The Influence of Crown Ethers on Cation Migration Processes. Part 4.[1] Some Simple Benzoquinone Radical Anions in the Presence of Dibenzo-18-crown-6 †

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The radical anions of 2,5-di-t-butyl- and 2,5-dimethyl-benzoquinone have been prepared in 1,2-dimethoxyethane with Li^+, Na^+, or K^+ as the counterion in the presence of dibenzo-18-crown-6. Linewidth alternation is observed in the e.s.r. spectra of these radical anions, with the lifetime of the counterion at one of the preferred sites near the radical anion varying in the sequence $Li^+ > Na^+ > K^+$ at a particular temperature. It is apparent that in the presence of the crown ether 'contact' ion pairs are still present in the majority of the systems studied. The relatively minor influence of the crown ether on these systems is probably a result of the similarity in cation solvation environment presented by 1,2-dimethoxyethane and the crown ether.

Linewidth alternation is often observed in the radical anions of simple benzoquinones when they are formed by alkali metal reduction; the phenomenon is due to the possibility of migration of the alkali metal ion between two equivalent sites in the radical anion.[2,3] Many other examples of cation migration processes have been observed, but few present the relatively simple spectra obtained from benzoquinone radical anions. It is not surprising to find that the rate of cation migration is often influenced by the nature of the solvent and of the cation.[2,3] The addition of cation binding agents, such as crown ethers, can also profoundly influence the rate of migration. Examples of this influence have been reported for the radical anions of pyrazine[4] and tetramethylbenzosemiquinone.[5,6] An important feature in determining the magnitude of the influence of the crown ether is the compatibility of the alkali metal ion with the binding site of a particular crown ether.[1,6]

In view of the recent interest in the role of crown ethers in influencing the rate of cation migration processes we report the results of our examinations of the radical anions of two simple quinones, 2,5-dimethyl- and 2,5-di-t-butylbenzoquinone, in the presence of dibenzo-18-crown-6 with Li^+, Na^+, or K^+ as the counterion. The interaction between the various alkali metal cations and this particular crown ether is thought to be greatest for K^+.[7,8] In view of the reported instability of the radical anions of these quinones in tetrahydrofuran,[9] 1,2-dimethoxyethane was selected as the solvent for these experiments.

Experimental

All vacuum operations were performed by use of standard high vacuum techniques.

Materials.—1,2-Dimethoxyethane was purified as described previously.[10] Both 2,5-dimethyl- and 2,5-di-t-butyl-benzoquinone were prepared by oxidation of the parent aniline with sodium dichromate and were purified by sublimation.[11] Dibenzo-18-crown-6 (Lancaster Synthesis) was used as supplied and the alkali metals were all washed in light petroleum before use.

Procedure.—Solutions of the quinones in 1,2-dimethoxyethane were prepared by the standard methods described previously.[12] The concentrations of the quinone and the crown ether were arranged to be as near as possible the same, and were in the range 2.5—2.8 × 10^{-3} mol dm^{-3}. The radical anions were prepared from these solutions as described, by using metal films in the experiments involving sodium or potassium and small metal pieces in the experiments involving lithium.

Spectroscopic Measurements.—All e.s.r. spectra were recorded with a Varian E3 spectrometer, the magnetic field sweep of which was calibrated with Fremy's salt.[13] The temperature of the samples was controlled by means of a Varian E4557 variable temperature unit.

Computer Simulation of E.s.r. Spectra.—Computer simulations of the e.s.r. spectra were obtained either with an I.C.L. 2960 computer linked to a Calcomp plotter or with a Data General Nova 1220 computer on line to the spectrometer. The program used in the simulation of the spectra of the 2,5-di-t-butylbenzoquinone radical anion employed the modified Bloch equations appropriate to a two-jump process with two protons interchanging their splitting constants. Allowance was not made within the program for hyperfine structure arising from the t-butyl protons as this was not resolvable within the natural linewidth of the spectra. The program used to simulate the spectra of the 2,5-dimethylbenzoquinone radical anion was similar to that just described except that allowance was made for the additional interchange of splitting constants between the protons of the two methyl groups.

Results

2,5-*Di-t-butylbenzoquinone.*—We describe first the results obtained for the radical anion of 2,5-di-t-butylbenzoquinone in 1,2-dimethoxyethane in the presence of dibenzo-18-crown-6. This quinone was readily reduced with each of the alkali metals to give a yellow solution of the radical anion. The radical anion was almost indefinitely stable when either Na^+ or K^+ was the counterion, but when Li^+ was the counterion the radical anion decayed relatively quickly at the higher temperatures at which spectra were recorded. E.s.r. spectra were recorded over the temperature range 200—340 K for each counterion and are readily interpreted with hyperfine structure observed from only two protons.

Potassium. When potassium was the counterion the ' slow exchange ' spectrum (*i.e.* a doublet of doublets) was not obtained even at the lowest temperature at which a spectrum was recorded [see Figure 1(a)]. It is immediately apparent

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† 6,7,9,10,17,18,20,21-Octahydrodibenzo[*b*,*k*][1,4,7,10,13,16]-hexaoxacyclo-octadecine.

Table 1. Parameters used in the computer simulation of the e.s.r. spectra of the K$^+$–dibenzo-18-crown-6–2,5-di-t-butylbenzoquinone radical anion system in 1,2-dimethoxyethane (splitting constants in μT)

T/K	a(H)	a(H′)	$10^8\tau$/s
202	185	265	52
215	185	264	40
226	185	264	29
236	184	264	23
244	184	264	17.5
254	182	261	12
266	182	261	7
280	182	261	3.5
288	182	261	2
300	182	261	1.3

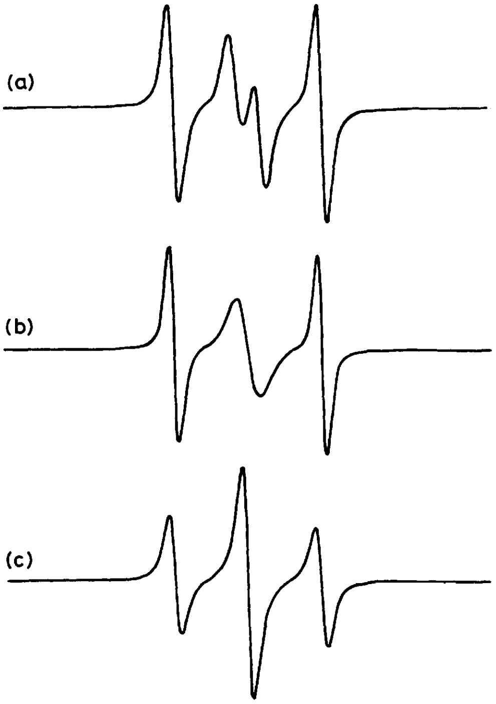


Figure 1. Experimental e.s.r. spectra of the K$^+$–dibenzo-18-crown-6–2,5-di-t-butylbenzoquinone radical anion system in 1,2-dimethoxyethane at (a) 202 K, (b) 244 K, and (c) 300 K

Table 2. Parameters used in the computer simulation of the e.s.r. spectra of the Na$^+$–dibenzo-18-crown-6–2,5-di-t-butylbenzoquinone radical anion system in 1,2-dimethoxyethane (splitting constants in μT)

T/K	a(H)	a(H′)	$10^8\tau$/s
259	161	287	$>$300
272	159	288	300
285	157	288	250
302	155	288	150
314	150	292	100
326	147	292	65
336	146	290	45
344	146	290	44
353	142	294	26

Table 3. Parameters used in the computer simulation of the e.s.r. spectra of the K$^+$-dibenzo-18-crown-6–2,5-dimethylbenzoquinone radical anion system in 1,2-dimethoxyethane (splitting constants in μT)

T/K	a(H)	a(H′)	$10^8\tau$/s
200	147	257	27
207	147	257	17
221	147	257	10.5
231	147	257	6
240	147	257	5
250	147	257	4
259	147	257	2.75
267	147	257	1.8
278	147	257	1.4

from the spectra recorded over the complete temperature range, that linewidth alternation is present and 'fast exchange' spectra are obtained at temperatures $>$*ca.* 300 K [see Figure 1(c)]. A computer simulation has been obtained for each spectrum and each of the various parameters employed in the simulation has been optimised as far as is possible. These parameters are summarised in Table 1.

Sodium. The e.s.r. spectrum of the radical anion with Na$^+$ as the counterion at 200 K is essentially a 1 : 1 doublet of 1 : 1 doublets but the intensity of the central pair of lines is distorted by the presence of a second species. This distortion becomes less noticeable as the temperature is raised until at *ca.* 250 K only the spectrum of the major species remains. This species is still near the 'slow exchange' region but linewidth alternation becomes apparent as the temperature is raised further. The parameters employed in the best fit computer simulations of the spectra of this species, recorded at $\geqslant$259 K, are summarised in Table 2. A comparison of Tables 1 and 2 shows that the lifetime of the counterion at one of the possible sites, at a particular temperature, is very much greater with Na$^+$ as the counterion than with K$^+$.

Lithium. The spectrum obtained for the 2,5-di-t-butylbenzoquinone radical anion when Li$^+$ is the counterion at 198 K is typical of a 'slow exchange' spectrum but more than one species is again present. A third derivative spectrum, recorded at the same temperature, reveals that at least two, and probably three, species are present. As the temperature is raised the spectrum is slowly simplified but still shows interference from at least one other species. However, even at 339 K the major species is still in the 'slow exchange' region. Because of the distortion of the spectrum by other species and the apparent lack of linewidth alternation in the major species, detailed computer simulations have not been attempted for this system. At *ca.* 300 K the two hyperfine splitting constants associated with the major species are a(H) 110 and 344 μT.

2,5-*Dimethylbenzoquinone.*—This quinone was readily reduced by sodium and potassium in 1,2-dimethoxyethane in the presence of dibenzo-18-crown-6 to give a yellow solution of the radical anion. However, there was no detectable reduction when lithium was employed. The radical anion was noticeably less stable than that of 2,5-di-t-butylbenzoquinone, decaying quite quickly at the higher end of the temperature range studied. E.s.r. spectra were recorded over the temperature range 200—333 K with both Na$^+$ and K$^+$ as counterions. The spectra were, naturally, more complex than those for 2,5-di-t-butylbenzoquinone with the methyl protons also involved in the linewidth alternation. In view of the length of the calculations involved only the low field half of the spectrum was computer simulated.

Potassium. At 200 K the e.s.r. spectrum of the 2,5-dimethylbenzoquinone radical anion is near the 'slow exchange' condition [see Figure 2(a)], and at 278 K is near the 'fast

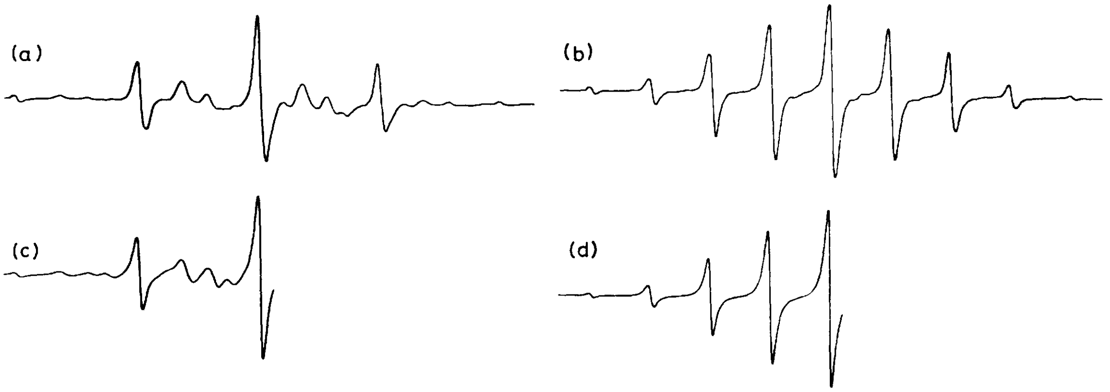


Figure 2. Experimental e.s.r. spectra of the K^+–dibenzo-18-crown-6–2,5-dimethylbenzoquinone radical anion system in 1,2-dimethoxyethane at (a) 200 K and (b) 278 K together with their computer simulations (c) and (d), respectively (parameters as given in Table 3)

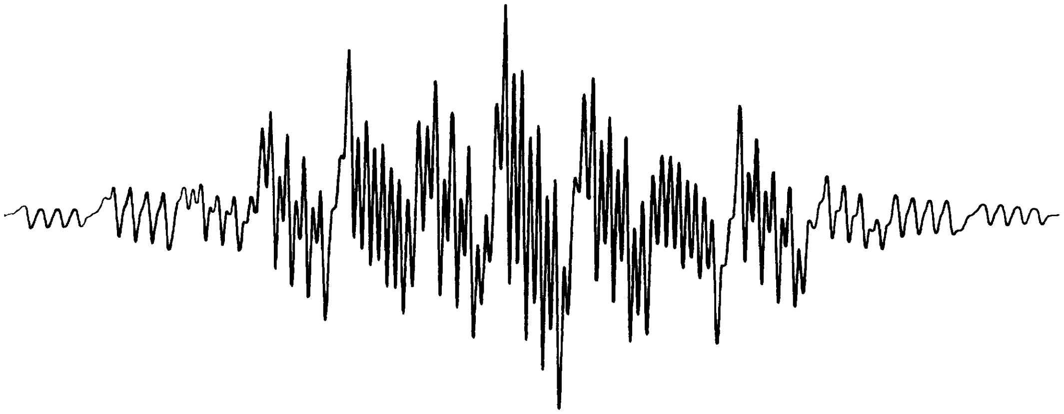


Figure 3. Experimental e.s.r. spectrum of the Na^+–dibenzo-18-crown-6–2,5-dimethylbenzoquinone radical anion system in 1,2-dimethoxyethane at 248 K

exchange ' condition [see Figure 2(b)]. Computer simulations of these two spectra are shown in Figure 2[(c) and (d), respectively]. The various parameters employed in the computer simulations at each temperature have been optimised as far as is possible and are summarised in Table 3.

Sodium. The e.s.r. spectra recorded with Na^+ as the counterion are considerably more complex than with K^+. This is due to the additional hyperfine structure arising from interaction with the ^{23}Na nucleus of the counterion. In view of this additional complication full detailed simulations of these spectra have not been attempted. Up to *ca*. 250 K the spectra are essentially in the ' slow exchange ' condition (see Figure 3); linewidth alternation only becomes noticeable in spectra recorded above this temperature. The magnitude of the sodium hyperfine interaction varies only slightly with temperature.

Discussion

A number of interesting points arise from the present results. The first is the nature of the ion pair in the presence of the crown ether. In the absence of the crown ether, in the same solvent (1,2-dimethoxyethane), the value of $a(H) - a(H')$ for the 2,5-di-t-butylbenzoquinone radical anion increases significantly as the size of the counterion decreases.[2] This points to a ' contact ' ion pair. The values for the same radical anion in the presence of the crown ether follow the same trend (224, 133, and 79 μT at *ca*. 300 K for Li^+, Na^+, and K^+, respectively) and are similar in magnitude to those obtained in the absence of the crown ether. It appears therefore that the addition of the crown ether has no dramatic influence on the environment of the cation relative to the radical anion. This is perhaps not surprising when two factors are considered. First, it is probable that the crown ether has similar solvating properties to 1,2-dimethoxyethane; we will return to this point later. Secondly, the linewidth alternation depends upon a significant interaction of the cation with the preferred site. It is doubtful whether the interaction of a heavily solvated cation with a particular preferred site would be sufficient to give rise to observable linewidth alternation on the e.s.r. timescale. These results indicate that the environment of the cation relative to the preferred site has not been greatly influenced by the addition of the crown ether. The minor contributions to the spectrum at the lower end of the temperature range, when Li^+ or Na^+ is the counterion, could well arise from solvent-separated or crown-separated ion pairs, or from free ions. Certainly a contact ion pair is present in the 2,5-dimethylbenzoquinone radical anion when Na^+ is the counterion, as ^{23}Na hyperfine splitting is observed in the spectrum over the temperature range studied.

In view of the above conclusion the influence of the crown ether on the rate constant and on the activation energy for the cation migration might not be very marked. A comparison of these parameters, in the presence and absence of the crown ether, is only possible for some of the systems studied here.[2,3] However, the addition of the crown ether does appear to modify the rate constant for the migration and, rather un-

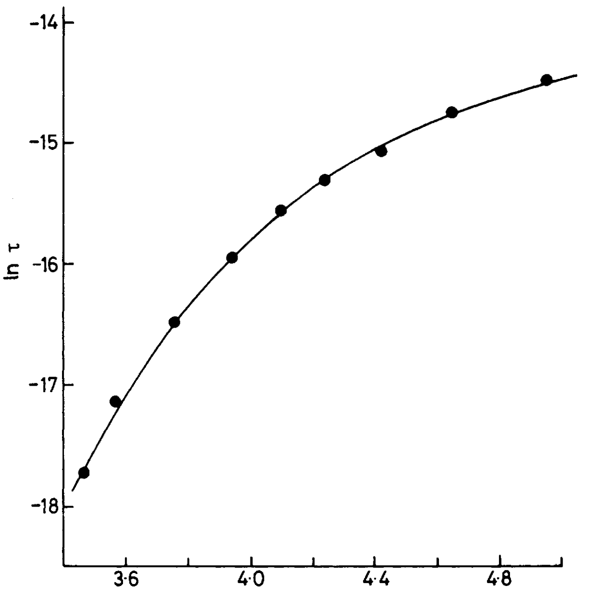
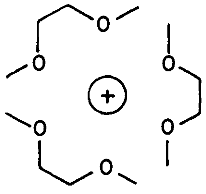
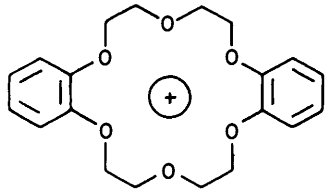


Figure 4. Arrhenius plot for the K$^+$–dibenzo-18-crown-6–2,5-di-t-butylbenzoquinone radical anion system in 1,2-dimethoxyethane

expectedly, also introduces some curvature to the log τ *vs.* $1/T$ plot (see Figure 4) for the K$^+$–2,5-di-butylbenzoquinone system. The other two systems studied in the presence of the crown ether (Na$^+$–2,5-t-butylbenzoquinone and K$^+$–2,5-dimethylbenzoquinone) give good linear plots (E_a 27.0 ± 2.5 and 17.2 ± 2.5 kJ mol^{-1}, respectively), and Warhurst *et al.* reported a linear plot for K$^+$–2,5-di-t-butylbenzoquinone in the absence of the crown ether.[2] There are no immediately obvious factors to which the non-linearity in the Arrhenius plot can be attributed. It is induced by the addition of the crown ether when K$^+$ is the counterion for one benzoquinone but not for the other, and it is induced for 2,5-di-butylbenzoquinone with K$^+$ but not Na$^+$ as the counterion. The most likely explanation is that $k_{obs.} = k_1 + k_2$, which, in turn implies that two different types of ion pair are present over the temperature range studied, with different lifetimes of the cation near to the preferred site in each ion pair. It is reasonable to suggest that in one of these ion pairs the cation is primarily solvated by the solvent, and that in the other it is primarily solvated by the crown ether. It is interesting that the curved Arrhenius plot is obtained for the 2,5-di-t-butyl- and not for the 2,5-dimethyl-benzoquinone radical anion; the main difference between those two is the steric environment adjacent to the preferred site.



(A)



(B)

Warhurst *et al.* concluded that for cation jumping in benzoquinone radical anions the transition state was more solvated than the initial state, but that the transition state was probably still a contact ‘ structure.’[2] Dibenzo-18-crown-6 is generally considered to have a ‘ cavity ’ well matched to the size of K$^+$.[7,8] This could help to explain the lower activation energy in the 2,5-di-t-butylbenzoquinone radical anion system when K$^+$ is the counterion in the presence of the crown ether. The comparatively minor influence of the crown ether on these systems as compared with for example, cation migration in the pyrazine[4] and tetramethylbenzosemiquinone[5,6] radical anions, is probably largely due to the similarity of 1,2-dimethoxyethane (A) to the crown ether (B) as a solvating agent. It is apparent that 1,2-dimethoxyethane can present a solvation environment for the counterion similar to that presented by the crown ether, and that this environment is adaptable to suit the nature, especially the size, of a particular cation. Presumably, therefore, in the cases of Li$^+$ and Na$^+$, solvation by 1,2-dimethoxyethane remains largely preferred to solvation by the crown ether.

References

1 A. J. Burke and B. J. Tabner, *J. Chem. Soc., Perkin Trans. 2*, 1983, 205.
2 J. C. Chippendale and E. Warhurst, *Trans. Faraday Soc.*, 1968, **64**, 2332.
3 P. S. Gill and T. E. Gough, *Trans. Faraday Soc.*, 1968, **64**, 1997.
4 G. F. Pedulli and A. Alberti, *Chem. Phys. Lett.*, 1977, **48**, 72.
5 M. P. Eastman, G. V. Bruno, C. A. McGuyer, A. R. Gutierrez, and J. M. Shannon, *J. Phys. Chem.*, 1979, **83**, 2523.
6 S. Konishi, S. Niizuma, and H. Kokubun, *Chem. Phys. Lett.*, 1980, **71**, 164.
7 N. S. Poonia and V. J. Bajaj, *Chem. Rev.*, 1979, **79**, 389.
8 D. E. Fenton, *Nato Adv. Study Inst. Ser. C*, 1980, **55**, 275.
9 M. P. Khakhar, B. S. Prabhananda, and M. R. Das, *J. Am. Chem. Soc.*, 1967, **89**, 3100.
10 D. Casson and B. J. Tabner, *J. Chem. Soc. B*, 1969, 572.
11 R. Nietzki, *Justus Liebigs Ann. Chem.*, 1882, **215**, 215.
12 D. Casson and B. J. Tabner, *J. Chem. Soc. B*, 1969, 887.
13 R. J. Faber and G. E. Fraenkel, *J. Chem. Phys.*, 1967, **47**, 2462.

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