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Formation of New Paramagnetic Complexes between Quinones and Their Semiquinone Anions in the Presence of a Cryptand or a Crown Ether

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The formation of new paramagnetic complexes is evidenced by the ESR spectra of anion radicals of duroquinone, *p*-benzoquinone, and 2,5-di-*t*-butyl-*p*-benzoquinone in tetrahydrofuran, which are recorded in the presence of their parent molecules and cryptand 222 or 18-crown-6. The numerical values for the equilibrium constant, standard enthalpy and standard entropy of the complex formation are also determined.

There are several reports about the formation of dimer cations between polyaromatic hydrocarbons and their cation radicals.[1,2] However, the formation of such dimer anions have scarcely been reported. In this paper, we report the formation of new paramagnetic complexes between several derivatives of *p*-benzoquinone and their semiquinone anions in the presence of a cryptand or a crown-ether in tetrahydrofuran at low temperature.

Experimental

p-Benzoquinone (BQ) was purified by sublimation. Other reagents; commercial duroquinone (DQ), 2,5-di-*t*-butyl-*p*-benzoquinone (DBQ), cryptand 222 (CRP) and 18-crown-6(CW) were used without further purification. The solvent, tetrahydrofuran (THF) was purified as described previously.[3] The method of deuteration followed the literature.[4] Semiquinone anion radicals (Q^-) were prepared in vacuo by reducing their parent molecules (Q) with anthracene anion radical, which was prepared by sodium or potassium reduction of anthracene. The respective test solutions used contained 0.5—1 mM (1 M=1 mol dm^{-3}) of Q^- ion-paired with an equivalent amount of Na^+ or K^+. When required, known amounts of Q, CRP, and CW were added. Simulated ESR spectra were calculated with a NEC PC-9801F2 personal computer.

Results and Discussion

The ESR spectra of Na^+DQ^- and K^+DQ^- recorded at −50 °C could be analyzed in terms of two sets of six equivalent hydrogens and one alkali metal atom, whose hyperfine splitting (hfs) constants (*a*) agree with the literature values.[5] An addition of DQ to these solutions caused electron-exchange broadening, but no new signals.

Figure 1 (a) shows an ESR spectrum of K^+DQ^- at −50 °C in the presence of CRP. Na^+DQ^- gave a similar spectrum under the same experimental conditions. These spectra, having no metal hfs, could be analyzed in terms of twelve equivalent hydrogens with a=1.9 G. This finding suggests that DQ^- should exist in the form of a free ion or an ion

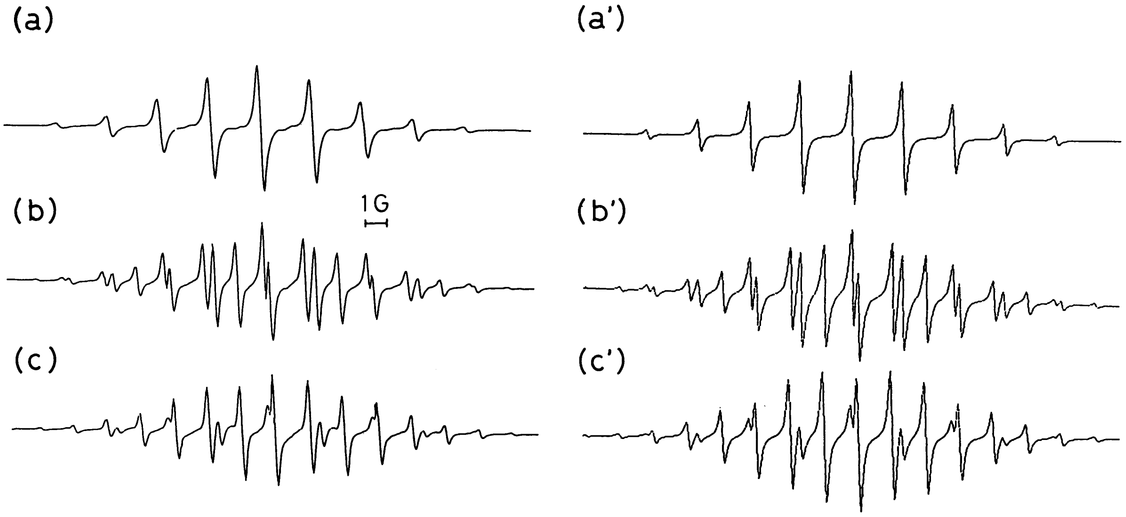

Fig. 1. ESR spectra of K^+DQ^- in THF containing 3.3 mM cryptand and (a) 0, (b) 6.4, (c) 12.8 mM DQ at −50 °C, and the corresponding computer simulated spectra; (a')—(c').

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pair whose cation is migrating rapidly between two oxygen sites.

Figure 1 (b) and (c) show that an increasing addition of DQ to the test solution gives rise to a new signal of increasing intensity, and the original signals of decreasing intensity. The new signal decreased in intensity with raising temperature, and became unobservable at 25 °C. This spectral change with temperature was reversible.

Figure 2 (a)—(c) show that a similar ESR pattern can be found for Na^+BQ^-, except that the hf structure is due to four equivalent hydrogens of a=2.38 G.

The ESR spectra of Na^+DBQ^- recorded at room temperature in the presence and absence of CRP exhibited hf structures due to two equivalent hydrogens and two nonequivalent hydrogens, respectively. The a value for the former hydrogens was 2.38 G, and the values for the latter agreed with the literature values.⁶⁾

According to Fig. 3 (a)—(c), the effect of DBQ addition to the solution containing Na^+DBQ^- and CRP is the same as in Fig. 1 (a)—(c) and Fig. 2 (a)—

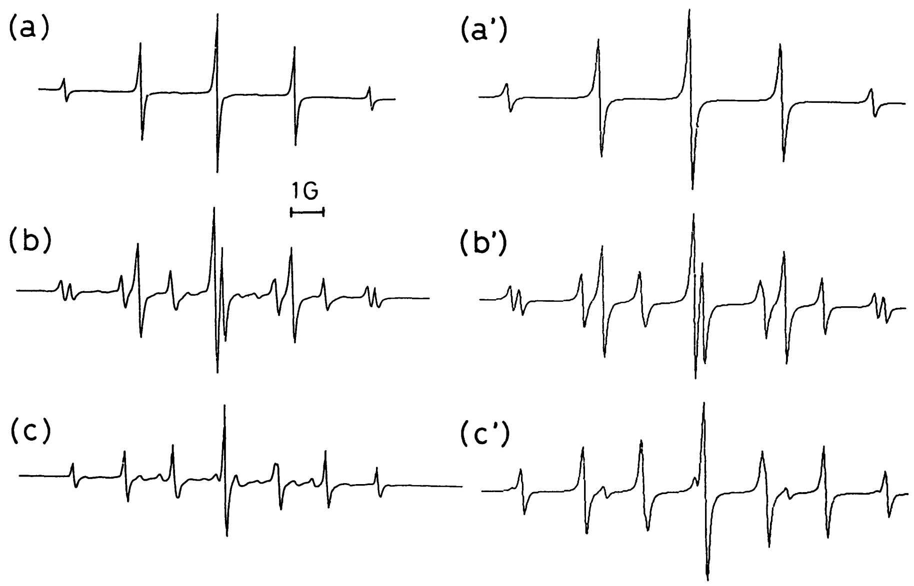

Fig. 2. ESR spectra of Na^+BQ^- in THF containing 3.1 mM cryptand and (a) 0, (b) 1.97 and (c) 4.12 mM BQ at −75 °C, and the corresponding computer simulated spectra; (a')—(c').

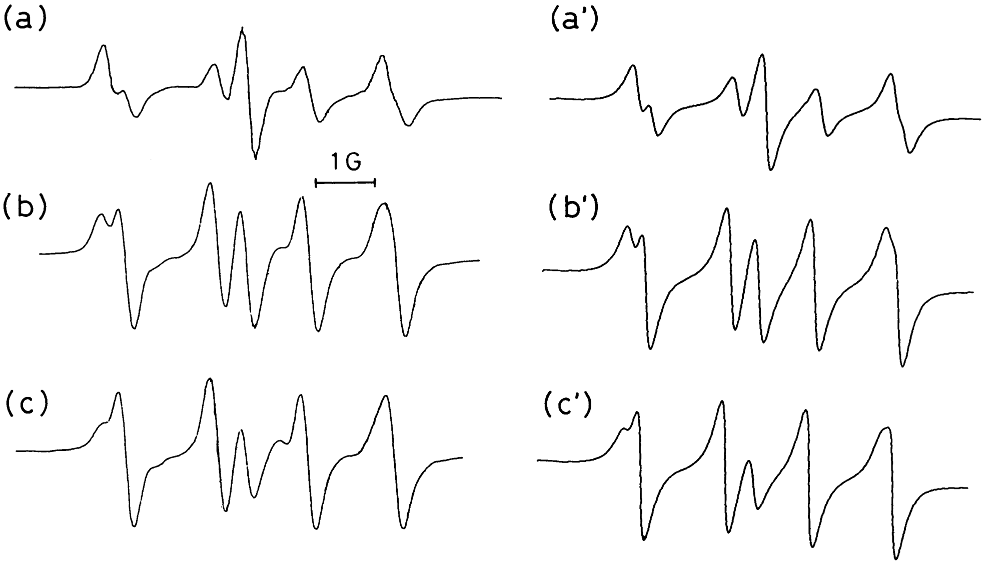

Fig. 3. ESR spectra of Na^+DBQ^- in THF containing 3.1 mM cryptand and (a) 0.3, (b) 17.1 and (c) 32.7 mM DBQ at −50 °C, and the corresponding computer simulated spectra; (a')—(c').

(c). Four new hf lines caused by DBQ addition, having equal intensities, can be attributed to two nonequivalent hydrogens of a=3.12 G and 1.56 G, respectively.

All features of the ESR spectra of Na$^+$DBQ$^-$ with and without DBQ were not changed by substituting CW for CRP, except for the broadening of two inner peaks of the original four lines.

Figure 1 (a′)—(c′) show computer simulated ESR spectra assuming the following situations; (A) The new paramagnetic species have two nonequivalent groups of hydrogens including 6 members respectively. (B) The hf constants for these two hydrogen groups of the new species are 2.54 and 1.27 G, and the hf constant for the equivalent 12 hydrogens of the original species is 1.90 G. (C) The observed ESR spectrum is the superposition of the original spectrum and the new spectrum having intensities corresponding to their concentrations. (D) The difference of the center field of each spectrum due to the difference of g values is 0.25 G. These simulated spectra agreed well with the observed spectra.

Figure 2 (a′)—(c′) show the similarly simulated spectra assuming that the hf constants of the two groups of hydrogens (2 members) for the new species are 3.38 and 1.74 G respectively; the hf constant for the 4 hydrogens of the original species is 2.56 G; and the difference of the center field is 0.25 G. Figure 3 (a′)—(c′) show the simulated spectra assuming that the hf constants of the two nonequivalent hydrogens for the new species are 3.12 and 1.56 G; the hf constant for the 2 equivalent hydrogens of the original species is 2.38 G; and the differnce of the center field is 0.25 G. These simulated spectra also agreed well with the observed spectra.

The. finding that these new signals can be found only in the presence of Q and increase in intensity with increasing Q concentration strongly suggests that they should be attributed to certain aggregates of Q and Q$^-$. Table 1 shows the equilibrium constants (K) for this association which were calculated from the relative intensities of the original and the new signals at different Q concentrations by assuming that the association occurred between one Q and one Q$^-$. The validity of this assumption may be supported by the K values which are nearly independent of the Q concentration.

Furthermore, the K values were little affected by the variations of the concentrations of CRP and CW, and of the kinds of alkali metal cations and crown compounds.

Figure 4 shows log K vs. T^{-1} plots for DBQ and BQ, and Table 2, the resultant values for the standard enthalpy (ΔH°) and entropy (ΔS°) of the association reaction. Both the ΔH° and ΔS° values are smaller for quinones of greater molecular size.

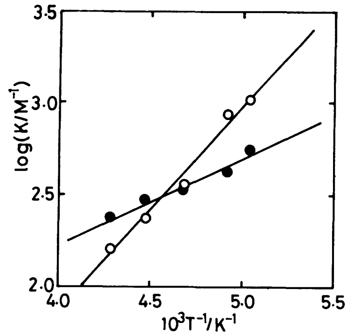

Fig. 4. Plots of log K vs. T^{-1} for the association reactions between (—●—) BQ and BQ$^-$, and (—○—) DBQ and DBQ$^-$, in the presence of Na$^+$ and cryptand.

Table 1. Equilibrium Constants, K, for Association Reactions between Q and Q$^-$ in the Presence of CRP and Alkali Metal Cations

Q	[Q]/mM	10^{-2} K/M^{-1} at T/K					
		T/K: 248	233	223	213	203	198
DBQ[a]	5.0		1.7	2.3	3.6	7.1	11.2
	14.3		1.5	2.4	3.8	10.4	9.4
BQ[b]	1.7		2.4	2.9	3.2	3.7	5.1
	6.2		2.5	3.2	3.7	5.1	6.3
DQ[c]	1.8	3.9		6.0			
	6.6	3.0		7.0			

a) The solution contains 3.1 mM CRP and equivalent concentration of Na$^+$ to DBQ$^-$. b) The solution contains 3.1 mM CRP and equivalent concentration of Na$^+$ to BQ$^-$. c) The solution contains 3.3 mM CRP and equivalent concentration of K$^+$ to DQ$^-$.

Table 2. Equilibrium Parameters at −50 °C for the Association Reactions between Q$^-$ and Q in the Presence of CRP and Alkali Metal Cations

Q	10^{-2} K/M^{-1}	ΔH°/kJ mol^{-1}	ΔS°/J mol^{-1} K^{-1}
p-BQ[a]	3.0	−9	8
DQ[b]	7.0	−10	−4
DBQ[c]	2.4	−21	−50

a) The solution contains 3.1 mM CRP and equivalent concentration of Na$^+$ to DBQ$^-$. b) The solution contains 3.1 mM CRP and equivalent concentration of Na$^+$ to BQ$^-$. c) The solution contains 3.3 mM CRP and equivalent concentration of K$^+$ to DQ$^-$.

The results described above strongly suggests that associations between quinones and their anion radicals occur in THF containing CRP and CW. If the associates are charge-transfer complexes like dimer cations,[1] the unpaired electron should be delocalized over two quinone molecules. Such a situation, however, is not in accord with the observed ESR pattern. On the contrary, if the unpaired electron is localized on one quinone molecule, the numbers of observed hf lines are reasonable. ESR spectrum of the deuterated BQ (BQ-d_1) anion in THF containing CRP and BQ-d_1 supported this situation.

In this case, however, no simple structural model can explain the formation of such aggregates containing two Q molecules. A tentative model is given as follows: A quinone anion ion-paired with an alkali metal cation, which is captured by CRP and CW, can further associate with a quinone molecule, where an unpaired electron is localized on one quinone molecule and the migration of the cation is hindered. Then, the hf constants of the two sets of half number of equivalent hydrogens are not averaged, and the ratio of these happens to be about 2.0 as is seen in the case of the 2,5-DBQ anion ion pair: $a(H_3)=1.50$ G, $a(H_6)=3.14$ G at 0 °C.

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