Radical	$\lvert a_O' \rvert$, G	$\lvert a_O'' \rvert$, G	Ref
FOO	22.17 ± 0.05	14.50 ± 0.05	3
CF_3OOO[a]	23.3 ± 0.1	14.0 ± 0.1	4
ROO[b]	23.0	18.0	2
$(CH_3)_3COO$	21.8 ± 0.1	16.4 ± 0.1	This work
$C_6H_5(CH_3)_2COO$	21.8 ± 0.1	16.4 ± 0.1	This work

[a] $a_O''' = 3.59 \pm 0.01$ G. [b] Produced by irradiation of 2,2,4-trimethylpentane containing ^{17}O enriched oxygen.

The line-width variation, which can be described by the equation[5,6]

$$T_2^{-1}(M_I) = C + LM_I + KM_I^2$$

is illustrated in Figure 2. The coefficient *C* arises primarily from *g* anisotropy, and so it is not surprising (since all isotopic species have the same *g* tensor) to find an indication that the $M_I = \pm 1/2$ lines of both enriched species are approximately the same width as the line from $R^{16}O^{16}O$.

The coefficient *L* describes the asymmetry in the line widths across the two ^{17}O hyperfine manifolds, and the sign of *L* depends on the sign of the inner product of the anistropic *g* and hyperfine tensors. For the terminal oxygen, these tensors will be approximately diagonal in an axis system *x* (the O–O bond), *y* (perpendicular to the C–O–O plane), and *z* (the mutually perpendicular direction). The corresponding principal values will be of the form $2\Delta g$, $-\Delta g$, $-\Delta g$ and B, $-2B$, B, respectively. Here, *B* is dipole–dipole contribution to the terminal ^{17}O hyperfine tensor into which the negative sign of the ^{17}O magnetogyric ratio has been absorbed. The inner product being $+3B\Delta g$, there is little doubt that the sign of *L* for the terminal ^{17}O will be positive, even if *x*, *y*, and *z* are not quite the true principal directions. Since both ^{17}O manifolds are such that lines on the high-field side are broader than the corresponding lines on the low-field side, the high-field side of the spectrum must be associated with positive values of M_I for the terminal ^{17}O nucleus. That is, the sign of the hyperfine constant of the terminal ^{17}O must be negative.

Moreover, a numerical analysis of the curves in Figure 1 yields $\lvert L'L''^{-1} \rvert = 2.2 \pm 0.3$ and $\lvert K'K''^{-1} \rvert = 5.1 \pm 0.5$. Since both primed and double-primed species must possess the same *g* tensor, the ratio $\lvert L'L''^{-1} \rvert$ is a measure of the spin-density ratio on the ^{17}O nuclei of the two species. The ratio $\lvert K'K''^{-1} \rvert$ should be the square of this quantity, as is seen to be approximately so.

It seems logical to conclude, therefore, that the primed species is $R^{16}O^{17}O$, having an ^{17}O hyperfine interaction of (−) 21.8 G; and that the double-primed species is

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(1) K. Adamic, J. A. Howard, and K. U. Ingold, *Chem. Commun.*, 505 (1969).

(2) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **44**, 434 (1966).

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(5) E. de Boer and E. L. Mackor, *ibid.*, **38**, 1450 (1963).

(6) A. Hudson and G. R. Luckhurst, *Chem. Rev.*, **69**, 191 (1969).

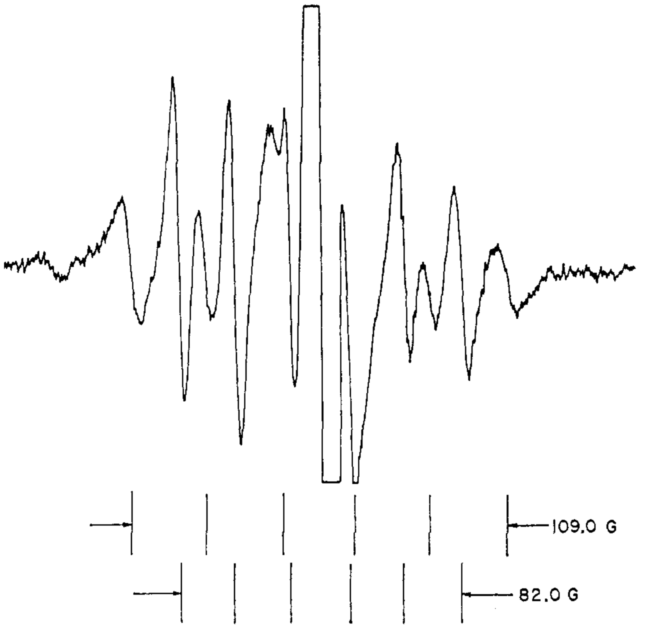

Figure 1. Esr spectrum of $C_6H_5(CH_3)_2COO$ cotaining ^{17}O enriched oxygen at −105°.

$R^{17}O^{16}O$, having an ^{17}O hyperfine interaction of $|16.4|$ G. In addition, the ratio of the spin densities on the two oxygens is approximately 2:1, in favor of the terminal oxygen.

Doubly Substituted Species. Part of the spectrum due to $R^{17}O^{17}O$ could also be detected. The lowest field line and the highest field line of $R^{17}O^{17}O$ were 187 ± 1 G apart, compared to the expected separation of 191 G, calculated from the values of a_O' and a_O''. An attempt was also made to measure the relative intensities of individual lines due to the different isotopic species. The intensity in a line was assumed to be proportional to $l(\Delta H_{ms})^2$, where l is the amplitude of the derivative presentation and ΔH_{ms} the maximum slope width. The intensity ratio between lines of either singly ^{17}O substituted species and the outside lines due to $R^{17}O^{17}O$ was 6 ± 1, compared to the expected 6.8. However, the ratio between the intensity of the center line, due to $R^{16}O^{16}O$, and a line due to either singly substituted species was 11.5 ± 0.5, approximately twice the expected 6.8. The simplest explanation of this anomaly would appear to be that the $R^{16}O^{16}O$ line has a different shape from that of lines from the ^{17}O containing species, but it is difficult to understand why this should be the case.

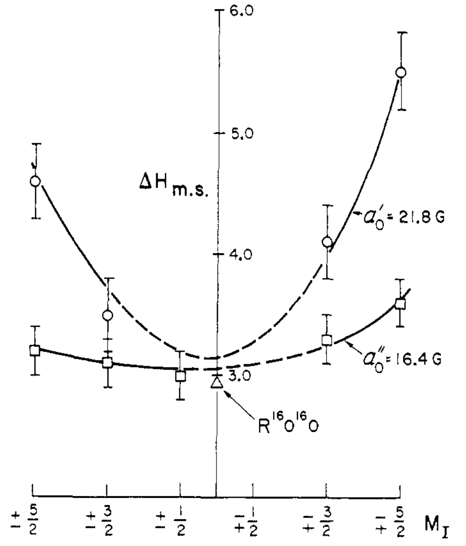

Figure 2. Variation in maximum slope line width across ^{17}O manifolds of esr spectrum of $C_6H_5(CH_3)COO$ at −105°.

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The Photochemistry of Isabelin

H. Yoshioka, T. J. Mabry, and A. Higo

Contribution from The Cell Research Institute and Department of Botany, The University of Texas at Austin, Austin, Texas 78712.

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Abstract: Irradiation of the germacranolide dilactone isabelin (**1**) at 253.7 nm in benzene afforded a single crystalline product resulting from a $(2\pi + 2\pi)$ cycloaddition process. The product, photoisabelin (**3**), absorbed 1 mol of hydrogen to yield dihydrophotoisabelin (**5**), a substance also obtained as a minor product from the photolysis of dihydroisabelin (**4**). However, the major compound from the ultraviolet irradiation of dihydroisabelin was the ene photoproduct lumidihydroisabelin (**9**). Thermolysis of dihydrophotoisabelin (**5**) gave a mixture of two germacranolides, dihydroisabelin (**4**) and pyrodihydroisabelin (**7**).

Isabelin (**1**),[1] a new germacranolide dilactone from *Ambrosia psilostachya* DC. (Compositae), exists in solution at room temperature in a 10:7 ratio of two nmr-distinguishable conformers (Table I); on the basis of nmr data, the two conformers were assigned structures **1a** and **1b**: in the major conformer (**1a**) the double bonds are in a crossed orientation while in **1b** they have a parallel alignment.

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[1] (a) H. Yoshioka, T. J. Mabry, and H. E. Miller, *Chem. Commun.*, 1679 (1968); (b) H. Yoshioka and T. J. Mabry, *Tetrahedron*, **24**, 4767 (1969).