

814. Ion-association and Specific Solvation in the Electron Spin Resonance Spectra of Semiquinones.

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By a study of their electron spin resonance spectra it is shown that alkali-metal semiquinones in anhydrous *t*-butyl alcohol exist as tightly bound ion pairs. For orthosemiquinones the ion-pairs are chelated. Hyperfine structure from the lithium-7 and sodium-23 nuclei is clearly visible. The ultra-violet and visible absorption spectra of these solutions show that further association to diamagnetic species also occurs. The complexes are destroyed and the "free" semiquinone regenerated by the addition of less than 1% water and the results of a preliminary study of the complex-breaking efficiency of a number of other solvents are reported.

THE electron spin resonance (e.s.r.) spectra of *p*-semiquinones in alkaline ethanol are those expected for the free anion radical¹ and only relatively small changes in the magnitudes of coupling constants result from a change in solvent or counter-ion.² Any ion-association which does occur is probably of a weak non-specific kind in which the cation and probably the anion are surrounded by a solvent sheath and where the ion-pair has no preferred configuration. In anhydrous *t*-butyl alcohol, however, we have observed that the spectrum of, for example, 2,5-dibutylsemiquinone, is no longer a 1 : 2 : 1 triplet but is complex and depends on the nature of the counter-ion. This is illustrated in Fig. 1 for the lithium,

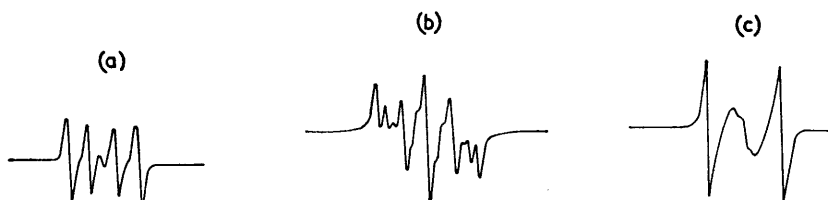
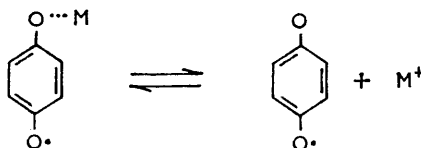


FIG. 1. The electron spin resonance spectra of the lithium (a), sodium (b), and potassium (c) salts of 2,5-di-*t*-butyl-1,4-benzosemiquinone in anhydrous *t*-butyl alcohol.

sodium, and potassium salts. For all three cations, however, the addition of a small quantity of water restores the spectrum to that usually observed. The solutions in anhydrous *t*-butyl alcohol are much more stable than those in either the wet solvent or ethanol.

We here describe our observations on a number of these systems and present evidence that the spectra can be explained in terms of an equilibrium between a tightly-bound ion-pair and the free or at most weakly associated anion and cation. Thus:



(a) *1,4-Benzosemiquinones*.—The hypothesis of the above equilibrium has several immediate consequences.

(i) Provided that the rate of interconversion of the two forms is slow, the spectra observed are due to the superposition of the spectra of the two separate radicals. The effect of ion-pairing on the spectrum of 1,4-benzosemiquinone is to remove the equivalence

¹ Venkataraman, Segal, and Fraenkel, *J. Chem. Phys.*, 1959, **30**, 1006.

² Stone and Maki, *J. Chem. Phys.*, 1962, **36**, 1944.

between the four protons which, with rapid rotation or libration of the metal cation about the carbon–oxygen bond, now become two pairs of equivalent nuclei. Simple molecular orbital theory shows that the complexing will increase the coupling constant of one pair while decreasing the other. If the effect of the cation is to increase the electronegativity of the oxygen atom to which it is attached and to lengthen the carbon–oxygen bond, then the pair *ortho* to the complexed oxygen atom has the lower coupling constant.³ As long as complexing does not produce too drastic a change in the conjugated system, the sum of the coupling constants will not, however, be greatly different from that of benzoquinone.

(ii) The spectrum of a complexed 2,5-disubstituted *p*-benzoquinone will thus be a quartet of lines of equal intensity while for a 2,6-disubstituted compound it will remain a 1 : 2 : 1 triplet but with a coupling constant greater or less than that of the uncomplexed semiquinone depending on which oxygen atom is attached to the cation.

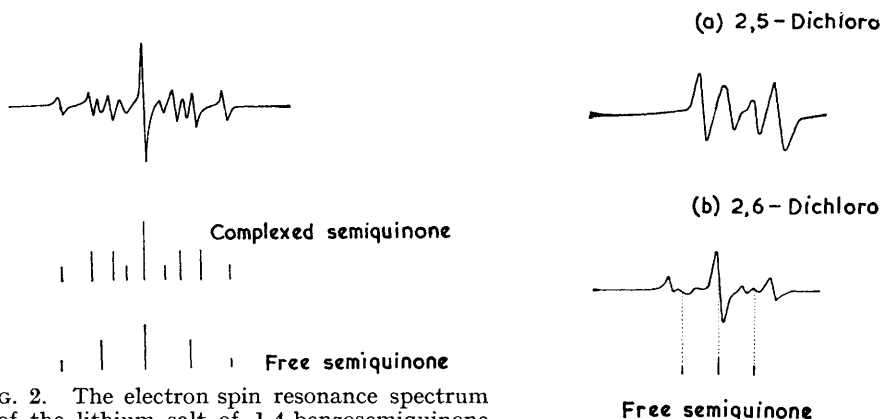


FIG. 2. The electron spin resonance spectrum of the lithium salt of 1,4-benzoquinone in anhydrous t-butyl alcohol and a theoretical reconstruction based on an equilibrium between a free anion and tightly-bound ion-pair.

FIG. 3. The electron spin resonance spectra of the lithium salts of two dichloro-1,4-benzoquinones in anhydrous t-butyl alcohol.

Fig. 2 shows the spectrum of the lithium salt of 1,4-benzoquinone and a reconstruction based on these hypotheses. The spectrum of the lithium salt in Fig. 1 can also be seen to be a superposition of a quartet and a triplet of the same over-all splitting.


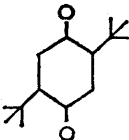
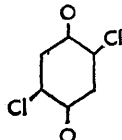
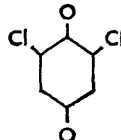
Fig. 3 shows the spectra of the complexed salts of 2,6- and 2,5-dichloro-1,4-benzoquinone, and again a satisfactory reconstruction is possible. In the case of the 2,6-disubstituted derivative complexing evidently occurs at both oxygen atoms, and if the predictions of simple M.O. theory are correct, more at that flanked by the chlorine atoms. This may indicate that the lone-pair electrons of the chlorine atoms also play a part in the bonding to the cation. In Table 1 the coupling constants of the lithium salts of these four semiquinones are shown together with those of the free anion. The spectra of the lithium salts, at least, seem to be well explained by the hypothesis of complex-formation.

The spectrum of potassium salt of 2,5-dibutyl-1,4-benzoquinone is also a superposition of a quartet and a triplet but the inner lines are considerably broader than those of the lithium salt, and this is probably due to a rapid interconversion of different forms of the complex. There is also a significantly greater amount of the free form present. The potassium salt of 1,4-benzoquinone only shows a line-broadening compared with the free anion and this again would be expected if there is a rapid exchange of metal ion between anions or between anion and solvent. Such a difference between lithium and potassium is to be expected in view of the much smaller radii of the lithium cation and the probably greater covalent character of the lithium–oxygen bond.

³ Lucken, unpublished calculations.

TABLE I.

Hyperfine splitting constants of lithium salts of semiquinones in gauss ± 0.05 .

							
Associated	Free	Associated	Free	Associated	Free	Associated	Free
2.75	2.37	2.90	2.13	2.75	2.03	2.85 *	2.32
2.00		1.35		1.30		1.40 †	

* Lithium attached to oxygen *ortho* to the substituents. † Lithium attached to oxygen *meta* to the substituents.

While the spectra of the lithium and potassium salts seem to be easily understandable, the spectra of the sodium salts is much more complex, as can be seen by reference to Fig. 1. This is further illustrated by the spectra shown in Fig. 4. In addition to the increased number of lines in the sodium complexes the total width of the spectra is greater than for

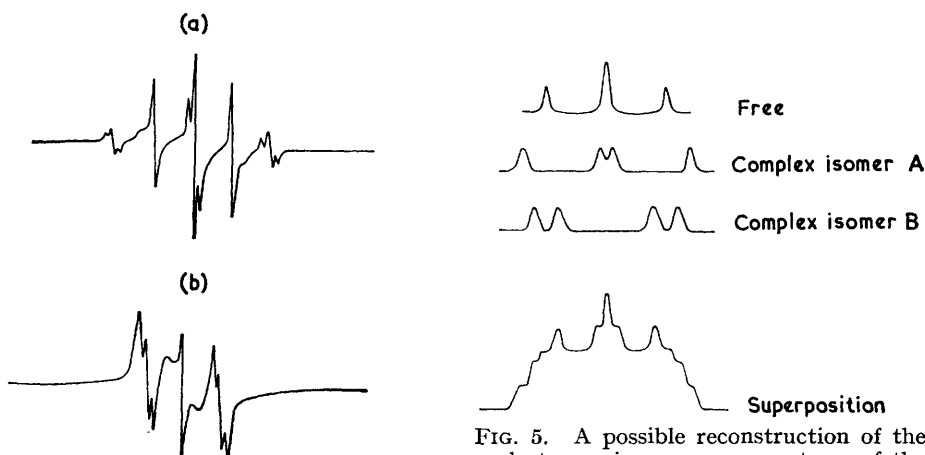


FIG. 4. The electron spin resonance spectra of the sodium salts of (a) 1,4-benzoquinone and (b) 2,5-dichloro-1,4-benzoquinone in anhydrous *t*-butyl alcohol.

FIG. 5. A possible reconstruction of the electron spin resonance spectrum of the sodium salt of 2,5-di-*t*-butyl-1,4-benzoquinone, based on the formation of two isomeric ion-pairs.

those of the other two alkali-metals. A possible explanation of this complexity would be the loss of free rotation about the carbon-oxygen bond. This in turn could be due to the usually higher solvation number of sodium compared to lithium which, despite the greater ionic radius of the former, might suffice to hinder rotation sufficiently to make separate isomers distinguishable by electron spin resonance. That such isomerism will affect the spin distribution is clearly shown by the spectra of the radical-anions of aromatic carbonyl compounds, where conjugation of the carbonyl group with the ring locks it in one of two positions, and for example in *p*-cyanobenzaldehyde makes all four ring-protons inequivalent.⁴ For a 2,5-disubstituted derivative two rotational isomers are possible and a reconstruction of the spectrum of 2,5-di-*t*-butyl-1,4-benzoquinone based on this hypothesis is shown in Fig. 5. Similar reconstruction of the spectrum of sodium *p*-benzoquinone where a spectrum due to four different proton coupling constants are likewise

⁴ Rieger and Fraenkel, *J. Chem. Phys.*, 1962, **37**, 2811.

possible, but the breadth of the lines makes it difficult to perform this reconstruction unambiguously.

Another possible and perhaps more likely explanation for the anomalous spectra of the sodium complexes is to assume that hyperfine splitting from the sodium-23 nucleus occurs. This hypothesis appears very attractive for 1,4-benzosemiquinone and a straightforward reconstruction of the observed spectrum is possible with a sodium-23 hyperfine coupling constant of 0.2 gauss. Moreover, the greater width of the sodium complexes is a *necessary* consequence of this hypothesis.

An objection to this theory is, however, the absence of hyperfine splitting from the lithium-7 nucleus for which the product of the nuclear moment (μ_N) and the value of the 1s wave function at the nucleus, $(\phi_{2s})_0^2$ (= 143 gauss), is not too different from the similar product $\mu_N (\phi_{3s})_0^2$ for the sodium-23 nucleus (= 316 gauss) and which is probably more strongly bound to the oxygen atom. The absence of splitting from the potassium-39 nucleus is less surprising for $\mu_N (\phi_{4s})_0^2$ is only equal to 83 gauss and it is probably only weakly attached to the oxygen atom. It is, however, possible that the lithium and sodium compounds do not have the same configuration and that the sodium atom interacts more efficiently with the π -system. Moreover, the strong bonding of the lithium and oxygen atoms might in fact militate against the occurrence of spin density at the lithium

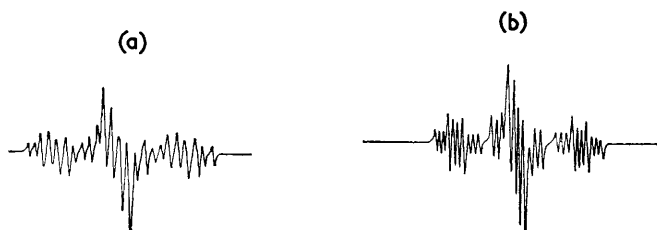


FIG. 6. Electron spin resonance spectra of the lithium (a) and sodium (b) salts of 1,2-benzosemiquinone in anhydrous t-butyl alcohol.

nucleus as it would favour resonance structures having a negative charge—and hence an even number of electrons—on the bound oxygen atom.

(b) *1,2-Benzosemiquinones.*—The broad lines of the spectra of 1,4-benzosemiquinone which render difficult their complete and unambiguous interpretation probably arise from interconversion of configurational isomers and exchange between free and complexed species. In particular this prevents the certain identification of alkali-metal hyperfine splitting which has been advanced above as an explanation of the spectra of the sodium complexes and which would remove any doubt that the phenomena described here are due to ion-association. It was thought likely that *ortho*-benzosemiquinones would be much more satisfactory from this point of view as chelation would render the complex more stable and remove the problem of rotational isomerism, so that the resonance lines would be sharp and alkali-metal fine structure thus observable, while the retention of the molecular symmetry of the uncomplexed ion would make the spectra particularly simple to interpret. The spectra of the lithium and sodium salts of 1,2-benzosemiquinone are given in Fig. 6 which shows that these hopes are amply fulfilled. Hyperfine structure from both the lithium ion (0.3 gauss) and the sodium ion (0.2 gauss) is visible while not unsurprisingly the spectrum of the potassium salt shows no fine structure. It is noteworthy that there is no significant difference in the ring proton coupling constants of the three salts and the free anion.

(c) *The Effect of Solvent Composition.*—It has already been mentioned that traces of water restore the spectra to those of the free semiquinones. Ion-pairing occurs in t-butyl alcohol presumably because the bulky solvent molecule is too large to pack the usual

number of hydroxyl groups around the cation, so that the semiquinone remains undissociated. Addition of water displaces the semiquinone from the metal and the solvation sheath of the cation is completed by water molecules.

It might in general be expected that any donor or hydrogen-bonding solvent, would be able to break up the semiquinone complex, and in Table 2 are shown the results of a preliminary investigation in which was determined the compositions of the mixtures of *t*-butyl alcohol and various solvents in which the concentration of free and associated

TABLE 2.
Composition of solvent at which the concentrations of complexed and free lithium *p*-benzoquinone are equal.

Adduct	Composition v/v % Adduct/ <i>t</i> -butyl alcohol	Dielectric constant of adduct at 25°
Propan-2-ol	23	18.3
Ethanol	6	24.3
Methanol	1	32.6
Water	0.2	78.5
Acetone	2	20.7
Tetrahydrofuran	No effect on complex	4.3 †
Pyridine		12.3
Triethylamine *		2.4
Phenol		9.8

* Reacts slowly with the semiquinone. † Dielectric constant of diethyl ether at 20°.

lithium 1,4-benzosemiquinone are equal. Pure ethanol contains 25% of dissociated semiquinone. A more detailed investigation of this phenomenon for a wider variety of solvents, cations, and semiquinones will be reported separately.

It is noteworthy that in accordance with the hypothesis that the cause of the ion-association is the size of the solvent molecules the efficiency of complex breaking for hydroxy-compounds is in the order water > methanol > ethanol > propan-2-ol, whereas their basicity, and hence presumably the strength of the metal-oxygen bond, is in the opposite sense. The dielectric constant, however, also increases in the same sense as the complex-breaking efficiency. Of the other common hydrogen-bonding solvents aniline and phenol react rapidly with the radicals and thus cannot be studied. Of the purely donor solvents studied only acetone had any complex-breaking effect and triethylamine if anything decreased the concentration of unassociated radical below that observed in pure *t*-butyl alcohol. The lack of complex-breaking power of ethers and tertiary amines, despite the fact that they are more basic than the alcohols, is possibly an indication that hydrogen-bonding to the other molecules solvating the cation is an important factor.

(d) *Electronic Absorption Spectra*.—By analogy with the structure of quinhydrone and the instability of neutral semiquinones it was thought possible that further association of the ion-pairs to diamagnetic products might occur. The observation that the concentration of unassociated free radical produced by addition of water to the anhydrous solvent was greater than that of the sum of free and associated radicals originally present supported this suggestion. The ultraviolet and visible absorption spectra of these solutions under a variety of conditions were, therefore, measured in the hope that they would provide additional evidence on this point and the results of these measurements on lithium 1,4-benzosemiquinone are shown in Fig. 7.

The addition of excess of lithium ions, by increasing the concentration of complexed anion, would be expected to favour further association and, indeed, the spectra in the visible region are changed markedly by the addition of either lithium chloride (B) or lithium *t*-butoxide (C), thus indicating that other species are formed. The striking change in the spectrum produced by the addition of water is illustrated by curve D.

The spectra of the sodium and potassium salts, shown in Fig. 8, can be seen to be quite different from each other and from that of the lithium salt, in agreement with the previous

observations. The presence of a high concentration of free semiquinone in spectrum D, where no excess of potassium ions is present, is in good agreement with the broadened quintuplet observed in the electron spin resonance spectrum.

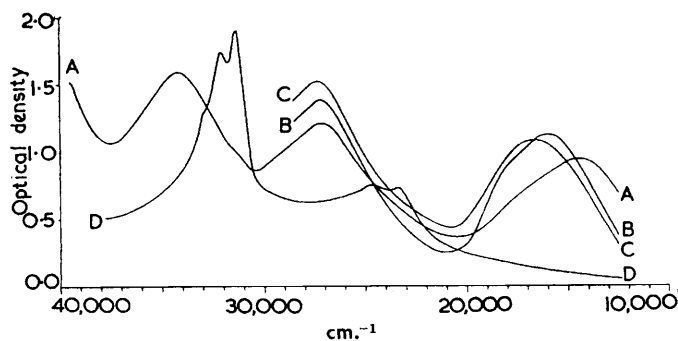


FIG. 7. Electronic absorption spectra of the lithium salt of 1,4-benzosemiquinone in anhydrous t-butyl alcohol.

- A = 0.02M benzoquinone, 0.02M hydroquinone, 0.04M lithium t-butoxide.
 B = A saturated with LiCl.
 C = 0.02M benzoquinone, 0.02M hydroquinone, 0.1M lithium t-butoxide.
 D = A + 5% water.

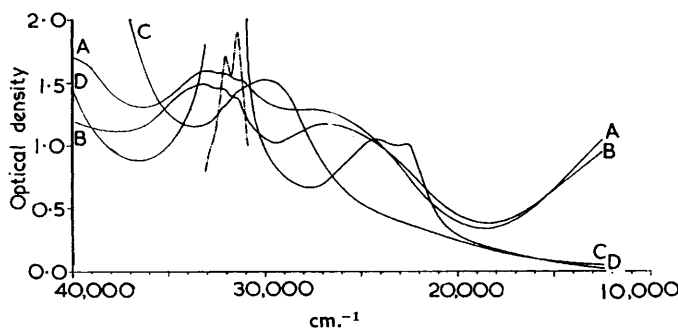


FIG. 8. Electronic absorption spectra of the sodium and potassium salts of 1,4-benzosemiquinone in anhydrous t-butyl alcohol.

- A = 0.02M benzoquinone, 0.02M hydroquinone, 0.12M sodium t-butoxide.
 B = 0.02M benzoquinone, 0.02M hydroquinone, 0.04M sodium t-butoxide.
 C = 0.02M benzoquinone, 0.02M hydroquinone, 0.12M potassium t-butoxide.
 D = 0.02M benzoquinone, 0.02M hydroquinone, 0.04M potassium t-butoxide.

EXPERIMENTAL

Electron spin resonance (e.s.r.) spectra were measured at 25° on a modified "Microspin" spectrometer at 9500 Megacycles/sec. The field was calibrated against 1,4-benzosemiquinone in ethanol. Ultraviolet (u.v.) and visible spectra were measured at 30° in a Cary model 11 spectrophotometer using a path length of 1.0 mm. Solutions of semiquinones were prepared by mixing 1.0 ml. of 0.1M-quinone, 1.0 ml. of 0.1M-quinol, and 1.0 ml. of 0.2M-alkali-metal butoxide, all in t-butyl alcohol, and making up to 5.0 ml. with pure solvent. All solutions and solvents were deoxygenated by bubbling nitrogen through them and mixing was carried out in an atmosphere of nitrogen.

Anhydrous alcohols (t-butyl, water <0.15%; isopropyl, water <0.5%; ethyl, water <0.2%; methyl, water <0.05%) and acetone (water <0.1%) were purchased from Fluka A.G., and used without further purification. Tetrahydrofuran and ether were dried over sodium, pyridine and triethylamine were dried over pellets of sodium hydroxide. Quinol was used

without further purification. All quinones were obtained commercially and purified by sublimation. 2,5-Di-*t*-butylquinol was a recrystallised commercial sample and the two dichloroquinols were prepared by reduction of the corresponding quinones with stannous chloride in acidified ethanol. Solutions of the alkali-metal butoxides were prepared by dissolving the weighed metal in an appropriate volume of anhydrous *t*-butyl alcohol.

CONCLUSION

There seems to be no doubt that the spectra of semiquinones observed in anhydrous *t*-butyl alcohol are due to ion-association, although the details for the sodium salts of 1,4-benzosemiquinones are not entirely clear. The complexed semiquinone is probably in equilibrium with a diamagnetic polymeric species. The formation of these complexes in this medium seems to be due to the inefficient solvation of the small cation by the bulky solvent molecule and they are destroyed by the introduction of more active solvating agents.

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