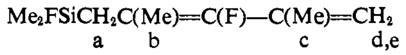
Table II

Nmr spectrum of IX (undeuterated)	Expected changes for incorporation of one deuterium atom at H_a	H_d	H_e
H_a 2.15 d (J = 9 Hz)	$^1/_2$ intensity		
H_b 5.79 t (J = 9 Hz)	d (J = 9 Hz)		
H_c 6.65 q (AMX, J_c = 10 Hz, J_t = 17 Hz)		d (J = 17 Hz)	d (J = 10 Hz)
H_d 5.2 d (J_c = 10 Hz)		Not present	
H_e 5.57 d (J_t = 17 Hz)			Not present

pared according to the procedure of Weyenberg, *et al.*,[23] bp 64–66° (44 mm), $n^{25}D$ 1.4570 (lit.[23] $n^{25}D$ 1.4574). Nmr (in CCl_4): δ 0.15 (s, 6 H, Me_2Si), 1.30 (s, 4 H, $SiCH_2$) (somewhat broadened), 1.68 (s, 6 H C–CH_3).

A solution of 1.65 g (11.8 mmol) of this silacyclopentene and 4.51 g (11.0 mmol) of $PhHgCCl_2Br$ in 30 ml of dry benzene was stirred under nitrogen at 80–82° for 3 hr. Filtration gave phenylmercuric bromide in 88% yield. The filtrate was trap-to-trap distilled at 0.01 mm (pot temperature to 80°). Glpc analysis of the distillate showed the presence of only a single product (74% yield) which was identified as $Me_2ClSiCH_2C(Me){=}C(Cl){-}C(Me){=}CH_2$. *Anal.* Calcd for $C_9H_{16}Cl_2Si$: C, 48.44; H, 7.23. Found: C, 49.16; H, 7.60. Nmr (in CCl_4): δ 0.43 (s, 6 H, Me_2Si), 1.86 (s with shoulder at *ca.* 1.84, 8 H, $SiCH_2$ + CH_3–C), 4.95 and 5.05 ppm, (2 H, $=CH_2$) two single resonances showing further fine splitting.

Reaction of 1,1,3,4-Tetramethyl-1-silacyclopent-3-ene with Me_3SnCF_3–NaI. A solution of 1.50 g (10.2 mmol) of anhydrous sodium iodide, 2.62 g (11.2 mmol) of trimethyl(trifluoromethyl)tin, and 1.41 g (10.0 mmol) of the silacyclopentene in 30 ml of DME (freshly distilled from potassium) was stirred under nitrogen at reflux for 10 hr. Trap-to-trap distillation of volatiles at 0.03 mm (pot temperature to 80°) was followed by glpc analysis of the distillate (at 130°). In addition to starting materials and trimethyltin iodide there were present one major product (46% yield) and two minor products with slightly longer retention times. The major product was identified as



$$Me_2FSi\underset{a}{CH_2}C(\underset{b}{Me}){=}C(F){-}C(\underset{c}{Me}){=}\underset{d,e}{CH_2}$$

Anal. Calcd for $C_9H_{16}F_2Si$: C, 56.80; H, 8.47; F, 19.97. Found: C, 56.28; H, 8.30; F, 20.04. Nmr (in CCl_4): δ 0.25 (d, 6 H, Me_2Si, J = 7.5 Hz), 1.72 (d, 3 H_b, J = 4 Hz), 1.86 (s, 3 H_c) (showing further fine splitting), 5.07 (s, H_c + H_d, broad). The H_a proton resonance appears to coincide with those of the CH_3 groups. Ir (liquid film): 3090 w, 2965 m, 2930 m, 2870 sh, 1640 w, 1460 m, 1410 sh, 1380 w, 1305 w, 1260 s, 1220 w, 1190 m, 1155 w, 1095 s, 1035 w, 1005 w, 950 w, 910 sh, 895 sh, 880 s, 845 s, 808 s, 765 w, 750 w, and 660 w cm^{-1}.

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[23] D. R. Weyenberg, L. H. Toporcer, and L. E. Nelson, *J. Org. Chem.*, 33, 1475 (1968).

Binding of Cyclic Polyethers to Ion Pairs of Carbanion Alkali Salts

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Abstract: Complexation of cyclic polyethers of the "crown" type to ion pairs of fluorenyl alkali salts was studied in ethereal solvents and pyridine by nmr and by uv–visible spectroscopy. The absorption spectra of these complexes are identical with the spectra of the solvent-separated ion pairs of the fluorenyl alkali salts. The complexing with the ion pairs leads to strong upfield shifts in the nmr spectrum of the polyether ring protons. The binding of fluorenylsodium with dimethyldibenzo-18-crown-6 is so strong that a slow exchange process with free cyclic polyether is observed, with an activation energy of 12.5 kcal/mole. The selectivity of this particular cyclic polyether with respect to alkali ions in THF was found to be $Na^+ \gg K^+ > Cs^+ > Li^+$, but this sequence is dependent on the solvent medium. In oxetane, the cyclic polyether prefers the fluorenylpotassium above the sodium salt. The complexing with some other cyclic polyethers was also investigated.

Various spectroscopic methods have recently been used to study structures of ion pairs and their solvates in aprotic solvents.[1,2] The ion pairs of carbanion salts have been of special interest to us for some time, since specific cation solvent interactions in a variety of aprotic media give rise to the formation of both contact- and solvent-separated ion pairs, and for certain types of carbanions, *e.g.*, fluorenyl alkali salts; the fractions of the two kinds of ion pairs can be quantitatively determined from their characteristic optical absorption spectra.[1] In addition, nmr spectroscopy has proven to be a valuable tool in the study of specific solvation phenomena and the fluorenyl alkali salts again provide us with a convenient probe to study structures of ion pairs in which certain agents are complexed to the cation.

In the study presented here we have investigated the complexes of fluorenyl alkali salts with cyclic polyethers

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(1) T. E. Hogen Esch and J. Smid, *J. Am. Chem. Soc.*, **87**, 669 (1965); **88**, 307 (1966); L. L. Chan and J. Smid, *ibid.*, **89**, 4547 (1967); **90**, 4654 (1968).

(2) G. W. Canters, E. de Boer, B. M. P. Hendriks, and H. Van Willigen, *Chem. Phys. Lett.*, **1**, 627 (1968); A. Fratiello, R. E. Lee, D. P. Miller, and V. M. Nishida, *Mol. Phys.*, **13**, 349 (1967); N. Hirota, R. Carraway, and W. Schook, *J. Am. Chem. Soc.*, **90**, 3611 (1968); R. V. Slates and M. Szwarc, *ibid.*, **89**, 6043 (1967).

or "crown" compounds of the type recently prepared by Pedersen,[3] who showed the very strong complexing ability of these ethers with a variety of cations, leading, for example, to improved solubility of many inorganic salts in media of low polarity. In our work, the complexing with fluorenyl salts leads to separated ion pairs, and the binding with cations turns out to be so strong that with Na^+ ions the rate of exchange with certain cyclic polyethers could be determined by nmr.

Experimental Section

Purification of solvents (THF, pyridine, and oxetane) has been described previously.[1] Three of the cyclic polyethers, *i.e.*, dibenzo-18-crown-6, dicyclohexyl-18-crown-6, and dibenzo-14-crown-4 (see ref 3 for structures and more exact nomenclatures), were kindly supplied to us by Dr. Pedersen. To obtain higher solubilities for nmr studies, the dimethyl derivative of dibenzo-18-crown-6 was prepared, starting from 4-methylcatechol and using the same procedure as given by Pedersen for the unsubstituted compound. The material was recrystallized from heptane and obtained in 40% yield, mp 132–135°. The dibenzo-16-crown-5 was prepared by method W[3] using benzyl instead of tetrahydropyran as the blocking group for one of the OH groups of catechol. The monobenzyl ether of cathecol obtained in 50% yield was treated with dibromopropane[3] to form the compound $C_6H_5CH_2OC_6H_4OCH_2CH_2CH_2OC_6H_4OCH_2C_6H_5$ (yield 80%), which was then debenzylated by Pd and H_2 in $CHCl_3$ at 25° to 1,3-bis(*o*-hydroxyphenoxy)propane (yield 95%). This compound was then treated with bis(2-chloroethyl) ether[3] to form the dibenzo-16-crown-5 in 25% yield, mp 117–118°.

In some experiments we used a dimethyldibenzo-18-crown-6 compound in which the CH_2 protons adjacent to the phenolic oxygens (the "a" protons of Figure 1) were replaced by deuterium. This compound was prepared by using diglycolic acid (Aldrich) as a starting material. The dimethyl ester of this compound was reduced with $LiAlD_4$ (Alfa Inorganics) and the resulting diethylenglycol was converted to the bis(chloro ethyl) ether ($ClCD_2CH_2OCH_2CD_2Cl$) with $SOCl_2$. The latter compound was then treated with 4-methylcathecol to yield the desired product. The purity of the compound was checked by nmr.

The preparation of carbanion salts have been reported previously.[1] For nmr experiments the fluorenylsodium was prepared in either THF or THF-d_8 by stirring fluorene on a sodium mirror. The potassium salt contains impurities when prepared in this way[4] and was therefore obtained by treating fluorene in THF with the potassium salt of the dianion of 1,1-diphenylethylene. For optical spectra studies, the sodium salt was prepared in a similar way. Fluorenyllithium was obtained by allowing butyllithium and fluorene to react in THF. When needed in other solvents, *e.g.*, pyridine, the THF was removed from the fluorenyl salts under vacuum and replaced by the desired solvent.

All uv-visible spectra were recorded on a Cary-14 spectrophotometer, while the nmr experiments were carried out with a Varian A60A spectrometer.

Results and Discussion

Studies of Ion Pair Structures by Nmr. Addition of dimethyldibenzo-18-crown-6 (I) to a solution of fluorenylsodium in THF in a 1:1 ratio causes the 356-mμ contact ion pair peak of F^-, Na^+ to be completely replaced by the 372-mμ absorption peak of the solvent-separated ion pair (see next section). This by itself is a strong indication that the Na^+ ion complexes with the cyclic polyether in THF. Even stronger evidence is found from the nmr spectrum of this complex as shown in Figure 1. Dissolved in THF-d_8, compound I shows the CH_3 protons at 136 cps, the aromatic protons at 406 cps, and the polyether ring protons as a somewhat broader band centered at 243 cps, all with respect to TMS (see Figure 1a). When fluorenylsodium is added in a 1:1 ratio (concentration of F^-,Na^+ = 5×10^{-2} *M*), the polyether ring protons are strongly shifted upfield, but not to the same extent. One set of protons is shifted upfield by 67 cps (to 176 cps), another set with equal number of protons is shifted by only 45 cps. The aromatic protons of the crown compound are also shifted upfield (by 11 cps), but the CH_3 protons are shifted slightly downfield by 4 cps.

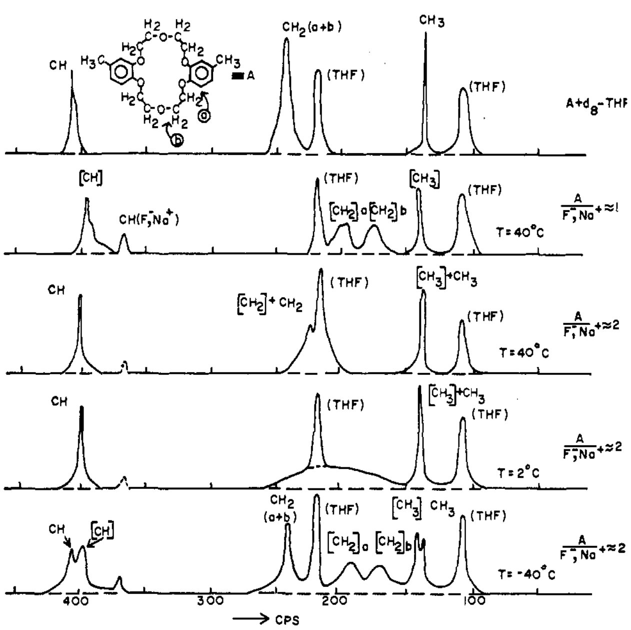

Figure 1. Nmr spectrum of the methyl derivative of dibenzo-18-crown-6 and its complex with fluorenylsodium in THF-d_8. The [] sign indicates that the proton peaks belong to that of the complexed cyclic polyether.

The strong upfield shift of protons in molecules complexed to compounds such as fluorenyl salts has been previously observed by Dixon, *et al.*, for complexes of fluorenyllithium with THF or DME[5] and by Chan and Smid for complexes of fluorenyl salts and linear polyethers.[1] The close proximity of the ether molecule above the aromatic ring causes the strong upfield shift in spite of the complexation with the alkali ion which in itself would induce a downfield shift of the polyether ring protons due to the increased electronegativity of the O atoms.

It should be stressed that the upfield shift itself does not necessarily indicate that one is dealing with a separated ion pair. In the fluorenyllithium–THF and –DME complexes of Dixon, *et al.*, the ion pair probably was a contact ion pair since benzene was used as solvent. With the linear polyethers, the optical spectrum clearly indicates the ion pair to be a glyme-separated ion pair, as is also the case with the cyclic polyethers.

The proposed structure of the F^-,Na^+–cyclic polyether complex is depicted in Figure 2. The large upfield shift of 67 cps (as compared to about 40 cps for the linear polyethers) not only indicates that the ether molecule must be located above the fluorenyl ring, but also strengthens the belief that the most effective conformation of the cyclic polyether molecule for coordination with the Na^+ ion is a nearly planar one (see also Pedersen, ref 3). The oxygen atoms of the dibenzo-18-crown-6 can arrange themselves in a coplanar configura-

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[3] C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967); *Fed. Proc.*, **27**, 1305 (1968).

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

[5] J. A. Dixon, P. A. Gwinner, and D. C. Lini, *J. Am. Chem. Soc.*, **87**, 1379 (1965).

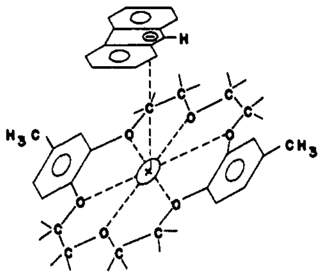

Figure 2. Suggested structure of the fluorenylsodium–cyclic polyether complex.

tion, with the apex of the C–O–C angle centrally directed in the same plane.[3] This leads to a comparatively tight separated ion pair with the polyether ring protons close to the fluorenyl moiety. It is also probable that the shielding of the external "a" protons (see Figure 1) caused by the diamagnetic anisotropy of the aromatic ring is less than that for the internal "b" protons. One would expect the fluorenyl carbanion to be pretty much centered above the ether molecule as depicted in Figure 2, particularly since repulsion by the aromatic rings of the ether molecule makes it more difficult for the carbanion to move freely above the crown compound.

It should be pointed out that a similar separation of the polyether protons may be obtained by assuming that the eight protons directly facing the fluorenyl ring are shifted more upfield than those on the other side of the ether molecule. However, this effect will be averaged out since the exchange between complexed molecules, *i.e.*, $(F^-,Na^+)^*,CPE + F^-,Na^+,CPE^* \leftrightarrows (F^-,Na^+)^*,CPE^* + F^-,Na^+,CPE$, is expected to be fast. Such an exchange may also proceed through the free ions. Of course, even a simple rotation of the CPE in the complex can lead to the same result. Such a process is very rapid, although the bulkiness of the ether may slow down this rotation to some extent, since it would probably require an increase in the separation of carbanion and cation.

To explore further the reason for the separation into the two separate bands of equal intensity, we complexed F^-,Na^+ with a compound I in which the CH_2 protons adjacent to the phenolic oxygen atoms were replaced by deuterium. The nmr spectrum now clearly shows only one peak at 174 cps which is also considerably sharper than the band in the nondeuterated compound. This is clear evidence that the inner "b" protons are shifted further upfield than the outer "a" protons.

The aromatic protons of the crown compound will of course be shifted to a much lesser degree, and those of the CH_3 group are even somewhat deshielded, presumably because they are located more on the side of the fluorenyl ring or because of the inductive effect of the Na^+ ion on the ether molecule.

A similar strong upfield shift is observed in pyridine. When the crown compound I is dissolved in pyridine, the polyether protons are again separated into two bands of equal number of protons, centered at 249 and 237 cps, respectively. While aromatic solvents like benzene usually line up in a plane parallel to a polar solvent molecule, giving rise to upfield shifts, solvation of pyridine is known to either shield or deshield the protons of the solute.[6] Owing to its unsymmetrical electronic structure, pyridine may specifically interact with the oxygens of the polyether ring, and the observed proton shifts will depend strongly on the average orientation of the pyridine ring with respect to the various protons. On addition of fluorenylsodium (1:1 ratio with the ether) the two peaks are now shifted much further upfield, namely, to 228 and 193 cps. This again indicates that the crown compound has complexed to the F^-,Na^+. Unlike THF, the optical spectrum does not give us any information whether complexation takes place since F^-,Na^+ is already a solvent-separated ion pair in pyridine, with an absorption maximum at 372 mμ, and no change is observed on addition of cyclic polyether. However, the nmr spectrum of the crown compound clearly shows that the solvent layer of pyridine molecules around the Na^+ ion is, at least partially, replaced by the cyclic polyether. The shift can also tell us whether extensive free ion formation takes place. The higher dielectric constant of pyridine (ϵ 14.0 at 25°) may conceivably lead to extensive dissociation of the separated ion pair. However, since the ether remains complexed to the alkali ion, dissociation would remove it from the fluorenyl moiety and a downfield, rather than an upfield shift should be observed. The observed strong upfield shift is therefore evidence that at 0.1 *M* concentrations, dissociation into free ions is not large.

Temperature Dependence of the Nmr Spectrum. The solvation of sodium ion pairs by linear polyethers involves a rapid process, as indicated from recent esr measurements[7] on the rate of collapse of a glyme-separated sodium naphthalene ion pair (the glyme involved was tetraethylene glycol dimethyl ether) to the contact ion pair in tetrahydropyran as solvent. The rate constant of this reaction was found to be $10^7\ M^{-1}\ sec^{-1}$, too fast to observe in the nmr. Since the cyclic polyethers have a much stronger coordinating ability then the linear polyethers, it was decided to investigate the temperature dependence of the nmr spectrum of the F^-,Na^+–dimethyldibenzo-18-crown-6 complex. The results are shown in Figures 1c, 1d, and 1e.

With a F^-,Na^+ to cyclic ether ratio of 1:2, the spectrum of the polyether ring protons at 40°, after correcting for the peak due to impurities in the THF-d_8, is clearly shown to result from the weighted average of the proton peaks of the complexed and free ether, indicating a rapid exchange between the two forms of the ether. However, on cooling the solution the proton peaks are broadening, with the coalescence temperature, t_c, being 2 ± 1° (Figure 1d) and at lower temperatures the spectrum of the free cyclic polyether and that of the complexed one are clearly visible.

Since the concentration of the complex and that of the free cyclic polyether are equal, one may calculate the rate constant of the reaction

$$F^-,CPE^*,Na + CPE \longrightarrow F^-,CPE,Na^+ + CPE^*$$

at the coalescence temperature from the equation $k = 1/2\tau[CPE]_{free}$, where the relaxation time $\tau = \sqrt{2}/2\pi\cdot(\nu_A{}^0 - \nu_B{}^0)$ (see ref 8). The exchange rate constant is thus calculated to be 3200 $M^{-1}\ sec^{-1}$ at 2°.

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(6) D. H. Williams, J. Ronayne, H. W. Moore, and H. R. Shelden, *J. Org. Chem.*, 33, 998 (1968).

(7) K. Höfelmann, J. Jagur-Grodzinski, and M. Szwarc, *J. Am. Chem. Soc.*, 91, 4645 (1969).

(8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw Hill Book Co., Inc., New York, N. Y., 1959.

At the same time one can observe the coalescence temperatures for the aromatic CH protons ($t_c \approx -18°$, $\Delta\nu = 10$ cps) and for the CH_3 protons which are shifted downfield in the complex ($t_c \approx -27°$, $\Delta\nu = 4$ cps). The calculated rate constants for these temperatures are $k = 550\ M^{-1}\ sec^{-1}$ at $-18°$ and $k = 200\ M^{-1}\ sec^{-1}$ at $-27°$. This would leave us with an activation energy of 12.5 kcal/mole for the exchange process, the *A* factor being $10^{13}\ M^{-1}\ sec^{-1}$. Although these values appear to be reasonable, more work is needed to establish whether the exchange is a simple bimolecular process, or whether it proceeds through free ions or possibly through the contact ion pair. The latter mechanism may involve a rate-determining dissociation step into the free cyclic ether and the contact ion pair, followed by a rapid association step leading to the exchange. These possibilities are currently under investigation.

A slow exchange rate between cyclic polyether and its complex with F^-,Na^+ has so far only been observed for the dibenzo-18-crown-6. The exchange rate is considerably faster for complexes of the hydrogenated compound, *i.e.*, dicyclohexyl-18-crown-6 (II), since no coalescence temperature for the polyether protons could be obtained even down to $-60°$. Also, an analysis of the nmr spectrum of a mixture of the two cyclic polyethers with F^-,Na^+ (molar ratio 1:1:1) in THF-d_8 shows that about 80% of the carbanion salt is complexed to I. Both observations may indicate that in THF I is more tightly bound to Na^+ than is II. The difference between the two cyclic polyethers in their complexation with F^-,Na^+ may also, at least partially, be due to a more tighter ion pair complex for I because of its planar structure. This might affect its rotation in the complex or the extent of free ion dissociation if the exchange took place through the free ions.

We also have found that above $-60°$ no coalescence phenomena of the polyether protons could be observed for the complexes of I with fluorenylpotassium and fluorenyllithium. The binding with Li^+, due to its smaller size and stronger solvation by THF, is expected to be less than for Na^+. This was also observed by Pedersen in CH_3OH as solvent. The weaker complexation with K^+ as compared to Na^+ is contrary to observations by Pedersen,[3] Eisenman, *et al.*,[9] and Izatt, *et al.*[10] The different behavior of the two ions is even more pronounced if one takes into account that the THF binds more strongly to Na^+ than to K^+, which in itself would favor complexation with K^+. We will return to this point when discussing the results of the optical spectra measurements.

Measurements of Optical Spectra. Selectivity of Alkali Ion Solvation by Cyclic Polyethers. Addition of cyclic polyether I or II to F^-,Na^+ in a 1:1 ratio in THF as solvent completely converts the contact ion pair spectrum of F^-,Na^+ (λ 355 mμ) to a spectrum identical with that of a F^-,Na^+ solvent-separated ion pair (*e.g.*, F^-,Na^+ in oxetane, λ 372 mμ). No contribution of a contact ion pair spectrum is noticeable even down to a complex concentration of 10^{-5} *M*. This means that the equilibrium constant for complex formation in THF

$$F^-,Na + CPE \rightleftarrows F^-,CPE,Na^+$$

must be larger than $10^6\ M^{-1}$. For the linear polyether pentaglyme which also contains six O atoms for coordination, *i.e.*, $CH_3O[CH_2CH_2O]_5CH_3$, the equilibrium constant is only 450 M^{-1}.[11] The difference is largely the result of the unfavorable entropy change on complexing linear polyethers compared to the cyclic polyethers.

It should be pointed out that at 10^{-5} *M* a considerable fraction of F^-, CPE, Na^+ may be dissociated into CPE, Na^+, and F^-, the latter having a similar spectrum to F^-, CPE,Na^+. In THF the dissociation constant of a solvent-separated ion pair would be in the order of 10^{-6} *M* at 25° (see F,Na^+ in DME, ref 4). However, when THF at 25° (ϵ 7.40) is replaced by tetrahydropyran (ϵ 5.60 at 25°) the complex still absorbs only at 372 mμ at 10^{-5} *M*. In this solvent the free ion fraction at this concentration will be less than 0.1.

In principle one can of course depress the free ion concentration through the common ion effect by adding a more dissociable salt like $NaBPh_4$. This was used previously as one of the evidences for the presence of solvent-separated ion pairs in solutions of fluorenyl salts.[1] It has also been frequently applied to decrease the effect of the highly reactive free ion in the anionic polymerization of styrene in THF or other ethereal solvents.[12] However, caution must be taken when dealing with separated ion pairs such as the F^-,CPE,Na^+ complex. In some recent work involving proton-transfer reactions between F^-,Na^+ and methylfluorene in THF[13] we found that, in spite of appreciable dissociation of F^-,Na^+, addition of $NaBPh_4$ had no effect on the rate of proton transfer, consistent with earlier observations in similar reactions.[14] On the other hand, addition of $NaBPh_4$ in the same reaction but carried out with the complex F^-,CPE,Na^+ strongly depressed the rate of the proton transfer from methylfluorene. This rate depression is not resulting from a decrease in the concentration of free fluorenyl ions. One clearly observes that on addition of $NaBPh_4$ the 372-mμ F^-,CPE,Na^+ ion pair peak reverts to the 355-mμ contact ion pair peak of F^-,Na^+, a species of lesser reactivity

$$F^-,CPE,Na^+ + NaBPh_4 \rightleftarrows F^-,Na^+ + Na,CPE,BPh_4$$

The equilibrium constant for this reaction was found to be approximately 2. The solvation of the $NaBPh_4$ by the cyclic polyether is probably accompanied by the release of a few THF molecules, since the salt is believed to be a solvent-separated ion pair in THF.[15] Other sodium salts show the same effect, although to a much lesser extent. For example, the equilibrium constant for $NaClO_4$ is only about 0.04. Conductance data indicate that this salt is very likely to be a contact ion pair,[12] and efficient binding with the ether may be accomplished only at the expense of a considerable amount of Coulombic interaction if the interionic distance of $NaClO_4$ is enlarged in the process. Moreover, less THF molecules will be released in the reaction.

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(9) G. Eisenman, S. M. Ciani, and G. Szabo, *Fed. Proc.*, **27**, 1289 (1968).

(10) R. M. Izatt, J. H. Rytting, D. P. Nelson, B. L. Haymore, and J. J. Christensen, *Science*, 164, 443 (1969).

(11) L. L. Chan, K. H. Wong, and J. Smid, to be published.

(12) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965).

(13) T. Ellingsen and J. Smid, unpublished results from this laboratory.

(14) T. E. Hogen Esch and J. Smid, *J. Am. Chem. Soc.*, **89**, 2764 (1967).

(15) C. Carvajal, K. J. Toelle, J. Smid, and M. Szwarc, *ibid.*, **87**, 5548 (1965).

It would seem to us that this method provides us with a simple way of acquiring quantitive information on the complexing ability of a variety of salts in solvents of low polarity. More detailed measurements to this effect are under way.

Using essentially the same method as described above, one can also determine quite easily the selectivity of cyclic polyethers with respect to various cations. For example, to check the complexation of CPE I with K^+ as compared with Na^+, we added in THF an equimolar quantity of F^-,Na^+ (λ_{max} 356 mμ) to the complex F^-,CPE,K^+ (λ_{max} 372 mμ). One observes an almost complete transfer of the dimethyldibenzo-18-crown-6 from F^-,K^+ to F^-,Na^+, as evidenced by the disappearance of the F^-,Na^+ contact ion pair and the formation of a new maximum at 362 mμ which is the absorption maximum of the contact ion pair of F^-,K^+. The same behavior was observed for the dicyclohexyl derivative.

Similar studies with other alkali ions show that the selectivity of these two cyclic polyethers with respect to complexation of alkali ions in THF is $Na^+ \gg K^+ > Cs^+ > Li^+$. The rather low selectivity for Li^+ ions is probably due to its small size (ionic diameter 1.20) as compared to the size of the hole of this cyclic polyether which has a diameter of 4 Å.[3] In addition, the specific solvation by the solvent medium itself is of prime importance in determining cation selectivity, and in this respect it will be more difficult to strip the solvent molecules from Li^+ than from the larger cations. This of course will depend very strongly on the nature of the solvent. Both Pedersen[3] and Eisenman, *et al.*,[9] found that in H_2O and CH_3OH the selectivity of CPE II with respect to alkali ions is $K^+ > Cs^+ > Na^+ > Li^+$. Also Izatt, *et al.*,[10] using calorimetric and potentiometric measurements, find an affinity order in water of $K^+ > Rb^+ > Cs^+ > Na^+,Li^+$. The main difference between our system and the other systems lies in the strong solvation of Na^+ and Li^+ by solvents such as H_2O and CH_3OH. In our case, THF is also more strongly bound to Na^+ then to K^+, but the difference is expected to be much less, and involves only a few solvent molecules since contact ion pairs are involved.

To check this point further, we repeated our selectivity experiments in oxetane. In this solvent, F^-,Na^+ is a solvent-separated ion pair at 25°,[1] but F^-,K^+ is a contact ion pair. Addition of CPE I to a mixture of F^-,Na^+ and F^-,K^+ in this solvent in a molar ratio 1:1:1 now shows only one absorption peak at 372 mμ. Apparently, the oxetane is too tightly bound to the Na^+, and the cyclic polyether therefore complexes preferentially with the K^+ ion, thereby changing the absorption maximum of F^-,K^+ from 362 to 372 mμ. We believe, however, that intrinsically the Na^+ ion is more strongly bound to the dibenzo- and dicyclohexyl-18-crown-6 cyclic polyethers than K^+, but that more polar solvents can reverse this order.

Some of the work of Pedersen[3] and Eisenman[6] has been based on solvent extraction data in which a picrate salt was extracted from the water layer into the organic layer containing the cyclo polyethers. Although free ions are present in the water layer, it is almost certain that in the organic layer (particularly cyclohexane, hexane, and toluene but probably also methylene chloride) the picrate salt is a contact ion pair. Ion pair formation in the organic layer should of course not have any effect on the nature of the salt in the water layer as long as a picrate salt is transferred. However, when the anion directly involved in the cyclic polyether–cation complex is changed (*e.g.*, a permanganate or fluoride instead of picrate), the extent of salt extraction is strongly affected[3] and this may largely be due to ion pair formation. Effective complexation of the cyclic polyether with the ion pair will depend on how tightly the ions are bound, since the interaction may involve a partial separation of the two ions.

As expected, the dibenzo-14-crown-4 is a rather poor solvating agent for F^-,Na^+. Although it forms solvent-separated ion pairs with F^-,Na^+ in THF, its complexation constant is only 150 M^{-1}, which, however, is still about 10 times higher than that for triglyme[1,11] which also has four coordination sites.

The dibenzo-14-crown-4 complexes very effectively with fluorenyllithium, but the resulting complex has a very poor solubility in tetrahydropyran. We also have found in many other cases that complexation of our salts with cyclo polyethers leads to products of much lower solubility. Hence, any complexation data based on increased solubility of inorganic salts in low polarity media may not yield a clear picture of how effective the various salts complex with ethers.[3]

The dibenzo-16-crown-5 has a complexation constant with F^-,Na^+ in THF of 7000 M^{-1}, much better than the crown-4 but still considerably less than the dibenzo-18-crown-6.

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