## Spin Relaxation in *t*-Peroxy Radicals

*Sir:*

Most organic free radicals which have been extensively studied by esr characteristically have had $g$ values near that of the free electron as a consequence of almost complete quenching of orbital angular momentum.[1] Normally the line widths of such radicals increase with increasing viscosity and decreasing temperature due to reduced averaging of anisotropic processes.[2-4] Certain metallic ions,[5,6] the stable radical $ClO_2$,[7] and probably the $O_2^-$ ion[8] have been observed to show the opposite behavior, namely, a decrease in line width with decreasing temperature. This behavior has been attributed to additional spin–orbit relaxation mechanisms[7,9-11] which appear particularly effective, in certain cases, for paramagnetic species with incomplete quenching of orbital angular momentum ($g$ value significantly different from that of the free electron).

The purpose of this note is to point out that *t*-peroxy radicals, unique among organic free radicals studied to date, exhibit spin-relaxation behavior apparently dominated by these latter spin–orbit effects. In particular, certain *t*-peroxy radicals are found to have esr line widths which depend strongly upon temperature and solution viscosity, as shown in Figures 1 and 2. In Figure 1 the X-band esr line width ($\Delta H$ in gauss, between points of maximum slope) of *t*-butylperoxy radical[12] is plotted as a function of $1/T$°K over the range −130 to 25°; $g$ values remained constant at 2.0146 ± 0.0001 from −80 to 25°. The radicals were generated by photolysis of a 10% *t*-butyl hydroperoxide solution in pentane containing 15% ethyl alcohol and were present at concentrations in the range of $10^{-4}$–$10^{-5}$ $M$. Concentrations were measured as previously described.[13] The solution remained homogeneous over the entire temperature range. Solutions were degassed, and measurements were made essentially as described previously.[14] As noted in Figure 1, the esr line width drops from a value of about 20 gauss at 25° to a limiting value of about 3 gauss at low temperatures. The possibility that a chemically shortened lifetime is responsible for the observed trend, *via* reactions of the radical with substrate materials or by self-reactions, including reversible formation of tetroxide, can be definitely eliminated by known reaction rate constants[13,15] and radical concentrations.

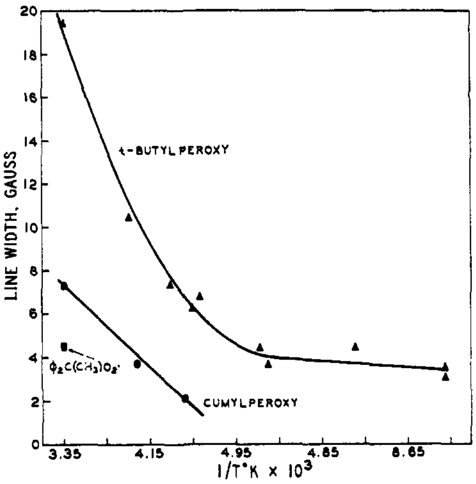

Figure 1. X-band line width of peroxy radicals *vs.* $1/T$°K.

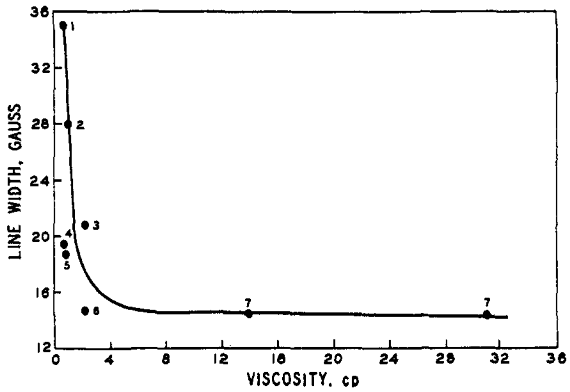

Figure 2. Line width of *t*-butylperoxy radical *vs.* solution viscosity at 25°; 10% *t*-butyl hydroperoxide in (1) pentane, (2) isooctane, (3) *t*-butyl hydroperoxide neat, (4) 15% ethyl alcohol in pentane, (5) benzene, (6) dimethyl sulfoxide, and (7) glycerol–methyl alcohol mixtures.

In Figure 2 the *t*-butylperoxy line width at 25° is plotted against measured solution viscosities of about 10% *t*-butyl hydroperoxide in a variety of solvents. Although specific solvent effects are evident, there is a general correlation between line width and viscosity until a limiting line width of about 14 gauss is reached at high viscosities. The possibility that the large line width of *t*-butylperoxy radical is due to unresolved proton hyperfine splitting and its variation with viscosity due to solvent effects is highly improbable. Hyperfine splittings of γ-protons are uniformly slight and the line width, due to this cause, of the related ketal of hexamethylacetone, $(t\text{-Bu})_2\text{-}\dot{C}\text{-}O^-$, is only about 2 gauss.[16] Furthermore, a 2.5-fold change in hyperfine splitting by solvent effects is much greater than any previously observed.[17,18] The possibility that the observed viscosity dependence may be attributed to exchange[19,20] can be discarded. The maximum measured concentration of this transient radical was $10^{-4}$ $M$, far too low for ex-

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(12) The esr spectra of the three peroxy radicals studied here consisted of single lines with no resolvable hyperfine splittings.

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change to contribute to the line width. Moreover, the line width remains constant over a tenfold range in concentration.

A characteristic of the additional spin-orbit relaxation mechanisms proposed[9,10,11] is that the line width is independent of frequency. To check this point, line widths of *t*-butylperoxy radical in 20% hydroperoxide in pentane were determined by Dr. W. C. Landgraf of Varian Associates at 35 Gc. At 25 and −35°, line widths of 27.8 and 16.0 gauss, respectively, were obtained. At X-band, in our laboratory, the same sample gave 29.0 and 18.9 gauss, respectively.[21] All measurements have about a ±0.7 gauss reliability. Consequently, it seems most plausible to attribute the dominant spin relaxation process in *t*-butylperoxy radicals to the spin-orbit processes of ref 9–11.

The exact nature of the most important spin-orbit mechanism is still a question under investigation. Most recently Atkins and Kivelson have concluded[11] that a spin-rotation interaction, involving the spin and the magnetic field created by rotation of the radical (coupled by an interaction tensor proportional to the square of the $g$ value variance from that of the free electron), is more important in most cases than the rotational spin-orbit mechanism of ref 9 which requires a combined spin and orbital electronic transition. When dominated by rotational motions of the radical, the line width is expected[11] to be proportional to $(g - 2.0023)^2T/a^3\eta$ where $a$ is the diameter of the radical, $\eta$ the viscosity, and $T$ the absolute temperature. Qualitatively the effects of temperature and viscosity shown in Figures 1 and 2 upon the line width as well as the influence of radical size shown in Figure 1 at 25° (*t*-butyl > cumyl > methyldiphenylmethyl)[22] are consistent with this expectation.

The vibrational spin-orbit process introduced by Lloyd and Pake[3,10] affords a possible mechanism to explain the drop of line width from its viscosity-limited value of 14 gauss at 25° to its low temperature limited value of 3 gauss in Figure 1. However, Atkins and Kivelson[11] conclude that this mechanism suffers the same restriction which limits the rotational spin-orbit mechanism and that it will, in general, be unimportant. In this event the discrepancy might possibly be accounted for by an effective increase in the size of the radical *via* hydrogen-bonding solvation with hydroperoxide at low temperatures.

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[21] Radical concentrations were not determined in these two sets of experiments. The radically different experimental equipment used, including method and intensity of irradiation, further dispels concern that the measured line widths are a function of radical concentration.

[22] Cumylperoxy was prepared in the same solvent as *t*-butylperoxy. Methyldiphenylmethylperoxy was prepared by oxidation of the hydroperoxide in methanol with $Ce^{4+}$; $g$ values were the same as for *t*-butyl to within ±0.0001 for cumyl and ±0.001 for methyldiphenylmethyl.

**J. R. Thomas**
*Chevron Research Company*
*Richmond, California*

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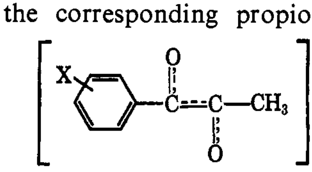
## Electron Spin Resonance Studies of Substituent Effects. Correlations with σ Constants

*Sir:*

Much data have been obtained in recent years concerning substituent effects on hyperfine splitting constants (hfsc) in radical ion series. Correlations of nitrogen hfsc with Hammett $\sigma$ constants have been sought for the nitrobenzene anion radicals[1] and the phenyl *t*-butyl nitroxides.[2] Even though the $\sigma$ constant is interpreted as a measure of a substituent effect on electron density at an atom,[3] a correlation with splittings of this type will not be very good because the nitrogen hfsc is a function of the spin density at the attached atoms as well as the spin density on nitrogen.[4]

We present here preliminary results on an anion radical system in which hyperfine splitting constants vary linearly with spin densities, which shows large sensitivity to substituent, and which gives an excellent correlation with $\sigma$ constants for many substituents. Radical anions of substituted 1-phenyl-1,2-propanediones (I) can be readily formed by base-catalyzed oxidation of the corresponding propiophenones in dimethyl sulfoxide (80%)–*t*-butyl alcohol (20%).[5] These radicals have sizable methyl splittings which are readily evaluated. Furthermore, the methyl splitting will be *directly proportional* to the spin density at the attached carbon atom.[6] Table I shows results for a variety of derivatives,[7] together with $\sigma$ constants taken from the compilation of McDaniel and Brown.[8]



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Four substituents, *p*-$CF_3$, *p*-Ph, *p*-F, and *p*-$N(CH_3)_2$, are anomalous in that the methyl splittings fall out of the order of the $\sigma$ constants while the methyl splitting for *p*-CN is obviously far less than would be predicted from its $\sigma$ constant. For all other substituents, however, the methyl splitting reproduces the vagaries of the $\sigma$ constants, *i.e.*, the strong electron-supplying effect of *p*-$OCH_3$ compared to the electron-withdrawing effect of *m*-$OCH_3$, the stronger electron-withdrawing effect of *meta* halogens compared to *para* halogens, and the order of electron withdrawal within the series Br, Cl, F.

Figure 1 shows a plot of $A^{H}_{Me}$ *vs.* $\sigma$ together with the least-squares line. The correlation coefficient for the 16 "well-behaved" points is 0.995. The correlation

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