Contact and Solvent-Separated Ion Pairs of Carbanions. V. The Role of Solvent Structure in Alkali Ion Solvation

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Abstract: The effect of solvent structure on the solvation of alkali ions was determined by measuring spectrophotometrically the extent of solvent-separated ion-pair formation from contact ion pairs for fluorenyllithium and 9-(2-hexyl)fluorenyllithium in a series of ethers. It was found that the 9-substituted derivative yields much higher fractions of solvent-separated ion pairs under otherwise identical conditions. For a series of unsubstituted cyclic ethers the order of increasing solvating power is largely determined by the basicity of the ether oxygen atom. However, steric factors are far more important when substituents are present close to the coordination site, as demonstrated by the behavior of a series of substituted tetrahydrofurans.

Recent studies dealing with the absorption spectra of carbanions in ethereal solvents have revealed conclusive evidence for the existence of two kinds of ion pairs, *viz.*, contact and solvent-separated ion pairs.[1] The larger interionic distance in the solvent-separated ion pair results in a distinct bathochromic shift in the uv and visible spectra of many carbanions. In this respect the alkali salts of the fluorenyl and substituted fluorenyl carbanions are particularly suitable to study the behavior of the two kinds of ion pairs since the overlap of the respective absorption bands is not large.

The dynamic equilibrium between the two ion pairs is strongly affected by the structure of the carbanion, the size of the alkali counterion, the temperature, and the nature of the solvent. Since the interaction between the solvating entity and the cation constitutes the main driving force for solvent-separated ion-pair formation, one may expect that the equilibrium between the two kinds of ion pairs as measured from their optical spectra represents a convenient way to investigate the factors governing the interactions between alkali ions and solvent molecules. The results of these studies, particularly in which interactions with ethereal solvents are considered, are presented in this article.

Experimental Section

All of the solvents employed in this investigation were commercially acquired. Where necessary, the solvents were fractionated, and a constant-boiling middle fraction was collected. The solvents were rigorously dried by stirring on calcium hydride and then distilled under vacuum into a flask containing sodium–potassium alloy to which some benzophenone or fluorene was added. After stirring the solution for some time, a persistent color was obtained representing that of the benzophenone radical ion or the fluorenyl carbanion. The solvents were then distilled under vacuum from these colored solutions into the appropriate ampoules. In some cases this purification procedure needed repeating (*e.g.*, oxetane) due to the presence of slowly reacting impurities.

The fluorenyl carbanions were prepared under vacuum, usually in tetrahydrofuran as solvent. The lithium salts were obtained by treating butyllithium (from which the heptane was removed) or ethyllithium (recrystallized from benzene) with a slight excess of fluorene dissolved in THF. The sodium, potassium, and cesium salts were prepared by treating fluorene with the corresponding polystyryl salts which were abundantly available in our laboratory. The salts can also be prepared by stirring fluorene in tetrahydrofuran on mirrors of the corresponding metals. Solutions prepared by these two methods yield identical absorption spectra. The carbanion solutions were stored in a freezer and were stable over prolonged periods of time.

The 9-(2-hexyl)fluorenyllithium was prepared by adding butyllithium to a slight excess of 9-ethylidenefluorene in THF. The reaction takes place instantaneously and quantitatively. The hydrocarbon was acquired from Aldrich and recrystallized from absolute alcohol. After drying under vacuum it was stored in an evacuated ampoule since it decomposes slowly when left in contact with air.[2]

The carbanion solutions in solvents other than tetrahydrofuran were prepared from the corresponding THF solutions by removing this solvent under vacuum and distilling the appropriate solvent onto the dry carbanion salt. Although complete removal of THF is difficult, the very small residual quantities of THF do not interfere with the measurements. In solvents of high polarity only solvent-separated ion pairs may exist, and in these cases measurements were carried out in the presence of a nonpolar solvent, usually dioxane. A solution of a carbanion salt in a mixture of dioxane and the polar solvent was added under vacuum from a buret provided with a Teflon stopcock to a solution of the same carbanion concentration in pure dioxane. After each addition of a known amount of the mixture, the spectrum of the new solution was recorded.

Spectra were recorded by means of a Cary Model 14 spectrometer, using 0.2-cm, optical vacuum cells provided with a 0.18-cm spacer. Measurements at low temperature were performed with a quartz dewar provided with optical windows and filled with precooled methanol. The temperature was recorded by means of a copper–constantan thermocouple located a few millimeters from the cell. The temperature change during the time of scanning amounted to less than 0.5°.

Results

The fluorenyl salts were found to be stable in all of the solvents used with the exception of oxetane, which immediately decolorized the lithium salts. In the latter solvent, the fluorenyl carbanion, aided by the strong interaction between the Li ion and the ether oxygen, most likely attacks the strained cyclic ether ring forming a lithium alkoxide. The fluorenylsodium is surprisingly stable in oxetane. However, when the solvent is not perfectly pure, the spectrum of the solvent-separated fluorenylsodium ion pair (maximum 373 mμ) rapidly changes to a spectrum identical in shape but with an absorption maximum at 382 mμ. Similar shifts are observed for the maxima in the visible region. The spectrum resembles that of the solvent-separated ion pairs of 9-alkyl-substituted fluorenyl salts. However, when the oxetane was repeatedly distilled from fluorenylsodium, a pure solvent was obtained in which the spectrum of fluorenylsodium was identical with that

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[1] T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **87**, 669 (1965); **88**, 307 (1966).

[2] D. J. Cram and D. R. Wilson, *ibid.*, **85**, 1249 (1963).

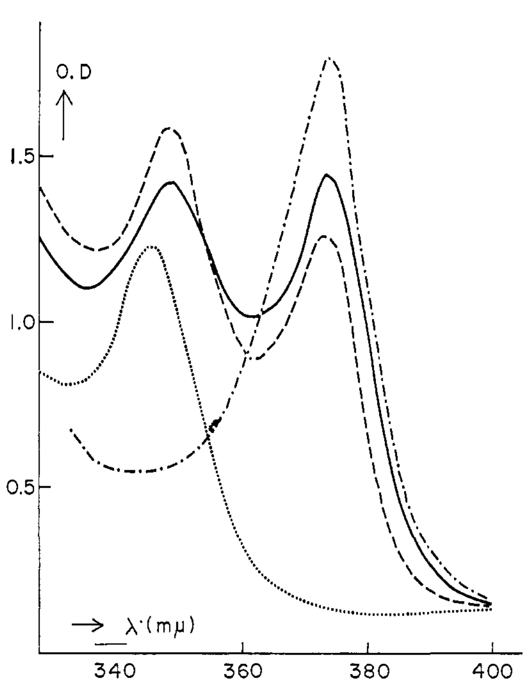

Figure 1. Ultraviolet spectrum of fluorenyllithium contact and solvent-separated ion pairs at 25° in 3,4-dihydropyran, ...; 3-methyltetrahydrofuran, ---; 2,5-dihydrofuran, ——; hexamethylphosphoramide, -·-·-·.

in other solvents which contain only solvent-separated ion pairs.

Most of the measurements were carried out with the fluorenyllithium salt since specific interactions with ethereal solvents are usually the strongest for the small lithium ion. Typical examples of the change in absorption spectrum with solvent are shown in Figures 1 and 2. Figure 1 represents part of the uv spectrum of fluorenyllithium in dihydropyran, 3-methyltetrahydrofuran, 2,5-dihydrofuran, and hexamethylphosphoramide, respectively, all spectra being recorded at 25°. A small bathochromic shift in the absorption maximum of the contact ion pair (which shifts to larger wavelengths with increasing radius of the alkali counterion[1]) is noticeable with increased solvent polarity. For example, increased quantities of hexamethylphosphoramide in a dioxane solution of fluorenyllithium not only increases the fraction of solvent-separated ion pairs, but also shifts the contact ion-pair absorption maximum gradually to higher wavelengths, although usually not more than about 5 mμ. The shifts are larger in the case of some amines, *e.g.*, ethylenediamine. Small quantities of this solvent in dioxane shifts the contact ion-pair peak from 345 to 354 mμ, and probably represents a species in which one ethylenediamine molecule solvates the lithium ion of the contact ion pair.[3]

The solvent-separated ion-pair absorption maximum (which does not change with the radius of the alkali counterion) is at 370–372 mμ and is hardly affected when the solvent is changed from tetrahydropyran (ε 5.6) to such strongly polar solvents as dimethyl sulfoxide (ε 45.0) or hexamethylphosphoramide.[4] In other words, the carbanion spectrum itself, apart from the effect of counterion, is nearly independent of the nature of the solvent, indicating the lack of solvation of the carbanion in most of these solvents. Some of the amines again appear to be an exception.[3]

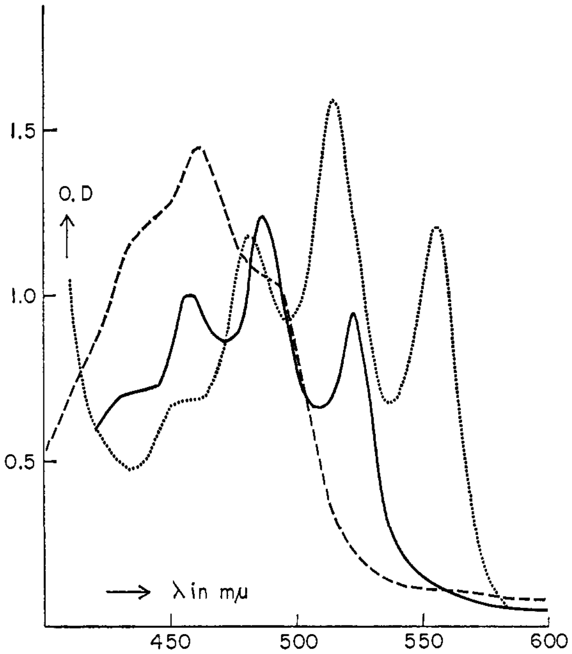

Figure 2. Visible spectrum of 9-(2-hexyl)fluorenyllithium in diethyl ether, ---; and in THF, ····; also of fluorenylsodium in oxetane, ——; all at 25°.

Similar changes as those observed in the uv spectrum can be found in the visible region of the fluorenyl carbanion spectrum (see Figure 2). The maxima are much lower (extinction coefficients in the range of 1000–1200 compared to 10,000–12,000 for the uv maxima), and the changes are rather complex since more than one peak is involved and considerable overlap exists. The maxima for the contact ion pair in this region are at 420, 437, and 460 mμ (*e.g.*, fluorenyllithium in diethyl ether) while those of the solvent-separated ion pairs (*e.g.*, fluorenylsodium in oxetane) appear at 458, 487, and 522 mμ and are much more distinct.

Alkyl substitution in the 9 position causes a bathochromic shift of about 2.4 kcal/mol in the transition energies for the various absorption bands (Figure 2). Such a shift is in agreement with that observed for alkyl substitution in other carbanions and has been discussed in detail by Waack and Doran.[5] The difference in the transition energies between corresponding bands (*e.g.*, 357 and 387 mμ) for the two kinds of ion pairs of the 9-(2-hexyl)fluorenyllithium salt is 6.2 kcal/mol, similar to that of fluorenyllithium.[1] Apparently the various transitions are again affected by the position of the cation to the same extent.

A measure of the solvent polarity of the various ethereal solvents can be obtained from the ratio of the

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(3) T. Ellingsen, R. Smyk, and J. Smid, unpublished results from this laboratory.

(4) Recent conductance studies by Szwarc, *et al.* (*J. Am. Chem. Soc.*, **89**, 7129 (1967)), indicate that the lithium salt of the anthracene monoradical anion is completely dissociated in hexamethylphosphoramide at 10^{-3} *M*. Our spectral measurements do not distinguish between a free ion or a solvent-separated ion pair, since the absorption maxima of both species are the same (see ref 1). Our measurements in HMPA were done at 10^{-2} *M*, and the charge in the fluorenyl carbanion is less delocalized than in the anthracene radical anion. Nevertheless, a considerable fraction of free ions may be present in pure HMPA. In the mixtures of HMPA with dioxane, however, the dielectric constant remains very low, and little or no free ions can be detected.

(5) R. Waack and M. A. Doran, *J. Phys. Chem.*, **68**, 1148 (1964).

fractions of the two ion pairs. This quantity can easily be calculated from the known absorption spectra of the "pure" ion pairs. For the contact ion pairs, fluorenyllithium in dioxane and 9-(2-hexyl)fluorenyllithium in diethyl ether were chosen, while the spectra in dimethoxyethane and tetrahydrofuran, respectively, were taken as that of the pure solvent-separated ion pairs. It was assumed that both the linear and integral extinction coefficients of the two peaks were independent of the nature of the solvent. There are small variations in the absorption bands with changing solvent polarity, but peak overlap of the spectra of the two ion pairs is not very extensive with lithium as counterion, hence the variations will not affect the calculation to any great extent.

In Table I the ratio of fractions of solvent-separated over contact ion pairs in a number of unsubstituted cyclic ethers are listed for both fluorenyllithium and its 9-substituted 2-hexyl derivative. Similar data for a number of substituted tetrahydrofurans are given in Table II. A few other solvents have also been added to this list. Values reported as >50 mean that no contact ion pairs can be detected at room temperature, while values <0.01 indicate that no solvent-separated ion pairs at that temperature can be observed in the spectrum.

Table I. Solvent-Separated Ion-Pair Formation for Fluorenyllithium (F^-,Li^+) and 9-(2-Hexyl)fluorenyllithium ($He\text{-}F^-,Li^+$) in Unsubstituted Cyclic Ethers at 25°

Solvent	$[F^-\|Li^+]/[F^-,Li^+]$	$[He\text{-}F^-\|Li^+]/[He\text{-}F^-,Li^+]$
Oxetane[a]	>50	. .
Tetrahydrofuran	4.6	>50
Tetrahydropyran	0.45	20
Hexamethylene oxide	0.24	2.3
2,5-Dihydrofuran	1.1	50
3,4-Dihydropyran	0.01	0.14
Furan	<0.01	0.02
Dioxolane	0.08	10
Dioxane[b]	0.01	0.3

[a] The lithium salts of fluorenyl carbanions were not stable in oxetane. The value listed for oxetane represents that of fluorenylsodium which is stable in this solvent. [b] When fluorenyllithium is prepared directly in dioxane, the fraction of solvent-separated ion pairs is about 0.1, and almost complete solvent separation was found for substituted fluorenyllithium salts. The reason for this peculiar behavior is being investigated.

Table II. Solvent-Separated Ion-Pair Formation for Fluorenyllithium (F^-,Li^+) and 9-(2-Hexyl)fluorenyllithium ($He\text{-}F^-,Li^+$) in Substituted Tetrahydrofurans and Some Other Solvents at 25°

Solvent	$[F^-\|Li^+]/[F^-,Li^+]$	$[He\text{-}F^-\|Li^+]/[He\text{-}F^-,Li^+]$
Tetrahydrofuran	4.6	>50
3-Methyltetrahydrofuran	0.85	>50
2-Methyltetrahydrofuran	0.33	1.50
2,5-Dimethyltetrahydrofuran	0.02	0.07
2,5-Dimethoxytetrahydrofuran	0.04	
2-(Methoxymethyl)tetrahydrofuran	>50	
3,3-Dimethyloxetane	1.2	>50
o-Dimethoxybenzene	>50	
m-Dimethoxybenzene	0.01	
Hexamethylphosphoramide[4]	>50	

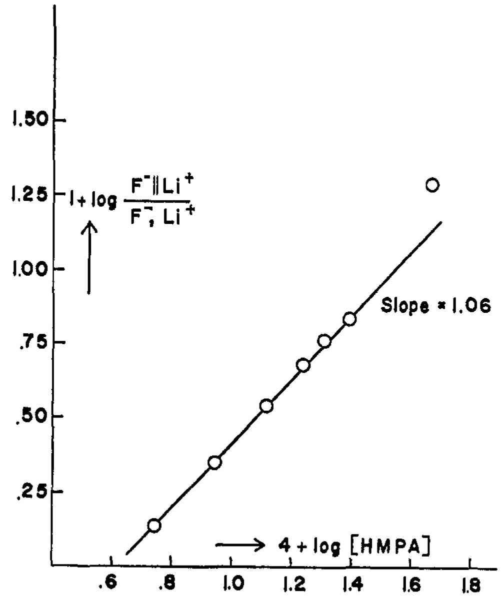

Figure 3. Solvent-separated ion-pair formation of fluorenyllithium as a function of [HMPA] in mixtures of dioxane–hexamethylphosphoramide; $[F^-,Li^+] \approx 1.5 \times 10^{-3}\ M$.

In more polar solvents, *e.g.*, hexamethylphosphoramide, no contact ion pairs may exist at room temperature or its fraction is too small to measure accurately. In that case a comparison of the polarity of such a solvent with other solvents may be obtained by using a solvent of low polarity like dioxane and adding small quantities of the strongly solvating agent. Dioxane contains only contact ion pairs in the case of fluorenyllithium, while for the substituted salt only about 10% are present. In the latter case, dimethyltetrahydrofuran would be better as the nonpolar medium. Toluene or benzene could also be used, but the possibility of aggregation of the lithium salts in these hydrocarbon media is a distinct possibility and could lead to complications.

Addition of a polar solvent to the contact ion pair in dioxane shifts the equilibrium in favor of the solvent-separated ion pairs according to the equation

$$F^-,Li^+ + nS \rightleftharpoons F^-\|Li^+ \qquad K_i$$

where n represents the number of solvent molecules S reacting with the contact ion pair F^-,Li^+ to form a solvent-separated ion pair $F^-\|Li^+$. A plot of log $[F^-\|Li^+]/[F^-,Li^+]$ *vs.* log [S] yields a straight line with slope equal to n. The average number of solvent molecules may not necessarily be an integral number and the plot is expected to show a curvature when n is changing. Only minute quantities of substances like dimethyl sulfoxide or hexamethylphosphoramide are required to form the solvent-separated ion pair and an isosbestic point is observed in these spectra (see also ref 1). An example of such a plot for the mixture of fluorenyllithium in dioxane and hexamethylphosphoramide (HMPA) is shown in Figure 3. The concentration of free HMPA is given by the difference of the total HMPA concentration added and the concentration of the solvent-separated ion pair, the assumption being that only one HMPA molecule is coordinated with the lithium ion. At low HMPA concentration (*i.e.*, comparable to that of fluorenyllithium which was about $1.5 \times 10^{-3}\ M$), the contact ion pairs are probably not solvated by HMPA, since this would lead to impossible values for the free HMPA concentration. However, at higher amide concentration the contact ion pairs may form species of the type $F^-,Li^+\cdots HMPA$, as indicated by a bathochromic shift of the absorption peak for the contact ion pair on addition of excess HMPA. In that case, the free HMPA concentration is somewhat less than calculated above, but it does not appear to affect the slope of the plot to any great extent.

Some peculiar observations were made when the 9-alkyl-substituted fluorenyllithium salt was directly prepared in dioxane as solvent.[3] As outlined in the Experimental Section, the carbanion salts were usually prepared in THF, and, if needed in other solvents, the THF was evaporated and the appropriate solvent distilled onto the dry salt. Prepared in this way, fluorenyllithium contains no solvent-separated ion pairs in dioxane, and the 9-substituted salt only about 10%. However, when the salt is directly prepared in dioxane (by adding a dioxane solution of the hydrocarbon to BuLi, yielding almost instantaneously the carbanion), the fluorenyllithium spectrum shows a measurable absorption peak at 372 mμ while the 9-(2-hexyl) salt has only one peak at 387 mμ, *i.e.*, it appears to exist only as a solvent-separated ion pair. The same behavior is observed for other 9-alkyl-substituted lithium salts (*e.g.*, 9-methyl, 9-ethyl, and 9-isopropyl). The absorption peak remains at 387 mμ when the dioxane is replaced by toluene. It is also interesting that the solubilities of the 9-alkyl fluorenyllithium salts are much higher when directly prepared in dioxane. Concentrations of more than 10^{-1} *M* were obtained. When first prepared in THF, the highest concentrations obtained in dioxane are about 2×10^{-3} *M*. Subsequent studies have shown that the conversion into the carbanion, which is essentially quantitative in THF, amounts to only about 50% when directly prepared in dioxane. This indicates that part of the butyllithium is lost through side reactions, probably with dioxane. Butyllithium and dioxane do not react rapidly at room temperature, *i.e.*, after about 10 min the mixture is still active and can produce the carbanion on addition of the 9-alkylfluorene. Since this reaction is instantaneous, it appears that somehow dioxane is involved when BuLi reacts with the fluorene hydrocarbon. It is not simply a matter of alkoxide formation, *e.g.*, species such as $BuCH_2CH_2OCH_2CH_2O^-,Li^+$ could conceivably be produced. However, addition of $CH_3OCH_2CH_2O^-,Li^+$ to the contact ion pair of an 9-alkyl fluorenyllithium salt in dioxane does not noticeably change the spectrum, *i.e.*, no increase in the concentration of solvent-separated ion pairs is found. We are continuing the investigation of this peculiar phenomenon.

Discussion

We reported in an earlier publication[1] that variations in temperature and solvent composition of solutions containing carbanions or radical anions resulted in reversible changes in their uv and visible absorption spectra. The observed changes were attributed to the existence of a rapid equilibrium between two kinds of ion pairs, *i.e.*, contact ion pairs (F^-,M^+) and solvent-separated ion pairs ($F^-||M^+$) according to the equation

$$F^-,M^+ + nS \rightleftharpoons F^-||M^+$$

n being the number of solvent molecules, S, reacting with the contact ion pair. The fraction of solvent-separated ion pairs was shown to decrease rapidly with increasing cation radius. For example, while the ion pairs of fluorenyllithium are solvent separated in dimethoxyethane at room temperature and those of the sodium salt for about 80%, the fluorenylcesium contains only contact ion pairs under these conditions.

The presence of two thermodynamically stable ion pairs was already postulated some time ago by Winstein,[6] to rationalize the stereochemical course of solvolysis reactions, and later by Cram, *et al.*,[7] for electrophilic substitution reactions at saturated carbon. At the same time, Fuoss and Sadek,[8] and also Grunwald[9] suggested that the association of free ions into ion pairs may involve a stepwise process involving two kinds of ion pairs. The first step would be formation of an ion pair in which either one or both ions essentially retain their solvation shell. A still closer approach of the two ions would then necessitate at least a partial desolvation of the ions requiring a substantial amount of energy. The increase in Coulombic attraction on formation of the contact ion pair as well as the gain in entropy on desolvation would constitute the driving force for this reaction. In Grunwald's model, the two kinds of ion pairs are represented by potential energy minima, each determined by the interionic distance in the respective ion pair.

The barrier separating the two potential energy minima will largely depend on such factors as size and charge of the ions, polarity, and geometry of the solvating molecules, temperature, etc. It is clear, therefore, that one may realize conditions favoring the existence of only one ion pair. In the case of alkali carbanion salts, the free energy of solvation of the alkali cation may be too small to overcome the strong coulombic attraction in the contact ion pair when dealing with such poorly solvating media as furan or diethyl ether, or when large cations are involved (*e.g.*, fluorenylcesium in THF). On the other hand, the presence of a bulky substituent close to the carbanion will increase the average interionic distance in the contact ion pair and, therefore, favor formation of solvent-separated ion pairs. An example of this effect of steric hindrance was recently reported by Roberts and Szwarc for the sodium salt of the monoradical ion of tetraphenylethylene in THF.[10]

It is tempting to suggest that the effect of steric hindrance in the contact ion pair is also largely responsible for the increased solvent-separated ion-pair formation in the 9-(2-hexyl)fluorenyllithium compared to the unsubstituted salt (see Tables I and II). There are other observations, however, which indicate that the difference in interionic distance between the contact ion pairs of the substituted and unsubstituted salt cannot be great. A large interionic distance in the contact ion pair of the 9-substituted fluorenyllithium would lead to a considerably smaller difference in the transition

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(6) S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *J. Am. Chem. Soc.*, 76, 2597 (1954); S. Winstein and G. C. Robinson, *ibid.*, 80, 169 (1958), and related papers by Winstein, *et al.*

(7) D. J. Cram, J. L. Mateos, F. Hanck, A. Langemann, K. R. Kopecky, W. D. Nielson, and J. Allinger, *ibid.*, **81**, 5774 (1959), and related papers by Cram, *et al.*

(8) H. Sadek and R. M. Fuoss, *ibid.*, **76**, 5905 (1954).

(9) E. Grunwald, *Anal. Chem.*, **26**, 1696 (1954).

(10) R. C. Roberts and M. Szwarc, *J. Am. Chem. Soc.*, 87, 5542 (1965).

energies of the absorption maxima of the two kinds of ion pairs, since this difference reflects the increase in interionic distance when changing from a contact to a solvent-separated ion pair. However, as shown above, the difference is the same as for fluorenyllithium, *i.e.*, 6.2 kcal/mol. Secondly, preliminary results show that in tetrahydrofuran the sodium salts of various 9-alkyl-substituted fluorenyl salts contain only slightly higher fractions of solvent-separated ion pairs than fluorenylsodium itself. Also, the exothermicity of solvent-separated ion-pair formation is 1 to 2 kcal/mol lower than for the unsubstituted sodium salt. This appears in sharp contrast with the results found for the lithium salts, where the exothermicities were found to be considerably higher for the substituted salts as compared to fluorenyllithium. We will discuss these results in more detail in a future publication dealing with the temperature dependence of the ion-pair equilibrium.

It should be stressed that the average interionic distance in both the solvent-separated ion pair and the contact ion pair may change with the nature of the solvating medium. In the fluorenyllithium solvent-separated ion pair the interionic distance was previously[1] calculated from conductance data to be 6.3 Å, which was interpreted as evidence for an ion-pair structure in which a THF molecule is situated between the fluorenyl ring and the cation. However, these calculations were based on the sphere in continuum model and could lead to ambiguous results when specific solvent–solute interactions are strong, even when these calculations refer to solvent-separated ion pairs. The two absorption bands in the optical spectrum of the carbanion only infer that in the solvent-separated ion pair the Li^+ ion has assumed a new average position in which the coordinated solvent molecules effectively shield the cation and reduce its positive field effect on the carbanion. In some cases this may mean that the solvating entity is situated right between the two ions, *e.g.*, in a molecule like tri-2-propanol amine borate or possibly dimethyl sulfoxide where both cation and carbanion may coordinate with different atoms of the molecule. In ethereal solvents only the cation is solvated, and depending on the geometry of the solvent molecule one can visualize different structures for the solvent-separated ion pair in which the interionic distance is less than calculated on the assumption of a solvent molecule squarely between the two ions. In the case of fluorenyllithium in THF the Li^+ ion could still occupy a position rather close to the fluorenyl ring since it may be expected to interact appreciably with the strongly polarizable π cloud.[11]

The interionic distance of the contact ion pair is also expected to be solvent dependent. As pointed out earlier, external solvation of the cation in organoalkali compounds is well known, and has been observed in solvent mixtures of hydrocarbons with ethereal solvents, amines, and other solvating agents.[12] Often the effect amounts to an increase in the ionic character of the organoalkali compound, *e.g.*, in complexes like butyllithium–tetramethylethylenediamine.[13] This is usually accompanied by a breakdown of rather unreactive aggregates, and both effects strongly increase the reactivity of these compounds. In the more resonance-stabilized carbanions like fluorenyllithium, the species are presumed to be ionic even in hydrocarbon solvents (the optical spectrum of contact ion pairs is essentially independent of solvent). However, external solvation will tend to disperse the cationic charge and weaken the Coulombic interaction, thereby increasing the average interionic distance in the contact ion pair, which in turn may affect its reactivity and other properties. It also explains the bathochromic shift of the contact ion pair peak in more polar solvents or solvent mixtures containing increasing quantities of powerful solvating agents like dimethyl sulfoxide. The effect of external solvation was also clearly observed in studies carried out recently by Slates and Szwarc[14] who found that the formation of the sodium biphenyl radical ion from sodium and biphenyl in tetrahydropyran was favored by addition of small quantities of glyme-type solvents, *e.g.*, diethylene glycol dimethyl ether. The shift in the equilibrium $Na + B \rightleftharpoons Na^+B^-$ to the radical ion was shown to be due to formation of both glymated contact and solvent-separated ion pairs.

Chang, Slates, and Szwarc[15] have stressed that in many systems the concept of two ion pairs as depicted by Grunwald[9] may not suffice to describe the actual situation. Recognizing the fluctuating environment of the surrounding solvent molecules which will affect the vibrating motion of the ions in the ion pair, one could visualize a broad potential energy well in which the two ions may vibrate between the two interionic distances characterizing the two kinds of ion pairs. In such a case, the concept of two thermodynamically stable ion pairs is not valid. Since the potential energy curve will be temperature dependent, the ion pairs may be contact ion pairs at room temperature, then, due to more favorable solvation conditions, change gradually to a solvent-separated ion pair at low temperature. The physical properties, at least those depending on the interionic distance, will in such a case not result from a superposition of the properties of two chemically distinct species but will show a gradual change with temperature. Spectroscopically, one would observe a spectrum at room temperature consistent with a contact ion pair followed by a gradual shift to larger wavelength on lowering the temperature, until an absorption maximum is reached representing the solvent-separated ion pair. The sodium salt of 9,10-dihydroanthracene was reported by Nicholls and Szwarc to exhibit this behavior.[16]

The spectra of carbanions and of radical ions studied so far seem to indicate that in most cases two kinds of ion pairs can be realized if conditions are properly chosen. However, in many cases, broadness of the absorption bands may cause extensive peak overlap and prevents a clear observation of two separate absorption bands. In such a case a maximum in the half-width of the band on cooling may reveal the presence of two distinct species. This was also observed by Waack, *et al.*, in studies dealing with the temperature

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

(12) D. J. Worsfold and S. Bywater, *Can. J. Chem.*, 40, 1564 (1962); R. Waack, M. A. Doran, and P. E. Stevenson, *J. Am. Chem. Soc.*, **88**, 2109 (1966); C. G. Screttas and J. F. Eastham, *ibid.*, **87**, 3276 (1965).

(13) A. W. Langer, *Trans. N. Y. Acad. Sci., Ser. II*, 27, 741 (1965).

(14) R. V. Slates and M. Szwarc, *J. Am. Chem. Soc.*, **89**, 6043 (1967).

(15) P. Chang, R. V. Slates, and M. Szwarc, *J. Phys. Chem.*, **70**, 3180 (1966).

(16) D. Nicholls and M. Szwarc, *Proc. Roy. Soc.* (London), **A301**, 223 (1967).

dependence of the spectrum of 1,1-diphenyl-*n*-hexyllithium in THF.[5] Even the absence of any broadening should not necessarily be interpreted as indicative for the absence of two kinds of ion pairs. Spectral bands usually narrow at lower temperatures, and particularly those of radical ions and carbanions in polar solvents were shown to narrow considerably, leading to an increase in the linear extinction coefficient. Hence, when two kinds of ion pairs are present, the expected broadening due to peak overlap could be obscured by a gradual narrowing of the individual absorption bands. In such a case, addition of a more polar solvent at constant temperature may be a better way to establish whether for a particular carbanion two thermodynamically stable ion pairs can exist. Careful analysis of the entire absorption spectrum, however, is required. For example, the spectra of the sodium naphthalene and sodium biphenyl radical ion in THF show some rather wide absorption bands which merely appear to shift at lower temperatures. However, the sharper bands (323 and 400 mμ for the respective radical ions) reveal a definite split at lower temperatures in two distinct absorption bands, although the two maxima differ by only 3 and 10 mμ, respectively.[1,14]

Effect of Solvent Structure

For a series of unsubstituted cyclic ethers, the extent of solvent-separated ion-pair formation (see Table I) appears to follow closely the change in the basicity of the O atom. The basicity of some of these ethers has been measured by various methods. Data based on the frequency shift of the O–D band in the infrared spectrum of methanol-*d* solutions[17] and those based on measurements of heat of mixing with chloroform[17,18] indicate that the basicity of saturated cyclic ethers changes with ring size in the order $4 > 5 > 6 > 3$. Similar results were reported by Tamres, *et al.*,[19] in studies of iodine complexes of cyclic ethers and by Barakat, *et al.*,[20] who measured the intensity of unbonded N–H stretching vibration of HCNS in cyclic ethers. Nmr data confirm this order of basicity for both cyclic ethers and for cycloimines.[21]

In our work we find a similar order for the saturated cyclic ethers with respect to the ease of solvent-separated ion-pair formation, the seven-membered ring compound, hexamethylene oxide, being the exception. This compound was found by Arnett and Wu[17b] to be slightly more basic than THF. Although no basicity values have been reported for unsaturated cyclic ethers, their behavior appears to reflect the expected basicity of the respective oxygen atoms. The basicity of 3,4-dihydropyran should be considerably less than that of the tetrahydropyran due to delocalization of the lone electron pair, and furan should have an even lower basicity. On the other hand, delocalization of the oxygen lone electron pair in 2,5-dihydrofuran will be very small, and its solvating ability is indeed not much less than that for tetrahydrofuran.

Presence of a second oxygen atom in the ring lowers the basicity of the coordinating oxygen atom. For example, dioxane has a considerably lower association constant with iodine than THP[19] and the same is found for complexes with thiocyanic acid.[20] The donor ability decreases even more when the distance between the oxygen atoms is decreased, *e.g.*, 1,3-dioxane was found to have a lower basicity than 1,4-dioxane.[22] Hence, it is not surprising to find that dioxolane, in spite of its five-membered ring, is a less effective solvent-separating agent than tetrahydropyran. In addition to a lower basicity, solvent-separated ion-pair formation in solvents like dioxane and dioxolane may also be hindered due to the expected repulsion between the π cloud of the fluorenyl ring and the noncoordinating oxygen atoms of the solvent molecules comprising the solvation shell or simply due to repulsion between these oxygen atoms themselves.

It should be emphasized again that formation of solvent-separated ion pairs also depends on the stability of the contact ion pair and while in a solvent like dioxolane the fluorenyllithium salt is essentially of the contact ion pair type at room temperature, the 9-(2-hexyl)-fluorenyllithium is predominantly a solvent-separated ion pair at 25°. This point has already been discussed.

Although basicity plays an important role in solvation of alkali ions by ethereal solvents, steric factors many times are even more dominant. Even in the unsubstituted cyclic ether series one does not expect close agreement between the extent of solvent-separated ion-pair formation and the change in basicity. In basicity studies, steric hindrance is often a minor factor since the measurements usually relate to the interaction of a proton (or a molecule like I_2) with only one ether molecule. In the solvent-separated ion pair the alkali ion is coordinated with the O atoms of a number of solvent molecules, and the over-all spacial arrangement of the solvent molecules in the solvation shell becomes critical. Bulky substituents close to the coordination sites will undoubtedly increase the average distance between the alkali ion and the coordination site and may also decrease the number of solvating molecules in the solvation shell. These effects may already play a role in the unsubstituted cyclic ethers, where the increase in ring size not only decreases the basicity of the molecule but also increases its volume. This could account for the lower solvating power of hexamethylene oxide compared to THF.

The data of Table II show more clearly the effect of steric hindrance. In spite of its higher basicity,[19] 2-MeTHF is a much poorer solvent for alkali ion solvation than THF, and 2,5-dimethyl-THF and 2,5-dimethoxy-THF are even worse. For 3-MeTHF the difference with THF is much less since the substituent is situated more to the periphery of the solvation shell. The 2-methoxymethyl-THF is an excellent solvating agent. Here of course the steric hindrance is nullified by the possibility of chelation, and it is well known that for linear ethers the chelation is most effective when the oxygen atoms are separated by two carbon atoms, at least for Li^+ and Na^+ ions.[23-25a] Experiments in

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[23] J. L. Down, J. Lewis, B. Moore, and G. Wilkinson, *J. Chem. Soc.*, 3767 (1959).

[24] A. I. Shatenstein, E. S. Petrov, M. I. Belousova, K. G. Yanova,

mixtures of dioxane and 2-methoxymethyl-THF show that this compound is even more effective than 1,2-dimethoxyethane, probably due to the higher basicity of one of its oxygen atoms and the smaller number of rotational conformations in this molecule as compared to DME.

The effect of chelation is even more pronounced in compounds like *o*-dimethoxybenzene, where, in spite of the expected low basicity, only solvent-separated ion pairs are found at room temperature for fluorenyllithium. Studies in mixtures with dioxane show that this solvent is about as effective as DME. Since the O atoms are fixed in the veratrole, the decrease in rotational entropy of this molecule on solvation with the Li^+ is much less than in DME where chelation is only favored for a particular conformation which also happens to be thermodynamically the least favorable. No chelation can be expected in *m*-dimethoxybenzene, and the low basicity of the O atoms strongly favors contact ion pairs. Other cases of chelating reagents favoring solvent-separated ion-pair formation, *e.g.*, the polyglycol dimethyl ethers, have recently been reported.[25b]

Another example of steric hindrance is found in the behavior of 3,3-dimethyloxetane. Although we do not have comparable data for fluorenyllithium in oxetane, the fact that even the sodium salt is completely solvent separated in this solvent indicates that the solvating ability of the substituted oxetane must be considerably less than that of oxetane itself. While the methyl groups are not attached to the α-carbon atoms, they considerably increase the total volume of the parent compound. If four oxygen atoms are assumed to be coordinated with the lithium ion,[25b] then their average distance to the Li^+ ion will be considerably larger when dimethyloxetane is the solvent. One also expects that steric hindrance will have a more serious effect in the coordination of the small Li^+ ion as compared to the larger Na^+ ions, where the crowding of solvent molecules in the solvation shell may be less. This may be the reason why in dimethyloxetane the fractions of solvent-separated ion pairs are not very different for the two fluorenyl salts, *i.e.*, 1.2 for F^-,Li^+ and 0.6 for F^-,Na^+. Usually the differences are much larger, *e.g.*, in THF 4.6 for F^-,Li^+ and 0.05 for F^-,Na^+.

One may argue that in comparing the various solvents the changing dielectric constant should also be taken into account since it might have an effect on the energy needed to partially separate the ions. The role of dielectric constant is not easy to assess, but its effect is probably not large. The effective dielectric constant in the vicinity of the ion pair is considerably less than the macroscopic dielectric constant, due to dielectric saturation, and in calculating the work required to separate the two ions from a contact to a solvent-separated ion pair a value for the dielectric constant must be used which is considerably less than the bulk dielectric constant.[8]

We have carried out a series of measurements in dioxane (ϵ 2.2), THP (ϵ 5.6), and THF (ϵ 7.4) in which the fluorenylsodium contact ion pair was changed to a "solvent"-separated ion pair by addition of small quantities of strongly solvating agents like tri-2-propanol amine borate or polyglycol dimethyl ethers.[3,25b] The results show that the equilibrium constant for solvent-separated ion-pair formation is only slightly increased when changing from dioxane to THP to THF.

The case of hexamethylphosphoramide resembles the earlier reported behavior of dimethyl sulfoxide.[1] Both are excellent solvating agents for alkali ions, and as indicated by the plot shown in Figure 3, only one HMPA molecule is coordinated with the alkali ion in the solvent-separated ion pair,[26] at least at low HMPA concentration. This ion pair, F^-,HMPA,Li^+ is clearly distinguished from the externally solvated F^-,Li^+,HMPA which may be present at higher HMPA concentrations as pointed out earlier. At the higher HMPA concentrations the separated ion pairs may be of the type F^-,HMPA,Li^+,HMPA, but their spectrum is apparently the same as for the F^-,HMPA,Li^+ ion pair and the additional correction needed to arrive at the free [HMPA] concentration does not affect the slope of Figure 3 to any great extent.

Some of the conclusions regarding alkali ion solvation arrived at in this work have also been obtained by using other methods. Down, *et al.*, studied solubility of alkali metals in a variety of ethereal solvents[23] by measuring the absorption spectra of the resulting blue solutions. No quantitative data were reported and the less basic ethers like THP do not give any color at all. Extensive measurements on the formation of radical anions (*e.g.*, lithium and sodium biphenyl and sodium naphthalene) in a series of ethers were reported by Shatenstein, *et al.*[24] In each case the hydrocarbon was treated with the metal in the appropriate ether, and the concentration of radical anions formed was determined spectrophotometrically. For the lithium salt the order of decreasing radical ion formation was found to be DME $\approx$ THF > THP > dioxolane > dioxane, similar to our results, although DME is clearly a better solvating agent than THF.[1] For the sodium salt the order is DME > THF > dioxolane > 2-MeTHF $\approx$ THP > dioxane, the main difference being the higher solvating power observed for dioxolane. A similar order for Na^+ ions (dioxolane not included) was found by Garst, *et al.*,[27] who measured spectral shifts in ethereal solutions of disodium benzophenone and sodium phenoxide. Our data, of course, refer to Li^+ ions, and one might expect a slightly different order for Na^+ since steric factors may affect the solvation in a different way. Also, the data of Shatenstein refer to 0° which may affect the order somewhat since the ΔH values vary substantially with solvent structure. Moreover, the equilibrium constant of radical ion formation is determined by the total free energy of solvation of the alkali ion since one measures both the contact and solvent-separated ion pairs. In our case, the difference in solvation state between solvent-separated and contact ion pair is the important factor. In the solvation process steric factors may affect the solvation of the two

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(26) We have continued to use the expression "solvent-separated ion pair" even in mixtures of solvents where the solvent-separating agent may be the component present in only small quantities, while the actual solvent, *e.g.*, dioxane, only plays a minor role. The term agent-separated[18] or simply separated ion pair may in this case be less ambiguous.

(27) J. F. Garst, R. A. Klein, D. Walmsley, and E. R. Zabolotny, *J. Am. Chem. Soc.*, **87**, 4080 (1965).

ion pairs in a different way. Therefore, one may anticipate that different approaches of measuring solvating power of ethers with respect to alkali ions will in some instances lead to different results.

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Anion Radicals in Liquid Ammonia

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Abstract: Anion radicals have been prepared by alkali metal reduction of various organic substrates in the relatively protic solvent, ammonia. The coupling constants of the anion radicals in ammonia are compared with their values in other solvents. The effects of ion pairing on the esr spectral parameters of the nitrobenzene anion radical **1** are minor.

Liquid ammonia alkali metal (LAAM) solutions have intrigued chemists for many years.[1] The physical properties of LAAM solutions have been studied by many physical methods, including electron spin resonance.[2] More recently, anion radicals have been electrolytically generated and observed by esr in liquid ammonia.[3] We report the formation of anion radicals by reduction of organic substrates with LAAM solutions, followed by their identification with esr. To our knowledge, this report represents the first time that anion radicals have been formed by alkali metal reduction and observed by esr in the relatively protic solvent ammonia.

Experimental Section

Since the esr sample tubes of these ammonia systems are at 11 atm at +30°, it is advised that the necessary safety precautions be considered.

Chemicals were obtained from the following sources: cyclooctatetraene (Chemical Procurement Laboratories), benzophenone (Matheson Coleman and Bell), and nitrobenzene, anthracene, and naphthalene from J. T. Baker. The solids were recrystallized to constant melting point. The liquids were degassed and distilled under high vacuum before use.

The spectra were recorded using the X band of a Varian V-4502-15 esr spectrometer with a 12-in. magnet. Temperature was controlled within ±1° by a Varian V-4557 variable-temperature controller. A copper-constantan thermocouple was used to calibrate the variable-temperature controller.

Coupling constants and line widths were taken directly from the calibrated chart paper.

Ammonia which was dried with potassium metal in bulb a (Figure 1) was distilled into the calibrated bulb b which contained a known amount of alkali metal. An aliquot of the solution in b was then poured into bulb c where it reacted with an equimolar quantity of the organic substrate in liquid ammonia at $-78°$. The blue color of the LAAM solution was quickly replaced by the color of the anion radical. Several samples having different concentrations of anion radicals were made by taking an aliquot of the anion radical solution into one of the calibrated side arms, d, then distilling liquid ammonia from bulb b into this side arm to the desired concentration and sealing it. Utilizing this procedure, a spectrum of the hydrocarbon anion radical having very narrow lines (40 mG) was obtained.

Results and Discussion

Previous attempts at generating anion radicals in LAAM may not have succeeded due to the fact that the anion radicals became diamagnetic upon addition of excess LAAM and/or some of the anion radicals were unstable at higher temperatures and were reduced by the solvent. Thus, we find that upon addition of more than 1 mol of LAAM/mol of substrate, the spectrum of the anion radical was replaced by the free electron line. Similarly, the napthalene and anthracene anion radicals were not thermally stable above 0°. However, the cyclooctatetraene, benzophenone, and nitrobenzene anion radicals were stable to at least +40°. A reduction of benzene to the anion radical could not be effected, and only the free electron line was observed.

Table I lists the coupling constants of representative anion radicals. The coupling constants of the hydrocarbon anion radicals in liquid ammonia vary no more than 5% from the values recorded in more aprotic solvents such as DME and THF.[4] However, the coupling constants of anion radicals with functional groups are very solvent dependent,[5] particularly if one is comparing data in protic and aprotic solvents. The a_N of the nitrobenzene anion radical **1** has frequently been used to monitor solvent effects.[5] Table II gives the coupling constants of anion radical **1** formed electrolytically or chemically in various solvents. Ion pairing modifies the properties of anion radical **1** in ether solvents,[5d] giving broad, overlapping lines and metal splitting in some instances.[5f] Nitrobenzene reduced by LAAM gives **1**, with a spectrum (Figure 2) similar

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