# Long-range Electron Spin Resonance Coupling Constants in Radical Adducts of Maleic Acid

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Received 11th March, 1974

The e.s.r. spectra of a number of radical adducts of maleic acid have been observed and hyperfine structure arising from  $\gamma$ -, from  $\delta$ - and from  $\varepsilon$ -coupling has been revealed. This provides a positive identification of the radicals involved. The origin of the long-range coupling constants is discussed in terms of simple molecular orbital theory and direct magnetic interaction. The difference between spectra observed in acidic and in alkaline conditions, is interpreted in terms of structural changes.

Aliphatic or aryl radicals may be trapped by maleic acid,<sup>1, 2</sup> and the short-lived adducts so-formed detected by means of e.s.r. spectroscopy. The sequence of reactions leading to the observed radicals have generally been as follows:

$$Ti^{III} + H_2O_2 \rightarrow Ti^{IV} + OH^- + OH$$
 (1)

$$\mathbf{R}\mathbf{H} + \mathbf{O}\mathbf{H} \rightarrow \mathbf{R} \mathbf{O} + \mathbf{H}_2 \mathbf{O} \tag{2}$$

(3)

 $\begin{array}{ccc} CHCO_2H & HOCHCO_2H \\ \parallel & + \cdot OH \rightarrow & \mid \\ CHCO_2H & \cdot CHCO_2H \end{array}$ 

| RCHCO <sub>2</sub> H |  |
|----------------------|--|
| <b>\</b> •→          | (4)  |
| •CHCO <sub>2</sub> H |  |
| (II)                 |  |
|                      | $ \begin{array}{c} \text{RCHCO}_2 H \\ \text{CHCO}_2 H \\ \text{CHCO}_2 H \\ (\text{II}) \end{array} $ |

(T)

Phenyl adducts have been generated from the corresponding diazonium salts by reduction.<sup>2</sup> In alkaline or neutral solution the reducing species has been  $Ti^{III}$  and in acidic solution the reduction has been achieved by radicals R• formed in reaction (2) where RH is a primary or secondary alcohol or formic acid.

$$PhN_{2}^{+} + [Ti^{III}(edta)] \rightarrow [Ti^{IV}(edta)] + N_{2} + Ph.$$
(5)

It is easy to arrange the conditions so that the consecutive reactions (2) and (4) dominate, and the e.s.r. spectra of the resulting radicals of type (II) consist of four lines. The two coupling constants obtained from each spectrum characterise the adducts but do not positively identify them. These splittings do not, for example, tell us whether or not the species, which has added to the double bond, is the same as that which would have been observed in the absence of maleic acid from the solutions. We now report successful attempts to improve the resolution of the four line spectra, so that in most cases further small splittings appear, which confirm the assumed nature of the adduct radicals.

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In the most straightforward cases each of the four lines was split further into a multiplet as appropriate for the number of  $\gamma$ -protons in the adduct. Thus the e.s.r. spectrum of the methyl radical adduct had a small quartet (1:3:3:1) splitting whereas there were small doublet (1:1) splittings when either dioxan or ethylenediaminetetra-acetic acid were the "primary" substrates in the Ti<sup>III</sup>/H<sub>2</sub>O<sub>2</sub> system (see table 1). In neutral or in alkaline solution the spectrum of the hydroxyl radical adduct itself has a small doublet splitting.



FIG. 1.—E.s.r. spectrum of maleic acid adducts with methyl and hydroxyl (asterisked) radicals.

The spectra obtained from the adducts of radicals of type RR'COH were not so straightforward, since they were less well resolved in neutral or in alkaline solution, but appeared to have small couplings corresponding to the appropriate number of  $\gamma$ and  $\delta$ -protons in acid. These "extra " splittings confirm the nature of these radicals. No additional splitting of the four lines was observed in the spectrum ascribed to the phenyl radical adduct, so 2-fluorophenyl was used in the hope that the fluorine splitting might be large enough to observe. In fact a fluorine splitting was observed and it was larger even than that expected from previous studies on aryl semiquinones.<sup>3</sup>

# EXPERIMENTAL

The conditions in our experiments were similar to those of Beckwith and Norman<sup>2</sup> except that the flow system was driven by a peristaltic pump which gave a fine control of the flow rate (*ca*. 10 cm<sup>3</sup> s<sup>-1</sup>). The concentrations used were approximately 0.05 mol dm<sup>-3</sup> for Ti<sup>III</sup> and peroxide, 0.25 mol dm<sup>-3</sup> for the diazonium salts and for the substrates about 0.5-1.0 mol dm<sup>-3</sup>. The acidic solutions contained 0.5 mol dm<sup>-3</sup> sulphuric acid and the "alkaline" solutions were at pH 7-9.

## **RESULTS AND DISCUSSION**

All of the results are summarised in table 1.

### THE ORIGIN OF THE LONG-RANGE COUPLING CONSTANTS

#### (i) $\delta$ -splittings

The patterns of the small coupling constants establish convincingly the structures of the adduct radicals. Relatively large  $\gamma$ -coupling constants have been observed many times, e.g. in radicals from t-butyl alcohol, ether, dioxan etc., <sup>1, 4</sup> and it seems likely that they arise from a combination of hyperconjugation and spin polarisation.<sup>5</sup> The observation of  $\delta$ -splittings is less common, however, and such splitting generally

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occurs only in rigid systems such as the adamantyl radicals.<sup>6, 7</sup> It is not difficult to see how coupling through so many  $\sigma$ -bonds arises, since the situation is essentially the same as that leading to large *meta*-coupling constants when aryl rings are twisted out of the nodal plane of a single occupied molecular orbital,<sup>3</sup> e.g. as in the rubrene radical ions.<sup>8</sup> The transmission of spin density through  $\sigma$ -bonded systems has already been explained in simple MO terms,<sup>4, 9, 10</sup> but in view of the complexity of the present problems it is rewarding to examine them in some detail.

TABLE 1.—Coupling constants (in  $10^{-4}$  T) of radicals RCH(CO<sub>2</sub>H)ĊHCO<sub>2</sub>H. Number of protons in brackets

|   | acid            |                |                    | alkali          |                |                    |
|---|-----------------|----------------|--------------------|-----------------|----------------|--------------------|
| R   | $a_{\alpha}(1)$ | $a_{\beta}(1)$ | further splittings | $a_{\alpha}(1)$ | $a_{\beta}(1)$ | further splittings |
| •OH   | 12.7            | 20.7           |                    | 15.3            | 20.2           | 0.2(1)             |
| •(edta—H)†  |                 |                | _                  | 7.5             | 19.8           | 0.9(1) 0.2(N)      |
| •CH <sub>2</sub> OH                                   | 13.7            | 20.8           | $0.6(1) \ 0.3(1)$  | 9.8             | 20.2           |                    |
| СН₃ĊНОН   | 9.5             | 20.6           | 0.4(4)             | 7.5             | 20.0           | 0.3(3)             |
| (CH <sub>3</sub> ) <sub>2</sub> ĊOH                   | 10.5            | 20.5           | 0.3(6)             | 5.1             | 20.0           | 0.3*               |
| (CH <sub>3</sub> ) <sub>2</sub> COH•CH <sub>2</sub> • | 9.0             | 20.3           | *                  | 7.1             | 19.9           | $0.6(1) \ 0.3(7)$  |
| CH <sub>3</sub> CHOEt                                 | 11.5            | 20.4           | 0.3*               | 6.7             | 20.0           | 0.3(3)             |
| [CH <sub>2</sub> ] <sub>2</sub>                       |                 |                |                    |                 |                |                    |
| Ó O   | 11.2            | 21.0           | 0.4(1)             | 8.0             | 20.3           | 0.3*               |
| CH2—ĊH  |                 |                |                    |                 |                |                    |
| •CO <sub>2</sub> H                                    | 15.2            | 20.9           |                    | 8.4             | 20.0           |                    |
| •CH <sub>3</sub>                                      | 13.5            | 20.8           | 0.6(3)             | 10.3            | 20.3           | 0.7(3)             |
| C <sub>6</sub> H <sub>5</sub> .                       | 14.6            | 20.9           |                    | 10.7            | 20.4           |                    |
| o-C <sub>6</sub> H <sub>4</sub> F•                    | 10.9            | 20.3           | 1.6(F)             |                 |                |                    |

\* Denotes incomplete resolution.

† Most probably a proton  $\alpha$  with respect to one of the carboxyl groups is abstracted.



 $c_1 = 0; \ c_2 = c_{2'} = -\gamma'_{\pi} \cos \theta_1 c_0; \ c_5 = -\gamma c_2; \ c_3 = (\gamma_{\pi} \cos \theta_2 + \gamma^2) c_2$ 

FIG. 2.—Diagram showing orbitals and interactions mainly responsible for the  $\sigma$ -spin delocalisation with coefficients of non-bonding orbital. Values of the non-zero parameters are

 $\alpha_{\rm C} = \alpha_{\rm H}, \gamma_{\pi} \approx \gamma'_{\pi} \approx \frac{1}{4}, \gamma \approx \frac{1}{4}\sqrt{3}$ 

 $\theta_1$  = dihedral angle of orbital 2 about  $C_{\alpha}$ — $C_{\beta}$  bond with respect to axis of orbital 0.  $\theta_2$  = dihedral angle about  $C_{\gamma}$ — $C_{\delta}$  bond.

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Using the MO parameters given in fig. 2, the average coupling constant of the  $\delta$ -protons, assuming free rotation about the C<sub> $\gamma$ </sub>—C<sub> $\delta$ </sub> bond is given approximately by:

$$a_{\delta} = \frac{1}{2} \gamma_{\pi}^2 (\gamma' \cos \theta_1)^2 \, 508 Z_{\text{eff}}^3 \times 10^{-4} \, \text{tesla} \tag{a}$$

where we take the hyperfine splitting due to the nucleus in a free hydrogen atom to be 50.8 mT and  $Z_{eff}$  is the effective atomic number for the hydrogen 1s orbital in a molecule. There are several ways of obtaining an order of magnitude for  $a_{\delta}$  from this. However, we shall take values of  $\gamma_{\pi}$  and  $\gamma'_{\pi}$  which have been shown to account for the coupling constants in the vinyl radical and also for the n.m.r. coupling constants in butadiene,<sup>11</sup> i.e.  $\gamma_{\pi} \approx \gamma'_{\pi} \approx \frac{1}{4}$  so that eqn (a) becomes :

$$a_{\delta} \approx \cos^2 \theta_1 Z_{\text{eff}}^2.$$
 (a')

If  $\cos^2 \theta_1$  is about 0.5 then for  $Z_{\text{eff}} = 1.0$ ,  $a_{\delta} \approx 0.5 \times 10^{-4}$  T.

This is of the correct order of magnitude and is close to the limits of resolution of our spectrometer under conditions of flow. If necessary,  $a_{\delta}$  can be quickly estimated for any dihedral angle using formula (a'). We can even go so far as to deduce the conformation about the  $C_{\alpha}$ — $C_{\beta}$  bond. The  $\delta$  coupling constants observed are of the order of 0.03 mT which corresponds to a dihedral angle of about 60°. Similarly the  $\beta$  coupling of about 1 mT (averaged over the different adducts) corresponds to a dihedral angle of about 60°. The resulting conformation is given in fig. 3.



FIG. 3.—One of the two conformations predicted for the (CH<sub>3</sub>)<sub>2</sub>COH adduct.



FIG. 4.—Diagram showing nearest approach of an  $\varepsilon$  proton to the  $\alpha$ -carbon atom in adduct  $\dot{C}HCO_2H CH(CO_2H)CH_2C(OH)(CH_3)_2$ .

Point X is nearest approach of a  $\delta$  proton. Adjacent C—C bonds are all taken to be 1.54 Å.

### (ii) *e*-coupling constants

The splittings from protons attached to  $\alpha$ -, to  $\beta$ -, to  $\gamma$ - and to  $\delta$ -carbon atoms can be explained in terms of transmission of spin density through bonds. The mechanisms involved may be separated approximately into two, i.e., (a) hyperconjugation and (b) spin polarisation. Appreciable splittings from  $\varepsilon$ -protons have already been observed <sup>12</sup> and they have been ascribed to "through-space" interactions. This term

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has not yet been clearly defined and in many cases where it has been invoked, an extended theory of hyperconjugation of the type given above for  $\delta$ -splittings can account for the observations. Also, because of the way spin densities tend to be transmitted to alternate orbitals, direct through-space interaction of a hydrogen orbital with the orbital containing the odd electron would result in spin density appearing not in the hydrogen orbital itself, in the first instance, but on the adjacent carbon atom.

In view of these thoughts we have investigated the possibility that  $\varepsilon$ -splittings arise not from spin density associated with the  $\varepsilon$ -hydrogen orbitals, but from a direct *magnetic* interaction between those protons and the cloud of spin density on the  $\alpha$ -carbon atom. The hypothetical situation which would give the maximum effect of this kind is shown in fig. 4.

The Slater-type orbital most commonly used for carbon 2p orbitals is :

$$\psi(2p_z) = (\frac{1}{4}\sqrt{2\pi})(Z/a_0)^{\frac{5}{2}}z \exp(-Zr/2a_0)$$

where the effective atomic number Z = 3.25 and  $a_0$  is the Bohr radius of the hydrogen atom.

The magnetic interaction of a proton with an electron in this carbon  $2p_z$  orbital is

$$(508/\pi a_0^3)[\psi(2p_z)]^2 = 2.06 \times 10^3 z^2 e^{-6.13r} mT$$

where distances are measured in Ångstroms.

For the proton in fig. 5 this becomes 10.2 mT. Now we would not expect that the proton could possibly get nearer to the  $\alpha$ -carbon atom than a distance somewhat greater than the C—H bond distance, so if we doubled the distance of closest approach the maximum direct coupling is reduced fifty times to 0.2 mT.

Allowing further free rotation of the methyl group and for other possibilities of bending or flapping in the molecule, the estimated  $\varepsilon$ -splittings are rather less than 0.05 mT. The main point here is that this direct magnetic interaction could be large enough to account for the observed splittings. The effect could be enhanced by steric repulsions of the  $\beta$ -carboxyl group.



The corresponding direct interaction with one of the  $\delta$ -protons has a maximum value of 0.05 mT. Allowing again for free rotation of methyl groups and for bending within the molecule, this is negligible compared with the coupling due to extended hyperconjugation, and is moreover extremely sensitive to the exact position of the  $\delta$  carbon atom.

## ADDUCTS OF RADICALS DERIVED FROM ALCOHOLS

The pattern of lines in the spectra from the adducts of maleic acid with radicals formed by  $\alpha$ -hydrogen abstraction from alcohols, were dependent on the pH of the

solutions. The maximum fine structure was observed in strongly acidic solutions and and in the case of the adduct formed from  $\cdot$ CH<sub>2</sub>OH, this fine structure unexpectedly showed two non-equivalent protons. A reasonable way of accounting for this, and for the apparent disappearance of some of the couplings when the solutions are made alkaline, is that there is some rigidity in the molecule, preventing free rotation and the corresponding equivalence of the two methylene protons of the CH<sub>2</sub>OH group. This rigidity could arise from hydrogen bonding between the hydroxyl group of CH<sub>2</sub>OH and the neighbouring carboxyl group (see fig. 5).

One might expect these structures to break down under alkaline conditions.

The results for simple addition of hydroxyl radicals indicate that the rate of exchange of the hydroxyl proton in the  $CH_2OH$  group is much faster in acidic solution than when conditions are more alkaline.

In conclusion it can be stated that the observed hyperfine splittings in the e.s.r. spectra of these adducts of maleic acid confirm their identities more completely than has previously been possible. The long-range  $\delta$ -coupling constants arise from extended hyperconjugation through the  $\sigma$ -bonds and  $\varepsilon$ -splittings from direct magnetic interactions. Both are observed because of favourable conformations.

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