An electron resonance study of rotational isomerism in the naphthazarin semiquinone cation

by J. R. BOLTON, A. CARRINGTON and P. F. TODD
Department of Theoretical Chemistry, University of Cambridge

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The naphthazarin semiquinone cation in sulphuric acid exhibits an electron spin resonance spectrum which varies with the temperature. This variation is ascribed to rotational isomerization and the shape of the spectrum at different temperatures is reconstructed using a theory based on the Bloch equations. From the temperature dependence of the rate of isomerization, the potential barrier to rotation is estimated to be 4 kcals. The mechanism of isomerization probably involves the breaking of an intramolecular hydrogen bond.

1. INTRODUCTION

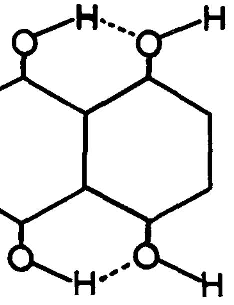
Several recent papers [1–4] have described the effects of rotational isomerism on the hyperfine structure in the electron resonance spectra of free radicals. In certain para disubstituted benzenes which can exhibit such isomerism the ring proton splittings are found to be quite sensitive to the orientation of the substituent groups. Consequently the shape of the electron resonance spectrum depends on the rate of isomerization and small changes in the rate can cause quite drastic alterations to the hyperfine pattern.

When the rate of isomerization is slow compared with the hyperfine frequency separations one expects to observe a superposition of the spectra of both cis and trans isomers. An example of this is the terephthaldehyde anion, studied by Maki [1]. In one isomer, probably the cis, the two ring proton splitting constants are 2·1 and 0·7 gauss; in the other isomer splittings of 1·2 and 1·6 gauss are observed. At room temperature the equilibrium concentrations of the two isomers are approximately equal.

If the isomerization is very rapid the observed hyperfine splitting due to a particular proton will be the average of its extreme values in the two isomers. In the dialdehyde mentioned above the four ring protons would give rise to a quintet of lines with spacing 1·4 gauss. However, when the rate of isomerization is comparable with the hyperfine frequency separation, interesting line width variations can occur and the shape of the spectrum can, in principle, be used to give kinetic information.

An example of the line width effects encountered is provided by the durosemiquinone cation in concentrated sulphuric acid [2]. At elevated temperatures (50°c) a well-resolved pattern is observed consisting of a multiplet of thirteen lines due to the twelve equivalent methyl protons, with an additional triplet splitting due to the two hydroxyl protons. When the temperature is lowered a marked alternation in the widths of the components of the methyl proton multiplet is observed. It was suggested that the methyl hyperfine splitting is sensitive to the orientation of the hydroxyl groups and that the resulting modulation of the isotropic hyperfine interaction was responsible for the line width alternation. A detailed theoretical study supports this hypothesis [3].

One would like to discover a system in which, by increasing the temperature, one could pass from slow to rapid isomerization, so that all the intermediate changes in the spectrum could be studied. In the case of the durosemiquinone cation it was not possible to decrease the rate sufficiently to obtain the extreme values of the methyl hyperfine constants. Without this information one cannot make a kinetic analysis of the system. However, in this paper we describe a more informative study of the naphthazarin semiquinone cation. This radical ion can exist in cis (I) and trans (II) conformations and the electron resonance spectrum is again markedly sensitive to temperature changes. Although here too we cannot study the complete temperature variation of the spectrum, we are able to obtain the extreme values of the proton hyperfine constants. Armed with this information we can reconstruct theoretically the shape of the spectrum at different temperatures, thus determining the temperature dependence of the rate of isomerization and hence the potential barrier to rotation.



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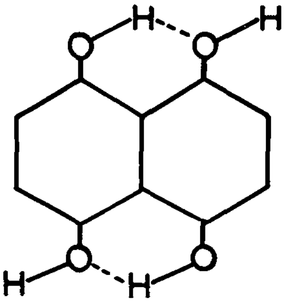


II

2. Analysis of the electron resonance spectra

The spectra were measured using a Varian 100 kc. E.P.R. spectrometer in conjunction with a Varian 6 in. magnet and the Varian variable temperature accessory.

Naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) was reduced with zinc dust in concentrated sulphuric acid and the electron resonance spectra obtained at different temperatures are shown in figure 1. At temperatures below 10°c the solution becomes extremely viscous and the spectra obtained were very poorly resolved and extremely asymmetric. Above 50°c the radical ion decomposes too rapidly to give a satisfactory spectrum.

In the absence of effects due to isomerism we would expect to observe a twenty-five line spectrum, arising from a quintet splitting due to the four equivalent ring protons, and a further quintet splitting from the four hydroxyl protons. We are unable to increase the rate of isomerization sufficiently to achieve these results, but nevertheless the 50°c spectrum can be interpreted in terms of two quintet splittings, the hyperfine constants being 2·3 and 1·2 gauss.

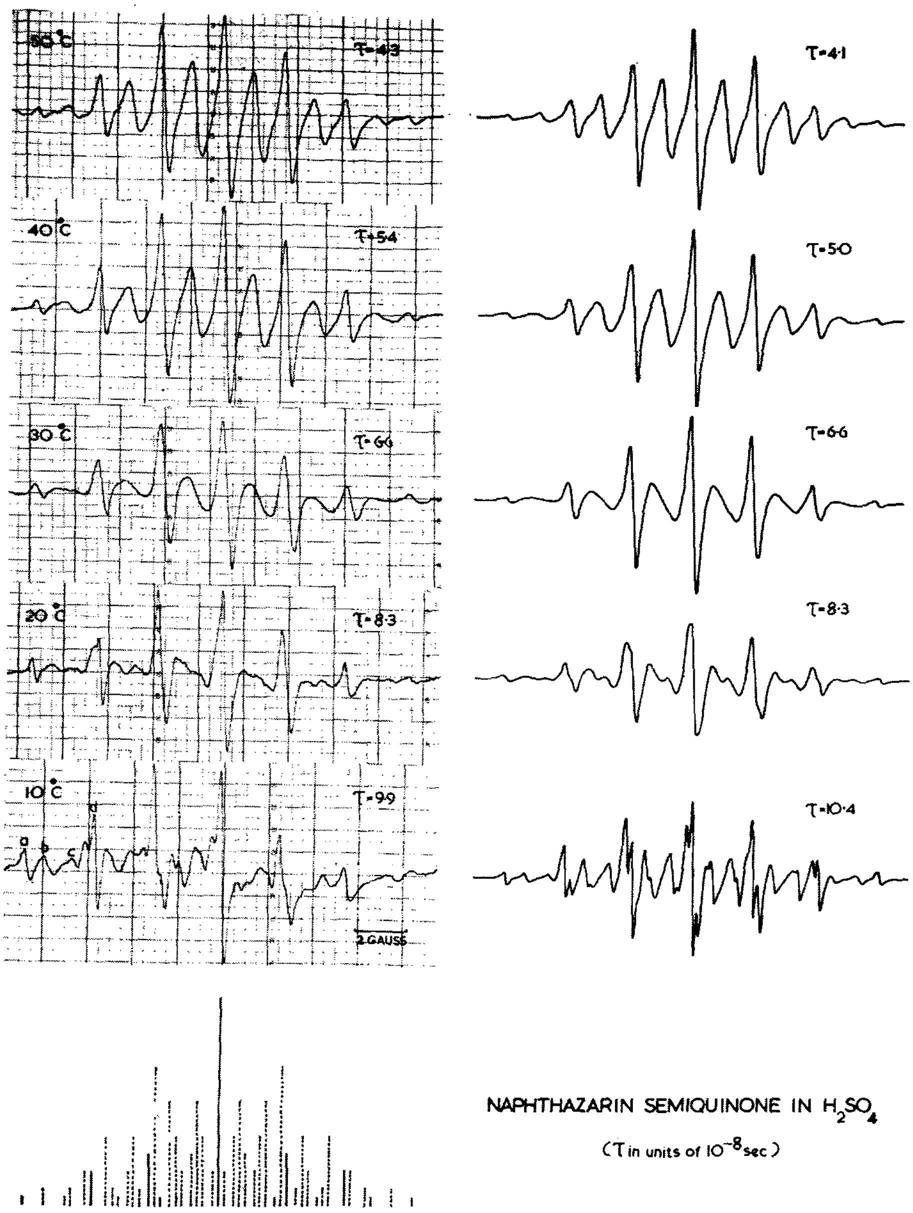


Figure 1. Electron spin resonance spectra of the naphthazarin semiquinone cation in concentrated sulphuric acid at different temperatures. The reconstructions shown on the right-hand side are derived from the theory outlined in § 3.

When the radical ion is prepared in concentrated dideuterosulphuric acid the hydroxyl protons are exchanged for deuterons; the electron resonance spectrum is shown in figure 2. It consists of five lines of spacing 2·38 gauss, with a further narrow splitting of each line into the expected nine components (spacing ~0·19 gauss) arising from interaction with four equivalent deuterons. Note

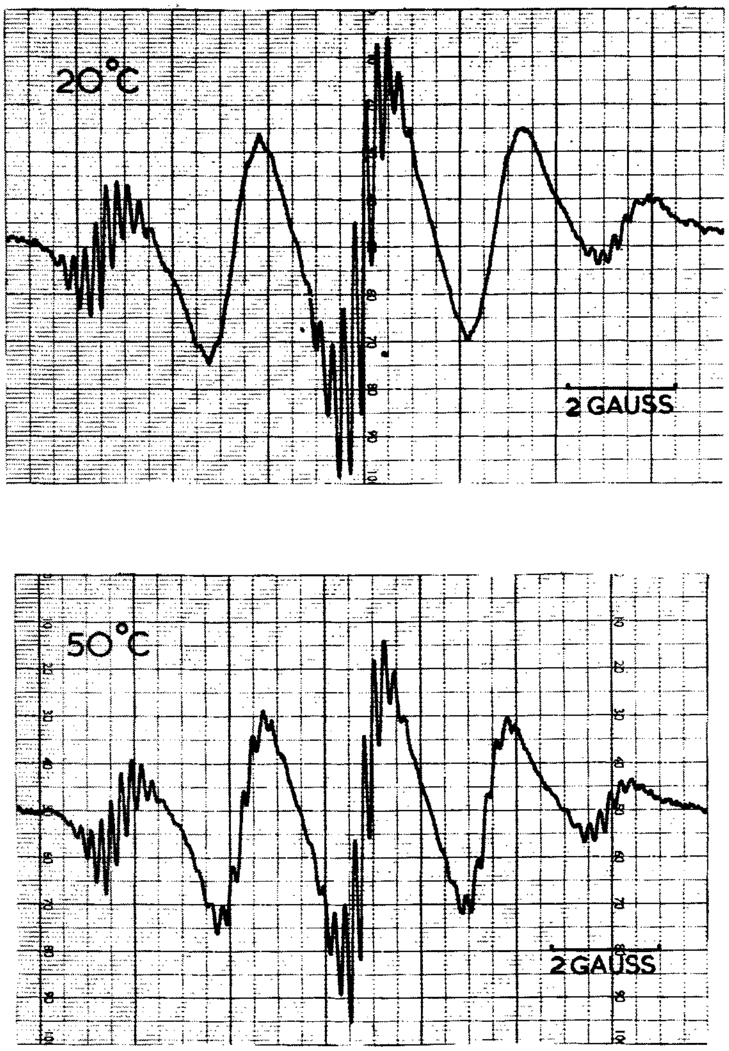


Figure 2. Electron spin resonance spectra of the naphthazarin semiquinone cation in concentrated dideuterosulphuric acid.

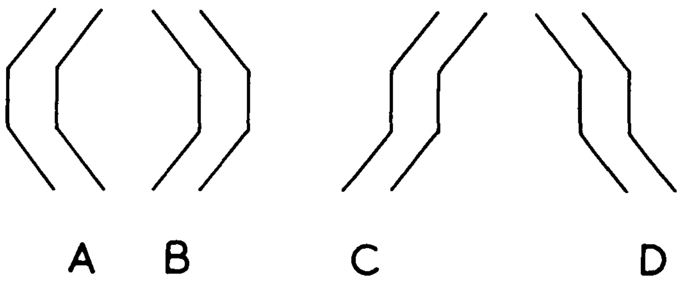
that the resolution of this extra structure on each of the five main lines alternates and is again temperature dependent. We shall return to this later. This spectrum confirms the proton splitting constants derived from the 50°c spectrum shown in figure 1; furthermore, it demonstrates that the 2·38 gauss splitting is due to the four ring protons. No exchange of ring protons for deuterons is apparent in the spectrum, even over a period of several days.

Before we can progress much further with the analysis we must briefly consider some physical aspects of the system. A particular hydroxyl proton can exist in one of two principal environments. It may be situated between two oxygen atoms and we will call this the 'bridge' position; alternatively, it may be associated with just one oxygen atom and this we will call the 'terminal' position. We will suppose that the splitting constants for bridge and terminal protons differ, but that these two constants do not vary from one isomer to the other. In this case each isomer will show the same electron resonance spectrum, determined by the same three splitting constants, and can be analysed in terms of one quintet splitting and two triplet splittings. The quintet splitting has already been obtained and the triplet splittings can be derived from the 10°C spectrum. We have labelled the outside four lines by the letters *a*, *b*, *c* and *d*. By a simple process of reconstruction one can see that the separations *b–d* and *c–d* give the two required hydroxyl proton constants, the sum of which should be equal to the *a–d* separation. The two constants thus obtained are 0·7 and 1·8 gauss, and the *a–d* separation is indeed 2·5 gauss. Furthermore the hydroxyl proton splitting constant derived from the 50°C spectrum is 1·2 gauss, very close to the average of the bridge and terminal constants, as it should be. Final confirmation is provided by the magnitude of the deuteron splitting, obtained from the spectra shown in figure 2.

Beneath the 10°C spectrum in figure 1 we show a reconstruction based on the above splitting constants. The continuous lines represent hyperfine components whose position and height are independent of the rate of isomerization. The dotted lines correspond to components which vary with the rate. Obviously the correspondence between the experimental 10°C spectrum and the theoretical spectrum is not close since the latter ideally refers to a solution in which the isomerization is too slow to affect the hyperfine pattern. However we can now test the physical model in more detail for, knowing all the hyperfine constants, we can reconstruct the shape of the spectrum for different rates of isomerization.

3. THEORY OF THE LINE SHAPES

The naphthazarin semiquinone cation can exist in any one of four conformations which we may represent symbolically as follows:



A and B represent cis conformations whilst C and D are trans; A and C in fact correspond to the structural formulae I and II shown in § 1. Hence, for a given fixed arrangement of proton nuclear spins the unpaired electron can find itself in four different environments in turn and it will have a different resonance frequency in each, due to different interactions with the protons. Our problem is to calculate the electron resonance absorption line shape for different rates of change in conformation. With certain restrictions this can be readily accomplished and it is desirable at this stage to state what these restrictions are, some of which have already been mentioned.

1. We assume that the four ring protons are always equivalent and have the same hyperfine interaction with the electron in all four conformations.
2. We assume that any particular hydroxyl proton can occupy either a bridge or a terminal position and that it has different hyperfine interactions in these positions. We further assume that the bridge and terminal proton hyperfine interactions do not vary in magnitude from one conformation to another.
3. We assume that conformation changes occur without change of proton spin orientations.
4. We assume that each conformation has the same average lifetime τ.
5. We do not consider the conformation changes $A \rightleftharpoons B$ and $C \rightleftharpoons D$ which involve simultaneous reorientation of all four hydroxyl groups.

We will return to these approximations later but for the moment they provide a satisfactory basis for line shape calculations.

The average magnetization of the electron in a particular environment can be calculated using the Bloch equations [5] for the precession of the electron spin magnetic moment about the direction of an applied steady magnetic field. The complications due to exchange between four environments have been examined by one of us [3] and the following expression for the net average electron magnetization $\langle G \rangle$ was derived,

$$\langle G \rangle = -i\omega_1 M_0 \tau \left\{ \frac{(\gamma_A+\gamma_B)(\gamma_C+\gamma_D+2\gamma_C\gamma_D)+(\gamma_C+\gamma_D)(\gamma_A+\gamma_B+2\gamma_A\gamma_B)}{4\gamma_A\gamma_B\gamma_C\gamma_D-(\gamma_A+\gamma_B)(\gamma_C+\gamma_D)} \right\}.$$

In this expression $\omega_1 M_0$ is a constant intensity factor and the subscripts A, B, C, D refer to the four conformations above. The γ's are defined in the following way. γ_A for example, is given by the expression

$$\gamma_A = 1 + \eta_A \tau, \quad \text{where} \quad \eta_A = T_2^{-1} - i(\omega_0 - \omega + \omega_A).$$

ω_0 is the natural precession frequency of the electron in the absence of hyperfine interactions and ω_A is the shift in resonance frequency due to interaction with the protons in conformation A. T_2^{-1} is the line width in the absence of conformation changes.

$\langle G \rangle$ represents the complex sum of the electron magnetizations in-phase and out-of-phase with the applied microwave field and therefore the imaginary part of $\langle G \rangle$ gives an equation for the absorption of energy from the radiation field, as a function of its frequency ω. We consider first the hydroxyl protons and calculate the appropriate values of ω_A, ω_B, ω_C and ω_D for each proton spin arrangement in turn, using the hyperfine constants derived in §2. The first derivative of the imaginary part of $\langle G \rangle$ with respect to ω is then calculated for each proton spin arrangement and the overall hyperfine pattern arising from interactions with the hydroxyl protons synthesized for varying values of τ. The further quintet splitting due to the ring protons is added finally, all the numerical calculations being carried out using the EDSAC II electronic computer.

In figure 1 we show the theoretical spectra which most nearly correspond to the experimental patterns. The correspondence is, in fact, extremely satisfactory for the 50°c and 40°c spectra, and it is as close as we can expect for the low temperature spectra, where there are several additional complications. Two of these deserve special mention. Firstly, as the solution becomes more viscous the relaxation effects due to g and hyperfine anisotropy become important, causing marked asymmetry in the widths of the hyperfine components. Secondly, it is clear from the spectra shown in figure 2 that there is actually a small line width alternation in the multiplet components arising from the four ring protons. This is the reason for the alternating resolution of the deuterium hyperfine structure, and it shows that the ring proton splitting is slightly sensitive to the orientation of the hydroxyl groups. This observation is not unexpected in view of previous results for the durosemiquinone cation and the terephthaldehyde anion [1, 2].

It is interesting to note that the deuterium structure shown in figure 2 is completely resolved when the secondary ring proton effect allows it to be. This implies that the rates of isomerization in sulphuric acid and dideuterosulphuric acid at the same temperature are comparable. Consequently when the hydroxyl protons are exchanged for deuterons we pass from a situation in which the rate of isomerization is comparable with the hyperfine frequency separation, to one in which it is much more rapid. We therefore observe the time-averaged deuterium splitting.

From a comparison of the experimental and theoretical spectra in figure 1 we are able to assign a value of τ to each experimental spectrum and hence to carry out the kinetic analysis described in the following section.

4. KINETICS AND MECHANISM OF ISOMERIZATION

Following the treatment of similar line broadening phenomena in nuclear magnetic resonance [6] we assume that the temperature dependence of the rate of isomerization is given by the expression

$$k = k_0 \exp(-E_A/RT),$$

where k is the rate constant $(1/\tau)$, k_0 is the frequency factor and E_A is the potential barrier to rotation. Since

$$\log_{10} k = \log_{10} k_0 - E_A/2{\cdot}303RT,$$

a plot of $\log_{10}(1/\tau)$ against $1/T$ should be a straight line. This plot is shown in figure 3 and from the slope we obtain an activation energy of 4 ± 1 kcals. The frequency factor k_0 is $10^{10} \pm 1\ \text{sec}^{-1}$, which is close to the normal range observed for unimolecular processes.

The most probable mechanism for the isomerization involves the breaking of one O–H . . . O hydrogen bond, so that the measured activation energy should correspond to the hydrogen bond energy. Hydrogen bonds of this type have estimated energies in the range 3 to 7 kcals so that our value is entirely reasonable. The arrangement of the oxygen atoms in naphthazarin certainly provides a favourable situation for the formation of a strong hydrogen bond, since they are only 2·4 Å apart. It is difficult to estimate the actual length of the hydrogen bond, however, for one cannot be sure of the O–H–O bond angle.

An alternative mechanism for the isomerization would involve the attachment of a proton from the solvent to an oxygen atom, with simultaneous ejection of the terminal proton on the adjacent oxygen. The experiments in dideuterosulphuric acid show clearly that exchange of both bridge and terminal protons does occur, but they also indicate that the exchange is much slower than the rate of isomerization. Were it not so, we would not obtain resolved hyperfine structure from the hydroxyl protons since there would be no proton spin conservation during conformation changes.

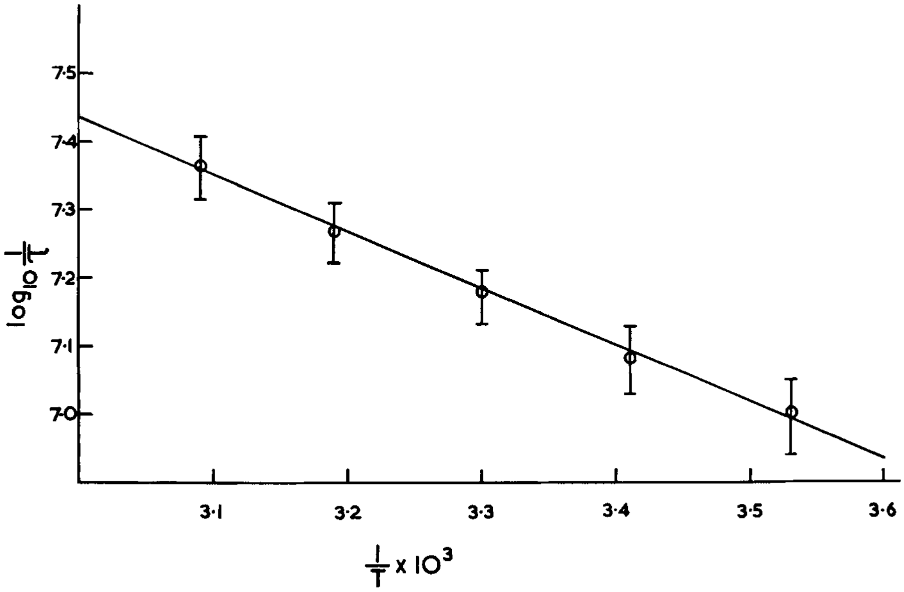


Figure 3. Plot of $\log_{10}(1/\tau)$ against $1/T$.

It has been pointed out to us [7] that the physical changes in the spectra of both the durosemiquinone and naphthazarin semiquinone cations could be interpreted in terms of two conformations (trans, say) rather than four. Thus, for example, the present results could be treated by considering only conformations C and D. For various reasons we do not favour this interpretation in the case of naphthazarin. Conformation changes between C and D alone would involve the breaking of two hydrogen bonds and would therefore be energetically unfavourable. This difficulty might be overcome by supposing that conformations A and B are involved, but that their lifetimes are very much shorter than those of C and D. This now becomes a more complicated interpretation than the one presented in this paper and there seems to be no reason for adopting it. The situation is less clear cut in the case of the durosemiquinone cation where intramolecular hydrogen bonds are not involved. If one supposes that the motions of the hydroxyl groups are linked because of steric interactions with the methyl groups then it is certainly true that the trans conformations are favoured. The experimental evidence does not enable one to decide the matter.

The observation that the bridge and terminal hydroxyl protons have quite different hyperfine constants is interesting, and should shed some light on the bonding differences. However, we have not yet resolved the ambiguity in assignment of the two splittings. Until this is done, and more information on similar systems has been obtained, we do not propose to speculate.

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REFERENCES

[1] MAKI, A. H., 1961, *J. chem. Phys.*, **35**, 761.
[2] BOLTON, J. R., and CARRINGTON, A., 1962, *Mol. Phys.*, **5**, 161.
[3] CARRINGTON, A., 1962, *Mol. Phys.*, **5**, 425.
[4] FREED, J. H., and FRAENKEL, G. K., 1962, *J. chem. Phys.*, **37**, 1156.
[5] BLOCH, F., 1946, *Phys. Rev.*, **70**, 460.
[6] GUTOWSKY, H. S., and HOLM, C. H., 1956, *J. chem. Phys.*, **25**, 1228.
[7] FRAENKEL, G. K. (private communication).