Radical-anion Intermediates. Part 8.[1] The Influence of a Crown Ether on the Fluorene and 9-Methylfluorene Radical-anions

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The addition of dibenzo-18-crown-6 has been found to influence the rate of decay of the fluorene and 9-methylfluorene radical anions. The influence is most significant when Li^+ is the counterion and the second-order kinetics observed with this counterion in the absence of the crown ether have been found to be prevented by its addition.

THE cation-complexing properties of crown ethers have recently attracted considerable attent[illegible] In particular it has been shown that the addition of a crown ether can profoundly influence the position of anion–cation equilibria. Detailed investigations have been made of this phenomenon in the fluorenyl anion [2-4] and 4,5-methylenephenanthrenyl anion systems.[5] In general it appears that the cation-complexing properties of the crown ether depend not only upon the size of the cation but also upon the size of the ' cavity ' in the crown ether. It appears that more than one type of ' crown separated ' ion pair may also be possible.[6] One of the most widely studied crown ethers is dibenzo-18-crown-6 for which it appears that the degree of interaction between the crown ether and the alkali metal cations varies in the sequence $Na^+ > K^+ > Li^+$.[2,7,8]

In previous publications we have reported a study of the decay of the radical anions of fluorene and of a variety of related molecules to the corresponding anions.[9-12] This rate is markedly influenced by the nature of the cation and consequently the addition of a crown ether to these systems can be expected to produce some interesting results. In this paper we report the influence of dibenzo-18-crown-6 on the rate of decay of the fluorene and 9-methylfluorene radical anions and also make the first report of an unexpected but dramatic effect upon the e.s.r. spectrum of the fluorene radical anion.

EXPERIMENTAL

All operations were performed using standard high-vacuum techniques.

Materials.—Tetrahydrofuran, fluorene, and 9-methylfluorene were purified as described.[5,9] Dibenzo-18-crown-6, prepared as described by Pederson,[13] was recrystallised from toluene, m.p. 166 °C (lit.,[14] 164 °C), and its purity checked by n.m.r. and t.l.c. Lithium, sodium, and potassium were washed in light petroleum before use.

Procedure.—Tetrahydrofuran solutions of fluorene and 9-methylfluorene with dibenzo-18-crown-6 were prepared as described.[9] For experiments involving fluorene and dibenzo-18-crown-6 and 9-methylfluorene and dibenzo-18-crown-6 the molar ratios were 1 : 1. Concentrations of reagents in all experiments were in the range $1—3 \times 10^{-3}$ mol l^{-1}. The radical anions were prepared from these solutions as described.[9]

Spectroscopic Measurements.—U.v.–visible absorption spectra were recorded on a Unicam SP 800 spectrophotometer over the required temperature range using the constant-temperature cell housing described.[13] E.s.r. spectra were recorded on a Varian E3 spectrometer and the temperature of these samples was controlled by means of a Varian E4557 variable temperature unit.

Calculations.—Values of velocity constants, $\Delta G^‡$, $\Delta H^‡$, and $\Delta S^‡$ were obtained with the aid of an ICL 1909 computer.

RESULTS

U.v.–Visible Absorption Spectra.—When a tetrahydrofuran solution of fluorene and dibenzo-18-crown-6 (mole ratio 1 : 1) was brought into contact with a lithium film at −70 °C an intense blue colour quickly developed. The resulting solution, which was relatively stable at −70 °C, gave an absorption spectrum characteristic of the fluorene radical anion previously studied in the absence of the crown ether.[9] Elevation of the temperature resulted in the decay of the blue radical anion solution to give a yellow solution of the fluorenyl anion with an absorption spectrum similar to those of the fluorenyl anion–crown ether–Li^+ systems previously reported.[4] Similar observations were made when the solution was brought into contact with either a sodium or a potassium film. However, in the case of the latter alkali metal the decay of the radical anion to the anion was too rapid, even at −70 °C, to record a reliable absorption spectrum of the radical anion.

Similar observations were made when a tetrahydrofuran solution of 9-methylfluorene and dibenzo-18-crown-6 (mole ratio 1 : 1) was brought into contact with a sodium film at −70 °C. Again elevation of the temperature resulted in a yellow solution of the anion with a characteristic absorption spectrum.[11] Unfortunately when the experiment was repeated with either a potassium or a sodium film the radical anion–crown ether complex was found to be insoluble and it was not possible, therefore, to obtain any data for this radical anion with these alkali metal counterions in the presence of the crown ether.

Kinetics.—*Fluorene radical anion decay.* The kinetics of the radical anion decay were studied by recording either the decrease in the intensity of the absorption in the region 680—695 nm or the decrease in the intensity of the e.s.r. absorption. Measurements using these two different techniques on the same system at the same temperature gave values for the velocity constant which agreed within experimental error. The reaction curves were analysed by plotting the functions log $(a - x)$ and $1/(a - x)$ *versus* time and were found to be first order with respect to the radical anion concentration for both counterions. The temperature dependence of the velocity constant for both of these systems is summarised in Table 1 and the values of $\Delta G^‡$, $\Delta H^‡$, and $\Delta S^‡$ in Table 3.

9-Methylfluorene radical anion decay. The decay of the

TABLE 1

Temperature dependence of the velocity constant for the decay of the fluorene radical anion in the presence of dibenzo-18-crown-6 (mole ratio 1 : 1) in tetrahydrofuran solution

Counterion	$10^3k/s^{-1}$	T/K	E/kJ mol^{-1}
Lithium	24.70	245	68.5
	9.99	239.5	
	6.08	234	
	2.22	228.5	
	1.02	223	
	0.32	217.5	
Sodium	28.70	272.5	87.8
	14.20	267.5	
	4.89	262	
	3.40	259	
	2.07	256	
	0.91	251	
	0.40	245	

Velocity constants are to within ±10%.

9-methylfluorene radical anion in the presence of dibenzo-18-crown-6 with sodium as the counterion was followed, as before, by recording the decrease in the intensity of the absorption in the region 670—690 nm or the decrease in the intensity of the e.s.r. absorption. Analysis of these reaction curves (as above) showed that the decay was first order with respect to the radical anion. The temperature dependence of the velocity constant is summarised in Table 2 and the values of $\Delta G^‡$, $\Delta H^‡$, and $\Delta S^‡$ in Table 3.

TABLE 2

Temperature dependence of the velocity constant for the decay of the 9-methylfluorene radical anion in the presence of dibenzo-18-crown-6 (mole ratio 1 : 1) in tetrahydrofuran solution

Counterion	$10^3k/s^{-1}$	T/K	E/kJ mol^{-1}
Sodium	17.30	267.5	66.0
	8.10	262	
	6.77	259.5	
	5.06	256.5	
	3.95	253	
	2.85	251	
	1.86	247.5	
	0.33	245	

Velocity constants are to within ±10%.

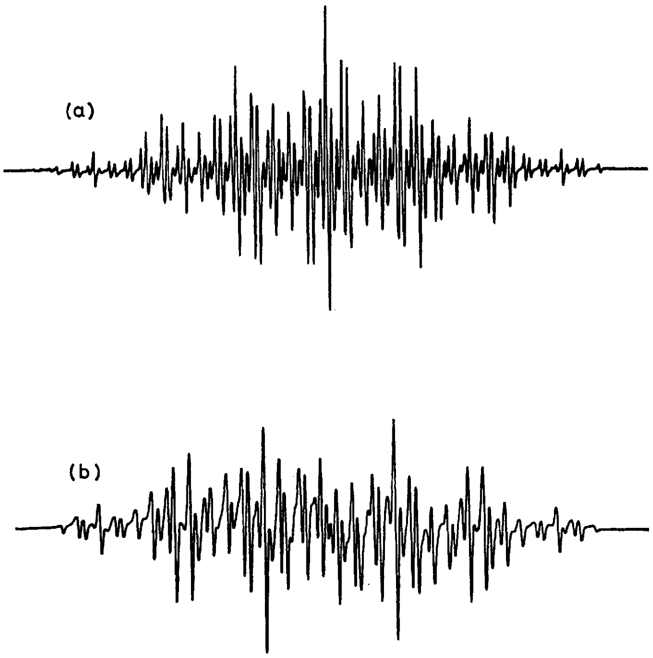
TABLE 3

Summary of the values of $\Delta G^‡$, $\Delta H^‡$, and $\Delta S^‡$ at 298 K (determined by computer extrapolation if necessary) for each of the systems studied

	$\Delta G^‡$/ kJ mol^{-1}	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J mol^{-1} K^{-1}
Li^+–fluorene [a]	86.9	45.1 ± 4.6	−140.4
Li^+–fluorene + crown ether	67.3	66.5 ± 2.5	−2.5
Na^+–fluorene [a]	75.7	54.6 ± 6.3	−69.8
Na^+–fluorene + crown ether	74.0	85.7 ± 3.3	39.3
Na^+–9-methylfluorene [b]	83.2	37.2 ± 3.3	−154.2
Na^+–9-methylfluorene + crown ether	75.5	64.0 ± 5.0	−39.3

[a] Taken from ref. 9. [b] Taken from ref. 11.

E.S.R. Spectra.—The e.s.r. spectrum of the fluorene radical anion in the presence of dibenzo-18-crown-6 is dramatically different to the spectrum in the absence of the crown ether (see Figure). In particular it is noticeable that the central line in the spectrum has a much reduced intensity in the presence of the crown ether. This effect is present when either Na^+ or Li^+ is the counterion but is more noticeable when Li^+ is the counterion. In addition this feature is temperature dependent, being less evident at higher temperatures. At sufficiently low temperatures the splitting constant with a(2H) 380 μT appears almost as a 1 : 1 doublet with a 740 μT. However the other triplets in the spectrum appear to retain their true 1 : 2 : 1 relative intensities with splitting constants differing only slightly in the presence of the crown ether. The splitting constants obtained from these spectra are summarised in Table 4.



The e.s.r. spectrum of the fluorene radical anion at 203 K with (a) Na^+ as the counterion and (b) with Na^+ as the counterion in the presence of dibenzo-18-crown-6. Both spectra recorded in tetrahydrofuran solution

TABLE 4

Hyperfine splitting constants (in μT) obtained for the fluorene radical anion in the presence and absence of dibenzo-18-crown-6 in tetrahydrofuran

Position	Fluorene–Na^+ [a]	Fluorene–Na^+–crown ether [b]
1	119	121
2	500	497
3	88	92
4	410	412
9	380	370 [c]

[a] Spectrum recorded at 203 K (taken from ref. 9). [b] Spectrum recorded at 203 K. [c] See text.

Hyperfine splitting constants are ±2 μT. The g values of the two spectra are the same to ±0.0005.

In contrast to the e.s.r. spectrum of the fluorene radical anion the e.s.r. spectrum of the 9-methylfluorene radical anion appears to be unaffected by the presence of the crown ether. This spectrum has a greater linewidth both in the presence and absence of the crown ether than that of the fluorene radical anion and within the linewidth of the spectrum the individual splitting constants appear to be little influenced by the crown ether.

DISCUSSION

Kinetics.—There are two interesting features of the observed kinetics. First, the crown ether influences the rate of the radical anion decay. Secondly, second-order kinetics are not observed in the Li^+–fluorene radical anion system at low temperatures when the crown ether is present.

When sodium is the counterion the influence of the crown ether on the rate of the radical anion decay for both the fluorene radical anion and the 9-methylfluorene radical anion is significant but not pronounced. However, over the accessible temperature range, the difference in the velocity constants in the presence and absence of the crown ether (at the same temperature) does not exceed a factor of 10. In contrast the difference in the velocity constants is more pronounced in the Li^+–fluorene radical anion system. At the same temperature the velocity constant is always larger in the presence of the crown ether (by a factor of *ca.* 300 at higher temperatures).

In the absence of the crown ether the greatest proportion of solvent separated ion pairs would be expected when Li^+ is the counterion. The addition of the crown ether might therefore be expected to have a dramatic influence on the ion-pairing properties of the Na^+–fluorene radical anion system where a change from contact to crown-separated ion pairs would be anticipated. However since this crown ether has reduced complexing properties towards the Li^+ ion its influence on the Li^+–fluorene radical anion system would be expected to be fairly marginal. The significant influence of the crown ether in this latter system is therefore surprising.

In each of the three systems studied (see Table 3) $\Delta H^\ddagger$ is greater in the presence of the crown ether and $\Delta S^\ddagger$ more positive. The increase in $\Delta H^\ddagger$ could be a consequence of the strong interaction between the cation and the crown ether. The rate of decay in the absence of the crown ether is very much dependent upon the nature of the cation. The environment of the cation with respect to the radical anion is therefore of fundamental importance in determining the rate of reaction. It follows therefore that the addition of the crown ether, with its strong interaction with the cation, will reduce the coulombic interaction particularly in the transition state, thus leading to an increase in $\Delta H^\ddagger$. The reduced coulombic interaction in the transition state in the presence of the crown ether could also explain the more positive $\Delta S^\ddagger$, as the crown ether–cation complex would be unable to approach the radical anion as closely as the uncomplexed cation.

It is also interesting to note that in the presence of the crown ether no second-order kinetics are observed in the Li^+–fluorene radical anion system. The addition of the same crown ether to the alkali metal cation–4,5-methylenephenanthrene radical anion system also resulted in the elimination of second-order kinetics.[12] If the second-order kinetics observed in the absence of the crown ether are a consequence of a bimolecular reaction between two radical anions this change of order might be anticipated. Presumably, in the presence of the bulky crown ether, a bimolecular collision is sterically hindered. A further example of a crown ether influencing a radical anion in this way can be found in the K^+–tetracyanoethylene radical anion system where the dimerisation of this radical anion is prevented by the addition of a crown ether.[15]

E.S.R. Spectra.—The addition of dibenzo-18-crown-6 has a dramatic effect upon the e.s.r. spectrum of the fluorene radical anion when either Li^+ or Na^+ is the counterion. The effect exhibits itself as a decrease in the intensity of the central line of the 1 : 2 : 1 triplet with a_H 380 μT which appears, at low temperatures, almost as a 1 : 1 doublet with a_H *ca.* 740 μT. The relative intensities of the remaining 1 : 2 : 1 triplets appear to be unaffected. The marked temperature dependence of this effect, which is associated with the pair of methylene protons at the 9-position, is typical of an alternating linewidth effect. A detailed investigation of this effect is in progress and will be the subject of a subsequent publication.

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