980. *The Electron Spin Resonance Spectra and Electronic Structure of Phosphobetaine Radicals.*

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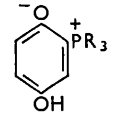
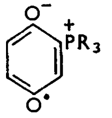
The electron spin resonance spectra of a variety of phosphobetaine radicals (II) have been measured and the splitting constants assigned to the various magnetic nuclei. The electronic structure of the radicals is discussed in the light of these results and it is concluded that the radicals are best described as phosphonium-substituted semiquinones.

It was recently observed[1] that oxidation of the phosphobetaines (I) obtained by addition of a tertiary phosphine to a 1,4-benzoquinone yields a free-radical phosphobetaine (II).

(I)





(II)

We now report measurements of the electron spin resonance spectra of various derivatives of these radicals which have enabled us to assign the hyperfine splitting constants to particular nuclei in the unsubstituted parents, and the electronic structure of the radicals is then discussed in the light of these results.

Experimental

Radicals of type (II) seem always to be formed in a reaction between a tertiary phosphine and a 1,4-quinone owing to oxidation of the initial adduct (I) by as yet unused quinone.[1] Apart, therefore, from the initial measurements already reported, all the spectra discussed here were measured on radicals produced by adding the phosphine to an excess of the quinone.

A 0·1M-solution (1·0 ml.) of the quinone in an electron spin resonance cell was deoxygenated by bubbling nitrogen through it for 5 min., and either a small crystal of a solid phosphine or a few drops of a 0·1M-solution of a liquid phosphine was added. The cell was immediately stoppered and placed in the spectrometer cavity. After attainment of a stationary radical concentration the solution was diluted with deoxygenated solvent until further dilution produced no further improvement in resolution of the spectra.

Materials.—Benzene was dried and stored over sodium. Tetrahydrofuran was refluxed over, and distilled from, sodium and stored over sodium. Methylene chloride (Fluka " puriss ") was stored over calcium chloride. With two exceptions the quinones were commercial samples (Fluka), purified by sublimation. Triphenylphosphine (Fluka " puriss ") and tributylphosphine (Fluka " purum ") were used without further purification. *NNN'N'*-Tetramethyl- and *NNN'N'*-tetraethyl-phenylphosphonous diamide were kindly supplied by Dr. P. A. Chopard of this Institute. Tri-(2-cyanoethyl)phosphine was supplied by Dr. L. Meriweather of the American Cyanamid Stamford Laboratories. 2,5-Diphenyl-1,4-benzoquinone was prepared by a standard method.[2] Perdeuteriobenzoquinone was prepared by refluxing a solution of quinol (1·1 g.) in 20% deuteriosulphuric acid (10·0 ml.) for 24 hr. and oxidising the resulting perdeuterioquinol by a standard method.[3]

Spectra were measured at room temperature on a modified " Microspin " electron spin resonance spectrometer functioning at a frequency of 9300 megacycles/sec. The field sweep was calibrated at frequent intervals against t-butylsemiquinone in ethanol.

Results and Discussion

In Table 1 are summarised the hyperfine constants of the electron spin resonance spectra of the various radicals, measured in methylene chloride solution. The reaction proceeds rapidly in this solvent and other radicals formed by side-reactions are not usually

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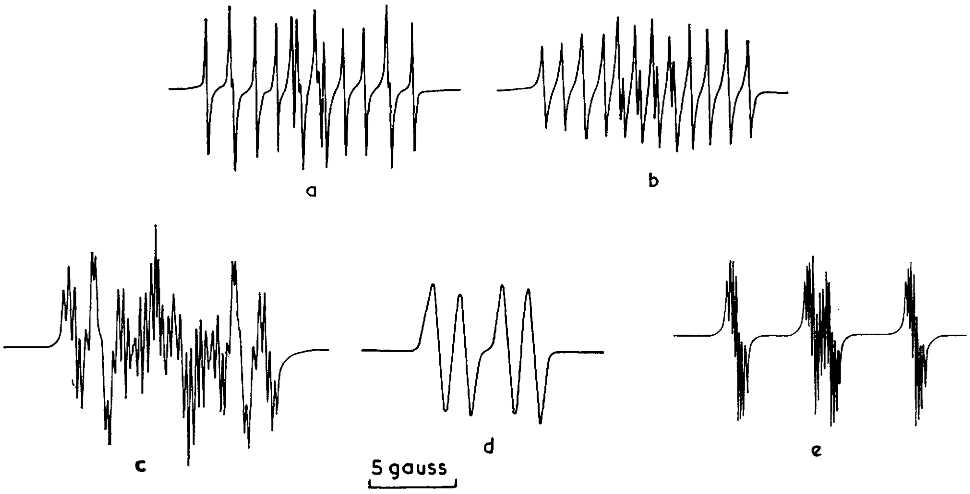
[1] Lucken, *Z. Naturforsch.*, 1963, **18**b, 166.

[2] Shildneck and Adams, *J. Amer. Chem. Soc.*, 1931, **53**, 2373.

[3] Billman, Wolnak, and Barnes, *J. Amer. Chem. Soc.*, 1944, **66**, 652.

observed. Assignments to particular nuclei have been made in the light of the discussion which follows. Typical spectra are shown in the Figure, and the references in column 9 of Table 1 are to these.

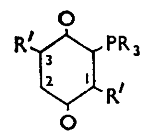
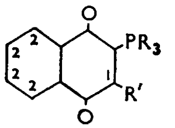
Solvent Effects.—Effects of solvent on electron spin resonance spectra have already been noted.[4] For the radicals discussed here, the changes in coupling constant are considerable, as illustrated in Table 2 (cf. Fig. a and b). The effect of phenols in low concentration is particularly striking, for, whereas similar low concentrations of phenol, *o*-chlorophenol, and *o*-cresol yielded essentially the same (altered) spectrum, the spectra of the radicals in a corresponding solution of ethanol, t-butyl alcohol, or pyridine was the same as that observed in pure methylene chloride. The hindered 2,6-di-t-butylphenol was similarly without effect.



Electron spin resonance spectra. For key see Table 1.

TABLE 1.

Electron spin resonance spectra of phosphobetaine radicals in methylene chloride. Splitting constants in gauss; error ±0·05 gauss, except where otherwise indicated.

Radical type	Phosphine	R′	a_1	a_2	a_3	a_p	Other coupling constants	Spectral type
	PPh_3	H	5·80	1·55	1·70	4·70		a
	PBu_3	H	5·15	1·70	1·70	5·00		a
	$P(CH_2{\cdot}CH_2{\cdot}CN)_3$ *	H	6·00	1·25	1·55	4·50		a
	$PPh(NMe_2)_2$	H	5·55	1·55	1·55	4·00	$a_N = 0{\cdot}2$—$0{\cdot}3$	c
	$PPh(NEt_2)_2$	H	5·60	1·50	1·50	3·85	$a_N = 0{\cdot}2$—$0{\cdot}3$	c
	PBu_3	Bu	—	1·60	—	4·40		d
	PBu_3	Ph	—	1·60	—	4·30		d
	PPh_3	H	6·70	—	—	5·70	$a_2 \approx 0{\cdot}2$—$0{\cdot}4$	e
	PBu_3	H	~6·25			~6·25	$a_2 \approx 0{\cdot}1$—$0{\cdot}3$	e
	$PPh(NMe_2)_2$	H	~6·05			~6·05		e
	PBu_3	CH_3	—	—	—	5·45	$a_{Me} = 6{\cdot}40$ $a_2 = 0{\cdot}1$—$0{\cdot}2$	

* Measured in tetrahydrofuran.

It is considered likely that in benzene or methylene chloride solution the zwitterionic radicals (II) are self-associated in dipole pairs, which are broken by hydrogen-bonding or, less efficiently, by donor solvents. The hyperfine splitting constants of such pairs are likely to be considerably modified by exchange effects, so that we consider the spectra of

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[4] Heineken, Bruin, and Bruin, *J. Chem. Phys.*, 1962, **37**, 452.

TABLE 2.

Solvent effect on spectrum of phosphobetaine from tributylphospine and benzoquinone. Splitting constants in gauss, ±0·05.

Solvent	a_1	a_2	a_3	a_p	Solvent	a_1	a_2	a_3	a_p
C_6H_6	5·25	1·60	1·60	4·90	Bu^tOH	4·90	1·60	2·00	4·90
CH_2Cl_2	5·15	1·70	1·70	5·00	o-$C_6H_4Cl{\cdot}OH$	4·30	1·30	2·35	5·05
Tetrahydrofuran	5·55	1·55	1·75	4·70	0·02M-Phenol in CH_2Cl_2	4·60	1·40	2·05	5·35, 4·60
Pyridine	5·15	1·55	1·55	4·70	0·02M-Phenol in tetrahydrofuran	4·90	1·50	1·90	5·05
Pr^iOH	4·90	1·50	2·15	4·80					

the radicals in hydrogen-bonding solvents to be closer to those which would be observed for the isolated molecules and in any case the proper ones to be compared with the spectra of semiquinones in alcohol or of hydrocarbon negative ions in ethers.

The efficacy of phenols can be understood as the result of the balance between self-association and hydrogen bonding to the radical:

$$n\mathrm{ROH} \rightleftharpoons (\mathrm{ROH})_n$$

$$m\mathrm{ROH} + \mathrm{A} \rightleftharpoons \mathrm{A(ROH)}_m$$

Although there have been many measurements reported of such equilibrium constants,[5] there are few cases in which it is possible to compare phenols and alcohols exactly. However, in general, while the self-association constants for phenols and alcohols are similar in similar solvents, the complex formation constants are greater for phenols than for alcohols with a particular donor type. This is undoubtedly a consequence of the greater basicity of alcohols.

In Table 3 are given the splitting constants of the phosphobetaine radicals formed from benzoquinone with four different tertiary phosphines, measured for both *o*-chlorophenol and propan-2-ol solutions. The phosphorus splittings have been determined from the spectra of the radicals obtained from tetradeuteriobenzoquinone (see next section), and the large change in the highest proton coupling constant on going from alcoholic to phenolic solution is noteworthy. This may be an indication of some more specific interaction (*e.g.*, charge-transfer) between the phenol and the radical and it is probably more reasonable to base a discussion of the electronic structure of these radicals on the hyperfine constants in alcoholic solution.

TABLE 3.

Spectra of benzoquinone-derived phosphobetaine radicals in hydrogen-bonding solvents. Splittings in gauss, ±0·05, unless otherwise indicated.

	In Pr^iOH				In o-$C_6H_4Cl{\cdot}OH$			
Phosphine	a_1	a_2	a_3	a_p	a_1	a_2	a_3	a_p
Ph_3P	5·15	1·40	2·05	4·90	4·60	1·30	2·25	4·95
Bu^3P	4·90	1·50	2·15	4·85	4·30	1·30	2·35	5·05
$(NC{\cdot}CH_2{\cdot}CH_2)_3P$	5·15	1·40	1·95	5·15	5·35	1·30	1·95	5·35
$(Et_2N)_2PPh$	~5·35	~1·7	~1·7	4·30 *				

* Also a_4 = 0·2—0·5.

Assignment of Splitting Constants.—The assignment of the ^{31}P splitting constant for the first three radicals follows unambiguously from the spectra of the radicals obtained from perdeuteriobenzoquinone. These values have been used to assign the ^{31}P splittings elsewhere. Thus, it is assumed that in the 2,5-diphenyl- and 2,5-di-t-butyl-quinone derivatives the ^{31}P constant is the larger of the two, and in the radical obtained from 1,4-naphthosemiquinone it is one of the two large coupling constants. With 2-methyl-1,4-naphthosemiquinone, the phosphorous coupling constant is unambiguously 5·45 gauss,

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[5] Pimental and McLellan, " The Hydrogen Bond," Freeman, San Francisco, 1960.

unless the unreasonable hypothesis is made that this coupling arises from one of the protons in the benzenoid ring.

With this allocation of the phosphorus splittings the low proton-splitting constant of the 2,5-disubstituted quinone derivatives and the high quinone ring-proton or methyl coupling constants of the naphthoquinone radicals make it certain that the highest proton-coupling constant of the unsubstituted benzoquinone radicals is due to the proton *ortho* to the phosphonium group.

The proton-coupling constant of the 2,5-diphenylquinone radical changes from 1·6 to 1·4 gauss when it is measured in 0·01M-solution in phenol. The line-width of this radical is unusually large and in pure *o*-chlorophenol the proton-coupling constant is so small (~1·0 gauss) that the doublet is only just separable. This leaves no doubt that the proton in the *para*-position produces the lowest splitting (~1·4 gauss), and consequently the intermediate splitting (~2·0 gauss) arises from the *meta*-proton.

The Electronic Structure of the Radicals.—(*a*) *The ring-proton coupling constants.* It has been shown[6] that the coupling constant (a_i) of a proton bound to an sp^2-hybridised carbon atom, i, forming part of a π-electron free-radical is given by the expression

$$a_i = Q_p \sigma_i$$

where Q_p is a constant (~28 gauss) and σ_i is the spin density in the p_z-orbital of atom i. For even-alternant systems, σ_i can be approximately replaced by p_i where ρ_i is the odd-electron density at atom i. A simple theory of the effect of inductive substituents on semiquinone electron spin resonance spectra, based on this equation and the molecular-orbital method, relates the splitting constants to the change produced by the substituent in the coulomb integral of the carbon atom to which it is attached.[7] It is here shown that if, in a monosubstituted benzosemiquinone, the substituent increases the coulomb integral by $0{\cdot}75\beta$ where β is the carbon–carbon resonance integral, then the *ortho*, *meta*, and *para* constants will be 5·00, 2·05, and 1·40 gauss, respectively. If the phosphonium group is to be considered as a purely inductive substituent, it will, of course, be electron-withdrawing and the similarity of the predicted coupling constants to those shown in Table 3 for the radicals in alcoholic solution is strong evidence that the electronic structure of (II) is best represented by the semiquinone-betaine formulation. The higher coupling constant observed in the naphthoquinone derivatives is then a consequence of the higher spin density at the quinonoid ring protons of naphthosemiquinone itself.

However, as McLachlan and his co-workers have pointed out,[8] ring-proton coupling constants alone cannot distinguish between inductive and conjugative substituents, for the algebraic form of the expression for their values is the same in both cases. Nevertheless, we may enquire whether $0{\cdot}75\beta \approx 1{\cdot}7$ ev is of an appropriate order of magnitude for the inductive parameter of the phosphonium group. An estimate is provided by the quantity $e/R \approx 7{\cdot}5$ ev, where R is the phosphorus–carbon bond length. This estimate assumes that the effective charge of the phosphonium group is unity; a more realistic guess to account for the polarisation of the four carbon–phosphorus bonds would be to divide the formal charge by the co-ordination number of the phosphonium group, yielding $\Delta\alpha \approx 1{\cdot}9$ ev, in very satisfactory agreement with the electron spin resonance results. These estimates certainly suggest that $\Delta\alpha = 0{\cdot}75\beta$ is not too large an inductive effect for a phosphonium group, so that it is not necessary to involve the use of acceptor *d*-orbitals by phosphorous to produce agreement between theory and experiment.

(*b*) *The phosphorus splittings.* The mechanisms by which the nucleus of such a polyelectronic substituent might couple with the spin of a conjugated radical, already numerous[9] with ^{13}C, become almost too varied with ^{31}P for any serious hope of a satisfactory analysis

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[6] McConnel, *J. Chem. Phys.*, 1959, **28**, 107.
[7] Fairbourn and Lucken, *J.*, 1963, 258.
[8] Bolton, Carrington, and McLachlan, *Mol. Phys.*, 1962, **5**, 31.
[9] Karplus and Fraenkel, *J. Chem. Phys.*, 1961, **35**, 1312.

of the problem at this stage. Moreover, the hyperfine coupling of a 3*s*-electron to the ^{31}P nucleus has been calculated to be 10,100 megacycles/second, so that an unpaired density of only 0·0015 in this orbital is required to produce the observed splitting. The coupling of 2*s*- and 1*s*-electrons would be expected to be even higher. It should be noted, however, that neither hyperconjugation nor $d\pi$–$p\pi$-double-bonding yields a first-order *s*-spin density at the ^{31}P nucleus.

A sensitive test for the mechanism of ^{31}P coupling would be a determination of the sign of the coupling constant. In favourable cases, it is possible to determine the relative signs of the coupling constants of non-equivalent nuclei by observation of the line-widths of the various components[10] and, since the ring-proton couplings are almost certainly negative, this would at once yield the sign for ^{31}P. This was not, however, possible in the present instance owing to the overlapping of the components in the central region of the spectra.

In conclusion, therefore, the electron spin resonance spectra of these radicals appears to be in satisfactory accord with their having the electronic structure shown in (II), where the unpaired electron is largely confined to the semiquinonoid part of the molecule, so that they are best considered as substituted semiquinones.

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[10] (*a*) Stephen and Fraenkel, *J. Chem. Phys.*, 1960, **32**, 1435; (*b*) Kivelson, *J. Chem. Phys.*, 1960, **33**, 1094; (*c*) de Boer and Mackor, *Mol. Phys.*, 1962, **5**, 493.