

## Radical-anion Intermediates. Part VI.<sup>1</sup> The Effect of a Crown Ether on the 4*H*-Cyclopenta[*def*]phenanthrene System

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The effect of the addition of dibenzo-18-crown-6-ether on the decay of the 4*H*-cyclopenta[*def*]phenanthrene radical anion has been examined. In contrast to the second-order kinetics observed in the absence of a crown ether, the decay of radical anion is first order for each of the counterions studied when the crown ether is present in an approximately equimolar quantity. The radical anion is also considerably more stable in the presence of the crown ether, particularly when either K<sup>+</sup> or Na<sup>+</sup> is the counterion. The crown ether also markedly influences the position of the contact-solvent separated ion pair equilibrium for the 4*H*-cyclopenta[*def*]phenanthryl anion, the selectivity being in the sequence Na<sup>+</sup> > K<sup>+</sup> > Li<sup>+</sup>.

THE ion pairing properties of a number of anions and radical anions have been investigated recently using a variety of techniques. Information obtained from the e.s.r. spectra of radical anions has been particularly valuable in this respect whilst for the anions studies of the u.v.-visible absorption spectra have been equally valuable. One anion which has been studied in detail is the fluorenyl anion for which it has been established that the relative proportion of solvent separated to contact ion pairs varies with solvent, temperature, and counterion.<sup>2</sup>

The influence of macrocyclic crown polyethers on the ion pairing properties of such systems has aroused considerable interest.<sup>3,4</sup> The crown ethers form complexes with alkali metal cations which, for example, result in a considerable increase in the solubility of salts in organic solvents.<sup>5,6</sup> The stability of the cation-crown ether complex depends upon the diameter of the cation and the size of the 'hole' in the polyether. For example, the dibenzo-18-crown-6-ether-alkali metal cation complex has a selectivity in the sequence Na<sup>+</sup> > K<sup>+</sup> > Cs<sup>+</sup> > Li<sup>+</sup><sup>3,4,7</sup> and it obviously influences the position of ion pair equilibria.

Recently we have been interested in the reactions of radical anions. For example, the fluorene radical anion, whilst being relatively stable at -70 °C, decays at higher temperatures to give the fluorenyl anion.<sup>8</sup> The kinetics of the radical anion decay have been found to be either of the first or of the second order, the latter being favoured by those conditions that favour solvent separated ion pairs. It was hoped, therefore, that the addition of a crown ether to one of these systems might help to clarify the mechanism of the radical anion decay. The system chosen for study was the 4*H*-cyclopenta[*def*]phenanthrene radical anion.

### EXPERIMENTAL

All operations were performed with standard high-vacuum techniques.

**Materials.**—Tetrahydrofuran and 4*H*-cyclopenta[*def*]phenanthrene were purified as described.<sup>9,10</sup> Dibenzo-18-crown-6-ether, prepared as described by Pederson,<sup>5</sup> was

<sup>1</sup> Part V, B. J. Tabner and T. Walker, *J.C.S. Perkin II*, 1972, 2010.

<sup>2</sup> T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, 1966, **88**, 307.

<sup>3</sup> C. J. Pederson, *J. Amer. Chem. Soc.*, 1970, **92**, 386.

<sup>4</sup> J. Smid, *Angew. Chem. Internat. Edn.*, 1972, **11**, 112.

<sup>5</sup> C. J. Pederson, *J. Amer. Chem. Soc.*, 1967, **89**, 7017.

recrystallised twice from toluene, m.p. 166 °C (lit.,<sup>11</sup> m.p. 164 °C), and its purity was checked by n.m.r. spectroscopy and t.l.c. Lithium, sodium, and potassium were washed in light petroleum before use.

**Procedure.**—Tetrahydrofuran solutions of 4*H*-cyclopenta[*def*]phenanthrene with dibenzo-18-crown-6-ether were prepared as described.<sup>10</sup> The concentration of 4*H*-cyclopenta[*def*]phenanthrene in the resulting solutions was in the range 1–5 × 10<sup>-3</sup> mol l<sup>-1</sup> and the 4*H*-cyclopenta[*def*]phenanthrene radical anion was prepared from these solutions as described.<sup>10</sup>

**Spectroscopic Measurements.**—U.v.-visible absorption spectra were recorded on a Unicam SP 800 spectrophotometer over the temperature range ±50 °C using the constant temperature cell housing described.<sup>4</sup> E.s.r. spectra were recorded on a Varian E3 spectrometer and the temperature of the samples was controlled by means of a Varian E4557 variable temperature unit. Temperature control was ±0.2 °C over this range.

**Calculations.**—Values of velocity constants, Δ*G*<sup>‡</sup>, Δ*H*<sup>‡</sup>, and Δ*S*<sup>‡</sup> were obtained with the aid of an I.C.L. 1909 computer.

### RESULTS

**Spectra.**—4*H*-Cyclopenta[*def*]phenanthrene reacts with lithium, sodium, or potassium in the presence of dibenzo-18-crown-6-ether at -70 °C to form a yellow solution. These solutions have u.v.-visible absorption spectra characteristic of the 4*H*-cyclopenta[*def*]phenanthrene radical anion and an e.s.r. spectrum identical to that obtained for the 4*H*-cyclopenta[*def*]phenanthrene radical anion in the absence of the crown ether.<sup>10</sup> At temperatures above -70 °C the radical anion decays to give a pink solution of the 4*H*-cyclopenta[*def*]phenanthryl anion (identified by its characteristic u.v.-visible absorption spectrum).

**Kinetics.**—*Radical anion decay.* Solutions were prepared for this study in which 4*H*-cyclopenta[*def*]phenanthrene and the crown ether were present in approximately equimolar quantities. Owing to overlap in the visible absorption spectrum of the radical anion and anion absorptions the decay was followed by measuring the decrease in the amplitude of the first derivative e.s.r. spectrum. The reaction curves were analysed by plotting the functions 1/(*a* - *x*) and log (*a* - *x*) against time and were found to be

<sup>6</sup> D. J. Sam and H. E. Simmons, *J. Amer. Chem. Soc.*, 1972, **94**, 4024.

<sup>7</sup> K. H. Wong, G. Konizer, and J. Smid, *J. Amer. Chem. Soc.*, 1970, **92**, 666.

<sup>8</sup> D. Casson and B. J. Tabner, *J. Chem. Soc. (B)*, 1969, 887.

<sup>9</sup> D. Casson and B. J. Tabner, *J. Chem. Soc. (B)*, 1969, 572.

<sup>10</sup> D. Casson and B. J. Tabner, *J. Chem. Soc. (B)*, 1970, 1560.

<sup>11</sup> C. J. Pederson and H. K. Frensdorff, *Angew. Chem. Internat. Edn.*, 1972, **11**, 16.

first order with respect to the radical anion for each of the counterions over the temperature range studied.

The temperature dependence of the velocity constant was determined for each of the counterions and is summarised in Table 1. The values of  $\Delta G^\ddagger$ ,  $\Delta H^\ddagger$ , and  $\Delta S^\ddagger$  are summarised in Table 4.

TABLE 1

Temperature dependence of the velocity constant for the decay of the 4*H*-cyclopenta[*def*]phenanthrene radical anion in the presence of a crown ether: radical anion mole ratio of 0.86 with tetrahydrofuran as solvent

Counterion	$k/s^{-1}$	$t/^\circ C$	$E/kJ\ mol^{-1}$
Lithium	$9.26 \times 10^{-3}$	25.3	92.4
	$4.64 \times 10^{-3}$	20.3	
	$2.37 \times 10^{-3}$	14.5	
	$1.29 \times 10^{-3}$	9.5	
	$5.58 \times 10^{-4}$	5.0	
	$2.75 \times 10^{-4}$	-0.5	
Sodium	$2.79 \times 10^{-2}$	25.3	93.2
	$1.55 \times 10^{-2}$	20.3	
	$6.93 \times 10^{-3}$	14.5	
	$3.19 \times 10^{-3}$	9.5	
	$1.90 \times 10^{-3}$	5.0	
		-0.5	
Potassium	$8.12 \times 10^{-3}$	-0.5	68.1
	$4.32 \times 10^{-3}$	-5.5	
	$1.78 \times 10^{-3}$	-11.0	
	$1.09 \times 10^{-3}$	-16.5	
	$6.31 \times 10^{-4}$	-22.0	

*Influence of the crown ether mole ratio.* In order to investigate the influence of the crown ether: radical anion mole ratio on the kinetics of this system the concentration of the crown ether was varied. The concentration of 4*H*-cyclopenta[*def*]phenanthrene was fixed (at *ca.*  $3 \times 10^{-3}$  mol l<sup>-1</sup>) and the crown ether: radical anion mole ratio varied from 0.13 to 1.56. Sodium was chosen as the counterion since the rate of the radical anion decay was reasonable over a convenient range of temperatures for this counterion. In addition the selectivity of dibenzo-18-crown-6-ether appears to be greatest for sodium.<sup>3,4,7</sup> The reaction curves were analysed as above and the order of the reaction was found to

*Equilibria.*—The effect of the crown ether on the ion pairing properties of the 4*H*-cyclopenta[*def*]phenanthryl anion. In the absence of the crown ether the visible absorption spectrum of the 4*H*-cyclopenta[*def*]phenanthryl anion can be interpreted in terms of an equilibrium between contact and solvent separated ion pairs.<sup>9</sup> The absorption maxima for the solvent separated ion pairs occur at 512 and 542 nm and for the contact ion pairs varies with counterion from 460 (when Li<sup>+</sup> is the counterion) to 492 nm (when K<sup>+</sup> is the

TABLE 2

Temperature dependence of the velocity constant for the decay of the 4*H*-cyclopenta[*def*]phenanthrene radical anion for different mole ratios of dibenzo-18-crown-6-ether, with sodium as the counterion in tetrahydrofuran

Mole ratio (crown ether : radical anion)	$k/s^{-1}$	$t/^\circ C$	$E/kJ\ mol^{-1}$
1.56	$2.01 \times 10^{-2}$	25.3	83.2
	$9.16 \times 10^{-3}$	20.3	
	$6.24 \times 10^{-3}$	14.5	
	$4.34 \times 10^{-3}$	9.5	
	$2.07 \times 10^{-3}$	5.0	
	$6.33 \times 10^{-4}$	-0.5	
0.52	$1.11 \times 10^{-2}$	20.3	94.0
	$5.52 \times 10^{-3}$	14.5	
	$3.92 \times 10^{-3}$	9.5	
	$1.39 \times 10^{-3}$	5.0	
	$5.92 \times 10^{-4}$	-0.5	
0.30	Mixed-order kinetics		
	$k/l\ mol^{-1}\ s^{-1}$		
0.13	50.5	14.5	51.4
	27.4	9.5	
	18.1	5.0	
	13.1	-0.5	
	9.5	-5.5	

counterion). Similar absorption spectra were obtained in the presence of the crown ether but the relative intensity of the absorption at each wavelength differed from those

TABLE 3

A summary of the values of  $k$ ,  $\Delta G^\ddagger$ ,  $\Delta H^\ddagger$ , and  $\Delta S^\ddagger$  at 25 °C for different dibenzo-18-crown-6-ether: 4*H*-cyclopenta[*def*]phenanthrene mole ratios with sodium as counterion in tetrahydrofuran

Mole ratio (crown ether : radical anion)	$k$	$\Delta G^\ddagger/kJ\ mol^{-1}$	$\Delta H^\ddagger/kJ\ mol^{-1}$	$\Delta S^\ddagger/J\ mol^{-1}\ K^{-1}$
1.56	$1.86 \times 10^{-2}\ s^{-1}$	82.8	$81.1 \pm 8.4$	-5.8
0.86	$2.73 \times 10^{-2}\ s^{-1}$	81.9	$91.1 \pm 2.5$	30.5
0.52	$2.34 \times 10^{-2}\ s^{-1}$	82.3	$92.0 \pm 8.4$	31.8
0.30	Mixed order kinetics			
0.13	$110\ l\ mol^{-1}\ s^{-1}$	61.9	$49.3 \pm 5.4$	42.2
0 <sup>a</sup>	$144\ l\ mol^{-1}\ s^{-1}$	60.6	$65.2 \pm 5.5$	15.0

<sup>a</sup> Taken from ref. 10.

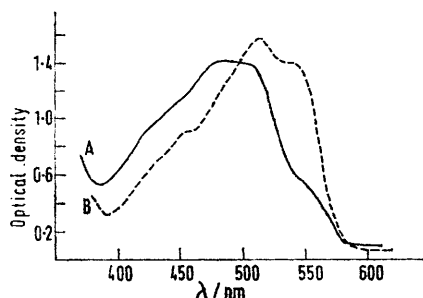
be dependent on the crown ether: radical anion mole ratio. With a crown ether: radical mole ratio of 0.13 the decay was second order with respect to the radical anion, mixed order kinetics were found for the mole ratio 0.30, and the decay was first order with respect to the radical anion for the mole ratios 0.52 and 1.56.

The temperature dependence of the velocity constant was determined for each of the crown ether: radical anion mole ratios and is summarised in Table 2. Values of  $\Delta G^\ddagger$ ,  $\Delta H^\ddagger$ , and  $\Delta S^\ddagger$ , together with the values of  $k$  at 25 °C (determined by computer extrapolation where necessary) are summarised in Table 3.

obtained previously. The effect of the crown ether on the absorption spectrum of the anion, with sodium as the counterion, is illustrated in the Figure.

In order to calculate the equilibrium constant  $K_e$  (= [solvent separated ion pairs]/[contact ion pairs]) from the observed spectra at each temperature it was necessary, as before, to determine the contribution made by each of the two types of ion pair to the spectrum.<sup>9</sup> This was done, as before, by obtaining relative values of the extinction coefficients of the two species and then employing Vierordt's method to determine the individual contribution of each species to the observed spectrum. The results obtained in

this way for each of the counterions are summarised in Table 5.



The effect of dibenzo-18-crown-6-ether on the visible absorption spectrum of the 4*H*-cyclopenta[*def*]phenanthryl anion at  $-10^{\circ}\text{C}$ , with  $\text{Na}^+$  as the counterion: A, no crown ether present; B, in the presence of a crown ether: anion mole ratio of 0.86

#### DISCUSSION

**Kinetics.**—There are two interesting features to the observed kinetics. First, the 4*H*-cyclopenta[*def*]phenanthrene radical anion is considerably more stable in the

of the crown ether when  $\text{Na}^+$  is the counterion, and similarly for  $\text{Li}^+$ , although the effect is less marked for this latter counterion. One further interesting feature of the radical anion decay in the presence of the crown ether is that the measured velocity constants are similar for each of the counterions. The values of  $k$  at  $25^{\circ}\text{C}$  range from  $8.9 \times 10^{-3}$  for ( $\text{Li}^+$ ) to  $96.4 \times 10^{-3} \text{ s}^{-1}$  (for  $\text{K}^+$ ). This range contrasts markedly with the range of values observed for the different counterions in the absence of the crown ether.

Perhaps just as remarkable is the change in reaction order which is observed in the presence of the crown ether for the  $\text{Li}^+$  and  $\text{Na}^+$  counterions. In fact all three counterions give first-order kinetics in the presence of the crown ether (0.86 mole ratio). The experiments in which the crown ether: radical anion ratio was varied, with  $\text{Na}^+$  as the counterion, also reveal that a relatively small mole ratio is necessary to produce this change. However, the actual crown ether: radical anion ratio at which the change of order occurs may well vary with the nature of the counterion particularly as the selectivity of the dibenzo-18-crown-6-ether is greatest for  $\text{Na}^+$ .

TABLE 4

A summary of the influence of dibenzo-18-crown-6-ether on the values of  $k$ ,  $\Delta G^{\ddagger}$ ,  $\Delta H^{\ddagger}$ , and  $\Delta S^{\ddagger}$  at  $25^{\circ}\text{C}$  for the decay of the 4*H*-cyclopenta[*def*]phenanthrene radical anion

Counterion	Mole ratio (crown ether: radical anion)	Reaction order	$\Delta G^{\ddagger}/\text{kJ mol}^{-1}$	$\Delta H^{\ddagger}/\text{kJ mol}^{-1}$	$\Delta S^{\ddagger}/\text{J mol}^{-1} \text{ K}^{-1}$
$\text{Li}^+$	0.86	1	84.8	$89.9 \pm 2.5$	+17.6
$\text{Li}^+ \text{ }^a$	0	2	73.1	$64.8 \pm 8.0$	-24.7
$\text{Na}^+$	0.86	1	81.9	$91.1 \pm 2.5$	+30.5
$\text{Na}^+ \text{ }^a$	0	2	60.6	$65.2 \pm 5.0$	+15.0
$\text{K}^+$	0.86	1	78.6	$66.0 \pm 5.0$	-42.5

<sup>a</sup> Taken from ref. 10.

TABLE 5

A summary of the influence of dibenzo-18-crown-6-ether on the fraction of solvent separated ion pairs (at  $0^{\circ}\text{C}$ ) and on the values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  (at  $-10^{\circ}\text{C}$ ) for the 4*H*-cyclopenta[*def*]phenanthryl anion equilibrium

Contact ion pairs  $\rightleftharpoons$  solvent separated ion pairs

Counterion	Mole ratio (crown ether: anion)	Fraction of solvent separated ion pairs	$\Delta H^{\circ}/\text{kJ mol}^{-1}$	$\Delta S^{\circ}/\text{J mol}^{-1} \text{ K}^{-1}$
$\text{Li}^+$	0.86	0.84	-23.8	-73.1
$\text{Li}^+ \text{ }^a$	0	0.80	-20.9	-67.3
$\text{Na}^+$	0.86	1.0		
$\text{Na}^+ \text{ }^a$	0	0.15	-52.7	-212.3
$\text{K}^+$	0.86	0.69	-13.4	-42.2
$\text{K}^+ \text{ }^a$	0	~0	-12.1	-68.1

<sup>a</sup> Taken from ref. 10.

presence of the crown ether. Secondly, the order of the radical anion decay changes from two (in the absence of the crown ether) to one (with a crown ether: radical anion mole ratio  $>0.50$ ).

Reference to Table 4 shows that the change in the stability of the radical anion is considerable. For example, in the presence of the crown ether the radical anion decayed at a conveniently measurable rate at  $-10^{\circ}\text{C}$  when potassium was the counterion. In the absence of the crown ether, however, the decay was too rapid to measure for this counterion at  $-50^{\circ}\text{C}$ . Similarly, the radical anion is much more stable in the presence

It is interesting to consider these two features of the reaction in the light of a possible mechanism for the radical anion decay. In the absence of the crown ether it is possible to observe either a first- or a second-order decay for related radical anions.<sup>8,10</sup> The experimental conditions which favour the formation of solvent separated ion pairs (*e.g.* low temperature, small counterion, good solvating ability of the solvent) are those conditions under which, typically, second-order kinetics are observed. One could therefore propose that the solvent separated ion pairs decay by a second-order process and the contact ion pairs by a first-order process.

This proposal contrasts markedly with the behaviour of the crown-separated ion pairs for which a second-order decay might have been expected. However, this observation may not be too difficult to interpret. For example, it has been shown that a number of crown ethers interact sufficiently strongly with the  $\text{Na}^+$  ion to replace completely the tetrahydrofuran molecules.<sup>12</sup> Considering the change in reaction order and stability, this should also be true for the other counterions. If therefore the crown ether interacts strongly with the counterion the influence of the counterion on the radical anion and transition state will be reduced. The relatively small variation in  $k$  with counterion in the presence of the crown ether supports this view. The first-order decay may well result due to steric hindrance to a bimolecular decay resulting from the large size of the crown ether. If therefore, steric factors result in a first-order decay, the rate of decay would be much reduced compared with that observed for contact or solvent separated ion pairs due to the very considerable reduction in the influence of the counterion. This picture agrees well with the experimental results.

*Anion Equilibrium.—The effect of the crown ether on the*

*fraction of solvent separated ion pairs.* The effect of the crown ether on the fraction of solvent separated ion pairs is interesting. Smid found that the selectivity of dibenzo-18-crown-6-ether towards alkali metal ion was  $\text{Na}^+ > \text{K}^+ > \text{Li}^+$ .<sup>4</sup> Our results (see Table 5) completely support this view. For example even at quite high temperatures (+40 °C) there is little evidence for the presence of the contact ion pair when  $\text{Na}^+$  is the counterion, and for  $\text{K}^+$  a dramatic increase in the fraction of solvent separated ion pairs at 0 °C is noted which contrasts with only a small change for  $\text{Li}^+$ .

The values of  $\Delta H^\ddagger$  both in the presence and absence of the crown ether are quite similar for each counterion. If anything the crown ether has a small stabilising effect on the solvent separated ion pair, presumably reflecting the increased interaction of the crown ether with the counterion compared with tetrahydrofuran.

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<sup>12</sup> A. M. Grotens, J. Smid, and E. de Boer, *Chem. Comm.*, 1971, 759.