An Electron Spin Resonance Study of the Photolysis of Tetrafluoro-*p*-benzoquinone

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The monoprotonated tetrafluoro-*p*-benzosemiquinone radical has been prepared from the parent quinone by photochemically induced hydrogen-atom abstraction in a variety of solvents. The radical dissociates readily in hydroxylic solvents and in some cases rapid proton-transfer equilibria were observed which gave time-averaged e.s.r. spectra.

Radicals derived from *p*-benzoquinone have been extensively investigated by e.s.r.; three different species may be distinguished, depending on the method of preparation and the experimental conditions. These are the radical anion,[1] the neutral monoprotonated radical,[2] and the diprotonated radical cation.[3,4] Rapid equilibria between these species have also been investigated and kinetic data have been derived from the pH dependence of the e.s.r. spectrum.[5,6] In contrast the corresponding fluorinated radicals have received little attention. The tetrafluoro-*p*-benzosemiquinone radical anion has been prepared by the oxidation of the corresponding hydroquinone [7,8] and shows the expected five-line hyperfine pattern with $a_{\mathrm{F}} = 4{\cdot}0$ G, but the protonated species are unknown. Recent investigations have shown that monoprotonated radicals may be generated photochemically by *in situ* irradiation of quinones in a variety of hydrogen atom-donating solvents.[2,9,10]

In this paper we report the results of similar investigations on tetrafluoro-*p*-benzoquinone. Interesting variations have been observed with changes in solvent which indicate that the fluorinated species readily dissociates under conditions in which the monoprotonated *p*-benzosemiquinone radical is stable.

EXPERIMENTAL

Solutions of tetrafluoro-*p*-benzoquinone (10^{-3}M) were irradiated in the multipurpose cavity of a Varian E3 spectrometer with an Osram ME/D 250 w high pressure mercury lamp. A quartz lens and water filter were used to focus the light and to prevent thermal effects.

The solvents were dried by a single distillation from calcium hydride except for the chloroform, which was first dried over concentrated sulphuric acid.[11]

Hyperfine couplings (Table) were measured relative to potassium peroxylaminedisulphonate [12] ($a_{\mathrm{N}} = 13{\cdot}091$ G) and are believed to be accurate to ±0·05 G.

U.v. spectra were measured on a Unicam SP 800 spectrophotometer.

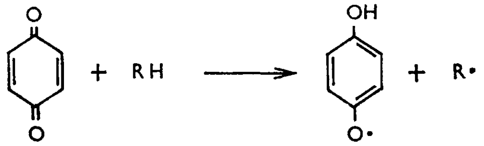
Tetrafluoro-*p*-benzoquinone was a gift from the Imperial Smelting Corporation, Avonmouth, and was purified by vacuum sublimation to resolve some anomalies observed with the original material.

Hyperfine coupling constants (G) for tetrafluoro-*p*-benzosemiquinone radicals in various solvents

Solvent	$\lvert a_{\mathrm{F}}{}^1\rvert$	$\lvert a_{\mathrm{F}}{}^2\rvert$	$\lvert a_{\mathrm{H}}\rvert$	$\lvert a_{\mathrm{F}}{}^1 + a_{\mathrm{F}}{}^2\rvert$
Chloroform	13·06	3·51	1·27	9·55
Methylene chloride...	12·64	3·20	1·17	9·44
Dioxan	12·89	3·51	1·11	9·38
Tetrahydrofuran ...	12·46	3·24	1·08	9·22
Acetone	12·35	3·17	1·07	9·18
Propan-2-ol...........	4·08	4·08		8·16
Ethanol	4·08	4·08		8·17
Methanol..............	4·02	4·02		8·04

DISCUSSION

Bridge and Porter [13] have found that in the flash photolysis of *p*-benzoquinone in solvents capable of donating hydrogen atoms, the *p*-benzosemiquinone radical is formed:



This reaction has also been investigated by means of e.s.r.[2,9,10] and we have employed the same technique to study tetrafluoro-*p*-benzoquinone.

The u.v. spectrum of tetrafluoro-*p*-benzoquinone exhibits two main peaks, the relative intensities of which are solvent-dependent. In chloroform the absorption maxima occur at *ca.* 3380 Å (ε *ca.* 200), and *ca.* 2580 Å (ε *ca.* 27,500); the latter peak consists of two overlapping maxima at 2640 Å and 2530 Å. The first peak corresponds to an n,π^* transition and the overlapping peaks to π,π^* transitions. In tetrahydrofuran (THF) two bands are seen, the relative intensities of which seem

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[11] D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, ' Purification of Laboratory Chemicals,' Pergamon Press, Oxford, 1966.

[12] R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, 1967, **47**, 2462.

[13] N. K. Bridge and G. Porter, *Proc. Roy. Soc.*, 1958, *A*, **244**, 259, 276.

to be concentration-dependent. At the concentrations employed in the e.s.r. experiments, the first (longest wavelength) band is very intense and is probably a charge-transfer band.

The mechanism of activation was investigated in a similar way to that employed by Brown and Williams.[14] The radiation corresponding to the shorter-wavelength band of tetrafluoro-*p*-benzoquinone in tetrahydrofuran was removed with an aqueous copper sulphate filter which cut off at *ca.* 3000 Å.[15] This hardly affected the intensity of the e.s.r. spectrum. When this filter was replaced by a saturated solution of sodium nitrite, which cuts out all radiation from *ca.* 4000 Å down to below 2000 Å,[15] the e.s.r. spectrum disappeared. It reappeared on removal of ths filter, which indicated that the longer-wavelength u.v. absorption band is responsible for the activation of tetrafluoro-*p*-benzoquinone in the reaction which produces the observed free radicals.

The e.s.r. spectrum observed during the continuous irradiation of tetrafluoro-*p*-benzoquinone in acetone is shown in Figure 1. It is attributed to the neutral radical (I), with couplings of 12·35 G from the fluorines *ortho* to the unprotonated oxygen and −3·17 G to those in the *meta*-positions. The signs are undetermined but have been assigned by analogy with similar radicals and on the basis of linewidth variations to be discussed later. In addition, there is a doublet splitting of ±1·07 G from the hydroxyl proton. Similar spectra were observed in other non-hydroxylic solvents. However, after sublimation of the quinone we were unable to detect radicals during irradiation until a trace of trifluoroacetic acid was added to the system, when spectra similar to that in Figure 1 were obtained. It would seem that our original success was due to the presence of a trace of an acidic impurity in the unsublimed material. Since the signals were always weak in these experiments, only a small reduction in radical concentration is required to explain the failure to observe radicals in the pure non-hydroxylic solvents.

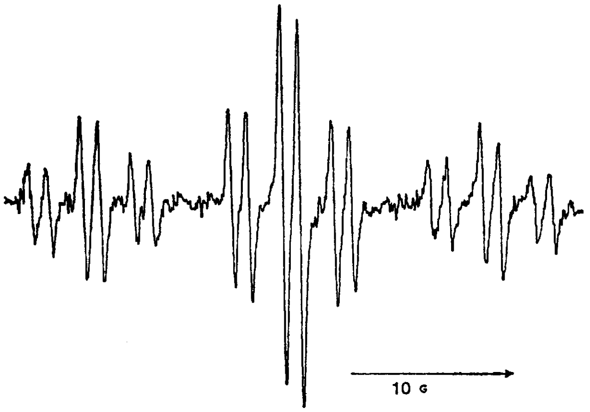


FIGURE 1 The e.s.r. spectrum of the monoprotonated tetrafluoro-*p*-benzosemiquinone radical in acetone

In contrast, for solutions in hydroxylic solvents such as methanol and ethanol, a five-line e.s.r. spectrum (Figure 2) was observed. The hyperfine splitting of 4·04 G is in accord with previous observations of the tetrafluoro-*p*-benzosemiquinone radical anion.[7,8]

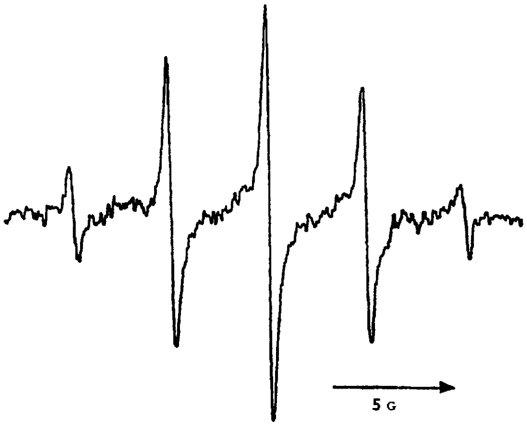
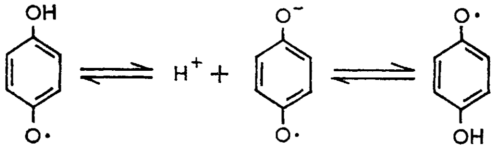


FIGURE 2 E.s.r. spectrum obtained by irradiation of tetrafluorobenzoquinone in ethanol

The spectrum suggests a rapid equilibrium between the protonated species and the radical anion (II).



(I) (II) (III)

A rapid proton transfer between the two oxygen atoms would give rise to an alternating linewidth effect if the rate of exchange were comparable in frequency with the difference between the two fluorine hyperfine coupling constants.[5,6] If the temperature were lowered, thus decreasing the exchange rate, such an alternation might be observable; however cooling to −80° produced no apparent effect, and it appears that the exchange is rapid compared with $a_F{}^1-a_F{}^2$.

Behaviour intermediate between that shown in Figures 1 and 2 was observed when AnalaR chloroform was used as solvent, to give the nine-line spectrum shown in Figure 3. The magnetic non-equivalence of the pairs of fluorines is retained but the doublet structure due to the hydroxyl proton has collapsed. When the chloroform was dried over concentrated sulphuric acid then distilled from calcium hydride,[11] an eighteen-line spectrum similar to that in Figure 1 was obtained. We believe these observations are explicable in terms of a small amount of alcohol in the AnalaR chloroform. The broadening pattern of the nine-line spectrum

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[14] J. K. Brown and W. G. Williams, *Chem. Comm.*, 1966, 495.

[15] E. J. Bowen, ' Chemical Aspects of Light,' Oxford University Press, 1946.

demonstrates clearly that the two fluorine couplings are of opposite sign. From it we can deduce that the rate of exchange is fast compared with the hydroxyl proton splitting of 3·6 MHz and is approaching the difference between a_{F}^1 and a_{F}^2 of 46·5 MHz. At faster rates of exchange the spectrum would be expected to collapse into a five-line pattern and this is what we observe in hydroxylic solvents.

Carrington and Smith[6] studied the analogous unfluorinated radicals in a rapid flow system. At pH 8·3 the radical anion was observed. When the pH was lowered, line-width alternation caused the 1 : 4 : 6 : 4 : 1 quintet to appear as a 1 : 4 : 1 pattern of sharp components. At still lower pH the broadened components sharpened again and the spectrum became a normal quintet. In concentrated sulphuric acid the diprotonated cation was observed. An analysis of the pH dependence gave the dissociation constant of the monoprotonated semiquinone. It would be of interest to determine the dissociation constant of the fluorinated radical in a similar fashion but large amounts of the hydroquinone would be required to do this in a rapid flow system. We have attempted to vary the hydrogen-ion concentration in ethyl alcohol by adding small amounts of acid or base. Unfortunately these experiments either have given a spectrum identical to that in Figure 2, or no signals have been detected. Only a small decrease in radical concentration or a small increase in linewidth would be required to explain our failure to detect the radical.

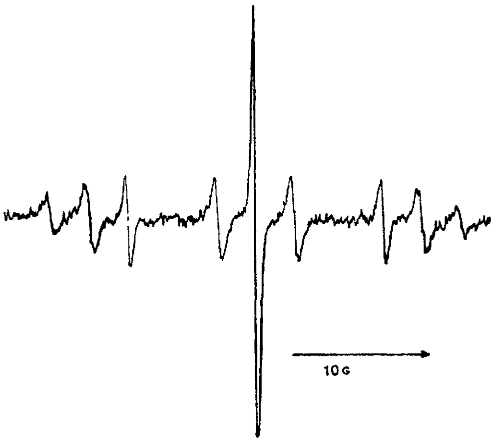

FIGURE 3 E.s.r. spectrum obtained on irradiation of tetrafluorobenzoquinone in chloroform containing a trace of trifluoroacetic acid

The coupling constants (Table) have two features, their magnitude and their solvent dependence, which require explanation. Several attempts have been made to correlate fluorine hyperfine couplings with electron densities,[16-22] by use of a relation of the form (1):

$$a_{\mathrm{F}} = Q^{\mathrm{F}}_{\mathrm{CC}}\rho_{\mathrm{CC}} + Q^{\mathrm{F}}_{\mathrm{FF}}\rho_{\mathrm{FF}} \qquad (1)$$

where ρ_{FF} and ρ_{CC} are the electron densities on fluorine and carbon, and the Q factors are constants. Recently it has been shown that off-diagonal elements of the spin-density matrix probably give a non-negligible contribution to the observed hyperfine splittings, and the extended relation (2) has been proposed,[23] where ρ_{CF} is the overlap spin density between the 2*p* atomic orbitals of fluorine and the bonded carbon atom.

$$a_{\mathrm{F}} = Q^{\mathrm{F}}_{\mathrm{CC}}\rho_{\mathrm{CC}} + (Q^{\mathrm{F}}_{\mathrm{CF}} + Q^{\mathrm{F}}_{\mathrm{FC}})\,\rho_{\mathrm{CF}} + Q^{\mathrm{F}}_{\mathrm{FF}}\rho_{\mathrm{FF}} \qquad (2)$$

Unfortunately the various Q factors are not known precisely.

A more direct approach is provided by the INDO (intermediate neglect of differential overlap) calculations of Pople and his co-workers.[24,25] These take into account both the σ- and π-electrons and give a direct estimate of hyperfine couplings without the use of relations such as (1) and (2). However for the present we shall use more qualitative arguments, and compare our radicals with the corresponding unfluorinated species.

Monoprotonated *p*-benzosemiquinone in THF[2] exhibits splittings of −5·56 G and +0·70 G from two pairs of protons and a hydroxyl proton splitting of −1·54 G. There seems to be little doubt that the largest splitting arises from the protons *ortho* to the unprotonated oxygen,[10] although the reverse assignment has been proposed.[26]

In many cases fluorine hyperfine couplings are *ca.* 2—2·5 times larger than those of protons in the same position and of opposite sign.[22] Such a proportionality follows from equation (1) if the ratio $\rho_{\mathrm{F}}/\rho_{\mathrm{C}}$ is constant, since proton couplings depend linearly on ρ_{C} to a good approximation. This works quite well for the 12·46 G splitting we have assigned to the *ortho*-protons but the −3·24 G splitting is rather larger than predicted. The results of Hinchliffe and Murrell show that the effects of the extra term in equation (2) are most marked in positions of small negative spin density.[23]

The absence of a direct proportionality between a_{F} and ρ_{C} is further demonstrated by the fact that the sum

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[21] A. Carrington, A. Hudson, and G. R. Luckhurst, *Proc. Roy. Soc.*, 1965, *A*, **284**, 582.

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of a_F^1 and a_F^2 is not equal to twice the coupling constant found for the radical anion, as is observed for the radicals derived from *p*-benzoquinone [2] and duroquinone.[9,10]

The influence of solvent on the proton coupling constants of a number of monoprotonated semiquinone radicals has been discussed by Symons and his co-workers.[2,9,10] The solvent effects apparent in the Table follow similar trends. The hydroxyl proton splitting varies smoothly with solvating power, which parallels the behaviour found for benzoquinone [2] but not for duroquinone.[9] The anomalous behaviour in the latter instance was attributed to the steric effect of the adjacent methyl groups. There is no evidence for steric hindrance in the fluorinated radical.

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