Line-width effects in the Electron Spin Resonance spectrum of the 2,5-dimethylhydroquinone cation radical

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where $x = \omega\tau_m$ and τ_m is the most probable relaxation time. Alternatively $x = \lambda_m/\lambda = f/f_m$. The other symbols have their usual significance. If α is small and points are considered where the dispersion is appreciable $(0.1 < x < 10)$ one may write $x^\alpha = 1 + \alpha \ln x$ which makes eq 1 and 2 considerably easier to handle by removing the fractional indices. The modified expressions are

$$\epsilon' = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)\left(1 + \frac{1}{2}\alpha x\pi\right)}{1 + \alpha x(\pi - 2x \ln x) + x^2} \qquad (3)$$

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)x(1 - \alpha \ln x)}{1 + \alpha x(\pi - 2x \ln x) + x^2} \qquad (4)$$

which, it must be emphasized, hold for values of α less than about 0.05 and for values of ϵ' and ϵ'' taken within the dispersion region corresponding to the range of x defined as above.

Assuming these conditions, expressions 3 and 4 can be rearranged to form the four following equations

$$\epsilon' - \frac{\epsilon''^2}{\epsilon_0 - \epsilon'} = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)\frac{\alpha\pi}{2}x^{-1} \qquad (5)$$

$$\epsilon' + \frac{\epsilon''^2}{\epsilon' - \epsilon_\infty} = \epsilon_0 - (\epsilon_0 - \epsilon_\infty)\frac{\alpha\pi}{2}x \qquad (6)$$

$$\frac{\lambda\epsilon''}{\epsilon' - \epsilon_\infty} = \lambda_m - \lambda\alpha x^2\left(\frac{\pi}{2} + x^{-1}\ln x\right) \qquad (7)$$

$$\frac{\lambda(\epsilon_0 - \epsilon')}{\epsilon''} = \lambda_m + \lambda\alpha\left(\frac{\pi}{2} - x \ln x\right) \qquad (8)$$

The final term in each of these equations shows the effect of a small α on standard expressions used for deriving the important dispersion parameters when a single relaxation time is present. In a previous publication[2a] the effect of a small α on the values of the left hand side of eq 5-7 has also been considered, but the resulting equations were unwieldy and difficult to handle due to the presence of terms containing $x^{1-\alpha}$. These difficulties are removed by making the derivations from eq 3 and 4 rather than 1 and 2.

Clearly, the usefulness of any of the above four equations depends upon the part of the dispersion region where the experimental points are available, since the terms containing α also contain x. For example, using eq 8 in conjunction with readings taken previously by the author[2a,4] on water at 0.86, 1.26, and 3.225 cm the left hand side becomes 1.74 ± 0.02, 1.77 ± 0.03, and 1.94 ± 0.07 cm, respectively. The quoted errors are appropriate to $\pm 1\%$ in ϵ' and $\pm 2\%$ in ϵ''. The three corresponding values of $\lambda\alpha$ $(\pi/2 - x \ln x)$ are 0.11α, 1.3α, and 6.2α which on substitution gives α lying in the range of 0.02 to 0.04. The precise value of α is of minimal importance however; the relevant observation is that the trend is away from single relaxation time be-

havior. Full discussions of the dielectric behavior of water appear elsewhere.[2a,2b,4]

For completeness it is worth noting that at frequencies well away from the relaxation frequency the curves for ϵ' against $\ln x$ become indistinguishable over a fair range of values of α. On the other hand, the differences between the ϵ'' curves for various values of α actually become more enhanced as $x \gg 1$ or $x \ll 1$ which makes these conditions very suitable for locating a small α, as was pointed out by Schwan.[2a] In these circumstances

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty)x^{1-\alpha} \quad (f \ll f_m) \qquad (9)$$

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty)x^{-(1-\alpha)} \quad (f \gg f_m) \qquad (10)$$

A logarithmic plot of ϵ'' against frequency or wavelength produces a straight line of slope $(1-\alpha)$; a similar plot can be deduced if values are available for conductivity rather than ϵ''.

Near the center of the dispersion the curves of ϵ'' against $\ln x$ lie almost on top of one another for the very small values of α being considered, and examination of eq 4 shows that one value of exists on either side of the central maximum where ϵ'' is the same for all values of α between 0 and about 0.05. This isobathic point is obtained by solving the equation $(x^2 - 1) \ln x = \pi x$ which gives the result $x = 3.1$ or 0.323.

In this note only small departures from Debye behavior have been considered; the case for a larger spread of relaxation times having been dealt with previously.[5-8]

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Line-Width Effects in the Electron Spin Resonance Spectrum of the 2,5-Dimethylhydroquinone Cation Radical

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As part of a study on the temperature dependence of the coupling constants of several cation radicals,[2a] the

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(2) (a) J. R. Bolton and P. D. Sullivan, unpublished results; (b) P. D. Sullivan and J. R. Bolton, *J. Amer. Chem. Soc.*, 90, 5366, (1968).
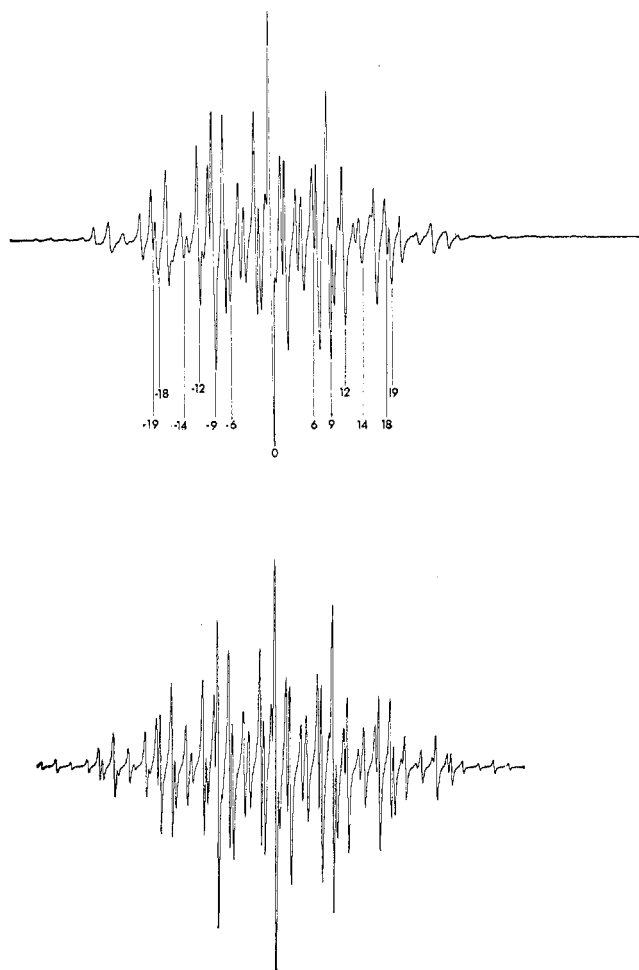
Figure 1. The esr spectrum (top) of the cation radical of 2,5-dimethylhydroquinone at 25°. Line numbers are indicated in the figure. A simulated spectrum (bottom) with a constant line width of 100 mG.

esr spectrum of the 2,5-dimethylhydroquinone cation radical was examined over the temperature range −70 to +25°. At the lowest temperatures line-width effects due to anisotropic dipolar and g tensor interactions were observed.[2b] At the higher temperatures (25°, see Figure 1), the spectrum is totally symmetric about the center line, however, a comparison of the experimental amplitudes with those predicted show certain deviations (Table I and Figure 1). First the lines arising from the methyl protons only (i.e., $\check{M}_{CH_3}$ = ±3, ±2, ±1, 0, $\check{M}_{CH}$ = $\check{M}_{OH}$ = 0) broaden symmetrically away from the center with an approximately quadratic dependence on $\check{M}_{CH_3}$ (cf. line no's ±18, ±9, 0 in Table I). Second, lines with $\check{M}_{CH_3}$ and $\check{M}_{CH}$ of the same sign have greater amplitudes than those with quantum numbers of opposite sign (compare line no's, ±12 with ±6, and ±19 with ±14 in Table I and Figure 1). These results cannot be explained in terms of the anisotropic dipolar and g tensor interactions.[3] It can be shown by observing the changes in line amplitudes with temperature that these effects

Table I: Experimental and Calculated Amplitudes for the 2,5-Dimethylhydroquinone Cation Radical at 25°

Line no.	$\check{M}_{CH_3}$[a]	$\check{M}_{CH}$	$\check{M}_{OH}$	Degeneracy, calcd	Exptl relative widths,[b] 25°	Calcd relative widths[c]
+19	1	1	1	15	1.18	
+18	2	0	0	24	1.53	1.56
+16	1	0	1	30	1.19	
+14	1	−1	1	15	1.35	
+12	1	1	0	30	1.01	0.98
+9	1	0	0	60	1.11	1.14
+7	0	0	1	40	1.08	
+6	1	−1	0	30	1.42	1.44
+3	0	1	0	40	1.06	1.09
+2	1	0	−1	30	1.15	
0	0	0	0	80	1.00	1.00
−2	−1	0	+1	30	1.24	
−3	0	−1	0	40	1.03	1.09
−6	−1	+1	0	30	1.45	1.44
−7	0	0	−1	40	1.04	
−9	−1	0	0	60	1.13	1.14
−12	−1	−1	0	30	1.00	0.98
−14	−1	+1	−1	15	1.35	
−16	−1	0	−1	30	1.18	
−18	−2	0	0	24	1.55	1.56
−19	−1	−1	−1	15	1.15	

[a] See B. L. Barton and G. K. Fraenkel, *J. Chem. Phys.*, **41**, 695 (1964) for explanation of spectral index numbers. [b] Normalized to the center line, which is assumed to have a line width independent of the modulating mechanisms. Relative widths were determined from relative amplitudes after corrections for overlap. [c] Calculated from eq (1) with $A = 0.14$, $B = 0.09$, $C = -0.21$.

are negligible at 25°, except perhaps for a small effect on lines associated with the hydroxyl protons. Most simply, the results may be explained in terms of "in-phase modulations."[3] Thus if the two methyl groups have splitting constants which are instantaneously equivalent at all times but which are modulated between two limiting values, then the line widths would be proportional to $(\check{M}_{CH_3})$.[2] Also if we assume that there is an "in-phase modulation" of the CH protons but that this modulation is "out of phase" with that of the methyl-group modulations (with respect to the absolute values of the methyl and CH proton splitting constants), the second effect is explained. That is, as the absolute value of the methyl group splitting constant increases the absolute value of the CH proton splitting constant decreases, thus making $|a_{CH_3}{}^H| + |a_{CH}{}^H| \cong$ constant. In relaxation matrix theory terms, the line widths would be expressed by[3]

$$T_2{}^{-1}(\check{M}_{CH_3},\check{M}_{CH}) = A(\check{M}_{CH_3})^2 + B(\check{M}_{CH})^2 +$$

$$C\check{M}_{CH_3}\cdot\check{M}_{CH} + T_{2,0}{}^{-1} \quad (1)$$

where, A, B, and C are spectral densities.[3] A least-squares fit of the experimental data for lines with $\check{M}_{OH}$

(3) G. K. Fraenkel, *J. Phys. Chem.*, **71**, 139 (1967).

= 0, gives values for A, B, and C of 0.14 ± 0.01, 0.09 ± 0.03 and −0.21 ± 0.02 respectively (see also Table I).

The physical explanation of this phenomenon is not straightforward. It is known that hydroxyl groups in hydroquinone and duroquinol are "fixed" at low temtemperatures and are "rotating" at high temperatures. It is presumed that the existence of only one distinct spectrum for 2,5-dimethylhydroquinone at low temperatures is due to the presence of the *trans* form only.[2] We may therefore speculate that it is the rotation of the hydroxyl groups at higher temperatures which cause the observed effects. The interesting point is, however, that for an "in-phase modulation" of the methyl and ring protons, both hydroxyl groups are required to rotate in an *instantaneously equivalent manner*. One wonders if, in fact, this may be a manifestation of a "cog-wheel" effect between the hydroxyl and methyl groups. Alternatively it may be that a more complex motion may also contribute to the observed line-width variations.

It is appropriate to mention that an apparently similar effect has been observed for the cation radical of 1,4-dideuteroxy, 2,3-dimethylnaphthalene at *low* temperatures, although in this case, due to the complexity of the spectrum it is more difficult to analyze in detail. It should also be noted that it has not been possible to study the cation radical of 2,3-dimethylhydroquinone at high temperatures due to the instability of this radical.

Steric Effects in the Decomposition
of Halogenated Nitrobenzene
Anion Radicals

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Numerous nitroaromatic compounds have now been successfully reduced to their corresponding anions in aprotic solvents.[1] Although many of these radicals are sufficiently stable to permit recording of their electron spin resonance (esr) spectra, a group of halogen-substituted nitroaromatic radicals constitutes a notable exception. For example, the reduction of the three isomers of iodonitrobenzene in dimethylform-

amide[2] and acetonitrile[3] gives not the corresponding iodonitrobenzene anion radicals, but rather the anion radical of nitrobenzene. Evidence was presented recently which indicates that this electrochemical reduction is an over-all two-electron process.[4] The initial one-electron reduction of an iodonitrobenzene was shown to give its anion radical which loses iodide ion to yield the corresponding nitrophenyl radical (eq 1)

$$IC_6H_4NO_2 + e \rightleftharpoons [IC_6H_4NO_2]^- \rightleftharpoons$$
$$[C_6H_4NO_2]\cdot + I^- \quad (1)$$
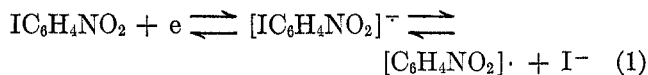
Nitrobenzene is then formed by the abstraction of a hydrogen atom from either the solvent or the supporting electrolyte by the nitrophenyl radical

$$[C_6H_4NO_2]\cdot + SH \longrightarrow C_6H_5NO_2 + S\cdot \quad (2)$$
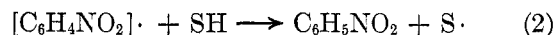
The subsequent one-electron reduction of nitrobenzene to its anion radical at slightly more negative potential completes the over-all two-electron process

$$C_6H_5NO_2 + e \rightleftharpoons C_6H_5NO_2^- \quad (3)$$

It was observed during the course of the earlier work that the *o*-iodo- and *o*-bromonitrobenzene anion radicals decomposed considerably more rapidly than their *meta* and *para* isomers. Those observations suggested that further studies should be made into the relationship between stability of the halogenated nitrobenzene anion radical and steric interactions. The results of such a study are reported herein.

Table I summarizes the electrochemical data for the compounds studied. Data for nonhalogenated nitrobenzenes are included for comparison. As the results for compounds 3, 4, 6, and 9–11 indicate, placement of a methyl group adjacent to the nitro group decreases the stability of the anion radical as evidenced by the enhanced rate of halide loss from a nonsterically affected position. For example, substitution of a methyl group in the 6 position of 3-iodonitrobenzene causes a 30-fold increase in the rate of iodide loss in the anion radical. Substitution of two methyl groups adjacent to the nitro group in 4-iodonitrobenzene results in a 280-fold increase in the rate of iodide loss. As expected from carbon-halogen bond energies, loss of halide ion from the 4-halogeno-2,6-dimethylnitrobenzene anion radicals is more rapid for iodide than for bromide (compare compounds 9 and 10). Loss of chloride is not observed electrochemically from any of the anion radicals.

Twisting of the nitro group by alkyl substituents in nitrobenzene anion radicals has been shown to be

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