Complexes of Macrocyclic Polyethers and Ion Pairs

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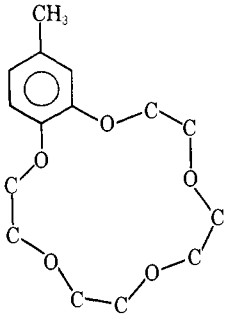
Abstract: The complexation of 4′-methylbenzo-15-crown-5 (C5), 4′-methylbenzo-18-crown-6 (C6), and the two isomers of dicyclohexyl-18-crown-6 (DC6) to the ion pairs of fluorenylsodium and -potassium was studied in tetrahydrofuran and tetrahydropyran by optical spectroscopy. The binding of a C5 molecule to F^-,Na^+ was shown to produce a mixture of crown-complexed contact ion pairs and crown-separated ion pairs, the proportion of the latter species being higher in more polar solvents. The same complexation mechanism was found to describe the interaction of C6 and DC6 with the F^-,K^+ contact ion pair. Interaction of C5 with F^-,K^+ produced separated ion pairs with two C5 molecules bound to the potassium salt. The stability of the respective ion-pair complexes was found to be a sensitive function of the temperature, solvent, size of the cation, and structure of the crown compound, especially the size of the polyether ring relative to that of the cation diameter.

Recent investigations on macrocyclic polyethers have generated considerable interest in the cation-binding properties of these materials.[1-7] The so-called crown compounds considerably increase the solubility of inorganic salts in nonpolar media[1] and can form crystalline stoichiometric complexes with a variety of salts.[1,2] When added to ethereal solutions of alkali or alkaline earth salts of carbanions, the crown ethers often modify the structure of the respective carbanion pairs.[3] Potentiometric and calorimetric measurements prove the existence of stable crown complexes of free alkali ions in water and methanol.[1,4,5] The macrocyclic polyethers are also found to strongly affect the reaction rate and stereospecific course of reactions involving ion pairs.[6] Of particular significance are recent studies by Eisenman, *et al.*, and others,[7] who established that crown compounds can exert specific effects on cation transport across biological membranes. This property makes them useful as model compounds of neutral ion carriers and resembles the behavior of the more complex macrocyclic antibiotics monactin and valinomycin which are known to make phospholipid bilayer membranes selectively permeable to cations.

We showed recently that complexation of certain crown compounds to fluorenyl salts in ethereal media produces crown-separated ion pairs.[3] The difference in optical spectra between contact and separated fluorenyl ion pairs was used as an analytical tool to establish the complexation order of dimethyldibenzo-18-crown-6 with respect to the different alkali fluorenyl ion pairs. Also, the strong upfield nuclear magnetic resonance shifts of the protons of the crown compound when complexed with the fluorenyl ion pair allowed us to study the exchange process between complexed and free crown species.

In the present work we report in detail the results of studies of the interaction of fluorenylsodium and fluorenylpotassium ion pairs with two crown compounds, *i.e.*, 4′-methylbenzo-15-crown-5 (I) and 4′-methylbenzo-18-crown-6 (II) (referred to in Pedersen's work as compounds IV and X, with methyl being the substituent in the aromatic ring). We specifically looked for evidence for the presence of crown-complexed contact ion pairs, in addition to crown-separated ion pairs, and also were concerned with the possible existence of 2:1 crown–ion pair complexes in the ethereal fluorenyl salt solutions. Species of a similar nature were recently reported by us in a study dealing with the interactions of polyglycol dimethyl ethers or glymes with fluorenylpotassium in tetrahydrofuran and tetrahydropyran.[8] The work presented in this paper also includes some results obtained with the two isomers of dicyclohexyl-18-crown-6 (III).



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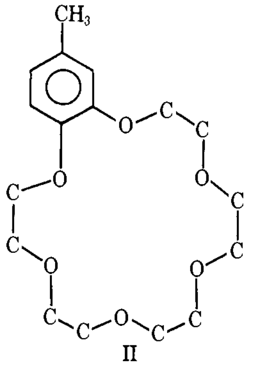

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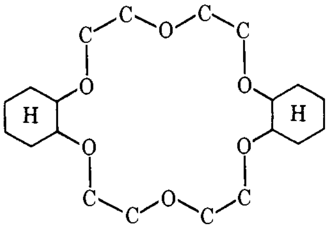

III

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(8) L. L. Chan, K. H. Wong, and J. Smid, *J. Amer. Chem. Soc.*, **92**, 1955 (1970).

Experimental Section

The two macrocyclic polyethers used in this investigation were synthesized according to method V as described in ref 1a. 2,3-(4′-Methylbenzo)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene or 4′-methylbenzo-15-crown-5 (abbreviated in this paper as C5) was prepared from recrystallized 4-methylcatechol (Aldrich Co.) and 1,11-dichloro-3,6,9-trioxaundecane.[1] The final product was recrystallized from petroleum ether (bp 30–60°, 1 g/50 ml), and obtained in 57% yield, mp 51.2–52.0°. The 2,3-(4′-methylbenzo)-1,4,7,10,13,16-hexaoxacyclooctadeca-2-ene or 4′-methylbenzo-18-crown-6 (abbreviated in this paper as C6) was synthesized by a similar procedure, using 4-methylcatechol and 1,14-dichloro-3,6,9,12-tetraoxatetradecane.[1] After purification, the compound was obtained in 52% yield, mp 54–55°. The two isomers of dicyclohexyl-18-crown-6, abbreviated as DC6A (mp 60°) and DC6B (mp 69°) were kindly supplied to us by Dr. K. H. Frensdorff of Du Pont, Wilmington, Del.

The sodium and potassium salts of fluorene were prepared under high vacuum in tetrahydrofuran by treating the respective alkali salts of the dianion of the 1,1-diphenylethylene dimer with a slight excess of fluorene.[9] The reaction is instantaneous and affords a quantitative yield of the fluorenyl salts. Their optical spectra show no evidence of any impurities. Solutions in tetrahydropyran (THP) were obtained by removing THF under vacuum from the salt solutions and replacing it by THP. Purification of the two solvents has been described elsewhere.[10]

Three procedures were utilized to study the complexation of crown compounds with fluorenyl salts, depending on the range of the respective concentrations. In method I (used with the systems fluorenylpotassium–C6 and fluorenylsodium–C5 and in the experiments involving the isomers of dicyclohexyl-18-crown-6), known quantities of dry macrocyclic polyether were added under vacuum (by means of breakseals) to an approximately 10^{-3} *M* THF or THP solution of the fluorenyl salt. After each crown addition, the optical spectrum of the solution was recorded on a Cary 14 or 15 spectrophotometer, using a 0.1- or 0.2-cm optical quartz cell attached to the apparatus. It was established that termination of the carbanion solution at the highest crown concentrations was less than 5%.

A different procedure (method II) was followed for low-concentration experiments to avoid the weighing of very small quantities of crown ether. A mixture of the fluorenyl salt and crown ether in an approximate ratio of one to two was prepared in THF or THP. The concentration of the two species was then varied over a 10^{-3}–10^{-5} *M* concentration range by each time pouring part of the solution in a side vessel and distilling the solvent back by cooling, all manipulations being carried out under vacuum. The ratio of crown ether to salt concentration remained constant. The optical spectrum was recorded after each dilution, using 0.2-, 1-, and 5-cm optical cells. This method was employed for the systems C5–F$^-$,Na$^+$ and C6–F$^-$,Na$^+$.

In a third method, described previously,[8,10] a fluorenyl salt solution was titrated with a fluorenyl salt solution of approximately the same concentration but containing the crown ether. The latter solution was contained in a buret and separated from the former solution by a small glass-enclosed steel rod acting as a shutoff device. Known quantities of the solution in the buret were added to the solution to be titrated by magnetically lifting the rod, the spectrum being recorded after each addition. The absence of stopcocks allowed us to work at a low but constant carbanion concentration. The system fluorenylpotassium–C5 was studied by this method.

Carbanion concentrations were calculated using the molar extinction coefficients, ϵ_m, referring to the respective absorption maxima. The ϵ_m of the F$^-$,Na$^+$ contact ion pair in THP (ϵ_m 12,000 at 354 nm) was obtained from that of F$^-$,Na$^+$ in THF (ϵ_m 10,800 at 356; see ref 10) by replacing THF with a known quantity of pure THP. Exactly the same value was recently reported from a preparation of fluorenylsodium directly in THP using a sodium mirror, and also from the reaction of fluorene with the dianion of the 1,1-diphenylethylene dimer in THP.[11] We used the latter reaction to determine the ϵ_m of the F$^-$,K$^+$ contact ion pair in THF and THP. A value of 12,000 at 362 nm was found in both solvents. Extinction coefficients for the crown-separated ion pairs were obtained from the respective contact-ion-pair salts by adding excess crown ether. A value of 14,300 at 373 nm was found for the ϵ_m of the F$^-$,K$^+$–C5 separated ion pair and 14,400 for that of the F$^-$,Na$^+$–C6 separated ion pair, its maximum also being at 373 nm. The conversion to separated ion pairs on addition of C6 to F$^-$,K$^+$ and of C5 to F$^-$,Na$^+$ was not complete. In these cases, a value of ϵ_m equal to 14,000 at 373 nm was assumed for the two crown-separated ion pairs.

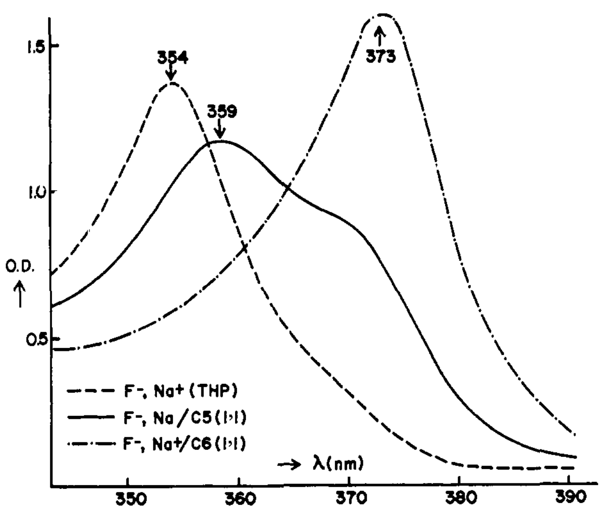

Figure 1. Optical spectrum of fluorenylsodium in tetrahydropyran in the absence and presence of macrocyclic polyethers; [F$^-$,Na$^+$] = 5×10^{-4} *M*; [C5] and [C6] = 6×10^{-4} *M*.

A calculation of the contact- and separated-ion-pair concentrations in a particular system also requires a knowledge of the extinction coefficients of the contact ion pair at the absorption maximum of the separated ion pair, and *vice versa*. This can be obtained from the "pure" ion-pair spectra. It should be pointed out that in certain cases the contact-ion-pair maximum shifts a few nanometers on addition of the crown compound (Results and Discussion). This changes the contribution of the contact-ion-pair absorption at the absorption maximum of the separated ion pair. In these cases we reevaluated this contribution by assuming that the shift did not alter the shape of the contact-ion-pair spectrum.

Results and Discussion

The maxima and shapes of the optical absorption bands of fluorenylsodium and -potassium in THF and THP at room temperature show that under these conditions the two salts exist as contact ion pairs.[10] However, changes in the fluorenyl spectra are observed on addition of the crown ethers C5 and C6, indicating that complexation occurs which results in a change in the ion-pair structure. A typical example is shown in Figure 1, which depicts the spectrum of F$^-$,Na$^+$ in THP and that of a similar solution but containing a slight excess of either C5 or C6. The spectrum of the F$^-$,Na$^+$–C6 mixture is clearly that of a F$^-$,Na$^+$ separated ion pair,[10] the absorption maximum being at 373 nm. The spectrum does not change on dilution even down to a concentration of 10^{-5} *M*. Since a contact-ion-pair fraction of less than 0.05 cannot be easily detected under our experimental conditions, one calculates that the equilibrium constant, K_i, of the complexation $F^-,Na^+ + C6 \rightleftarrows F^-,C6,Na^+$ must be larger than 4×10^7 M^{-1}. The value in THF is larger than 2×10^7 M^{-1}, taking into account that in this solvent a considerable fraction of free ions is present at 10^{-5} *M* F$^-$,C6,Na$^+$, with the two species possessing essentially identical absorption spectra. The value of the free-ion dissociation constant, K_d, of this complex should be close to 4×10^{-6} *M*, which is the K_d value found for the ion-pair

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[9] T. Ellingsen and J. Smid, *J. Phys. Chem.*, 73, 2712 (1969).

[10] T. E. Hogen Esch and J. Smid, *J. Amer. Chem. Soc.*, 88, 307 (1966).

[11] S. Boileau, private communication.

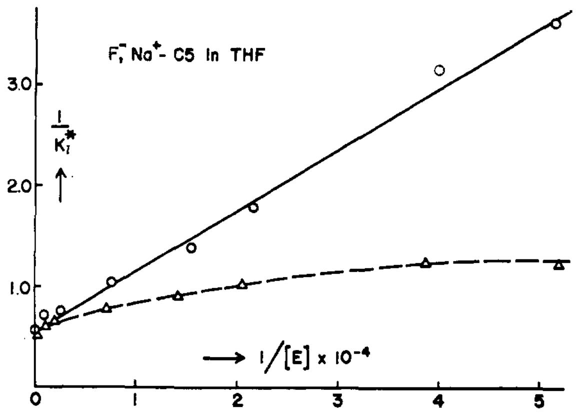

Figure 2. Plots of $1/K_i^*$ *vs.* $1/[E]$ (E being C5) for F^-,Na^+ in THP before (△) and after (○) correction for free ions is made.

complex of F^-,Na^+ and dimethyldibenzo-18-crown-6 in THF.[12] In THP the K_d value for this crown-separated ion pair is only 4×10^{-8} M.[12]

Crown-Complexed Contact and -Separated Ion Pairs. The behavior of the system $C5{-}F^-,Na^+$ in THF or THP is different from that involving C6. First of all, the absorption maximum of the contact ion pair shifts from 354 to 359 nm. Secondly, although the shoulder around 370 nm in the spectrum of $F^-,Na^+{-}C5$ clearly reveals the presence of a small fraction of C5-separated ion pairs, the spectrum shows very little change on addition of more C5, even when a tenfold excess is used. Both observations point to a complexation mechanism which we previously observed in mixtures of fluorenylpotassium and polyglycol dimethyl ethers;[8] *i.e.*, the crown compound either complexes externally to a fluorenyl contact ion pair or the interaction leads to ion-pair separation. The ion-pair complexation equilibria can be represented in the following way.

$$F^-,Na^+ + C5 \rightleftharpoons F^-,Na^+,C5 \qquad K_1$$

$$F^-,Na^+ + C5 \rightleftharpoons F^-,C5,Na^+ \qquad K_i$$

$$F^-,Na^+C5 \rightleftharpoons F^-,C5,Na^+ \qquad K_2$$

Although the species $F^-,Na^+,C5$ may still be classified as tight ion pairs, the strong interaction of C5 with Na^+ apparently results in a slight increase in the average interionic distance between the Na^+ and fluorenyl anion, causing the 5-nm bathochromic shift. Such shifts in contact-ion-pair maxima were also previously observed in the presence of other complexing agents such as hexamethylphosphoramide[13] and ethylenediamine.[14] Additional evidence that the 359-nm peak can be attributed to a C5-complexed F^-,Na^+ contact ion pair is obtained when $NaBPh_4$ is added to the 1:1 mixture of $F^-,Na^+{-}C5$ in THP. In the presence of excess boron salt, the absorption maximum is again at 354 nm, due to the transfer of C5 to the $NaBPh_4$.

$$F^-,Na^+,C5 + Na^+,B^-Ph_4 \rightleftharpoons F^-,Na^+ + Na^+,C5,B^-Ph_4$$

Displacement reactions of this type have also been observed with other crown compounds.[3]

Experimentally, one measures the concentrations of separated and contact ion pairs; hence, the ratio $[F^-,C5,Na^+]/[F^-,Na^+,C5 + F^-,Na^+] = K_i^*$ may be calculated. One can easily show that

$$1/K_i^* = 1/K_2 + 1/K_1K_2[C5]$$

The complexation constant K_1 turns out to be high and can only be determined by sufficiently diluting the $F^-,Na^+{-}C5$ mixture. Dilution in THF clearly results in a shift of the contact-ion-pair maximum from 359 to 357 nm, indicating formation of the F^-,Na^+ ion pair which absorbs in THF at 356 nm. Also, dissociation into free ions affects the ratio K_i^* at low dilution, and it is necessary to correct for this. This was done by assuming K_d of $F^-,C5,Na^+ \gg K_d$ of F^-,Na^+, the former K_d probably being close to that of the dibenzo-18-crown-6-separated F^-,Na^+ ion pair.[12] Plots of $1/K_i^*$ *vs.* $1/[C5]$ before and after correction for free ions are shown in Figure 2. The ratio of carbanion to C5 concentration was constant (approximately 0.5); hence, a high C5 concentration means a high ion-pair concentration. The correction for free ions does not affect the intercept $1/K_2$ to any appreciable extent, but the slope and therefore the K_1 value may be in error by 20–30% in spite of the linear relationship which is obtained. The respective K_1 and K_2 values are 9.2×10^3 M^{-1} and 1.80. In THP, a shift of the 359-nm peak back to the 354-nm F^-,Na^+ contact-ion-pair peak is barely observable on dilution, indicating a considerably higher value for K_1 than in THF.

Crown-Separated Ion Pairs with More Than One Crown Ether. The complexation mechanism outlined above predicts a constant ratio K_2 of crown-separated ion pairs to crown-complexed contact ion pairs at high crown concentrations. To verify this, the ratio K_i^* was determined for different C5 concentrations, keeping the carbanion concentration constant at approximately 10^{-3} M. The results of these measurements, carried out for a number of systems, are shown in Figures 3 and 4. It appears that K_i^* is indeed constant or nearly constant for the systems $F^-,K^+{-}C6$ in THF and THP and for the system F^-,K^+ with both isomers of dicyclohexyl-18-crown-6. A slight increase is observed for $F^-,Na^+{-}C5$ in both THP and THF. The most outstanding system is that of C5 with F^-,K^+ in THF, which shows a strong dependence of K_i^* on the crown ether concentration.

The latter system resembles the complexation behavior of the linear polyglycol dimethyl ethers, glyme 4 and glyme 5, with F^-,K^+.[8] Apparently, a second C5 molecule complexes with a crown-complexed contact ion pair, thereby converting it to a separated ion pair

$$F^-,K^+,C5 + C5 \rightleftharpoons F^-,C5,K^+,C5 \qquad K_3$$

As shown previously,[8] the relationship between K_i^* and [C] now becomes

$$K_i^* = (K_2 + K_3[C5])/(1 + 1/K_1[C5])$$

Under conditions where $K_1[C5] \gg 1$, the above relationship can be approximated by

$$K_i^* = K_2 + K_3[C5]$$

Two plots of K_i^* *vs.* [C5] for the system $F^-,K^+{-}C5$ in THF are shown in Figure 5. In one plot it is assumed that only one C5 molecule is bound to K^+ in the crown-separated ion pair, *i.e.*, $F^-,K^+ + C5 \rightleftarrows$

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[12] T. E. Hogen Esch and J. Smid, manuscript in preparation.

[13] L. L. Chan and J. Smid, *J. Amer. Chem. Soc.*, **90**, 4654 (1968).

[14] R. Smyk, M.Sc. Thesis, College of Forestry, Syracuse, N. Y., 1966.

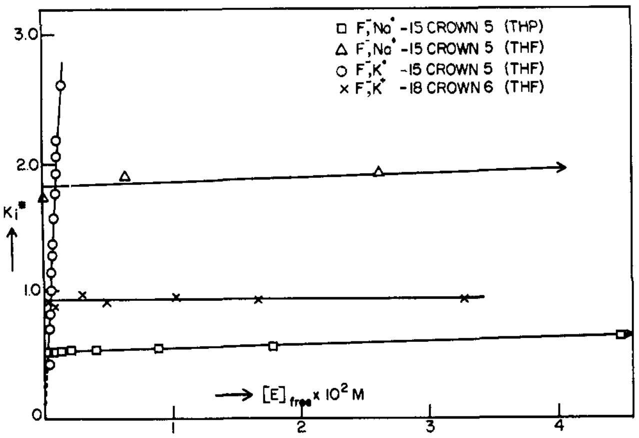

Figure 3. Plots of K_i^* *vs.* crown concentration (E) for the systems C5-F^-,Na^+ (THP and THF), C5-F^-,K^+ (THF), and C6-F^-,K^+ (THF); [fluorenyl salt] $\approx 6 \times 10^{-4}$ *M*.

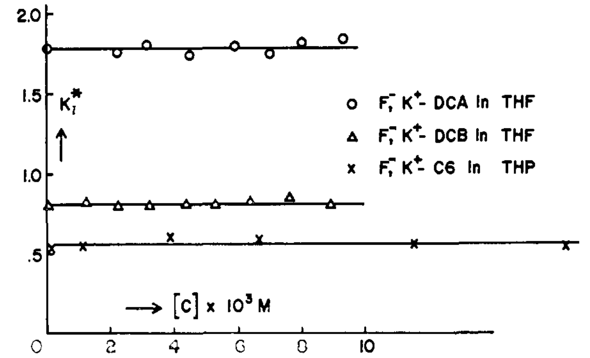

Figure 4. Plots of K_i^* *vs.* crown concentration for the systems C6-F^-,K^+ (THP), DC6A-F^-,K^+ (THF), and DC6B-F^-,K^+ (THF); [F^-,K^+] $\approx 6 \times 10^{-4}$ *M*.

F^-,C5,K^+. In this case, [C5] = $[C5]_0$ − [F^-,C5,K], $[C5]_0$ being the total crown concentration. The second plot is based on the equation

$$F^-,K^+,C5 + C5 \rightleftharpoons F^-,C5,K^+,C5$$

and now [C5] is given by [C5] = $[C5]_0$ − [F^-,K^+,C5] − 2[F,C5,K^+,C5]. Since the concentration of the crown-separated ion pairs (F^-,C5,K^+ or F^-,C5,K^+,C5) can be determined experimentally, [C5] can be calculated. A comparison of the two plots suggests that the assumption of two C5 molecules bound to F^-,K^+ appears to be correct. The deviation observed at lower [C5] means that under these conditions the product K_1[C5] apparently is not much larger than unity. One estimates that K_1 should be on the order of 5×10^3 M^{-1}. Using this value, the [C5] can now be determined more accurately by an iterative procedure. A plot of K_i^* [1 + 1/K_1[C5]] *vs.* [C5] is shown in Figure 6. The observed straight line leads to a value of K_3 = 1840 M^{-1} and K_2 = 0.2, the latter value being not much different from the K_2 values found for the systems F^-,K^+–glyme 4 and F^-,K^+–glyme 5.

To obtain further evidence for the existence of a 2:1 complex of C5 with F^-,K^+, a mixture of F^-,K^+ and C5 in a ratio 1:4 was prepared in THF. The solution was then concentrated by evaporating the solvent, which resulted in the formation of an orange-colored precipitate. The latter was filtered, washed with cold THF, and dried, all manipulations being carried out under vacuum. After protonating the carbanion salt with methanol–water, the now colorless solution was dried and the resulting solid was dissolved in $CDCl_3$ and analyzed by nmr. Only two compounds were found, *viz.*, fluorene and monobenzo-15-crown-5, in the almost exact molar ratio of 1:2. While we realize that this result does not necessarily prove the existence of 1:2 F^-,K^+–C5 complexes in solution, it nevertheless shows the feasibility of complexing two C5 molecules with a K^+ ion.

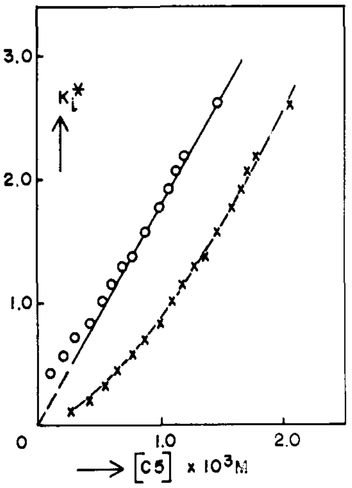

Figure 5. Plots of K_i^* *vs.* [C5] for the system F^-,K^+–C5 in THF at 25°: ×, plot of K_i^* *vs.* [C5], assuming equilibrium F^-,K^+ + C5 $\rightleftharpoons$ F^-,C5,K^+; ○, plot of K_i^* *vs.* C5, assuming equilibrium F^-,K^+,C5 + C5 $\rightleftharpoons$ F^-,C5,K^+,C5; $[F^-,K^+]_{total} \approx 6 \times 10^{-4}$ *M*.

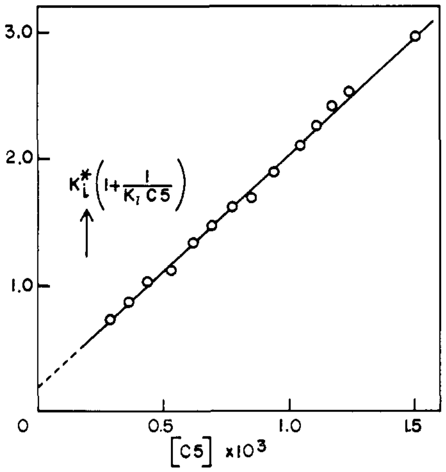

Figure 6. Plot of K_i^* [1 + 1/[K_1C5]] *vs.* [C5] for the system F^-,K^+–C5 in THF at 25°.

There is a slight increase in K_i^* when the C5 concentration is increased in the system F^-,Na^+–C5, both in THF and in THP as solvents. This indicates that F^-,Na^+ may also acquire a second C5 molecule, but the K_3 value is much lower than for the system F^-,K^+–C5.

To further test the reliability of our procedures, a series of experiments was carried out at constant C5 concentration but varying carbanion concentration, keeping the ratio [C5]/[fluorenyl] at all times considerably larger than one. The results of these measurements, carried out in THP to avoid corrections for free-ion formation, are shown in Table I. The value

Table I. Dependence of K_i^* on the Fluorenylsodium Concentration[a]

$[F^-,Na^+]_0 \times 10^4$ *M*	$[C5]^b \times 10^2$ *M*	K_i^{*c}
0.233	3.60	0.595
1.27	3.58	0.588
4.01	3.56	0.579
5.61	3.54	0.573
13.5	3.45	0.599
75.0	2.85	0.769

[a] Solvent THP; temperature 25°. [b] [C5] denotes the concentration of uncomplexed monobenzo-15-crown-5. [c] $=(F^-,C5,Na^+ + F^-,C5,Na^+,C5)/F^-,Na^+,C5$.

of K_i^* should be independent of the carbanion concentration, and this is indeed observed over a large concentration range. However, a considerable increase is found at $[F^-,Na^+]_0$ above 2×10^{-3} *M*. The cause of this increase, which is solvent dependent and also found in other systems, will be the subject of a separate study.

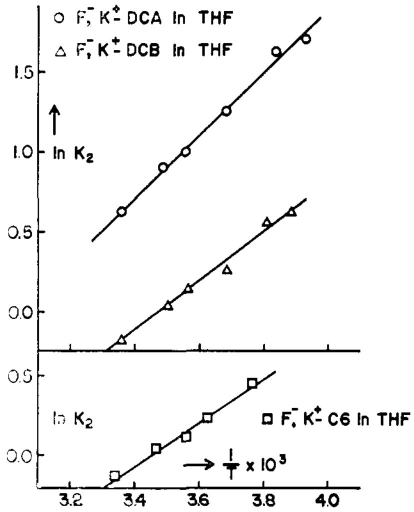

Figure 7. Plots of ln K_2 *vs.* $1/T$ in THF for the systems C6–F^-,K^+ (□), DC6A–F^-,K^+ (○), and DC6B–F^-,K^+ (△).

The values obtained for the various equilibrium constants are compiled in Table II. The constants K_2 and K_3 were calculated from plots shown in Figures 3 and 4. A lower limit can be obtained for most K_1 values by determining the lowest crown concentration for which the condition K_1[crown] $\gg 1$ is still fulfilled.

Table II. Complex Formation Constants of Macrocyclic Polyethers with Fluorenyl Ion Pairs in Ethereal Solvents at 25°

Ion pair	Crown	Solvent	$K_1 \times 10^{-3}\ M^{-1}$	K_2^a	$K_3,^a\ M^{-1}$	$K_i \times 10^{-3}\ M^{-1}$
F^-,Na^+	C5	THF	9.2	1.8	3.5	16.5
		THP	>20	0.52	2.8	>10
	C6	THF				>20,000
		THP				>40,000
	DC6	THP				>40,000
F^-,K^+	C5	THF	~5	~0.2	1840	~1
	C6	THF	>10	0.93		>9
		THP	>10	0.55		>5.5
	DC6A	THF	>30	1.80		>54
	DC6B	THF	>40	0.80		>32

[a] The accuracy of the K_2 values is estimated to be better than 10% for F^-,Na^+ and better than 20% for F^-,K^+. A similar accuracy is estimated for the K_3 values.

Table III. Enthalpy and Entropy Changes for the Equilibrium $F^-,K^+,C \rightleftarrows F^-,C,K^+$, with C Being C6, DC6A, or DC6B

System	ΔH_2,[a] kcal/mol	ΔS_2,[a] eu
C6-F^-,K^+ (THF)	−3.0	−10.4
DC6A-F^-,K^+ (THF)	−3.9	−11.7
DC6B-F^-,K^+ (THF)	−3.1	−10.7

[a] The accuracy of ΔH_2 is estimated to be ±0.3 kcal/mol; that of ΔS_2 is about 1 eu.

A few systems were studied as a function of temperature. To simplify calculations (for details, see Experimental Section), systems were selected for which K_i^* is independent of the crown concentration; hence, one measures the temperature dependence of K_2. The ratio of crown to fluorenyl concentration was taken slightly higher than one, the concentration being approximately 10^{-3} *M*. The results obtained for the systems F^-,K^+–C6, F^-,K^+–DC6A, and F^-,K^+–DC6B are depicted in Figure 7 as plots of ln K_2 *vs.* $1/T$. Linear relationships are observed from which the thermodynamic quantities ΔH_2 and ΔS_2 are derived. Their values are listed in Table III.

General Discussion

Complexation of macrocyclic polyethers to sodium and potassium fluorenyl ion pairs appears to proceed in a manner similar to that reported for linear polyethers.[8] Binding of a crown molecule to contact ion pairs produces a mixture of crown-separated ion pairs and crown-complexed contact ion pairs. The concentration ratio of the two species, given by the constant $K_2 = K_i/K_1$, depends on solvent, temperature, nature of the cation, and structure of the crown ether, particularly the size of the polyether ring relative to that of the cation.

The lower K_2 values in less polar solvents indicate that these media favor the externally complexed contact ion pairs (K_1 values are higher in less polar solvents, as was also observed for the glymes[8]). External complexation to the contact ion pair requires removal of the few solvent molecules still bound to the cation, and more energy is needed to accomplish this in a solvent of higher polarity, *e.g.*, THF as compared to THP. As the cation moves further into the polyether ring, ion-pair separation occurs. Frensdorff pointed out recently that complexation of a free alkali ion by the planar macrocyclic polyethers does not necessitate a removal of the entire solvation shell.[5] This is probably also true for the crown-separated ion pair. The transformation from one kind of ion pair to the other kind is therefore more accurately represented by

$$\mathrm{F^-,M^+,C} + n\mathrm{S} \leftrightarrows \mathrm{F^-,C,M^+,S}_n$$

where S denotes a solvent molecule. This equilibrium is expected to shift in favor of the crown-separated ion pairs in more polar media. The enlargement of the ion-pair dipole and the binding of solvent molecules contribute to the negative enthalpy and entropy values observed for this transformation. The values found for ΔH_2 and ΔS_2 in THF (see Table III) appear to be reasonable and are of the same order as those obtained for linear polyglycol dimethyl ethers.[8] They are expected to be less in THP.

One anticipates that in hydrocarbon solvents the stability of the complexed contact ion pair increases relative to that of the crown-separated ion pair. This probably enhances the binding efficiency of a crown ether with a small polyether ring relative to that of ethers possessing a large hole. It is interesting that in hexane the macrocyclic antibiotic monactin binds cations (particularly the K^+ ion) much less effectively than dicyclohexyl-18-crown-6, while the reverse is true when dichloromethane is the solvating medium.[7a] The monactin, with its large ring structure, is known to wrap itself completely around the cation for an effective binding.[5,15] To accomplish this in hexane, where most likely tight ion pairs exist, the interionic distance in the ion pair must be enlarged. On the other hand, the crown ether with its smaller ring can rather easily bind itself externally to the tight ion pair, and in this case no energy is needed to separate the ions. No ion-pair separation is necessary in dichloromethane, as free ions are the predominant species, at least at low salt concentrations.[5,7a]

The structure of the anion affects the tightness of the ion pair and should, therefore, influence the above ion-pair transformation. Bulky substituents on the anion and charge delocalization facilitate ion-pair separation and enhance the stability of the separated ion pair relative to that of the complexed contact ion pair. The latter species are probably prevalent in solutions of alkoxides, which are expected to form tight ion pairs in low polarity media.

Ion-pair separation is favored, as more oxygen atoms are available for coordinating with the alkali ion and the polyether ring is large enough to accommodate the cation. For example, only separated ion pairs are observed in ethereal solutions of F^-,Na^+ with C6, DC6, or dibenzo-18-crown-6.[3] A smaller ring favors formation of externally complexed contact ion pairs, as is observed with C5 and F^-,Na^+, especially in less polar solvents. The hole of this crown ether is barely large enough to fit the Na^+ ion,[1,5] and the cation protrudes from the plane of the ring, with the oxygen atoms most probably in a nearly planar conformation such that an electron-rich environment exists just above the ring. This situation resembles that found by X-ray crystallography for solid complexes of dicyclohexyl-18-crown-6 and RbCNS.[2]

It is interesting that the linear polyether tetraglyme (glyme 5) forms only separated ion pairs with F^-,Na^+,[8] although the complexation constant is more than three powers of ten lower than that of C5. A closed-ring structure such as in C5 apparently favors external complexation. This is difficult to achieve with linear polyethers because of the unfavorable entropy change and the repulsion of the terminal methoxy groups. The glyme therefore will have a tendency to more fully wrap itself around an alkali ion to achieve effective binding, especially with small cations, forcing thereby the ion pair to separate.

The C5 hole is too small to accommodate the K^+ ion,[1,5] and external solvation becomes predominant with F^-,K^+ ion pairs, although a small fraction of $F^-,C5,K^+$ ion pairs is apparently formed (K_2 = 0.2). The fraction of separated ion pairs, however, rapidly increases when a second C5 molecule is complexed to F^-,K^+. The feasibility of forming stable 2:1 complexes of K^+ with C5 was recently confirmed from a study of the cation binding properties of poly(vinyl macrocyclic polyethers).[16] Compared to monomeric C5, polymers containing the C5 moiety as pendent groups show a pronounced increase in the efficiency of binding large cations such as K^+ and Cs^+, owing to cooperative effects of neighboring C5 groups. Also, the maximum number of fluorenylpotassium ion pairs bound to the polymer is slightly less than half the total number of available C5 units. With F^-,Na^+, the ratio of bound ion pairs to crown units approaches unity. Frensdorff,[5] using a potentiometric technique, has found stable 1:1 and 1:2 complexes of K^+ with cyclohexyl-15-crown-5 in methanol at 25°, and states that a ring size smaller than the cation diameter is probably a necessary but not always sufficient condition for a 2:1 complex. Other evidence for 2:1 complexes has been derived from studies in the solid state,[1b,2] and Truter, *et al.*, have recently characterized by X-ray a 2:1 complex of C5 with the K^+ ion sandwiched in between the two crown ether molecules.[17]

As pointed out earlier, the interaction of C5 with F^-,K^+ resembles that of tri- and tetraglyme,[8] both of which can form 1:1 and 2:1 complexes with F^-,K^+ in ethereal solution, but the complexation constants in comparison with that of C5 are lower by about three powers of ten.

The increase in $K_i{}^*$ for the system C5–F^-,Na^+ at higher C5 concentration (see Figure 2) appears to be real and is evidence for 2:1 complex formation of C5 with F^-,Na^+. However, the low K_3 value for this system shows that the 2:1 complex is not very stable. This is probably due to increased repulsion between the oxygen atoms of the two C5 molecules when small cations are sandwiched in between the two crown ethers. Moreover, in the separated $F^-,C5,Na^+$ ion pair, the Na^+ ion can be located in the center of the hole, and a second C5 molecule would not contribute much to the solvation energy. The same can be said for the C6 complexation with F^-,K^+. In this system, external complexation to the contact ion pair competes favorably with ion-pair separation, but 2:1 complexes are unstable.

The behavior of the two dicyclohexyl-18-crown-6 isomers DC6A and DC6B shows that the lower melting isomer DC6A appears to be the stronger complexing

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agent for K^+ ions. It produces a considerably higher fraction of F^-,K^+ separated ion pairs. The same observation was made by Izatt, *et al.*,[4] and by Frensdorff,[5] although in their experiments free K^+ ions in water and methanol, respectively, were involved in the complexation. It is interesting that even this powerful complexing crown ether (Pedersen[1] classified this ether in comparison to other crown ethers as the strongest complexing agent for K^+ ions) does not easily separate the F^-,K^+ ion pair. Its conformation may favor a complex where the K^+ ion slightly protrudes from the polyether, enhancing the stability of externally complexed contact ion pairs.

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Nitroxides in the Oxidation of Bicyclic Oximes. An Electron Paramagnetic Resonance Study

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Abstract: The nitroxide radicals RR′NO which appear in the oxidation of bicyclic oximes with lead tetraacetate have been investigated by means of epr spectroscopy. Three types of radicals were found to have the following characteristics: type i, $a_N \sim 13$ G, $g \sim 2.0061$; type ii, $a_N = 11.7$ G, $a_H = 9.6$ G, $g = 2.0061$; type iii, $a_N \sim 8$ G, $g \sim 2.0069$. Their structure and formation are discussed.

The oxidation of oximes with lead tetraacetate is known to yield iminoxy radicals $R_1R_2C{:}NO$, the characteristics of which have been extensively discussed[1,2] in earlier papers. Sometimes nitroxide radicals RR′NO are also pointed out.[2-4] As yet the question of their structure and origin has not been completely answered.[5]

In our epr study of the oxidation of bicyclic oximes, we have observed, besides the iminoxy radicals,[4,6,7] various nitroxides whose structure and relative concentrations seem to depend on the nature of the parent compound. It is the aim of this paper to report our observations on this subject.

Results and Discussion

The investigated oximes were derivatives of bicyclo[3.3.1]nonane (I, II, III, IV, V, VI), bicyclo[3.2.1]octane (VII, VIII, IX, X), and bicyclo[4.2.1]nonane (XI, XII, XIII). Typical spectra are given in Figure 1. The parameters of the epr spectra of the observed nitroxides are summarized in Tables I and II.

As may be observed in most cases, proton hfs is lacking, so the a_N and g parameters had to be used in order to determine the structures of the nitroxide radicals.

Table I. Parameters of the Epr Spectra of the Indicated Nitroxides

Parent oximes	Radical type i		Radical type iii	
	a_N, G	g	a_N, G	g
I	12.9	2.0062	7.8	2.0068
II	12.4	2.0061	. . .	. . .
III	12.4	2.0061	7.4	2.0068
IV	12.5	2.0061	. . .	. . .
V	13.6	2.0060	7.7	2.0068
VI	13.6	2.0061	. . .	. . .
VII	12.6	2.0063	7.3	2.0069
VIII	13.3	2.0061	8.0	2.0068
IX	12.8	2.0061	. . .	. . .
X	13.2	2.0062	7.8	2.0069
XI	13.2	2.0062	7.3	2.0070
XII	13.6	2.0061	8.0	2.0070
XIII	13.6	2.0061	. . .	. . .

Table II. Parameters of the Epr Spectra

Parent oximes	Radical type ii		
	a_N, G	a_{NH}, G	g
II	11.7	9.6	2.0061
III	11.7	9.6	2.0061

According to their epr parameters, the radicals are divided into three groups.

Radical Type i. This type of radical (Table I) has $a_N \sim 13$ G, a value characteristic of a few types of nitroxides only. Among them, bis(1-acetoxycyclohexyl) nitroxide ($a_N = 13.2$ G, $g = 2.0061$) (XIV), which was described by Wajer, Mackor, and de Boer,[8] suggests a similar structure (XV) for our type i bicy-

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