The Influence of Crown Ethers on the Rate of Intramolecular Cation Exchange involving the 5,12-Dihydrotetracene Radical Anion

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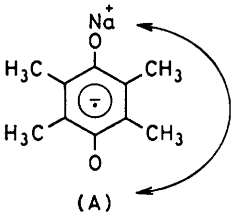
The addition of dibenzo-18-crown-6 to the Na^+–5,12-dihydrotetracene radical-anion ion pair has been found dramatically to reduce the rate of cation migration. The resulting e.s.r. spectra (which exhibit linewidth alternation) have been computer-simulated employing modified Bloch equations. The activation energy for the cation migration process has been found to be 19.3 kJ mol^{-1}.

CROWN ethers have attracted considerable attention recently due to their often dramatic influence on anion–cation and radical-anion–cation ion pairs. For example, the proportion of contact ion pairs in the equilibria involving alkali-metal cations with the fluorenyl and 4,5-methylenephenanthrenyl anions is considerably influenced by the addition of a crown ether.[1,2] This influence is undoubtedly a consequence of the interaction between the macrocyclic ether and the cation. The degree of this interaction, however, varies with the size of the cation and the size of the ' cavity ' in the crown ether.

Although less widely investigated, crown ethers also influence the rate of radical-anion reactions. For example the addition of dibenzo-crown ethers has little effect on the rate of electron transfer between tetracyanoethylene and its radical anion. However, the dimerisation of this radical anion was inhibited by the addition of crown ethers.[3] In a previous publication we reported that crown ethers can not only influence the rate of decay of the fluorene radical anion but also the order of the decay reaction.[4]

Recently evidence has been presented that crown ethers can also influence the rate of cation migration reactions. For example Eastman *et al.* have shown that the addition of various crown ethers dramatically influences the rate of intramolecular Na^+ exchange in the durosemiquinone radical anion (A).[5] Similar observations have been reported by Konishi *et al.*[6] The rate of cation migration in the fluorene radical anion is dramatically reduced in the presence of two dibenzo-crown ethers.[7]



(A)

In this paper we report a further example of this effect in the Na^+–5,12-dihydrotetracene radical anion system.[8]

EXPERIMENTAL

All operations were performed using standard high vacuum techniques.

Materials.—Tetrahydrofuran was purified as described.[9] Dibenzo-18-crown-6, prepared as described by Pederson,[10] was purified as described.[4] 5,12-Dihydrotetracene (Aldrich) was recrystallised from 95% ethanol before use. Lithium, sodium, and potassium were washed in light petroleum before use.

Procedure.—Tetrahydrofuran solutions of 5,12-dihydrotetracene and of a mixture of 5,12-dihydrotetracene and dibenzo-18-crown-6 were prepared by the methods described previously.[11] For experiments involving 5,12-dihydrotetracene only the concentration was 2.7×10^{-3}M. For experiments involving 5,12-dihydrotetracene with dibenzo-18-crown-6 the concentrations were 2.3×10^{-3} and 2.5×10^{-3}M, respectively. The radical anion was prepared from these solutions as described.[11]

Spectroscopic Measurements.—E.s.r. spectra were recorded on a Varian E3 spectrometer and the temperature of the samples was controlled by means of a Varian E 4557 variable temperature unit.

Calculations.—Computer simulations of e.s.r. spectra showing linewidth alternation were obtained using an ICL 1905 F computer. The first part of the program uses modified Bloch equations to derive the spectrum of a radical anion containing two pairs of two protons with interchanging splitting constants and is similar to that already published.[12] The second part of the program introduces the hyperfine splitting from the remaining (non-alternating) protons and records the first derivative spectrum on a Calcomp plotter. A second program, which simulates spectra of constant linewidth was used in conjunction with a Data General Nova 1220 computer on line to the e.s.r. spectrometer.

RESULTS AND DISCUSSION

5,12-Dihydrotetracene (B) is readily reduced by alkali metals in tetrahydrofuran to give a green solution of the radical anion. The principle features of the e.s.r. spectrum of this radical anion, however, vary with the nature of the alkali-metal counterion. The spectrum is easiest to interpret when Li^+ is the counterion and consists of four 1 : 2 : 1 triplets and a 1 : 4 : 6 : 4 : 1 quintet. The fifth triplet is only just visible within the linewidth of the spectrum and it was not possible to measure its splitting constant accurately. The splitting constants obtained by computer simulation of this spectrum are summarised in Table 1 and are in good agreement with published values.[8]

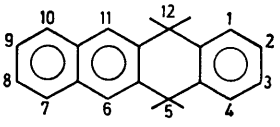
When Na^+ is the counterion the spectrum is again easily interpreted at 203 K to give the splitting constants, obtained by computer simulation, summarised in Table 1. However above this temperature the spectrum is complicated by additional hyperfine splitting arising from the interaction of the unpaired electron with the alkali-metal counterion.

TABLE 1

Parameters used in the computer simulation of the e.s.r. spectra of the 5,12-dihydrotetracene (B) radical anion in tetrahydrofuran at 203 K (splitting constants are in μT)

	Counterion		
	Li^+	Na^+	K^+
$a_{1,4}$	15	20	
$a_{2,3}$			
$a_{6,11}$	417	434	466
$a_{7,10}$	493	516	480
$a_{8,9}$	170	164	174
$a_{5,12}$	339	347	340
$a_{5'.12'}$	339	347	265

In the absence of dibenzo-18-crown-6, when K^+ is the counterion, an alternating linewidth effect is observed. The splitting constants obtained from a computer simulation of the slow exchange region of the spectrum are summarised in Table 1; the various parameters required to simulate these spectra are in good agreement with those reported by Iwaizumi.[8] In tetrahydrofuran the alternating linewidth effect is present only when K^+ is the counterion in the absence of a crown ether.



(B)

Dibenzo-18-crown-6 was added to the Na^+–5,12-dihydrotetracene radical anion system in which interaction of the unpaired electron with the alkali metal counterion had been observed in the absence of the crown ether. The convenient size of this alkali metal ion compared with the size of the ' cavity ' in this crown ether is believed to lead to a strong cation–crown ether interaction. A profound influence on the magnitude of the alkali-metal splitting in this spectrum was therefore anticipated. E.s.r. spectra were recorded over the temperature range 193—273 K and indicated a complete absence of any alkali-metal hyperfine structure originating from interaction of the unpaired electron with the cation over this temperature range. It would therefore appear that the cation–crown ether interaction is sufficiently strong in this system to remove the cation from the immediate vicinity of the radical anion. However, these spectra were quite different in appearance to the spectrum at 203 K in the absence of the crown ether (a_{Na} *ca.* 0). In fact the spectra for this system are very similar to those obtained in the K^+–5,12-dihydrotetracene radical-anion system and it appears therefore that in the presence of the crown ether the four methylene protons are no longer equivalent and that the crown ether has therefore induced an alternating linewidth effect in the Na^+–5,12-dihydrotetracene radical anion system.

It is apparent from an inspection of the e.s.r. spectra obtained from the Na^+–5,12-dihydrotetracene radical-anion–dibenzo-18-crown-6 system that at 273 K the intensity of each line is approximately that expected from a comparison with spectra obtained for the Li^+–5,12-dihydrotetracene system. However at lower temperatures the amplitude of certain lines decreases until at the lowest temperature at which spectra were recorded (193 K) new lines (of relatively low amplitude) appear. A further examination of these spectra reveals that it is the lines associated with the quintet which are involved in this process, the ' pure ' lines of the 1 : 2 : 1 triplets retaining their correct intensities. It is evident therefore that it is the four methylene protons that are involved in this process and that at low temperatures they are not equivalent in the presence of the crown ether.

We have attempted a computer simulation of each spectrum assuming that it is the methylene protons whose splitting constants undergo out-of-phase modulation. ' Slow exchange ' spectra were obtained at the lower temperatures and from these spectra it was possible to obtain the splitting constants of each of two pairs of methylene protons. The lineshape arising from the interaction of the unpaired electron with these protons was then computed employing the modified Bloch equations appropriate to a two-jump model in which the interconverting species have equal lifetimes and spin–spin relaxation times.[12] The remaining 1 : 2 : 1 triplets were then introduced into the computation to give the resulting computer simulation of the complete spectrum. At each temperature very many computer simulations were attempted to obtain the best possible fit to the experimental spectrum. Of these simulations two have been selected for illustration in Figure 1. We believe that the simulations have been optimised as far as possible, and while any further modification of the parameters used in each simulation might result in an improvement of a particular feature, it does so at the expense of some other feature. The parameters used in obtaining the best simulation at each temperature are summarised in Table 2.

The influence of τ on the lineshape resulting from the interaction of the unpaired electron with the methylene protons is obscured to some extent by the overlapping of lines arising from the ring protons. However it is possible to deconvolute the computer simulations and so examine the variation in this lineshape in the absence of these lines. A selection of these deconvolutions is illustrated in Figure 2.

The question remains as to the nature of the process which leads to the observed linewidth alternation in the Na^+–5,12-dihydrotetracene radical anion–dibenzo-18-crown-6 system. Iwaizumi and Isobe consider that in the K^+–5,12-dihydrotetracene radical anion system the linewidth alternation does not result from the ' inversional motion ' of the radical anion.[8] This conclusion is based upon the observation that the ratio $a_{\beta a}/a_{\beta e}$

($=\cos^2\theta_a/\cos^2\theta_e$) should be 4 in such cases.[12] Indeed values of this magnitude have been observed for such interconversions.[13] However, the ratio of the values observed for the methylene protons in the K^+–5,12-dihydrotetracene radical-anion system is 1.29, and for the Na^+–5,12-dihydrotetracene radical anion–dibenzo-18-crown-6 system (see Table 2) is also 1.29. Iwaizumi and Isobe interpreted this value as indicating that the inversion process was rapid and that the different methylene splitting constants were a consequence of a polar effect resulting from two different sites for the alkali-metal counterion. In order to produce the linewidth effects observed both in the presence and absence of the crown ether these two sites must be above and below the molecular plane. We would support this view and have found an additional example of this effect in the fluorene radical anion (also in the presence of a crown ether).[7] In this radical anion inversional motion is not considered to be a possible explanation of the observed linewidth alternation. Again an exchange of the crown ether–cation complex from one side of the molecular plane to the other has been proposed and in this radical anion the ratio of the methylene proton splitting constants is 1.29. The similarity of this value in all three systems supports the view that the linewidth alternation is a consequence of the migration of the cation from one side of the molecular plane to the other.

TABLE 2

Parameters used in the computer simulation of the e.s.r. spectra of the Na^+–dibenzo-18-crown-6–5,12-dihydrotetracene radical anion system in tetrahydrofuran (splitting constants are in μT)

T/K	193	203	213	223	233	243	253	263	273
$a_{1,4}$	20	20	20	20	20	20	20	20	20
$a_{2,3}$									
$a_{6,11}$	426	424	426	426	426	426	426	426	426
$a_{7,10}$	506	502	507	507	512	512	512	512	512
$a_{8,9}$	160	164	164	164	164	164	164	164	164
$a_{5,12}$	379	373	376	376	378	378	378	378	378
$a_{5',12'}$	295	288	292	292	294	294	294	294	294
τ/s	1.4×10^{-6}	9.0×10^{-7}	4.5×10^{-7}	3.3×10^{-7}	2.0×10^{-7}	1.4×10^{-7}	9.0×10^{-8}	6.0×10^{-8}	4.5×10^{-8}

It is interesting that this type of cation migration process appears to be susceptible to the presence of a crown ether. It is not possible, of course, in the absence of linewidth alternation to estimate the frequency of the cation migration process, but the absence of observed linewidth effects would suggest a frequency $>10^8$ s^{-1}. The crown ether therefore slows down this migration process by a factor of between 10 and 100 (and possibly by a greater amount). Presumably this change in migration rate is a direct consequence of the large size of the counterion–crown ether complex.

The data required to simulate each spectrum in the Na^+–5,12-dihydrotetracene radical anion–dibenzo-18-crown-6 enables a value of the velocity constant ($=1/\tau$) to be obtained for the migration process at each temperature. Figure 3 shows the resulting $\log_{10}k$ *versus* $1/T$ plot from which an activation energy 19.3 kJ mol^{-1} has been obtained. The corresponding values of $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ are 27.0 kJ mol^{-1} (at 234 K), 17.3 kJ mol^{-1}, and -39.9 J mol^{-1} K^{-1}, respectively. It is perhaps misleading to compare these values too closely

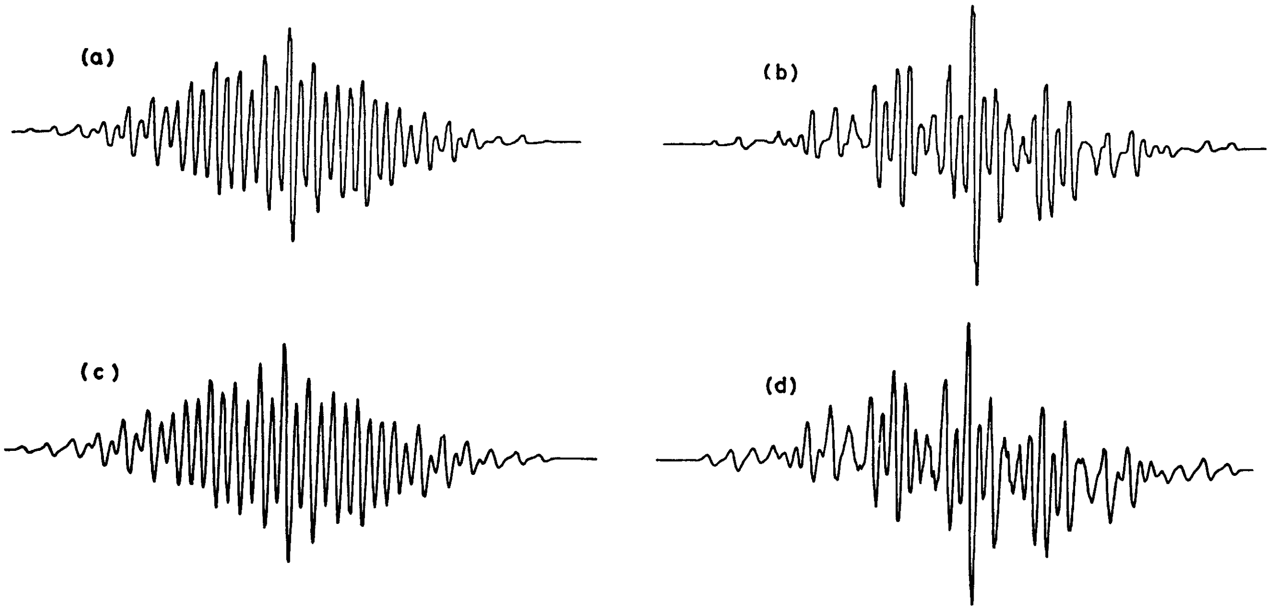


FIGURE 1 The experimental e.s.r. spectra of the Na^+–dibenzo-18-crown-6–5,12-dihydrotetracene radical anion system in tetrahydrofuran at (a) 253 K, and (b) 213 K together with their computer simulations (c) and (d) respectively (parameters as given in Table 2)

with the values obtained for the K^+–5,12-dihydrotetracene system due to the uncertainty attached to the influence of a change in the nature of the counterion. However, the larger $\Delta H^\ddagger$ observed in the presence of the crown ether could perhaps be anticipated as a consequence of the very bulky crown ether–cation complex compared with the size of the uncomplexed cation. Similarly, the more positive value of $\Delta S^\ddagger$ in the presence of the crown ether could again be anticipated as the strong cation–crown ether interaction would result in a vary much reduced cation–radical anion interaction. The crown ether–cation complex would therefore only interact loosely with the radical anion in the transition state.

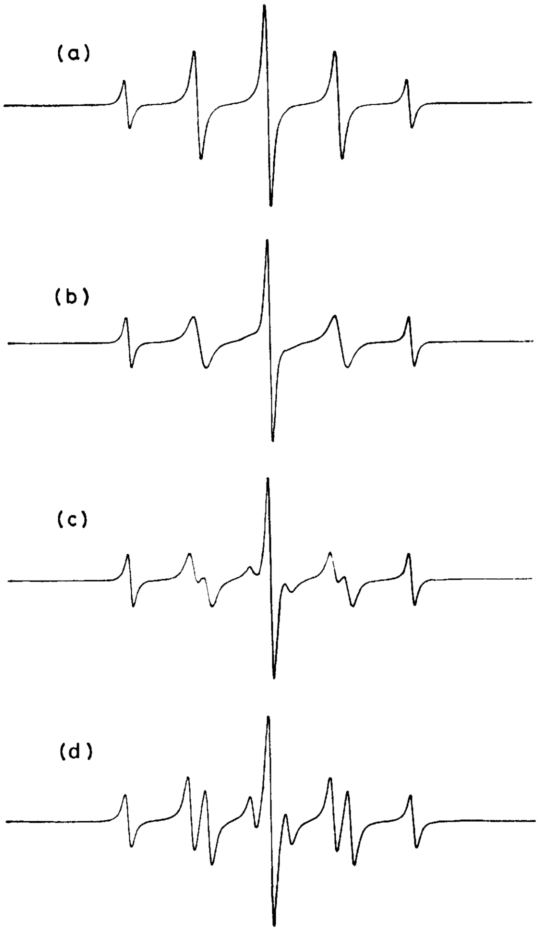


FIGURE 2 Deconvoluted computer simulations of the e.s.r. spectra of the Na^+–dibenzo-crown-6–5,12-dihydrotetracene radical anion system at (a) 273, (b) 243, (c) 223, and (d) 193 K

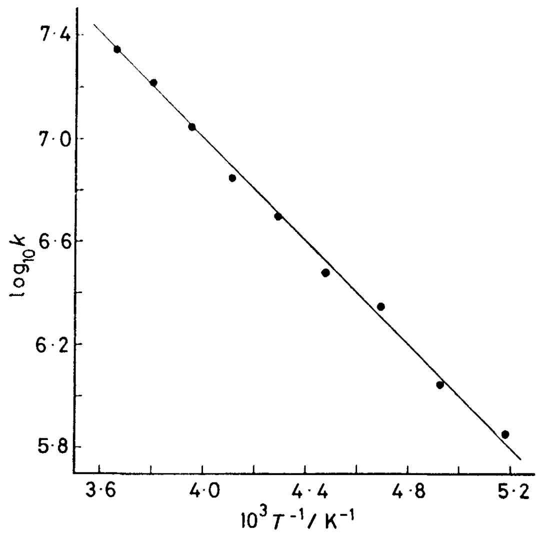


FIGURE 3 The Arrhenius plot for the Na^+–dibenzo-18-crown-6–5,12-dihydrotetracene radical anion system in tetrahydrofuran

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