Organic and Biological Chemistry

Studies of Contact and Solvent-Separated Ion Pairs of Carbanions. I. Effect of Temperture, Counterion, and Solvent

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Abstract: Evidence has been presented for the existence of contact and solvent-separated ion pairs in solutions of carbanions and radical ions. The changes observed in the absorption spectra of 9-fluorenyl and substituted 9-fluorenyl salts as well as in other carbanions and radical ions on lowering the temperature have been interpreted in terms of the two kinds of ion pairs. The change in enthalpy on formation of the solvent-separated ion pair of fluorenylsodium in THF from its contact ion pair was found to be −7.6 kcal./mole, the change in entropy being −33 e.u. Bathochromic shifts have been observed for all carbanions and radical ions on increasing the radius of the cation in the contact ion pair. The fraction of solvent-separated ion pairs has been shown to decrease rapidly in the order Li > Na > K > Cs, and is a sensitive function of the solvating power of the medium. Complete solvent separation of Li and Na salts occurs on addition of small quantities of dimethyl sulfoxide or triisopropanolamine borate. It has been shown that only one DMSO molecule reacts with the contact ion pair (or solvated contact ion pair) to form the solvent-separated ion pair. Preliminary studies of reactivities of the two kinds of ion pairs have indicated the solvent-separated ion pair to be much more reactive than the contact ion pair. Spectral shifts observed previously by other investigators have been discussed and appear to be consistent with the concept of the two kinds of ion pairs. The effect of the two ion pairs on reaction rates (*e.g.*, activation energies in anionic homopolymerization) has also been discussed briefly.

The effect of solvents on the behavior of organometallic compounds recently has received considerable attention. Solvent-induced shifts in absorption spectra have been observed for a number of ketyls,[2-4] and similar effects have been found for carbanionic species[5,6] and alkali salts of phenols and enols.[7] The position of the absorption maxima appears to depend on the type of cation and is temperature sensitive. Temperature-dependent shifts also have been observed for radical ions of many aromatic hydrocarbons[8,9] and have been attributed to free ion formation on lowering the temperature.

Most of these studies have been carried out in ethereal solvents. It is generally accepted that the capacity of these solvents to solvate anions is rather poor. Therefore, the reported solvent effects have, in most instances, been rationalized in terms of specific interactions between the solvent molecules and the cation (usually one of the alkali ions).[3,6,7] This specific interaction is thought to effectively reduce the influence of the cationic field on the transition energy of a $\pi \rightarrow \pi^*$ transition of the anion. It has been argued that an increasing solvent polarity would lead to greater dispersion of the cationic charge, and this in turn would have the same effect as increasing the radius of the cation.[2,3,10]

In a short communication[11] we have presented recently evidence for the existence of two kinds of ion pairs in ethereal solutions of carbanions and radical ions. The relative amounts of these two ion pairs, *viz.*, contact or intimate ion pairs and solvent-separated ion pairs, were found to be sensitive functions of the solvating power and temperature of the medium and of the type of carbanion or radical ion and its counterion. In this paper we present a full account of these investigations. They have been extended to include different carbanions and solvents, in particular mixtures of solvents (*e.g.*, dioxane–tetrahydrofuran, dioxane–dimethyl sulfoxide). The results seem to fully justify the concept of the two ion pairs, and in many instances lead to a more satisfactory explanation of previously observed phenomena in this field.

Experimental Section

All of the materials used in this investigation were commercially available. Fluorene, 1-methoxyfluorene, and the benzofluorenes were acquired from Aldrich Chemical Co. and purified by repeated recrystallization from absolute alcohol. The purity was checked by melting point and v.p.c. Tetrahydrofuran, 2-methyltetrahydrofuran, and 1,2-dimethoxyethane were refluxed over Na–K alloy and distilled onto fresh alloy. A small amount of benzophenone was added to form the benzophenone dianion. Dioxane was dried over CaH$_2$ and distilled onto Na–K alloy. A small amount of fluorenone was added to this solvent. Toluene, pyridine, and dimethyl sulfoxide were distilled under vacuum after being thoroughly dried over CaH$_2$. In many cases, the solvents used in the

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(1) To whom correspondence should be addressed.

(2) D. G. Powell and E. Warhurst, *Trans. Faraday Soc.*, **58**, 953 (1962).

(3) J. F. Garst, D. Walmsley, C. Hewitt, W. R. Richards, and E. R. Zabolotny, *J. Am. Chem. Soc.*, **86**, 412 (1964).

(4) N. Hirota and S. I. Weissman, *ibid.*, **86**, 2538 (1964).

(5) R. Waack and M. A. Doran, *J. Phys. Chem.*, **67**, 148 (1963).

(6) A. Streitwieser, Jr., and J. I. Brauman, *J. Am. Chem. Soc.*, **85**, 2633 (1963).

(7) H. E. Zaugg and A. D. Schaefer, *ibid.*, **87**, 1857 (1965).

(8) J. Dieleman, Thesis, Free University, Amsterdam, 1962; K. H. J. Buschow, Thesis, Free University, Amsterdam, 1963.

(9) (a) K. H. J. Buschow and G. J. Hoijtink, *J. Chem. Phys.*, **40**, 2501 (1964); G. J. Hoijtink, *Ind. Chim. Belge*, **12**, 1371 (1963); K. H. J. Buschow, J. Dieleman, and G. J. Hoijtink, *J. Chem. Phys.*, **42**, 1993 (1965); (b) N. H. Velthorst and G. J. Hoijtink, *J. Am. Chem. Soc.*, **87**, 4529 (1965).

(10) B. J. McClelland, *Trans. Faraday Soc.*, **57**, 1458, 2073 (1961).

(11) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **87**, 669 (1965).

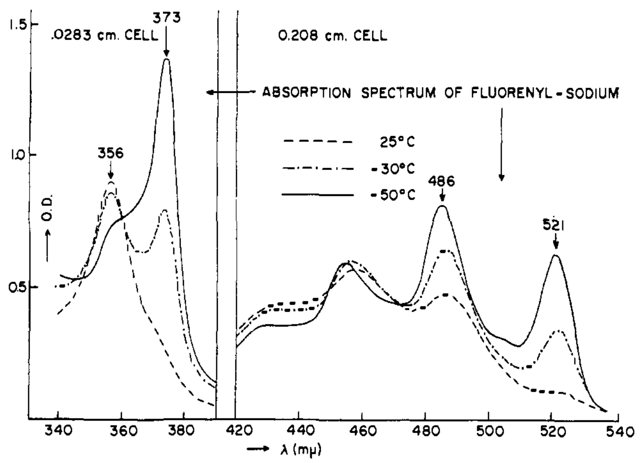

Figure 1. Absorption spectrum of fluorenylsodium in THF as a function of temperature.

actual experiments were distilled once more onto a fluorenyl salt, left to stand for a few hours, and then distilled under vacuum into ampoules, using an all-glass apparatus equipped with breakseals.

The fluorenyl salts (lithium, sodium, potassium, and cesium) were prepared from the corresponding polystyryl salts which were available in our laboratory. The reactions, carried out in THF under vacuum with a slight excess of fluorene or its derivative, were found to be instantaneous and quantitative. Alternatively, fluorenyllithium and -sodium were prepared by stirring a THF solution of the hydrocarbon on freshly cut lithium metal or a sodium mirror, respectively.[12] After a few hours, the orange-colored solutions were filtered through sintered glass and sealed off in ampoules. The salt solutions in THF showed absorption spectra independent of the method of preparation. They were found to be stable for prolonged periods of time when kept in a freezer. The tetrabutylammonium salt was obtained by adding tetrabutylammonium tetraphenylboron to a THF solution of fluorenylcesium. The sparsely soluble cesium tetraphenylboron precipitated out and was removed by filtration.

Carbanion solutions in other solvents usually were prepared from the corresponding THF solution by removing the THF under vacuum and distilling the appropriate solvent onto the dry salt. This procedure was repeated once to assure complete removal of THF.[13] In the experiments carried out with mixed solvents, solutions of the carbanion salt in the pure solvents were mixed together in known quantities. In the studies involving dioxane-DMSO mixtures, a solution of fluorenyllithium in a mixture of dioxane and DMSO was gradually added from a buret, provided with a Teflon stopcock, to a fluorenyl solution of the same concentration but in pure dioxane. After each addition of a known quantity of the dioxane-DMSO mixture, the spectrum of the new solution was taken.

Spectra were recorded by means of a Cary Model 14 spectrophotometer, using 0.2-cm. optical vacuum cells provided with a 0.18-cm. spacer. Concentrations could be varied by transferring part of the sample to an adjacent ampoule and distilling the solvent back by cooling the cell. In some runs alkali tetraphenylboron salts were added to the fluorenyl solutions. The purification of these salts has been described elsewhere.[14] A quartz dewar with optical windows was used for the low-temperature measurements. Precooled methanol was chosen as the cooling liquid. This liquid was stirred continuously, and its temperature was recorded by means of a copper-constantan thermocouple located a few millimeters from the cell. It was established that during the time of scanning, the temperature change amounted to less than 0.5°.

Extinction coefficients of the fluorenyl salts were determined by adding a THF solution of a polystyryl salt to a slight excess of dry and pure fluorene. Before and after addition, the spectrum of the solution was recorded. Since the molar extinction coefficients of the polystyryl salts at 340 mμ are known[15] and the reaction is quantitative without any evidence of reaction with impurities, the molar extinction coefficients of the fluorenyl salts could be calculated. Reaction with methyl iodide and titration of the resulting iodide with silver nitrate also has been used.[15] The data obtained by both methods are in agreement within 5%. The following λ_{max} (ϵ) were found: fluorenyllithium 373 (9600), fluorenylsodium 356 (10,800), and fluorenylcesium 364 (12,000).

Results and Discussion

The Behavior of Fluorenyl Salts. The Effect of Temperature. Changes in the absorption spectra of the fluorenyl salts were first observed on cooling a THF solution of this carbanion.[11] The spectrum of its sodium salt in THF at three different temperatures is depicted in Figure 1. At room temperature, the carbanion has a narrow absorption band at 356 mμ (ϵ_m 10,800), in addition to some weaker bands in the visible region (ϵ_m ~1000–1200). At −30°, a new peak is clearly visible at 373 mμ, and has fully developed at −50° at the expense of the 356-mμ band. Similar changes can be seen in the visible region although they are more complex due to extensive peak overlap. It was established, however, that the new band at 521 mμ belongs to the same species as the peak developing at 373 mμ.

The reversibility of the process and the existence of two separate bands indicate the presence of a new entity at low temperatures in equilibrium with that existing at room temperature. It was found that a 100-fold dilution did not alter the relative heights of the two bands (*i.e.*, those at 356 and 373 mμ). Only at very low carbanion concentration (below 10^{-5} mole/l.) were significant changes observed. The concentration independence of the peak height ratio excludes any explanation based on equilibria of the type

$$(F^-,M^+)_2 \rightleftarrows 2F^-,M^+ \tag{1}$$

$$F^-,M^+ \rightleftarrows F^- + M^+ \tag{2}$$

Equilibrium (eq. 2) also must be rejected on account of the absence of any common ion salt effect. Addition of sodium tetraphenylboron, which is reasonably well ionized in THF at 25°[14] did not change the peak height ratio. Moreover, conductance studies[16] showed only a few per cent of free ions present under the conditions of our experiments (concentrations were usually between 10^{-2} and 10^{-3} mole/l.). The latter two observations also exclude triple ion formation ($2F^-,M^+ \rightleftarrows F^-M^+F^- + M^+$) as the cause of the spectral shifts. All these equilibria may, of course, exist under the prevailing conditions. Dimerization of ion pairs has been shown to occur for ketyls[4] and certain types of carbanions.[17] However, none of these equilibria apparently occur to such an extent as to be held accountable for the observed spectral changes.

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[12] G. W. H. Scherf and R. K. Brown, *Can. J. Chem.*, **38**, 2450 (1960).

[13] Complete removal of THF by this method appears to be difficult when hydrocarbon solvents are employed. A few molecules of THF seem to remain associated with the alkali fluorenyl ion pairs. In the case of dioxane or more polar solvents, complete removal of THF by this method appears to be assured, since no THF could be detected by v.p.c. when water was added to a fluorenyl solution in these solvents; see also J. A. Dixon, P. A. Gwinner, and D. C. Lini, *J. Am. Chem. Soc.*, **87**, 1379 (1965).

[14] D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 608 (1965).

[15] D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *ibid.*, **69**, 612 (1965).

[16] T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 318 (1966).

[17] D. J. Worsfold and S. Bywater, *Can. J. Chem.*, **38**, 1891 (1960); M. Morton, E. E. Bostick, R. A. Livigni, and L. J. Fetters, *J. Polymer Sci.*, **A1**, 1735 (1963).

The experimental evidence, therefore, strongly suggests the new entity at low temperatures to be a solvent-separated ion pair

$$F^-,Na^+ + n\text{THF} \rightleftarrows F^- \,||\, Na^+ \qquad (3)$$

Here, F^-,Na^+ and F^- Na^+ denote a contact and a solvent-separated ion pair, respectively, while n represents the number of solvent molecules involved in the equilibrium reaction. It is obvious that this equilibrium is not affected by dilution (solvent in large excess) or by addition of a common ion salt.

Equilibrium 3 is apparently strongly exothermic. In order to measure the thermodynamic quantities associated with this equilibrium, we measured carefully the absorption spectrum of fluorenylsodium in THF over the temperature range of +25 to −70°. If the solvent is in large excess, the ratio $[F^-||Na^+]/[F^-,Na^+]$, denoted by K_i, should be constant at a particular temperature. We determined the ratio of the optical densities at each temperature for the two ion pairs and assumed the extinction coefficients at room temperature to be the same.[18] Corrections were made for the known change of density with temperature and the mutual overlap of the two peaks. This latter operation was accomplished by determining the contribution of each band at the λ_{max} of the other band, utilizing the spectra of the two ion pairs in solvents where only one type of ion pair exists. The changes of these "pure" spectra with temperature were incorporated in the calculations.[19] The absorption band of the solvent-separated ion pair narrows on lowering the temperature to −70°, thereby increasing the linear extinction coefficient at 373 mμ by a factor of about 1.5. The band for the contact ion pair (*e.g.*, fluorenylcesium in THF) changes also the linear extinction coefficient (after correcting for density changes) being higher by 30%.

The results of the calculation are shown in Table I and the temperature dependence of K_i is illustrated in Figure 2. A straight line is obtained for the log K_i *vs.* $1/T$ plot, from which slope an enthalpy, $\Delta H_i°$, of −7.6 kcal./mole can be computed. Deviations from the straight line occur at low and high temperature, but these regions are the least accurate for the determination of K_i.

Table I. Temperature Dependence of the Equilibrium Constant K_i ($F^-,Na^+ + n\text{THF} \rightleftarrows F^-||Na^+$)[a]

Temp., °C.	K_i	Temp., °C.	K_i
24.2	0.064	−26.3	0.619
14.7	0.088	−29.1	0.741
1.8	0.129	−36.2	1.22
−14.6	0.313	−42.0	1.84
−17.8	0.380	−51.0	3.75
−21.8	0.468	−63.0	6.15

[a] $K_i = [F^-||Na^+]/[F^-, Na^+]$.

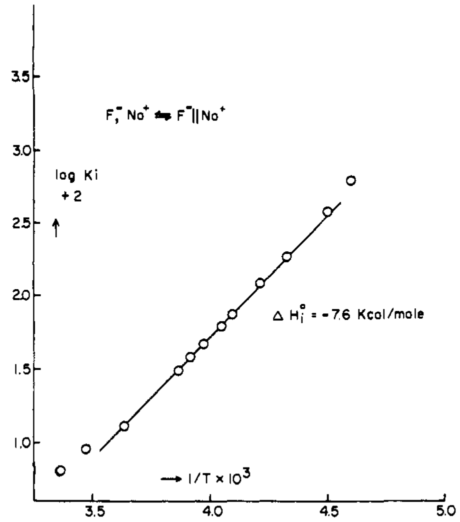

Figure 2. Temperature dependence of the equilibrium $F^-,Na^+ + n\text{THF} \rightleftarrows F^-||Na^+$ ($K_i = [F^-||Na^+]/[F^-,Na^+]$).

The strong exothermicity of the equilibrium is due to the large gain in solvation enthalpy on formation of the solvent-separated ion pair. The increase of $-\Delta H_i°$ at low temperature, as suggested by the deviation from the straight line (Figure 2) may be genuine, since one may expect the average number of solvent molecules associated with the Na^+ ion to increase at low temperature. The immobilization of solvent molecules on formation of the solvation shell around the sodium ion leads to a large entropy change of about −33 e.u.[16]

For F^-,Li^+, a value for $\Delta H_i°$ of −7.0 kcal./mole was found, but its determination is less accurate, since at 25°, K_i is already >3.0.

Effect of Counterion. Bathochromic shifts in absorption maxima have been shown to occur for a variety of anionic species on increasing the radius of the cation.[6–9,20] The same phenomenon is also observed for the fluorenyl carbanion. Table II lists the position of the absorption maximum for a number of fluorenyl salts. The maxima refer to those for the contact ion pairs, and it is clear that a bathochromic shift occurs as the cation radius increases.

Table II. Dependence of λ_{max} on the Radius of the Cation for 9-Fluorenyl Salts in THF at 25°

Cation	r_c, Å.	λ_{max}, mμ
Li^+	0.60	349
Na^+	0.96	356
K^+	1.33	362
Cs^+	1.66	364
N^+Bu_4	3.5	368
$||M^+$	~4.5	373
Free ion	∞	374

The cause of this shift has been explained[9,20] as a perturbation of the molecular energy levels by the

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[18] The extinction coefficients of the two ion pairs at their respective absorption maxima were found to be very nearly the same at room temperature. This was established by determining their values in two different solvents in which only one of the ion pairs is stable. Usually ϵ_m of the solvent separated ion pair is slightly higher. This will affect somewhat the absolute values found for K_i but not the temperature dependence of log K_i.

[19] As the "pure" contact ion pair, fluorenylcesium in THF was selected, while fluorenyllithium in dimethoxyethane turned out to be a solvent-separated ion pair over the whole temperature range. The shape of the spectrum of the pure ion pairs appears to be affected very little by the counterion or the solvent. Therefore, the narrowing of the spectral bands of these two salts with temperature has been applied to the two ion pairs of fluorenylsodium in THF.

[20] H. V. Carter, B. J. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, **56**, 455 (1960).

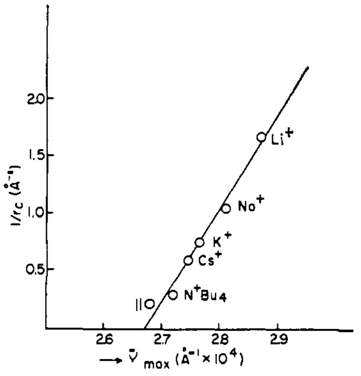

Figure 3. Correlation between wave number and the inverse of the cationic radii for contact ion pairs of fluorenyl salts in THF at 25°.

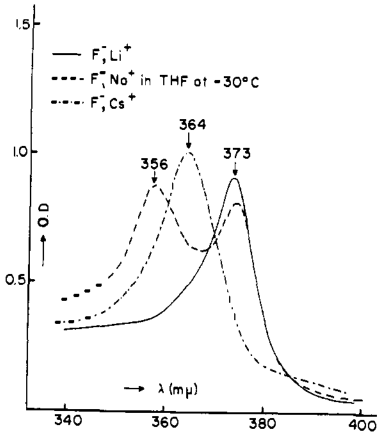

Figure 4. Absorption spectrum of fluorenyl salts in THF at −30° as a function of counterion.

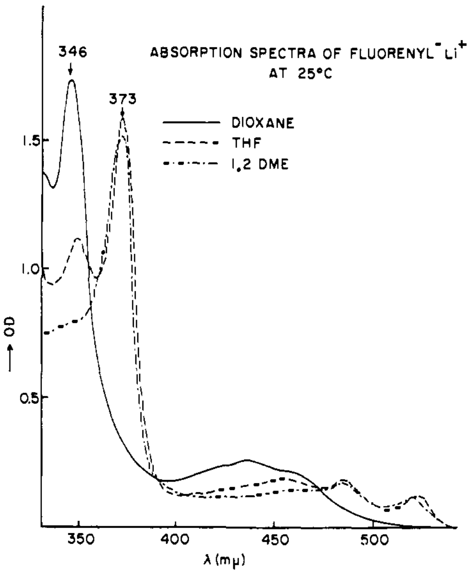

Figure 5. Fluorenyllithium spectrum in dioxane, THF, and DME at 25°.

positive field of the cation. In the ground state the cation is located so as to form the smallest dipole. On excitation, the dipole increases, *i.e.*, the negative charge moves away from its original position in the ground state while the position of the cation is not affected (Franck-Condon principle). Hence, an increase in cation radius destabilizes the ground state more than the excited state, leading to the observed bathochromic shift. Carter, *et al.*,[20] have pointed out that the perturbation of the energy levels should be roughly proportional to the reciprocal of the appropriate interionic separation. In our case, a reasonably linear relationship is observed (Figure 3) between the inverse of the cationic radius r_c and the wave number ν_m of the transition, similar to that found by Zaugg and Schaefer for the anions of phenols and enols.[7] For the radius of the solvated sodium ion, a value of 4.5 Å. was used. Actually, the presence of a solvent molecule between anion and cation appears to reduce the effect of the cationic field on the carbanion even more than would be the case for a cation of radius 4.5 Å., and this seems plausible.

The intercept $\tilde{\nu}_m{}^\circ$ on extrapolation to $1/r_c \rightarrow 0$ represents the wave number of the solvated free ion, and leads to a λ_{max} of 374 mμ for the free fluorenyl carbanion in THF. This is confirmed from spectra obtained at very low dilution ($<10^{-5}$ mole/l.). Conductivity data show that under these conditions a substantial fraction of the ion pairs is present as free ions.[16] This causes the peak height ratio of the respective absorption maxima of the two ion pairs to change, but no difference could be detected in the position of the absorption maxima of the solvent-separated ion pair and the free ion.

The difference in transition energy between the contact and the solvent-separated ion pair maxima for F$^-$,Na$^+$ (*i.e.*, the 356- and 373-mμ peak) amounts to 4.0 kcal./mole. Exactly the same difference is found in the visible region between the 486- and 521-mμ peaks. In general, the cationic effect on different $\pi \rightarrow \pi^*$ transitions will not be the same. Depending on the polarization direction of the transitions with respect to the line connecting the centers of the opposing ions in the ion pair, the cationic field will usually affect the various transitions to different degrees. Cases are known in which one electronic transition in the same organometallic compound is cation dependent, while another is not.[21]

The type of counterion strongly affects the fraction of solvent-separated ion pairs formed under otherwise identical conditions. This is clearly demonstrated by the spectra shown in Figure 4. At −30°, the fraction of solvent-separated ion pairs in THF is essentially 1.0 for fluorenyllithium, about 0.5 for the sodium salt, and no evidence for solvent separation in the cesium ion pair can be seen. This behavior illustrates the difference in specific interaction energy between the THF molecules and the respective cations. The poorly solvated Cs$^+$ does not even show any solvent separation in THF at −70°. At this temperature, the Na and Li salts are completely solvent separated. At room temperature, the fraction of solvent separated ion pairs for the Li salt is about 0.75, for F$^-$,Na$^+$ only 0.05. The potassium salt still shows very little solvent separation at −70°. The tetrabutylammonium ion essentially is not solvated, and its fluorenyl salt therefore behaves similar as the cesium salt.

Effect of Solvents. The formation of solvent separated ion pairs is greatly facilitated by changing to more polar solvents. This point is illustrated in Figure

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(21) N. S. Hush and J. R. Rowlands, *Mol. Phys.*, 6, 201 (1963).

5. In dioxane at room temperature, the spectrum of F^-,Li^+ shows only contact ion pairs. In THF the fraction of $F^-||Li^+$ is already 0.75, while in 1,2-dimethoxyethane all ion pairs are solvent separated.

Table III summarizes the spectral data found for different fluorenyl salts in various solvents. The fraction of solvent separated ion pairs was calculated utilizing the known shape of the "pure" ion pairs, assuming that the change in solvent affects their shape only very little.[19]

Table III. Absorption Maximum of Contact and Solvent-Separated Ion Pairs of the 9-Fluorenyl Carbanion in Various Solvents

Counterion	Solvent	D (25°)	λ_{max}, mμ		Fraction of $F^-||M^+$ at 25°
			F^-, M^+	$F^-||M^+$	
Li	Dioxane	2.20	346	...	0.0
Na	Dioxane		353	...	0.0
Li	Toluene	2.38	348	...	0.0
Li	MeTHF	6.29	347	373	0.25
Na	MeTHF		355	373 (−80°)	0.0
Li	THF	7.39	349	373	0.80
Na	THF		356	373 (−50°)	0.05
K	THF		362	...	0.0
Cs	THF		364	...	0.0
NBu_4	THF		368	...	0.0
Li	DME	7.15	...	373	1.00
Na	DME		358 (50°)	373	0.95
K	DME		362		~0.10
Cs	DME		364	...	0.0
Li	Pyridine	12.2	...	373	1.0
Na	Pyridine		...	373	1.0
Li	DMSO	45	...	373	1.0
Na	DMSO		...	373	1.0

The following facts emerge from an inspection of this table.

(a) Bathochromic shifts for contact ion pairs on increasing the cationic radius are observed in all solvents. Moreover, as far as has been checked, the lithium salt always yields the highest fraction of solvent-separated ion pairs, followed by sodium, potassium, and cesium, in this order. Both these points have been discussed before.

(b) The λ_{max} of the solvent-separated ion pair appears not to be influenced by the polarity of the solvent, while that of the contact ion pair is affected only slightly. The significance of these observations will be discussed later.

(c) In toluene[22] and dioxane, only contact ion pairs can be detected. In this respect, both solvents appear to be poor solvating agents for alkali cations. This conclusion appears to be surprising for dioxane. In mixtures with water it is known to solvate small alkali cations better than water.[23] However, the latter observation was made under conditions of free alkali ions, and it was argued that the strong electric field of the cation may displace the chair–boat equilibrium for dioxane from its thermodynamically stable chair form to the boat conformation.[24] This would bring both oxygen atoms simultaneously into a favorable position for cation solvation. Apparently, the reduced positive field in the contact ion pair cannot accomplish this change. The ion pair of course may still be peripherally solvated by the dioxane, but a stronger interacting solvating agent is needed to bring about solvent separation.

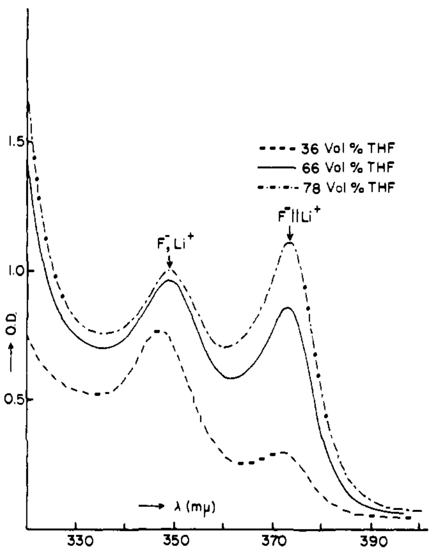

Figure 6. Spectrum of fluorenyllithium in mixtures of dioxane and THF.

Tetrahydrofuran, and its 2-methyl derivative, cause solvent separation of the ion pair, the latter to a lesser extent, presumably because of steric crowding around the ether oxygen. Dimethoxyethane, because of the possibility of bidentate coordination, is a powerful solvating agent for alkali ions, and this is reflected in the high fraction of solvent-separated ion pairs for the sodium salt in this solvent. The cesium salt is again unaffected, although its spectrum in DME at −70° indicates the presence of a sizable fraction of solvent-separated ion pairs.

In pyridine, no contact ion pairs could be detected for both the lithium and sodium salt. Although λ_{max} of the solvent-separated ion pair is again at 373 mμ, the band appears to be definitely broader. The spectrum in dimethyl sulfoxide, an extremely powerful solvating agent, shows only solvent-separated ion pairs. In spite of its high dielectric constant, the salts appear to be only moderately dissociated at 10^{-3} mole/l. However, the 373-mμ peak is gradually replaced by a peak at 364 mμ upon further dilution. The new peak apparently is that of the free ion, although the reason for the blue shift is not immediately apparent.

Mixtures of Solvents. The ratio of solvent-separated ion pairs to contact ion pairs in mixtures of solvents containing a polar and a nonpolar component is a sensitive function of the composition of the medium. An example of such a system is illustrated in Figure 6. The fraction of $F^-||Li^+$ (373-mμ peak) increases in a dioxane–THF mixture as the THF con-

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[22] Our method of preparing the fluorenyl salt in toluene from a THF solution of the salt makes it likely that the contact ion pairs in this solvent are associated with one or two THF molecules.[13] In the absence of any THF, one may expect dimerization of the lithium ion pairs, as was found to be the case for lithium polystyryl in benzene[17] and probably also for 1,1-diphenylhexyllithium in hydrocarbon solvents: R. Waack, private communication. The dimerization may lead to a further shift to the blue, and preliminary data, obtained in pure toluene, seem to confirm this.

[23] E. Grunwald, G. Baughman, and G. Kohnstam, *J. Am. Chem. Soc.*, **82**, 5801 (1960).

[24] J. B. Hyne, *ibid.*, **85**, 304 (1963).

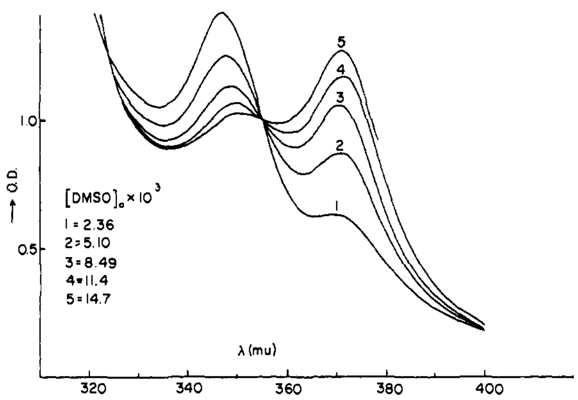

Figure 7. Spectrum of fluorenyllithium in dioxane on addition of small quantities of dimethyl sulfoxide.

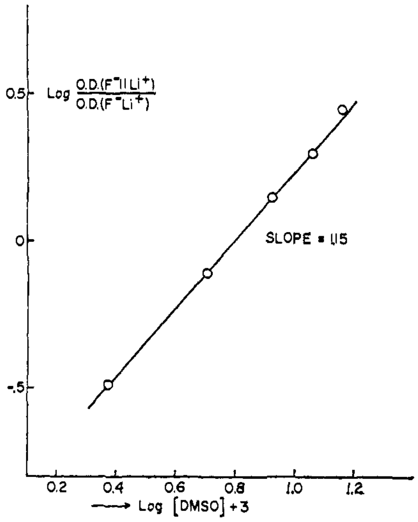

Figure 8. Effect of DMSO concentration on the fraction of solvent-separated ion pairs for $\mathrm{F^-,Li^+}$ in dioxane-DMSO mixtures at 25°.

centration is increased (the concentration of the salt was not kept constant in these experiments). A more pronounced change is achieved by using a component of stronger solvating power. For example, much smaller quantities of 1,2-dimethoxyethane as compared to THF are needed to obtain the same fraction of $\mathrm{F^-||Li^+}$. A dramatic change is observed when dimethyl sulfoxide is added (Figure 7). Only minute quantities of this powerful solvating agent are necessary to convert all contact ion pairs $\mathrm{F^-,Li^+}$ into $\mathrm{F^-||Li^+}$. The appearance of an isosbestic point is again evidence that one is dealing with an equilibrium between two species. The macroscopic properties of the dioxane-DMSO mixtures change only very little, in contrast to the dioxane-THF mixtures. For example, it was established that the presence of the small quantities of DMSO does not induce any conductance in the carbanion solution. The dielectric constant of the mixture is essentially that of dioxane, in which no conductance was observed.

Let us assume that n molecules of DMSO react with one $\mathrm{F^-,Li^+}$ molecule to form a solvent-separated ion pair containing the n DMSO molecules

$$\mathrm{F^-,Li^+} + n\mathrm{DMSO} \rightleftarrows \mathrm{F^-\ ||\ Li^+}\ (K_{\mathrm{eq}}) \tag{4}$$

This leads to the relationship

$$\log[\mathrm{F^-||Li^+}]/[\mathrm{F^-,Li^+}] = n \log[\mathrm{DMSO}] + \log K_{\mathrm{eq}} \tag{5}$$

A plot of log $[\mathrm{F^-||Li^+}]/[\mathrm{F^-,Li^+}]$ *vs.* log [DMSO] should then yield a straight line with slope equal n. Instead of the ratio of the concentrations, one may also utilize the ratios of the optical densities of the two species at their absorption maximum, making appropriate corrections for overlap of the bands. It is assumed in the calculations that the small quantities of DMSO do not alter the shape of the bands of the two ion pairs, and the appearance of an isosbestic point seems to support this. The results are shown in Figure 8. The value of the slope, *i.e.*, 1.15, indicates that probably not more than one DMSO molecule is inserted between the two ions. Therefore, the concentration of DMSO in eq. 1 was corrected assuming that one DMSO molecule becomes bound in the solvent-separated ion pair.

The value of 1.15 indicates that the mechanism is probably more complicated. It is known that polystyryl lithium in benzene forms mono- and dietherates when small quantities of THF are added to the solution.[25] It is therefore probable that a powerful solvating agent like DMSO will also specifically solvate the contact ion pairs, forming species like $\mathrm{F^-,Li^+,}$-DMSO. The spectrum of $\mathrm{F^-,Li^+}$ in the dioxane-DMSO mixtures does not show evidence for these two types of contact ion pairs. This is not surprising, since we have found little effect of solvent polarity on the absorption maxima of contact ion pairs.

If we assume all contact ion pairs to be present in the form $\mathrm{F^-,Li^+,DMSO}$, as suggested above, then the [DMSO] in eq. 5 can be corrected easily for the amount of DMSO associated with this contact ion pair. The corrected plot appears again to result in a reasonably good straight line, but its slope is much closer to one. The DMSO molecule present in the solvation shell of the contact ion pair (and likely to be associated with the Li ion) will certainly facilitate the process of insertion of another DMSO molecule to form a solvent-separated ion pair.

When small quantities of DMSO are added to a 10^{-2} M solution of $\mathrm{F^-,Na^+}$ in THF, the contact ion pair again is converted into a solvent-separated ion pair. It is interesting to observe that the DMSO addition causes the highly soluble $\mathrm{F^-,Na^+}$ to precipitate, and a red, crystalline solid can be isolated. It is possible that the solvent-separated ion pairs form insoluble polymeric aggregates of the type $(\mathrm{F^-,DMSO,Na^+,}$-$\mathrm{DMSO})_n$. The exposed positive dipole end of the DMSO molecule (the sulfur atom) may interact quite strongly with the fluorenyl carbanion and favor such a type of polymeric structures. Depending on the number of DMSO molecules coordinated with the Na ion, one could obtain reasonably stable two or three dimensional networks. It was observed that the precipitate dissolved again when larger quantities of DMSO were added, presumably because of the increasing dielectric constant. The detailed structure of the precipitate is currently under investigation. No precipitate was observed in the dioxane-DMSO mixtures of fluorenyl lithium, but the low solubility of $\mathrm{F^-,Li^+}$ in dioxane ($<10^{-3}$ M) makes it impossible to work in more concentrated solutions.

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(25) D. J. Worsfold and S. Bywater, *Can. J. Chem.*, 40, 1564 (1962).

Whether the contact ion pairs are associated with one DMSO molecule is still an open question, although the data appear to favor this proposition. Kinetic measurements, like those performed for polystyryl salts in benzene–THF mixtures,[25] may shed more light on this problem. The solvated and nonsolvated contact ion pairs would be expected to have different reactivities.

Other solvating agents are now being tested. For example, triisopropanolamine borate $N(CH_2 \cdot CH \cdot CH_3 \cdot O)_3B$, a crystalline compound with a highly polar transannular N:B bond,[26] was shown to form solvent-separated ion pairs very easily when added in small quantities to a THF solution of F^-,Na^+.

The experiments carried out with F^-,Li^+ in mixtures of dioxane and THF show that in this case a plot of log $OD(F^- \| Li^+)/OD(F^-,Li^+)$ *vs.* log [THF] yields a curve with a slope of 2 at low THF concentration and increasing to about 3 at higher THF concentrations. Since the macroscopic properties of the medium change considerably, the results are more difficult to interpret. Nevertheless, it appears that in this case formation of solvent-separated ion pairs occurs by reaction of at least two THF molecules. The average number of THF molecules coordinated with the cation in the solvation shell is of course not necessarily an integral number, but will depend on the concentration of THF. This coordination number may be as high as 4, or more, since the contact ion pairs may already be associated with one or two molecules of THF. It would be interesting in this respect to investigate more carefully the behavior of mixtures of dioxane and 1,2-dimethoxyethane, since one DME molecule can provide two coordination sites.[27] In this case, one may anticipate only one DME molecule reacting with the contact ion pair to form the solvent-separated ion pair.

Other Carbanions and Radical Ions. Formation of solvent-separated ion pairs was also observed for carbanions of substituted fluorenes, for the dianions of 1,1,4,4-tetraphenylbutane, and for radical ions. The data are summarized in Table IV.

The spectrum of 2,3-benzofluorenylsodium in THF at room temperature and at −50° is shown in Figure 9. Again two distinct absorption maxima are present, that of the contact ion pair at 407 mμ and the solvent-separated ion pair (which is the stable entity at low temperatures) at 431 mμ. The difference in transition energy is again 4.0 kcal./mole. Similar changes occur in the 550- to 700-mμ region, but here the changes are complicated by extensive peak overlap. The fraction of solvent-separated ion pairs at room temperature is higher for this compound than for fluorenylsodium (about 0.15 as compared to 0.05). The increased charge delocalization in the 2,3-benzofluorenyl carbanion facilitates the separation of the two ion pairs.

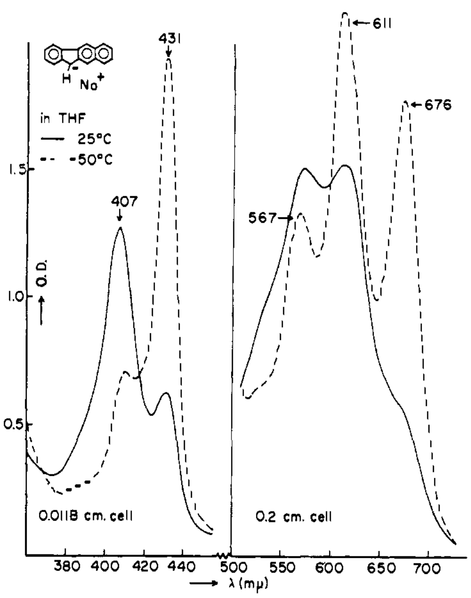

Figure 9. Spectrum of 2,3-benzofluorenylsodium in THF at 25 and −50°.

The behavior of 3,4-benzofluorenyl$^-$, Na$^+$ is more complex. The 324-mμ peak shifts to a peak at 340 mμ on cooling. The broadness of the band prevents observation of two separate peaks. The contact ion pair has two smaller peaks at 368 and 388 mμ. On cooling, a distinctly new peak develops at 410 mμ, which is probably the same transition as the 388-mμ band of the contact ion pair. The 368-mμ band also disappears on cooling and reappears probably at 388 mμ, since this band only changes in height at low temperatures. The shifts amount again to 4.0 kcal./mole.

Table IV. Absorption Maxima of Contact and Solvent-Separated Ion Pairs of Various Carbanions and Radical Ions in THF[a]

Compound	Contact ion pair[b] λ_{max}, mμ	Solvent-separated ion pair[b] λ_{max}, mμ
2,3-Benzofluorenyl$^-$, Na	407, 567, 611	431, 611, 676
3,4-Benzofluorenyl$^-$, Na$^+$	324, 368, 388	340, 388, 410
1-Methoxyfluorenyl$^-$, Li$^+$ (in MeTHF)	344	368, 498
1,1,4,4-Tetraphenylbutane dianion Li$^+$	460 (50°)	500
Na$^+$	472	501
Cs$^+$	481	. . .
Polystyryl[c] Li$^+$	337	. . .
Na$^+$	340	. . .
Cs$^+$	343–345	. . .
Naphthalene,$^-$ Li$^+$	322	326
Na$^+$	323, 364	326, 369

[a] Not all absorption peaks observed in the spectra of the two kinds of ion pairs are listed in this table. [b] The maxima of the contact ion pairs were usually determined at 25°, those of the solvent-separated ion pairs were obtained at low temperatures (−50 to −70°). [c] See ref. 15.

The behavior of 1-methoxyfluorenyllithium was found to be very similar to that of its unsubstituted analog. The absorption maxima of the two ion pairs in MeTHF are 344 and 368 mμ, respectively, amounting to a small blue shift compared to the maxima found for fluorenyllithium. The fraction of solvent separated ion pairs at room temperature appears to be slightly less than that for fluorenyllithium, particularly in THF. The electron-donating effect of the methoxy group slightly enhances the electron density at the 9-position of the carbanion, making separation of the two ions more difficult. The similarity in behavior of these two

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(26) T. L. Fabry and R. M. Fuoss, *J. Phys. Chem.*, **68**, 907 (1964).
(27) F. Cafasso and B. R. Sundheim, *J. Chem. Phys.*, **31**, 809 (1963).

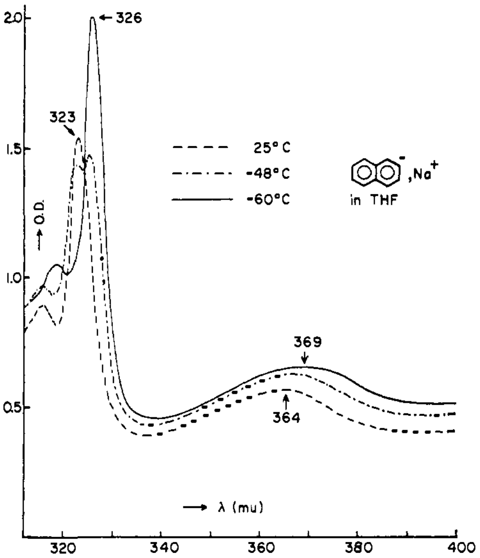

Figure 10. Effect of temperature on the spectrum of naphthalene⁻,Na⁺ in THF.

fluorenyl salts also indicates that none or very little intramolecular association between the Li^+ ion and the oxygen of the methoxy group takes place, probably because of the unfavorable position of the methoxy group with respect to the Li^+ ion. Such an association would have made solvent separation more difficult.

Ethereal solutions of the dianions of 1,1,4,4-tetraphenylbutane (*i.e.*, $M^+\bar{C}(C_6H_5)_2 \cdot CH_2 \cdot CH_2 \cdot \bar{C}(C_6H_5)_2, M^+$)[28] were also investigated, and the pertinent data are reported in Table IV. The absorption maximum of the Cs salt at 481 mμ is not affected by temperature. Due to the broadness of the absorption band (half width about 90 mμ at 25° for the Na salt), no separate peaks are observed, as was found for the fluorenyl salts (its sodium salt having a half-width of only about 15 mμ at 25°). However, there is little doubt that one is dealing again with two distinct ion pairs, the observed spectrum being a superposition of the absorption bands of the respective ion pairs. This overlap of two absorption bands is indicated by the change of the half-width of the band, its value going through a maximum on cooling. The fraction of solvent-separated ion pairs, which is more difficult to estimate due to complete peak overlap, is definitely lower than for the fluorenyl salts under otherwise identical conditions. This is to be expected since in addition to being coplanar, the fluorenyl carbanion possesses the stable cyclopentadienyl anion ring system.[29] Both contribute to delocalization of the negative charge.

No spectral shifts were observed on cooling THF solutions of polystyryl salts. The difference in absorption maximum[15] of the lithium salt (337 mμ) and the cesium salt (343–345 mμ) suggests that the shift in absorption maximum from contact to solvent-separated ion pairs would be about 10 mμ at the most. Since the absorption band is broad, amounts up to 20% of solvent-separated ion pairs in the Li salt would be difficult to detect. However, kinetic measurements of homopolymerization of living polystyrylsodium at low temperatures indicate the presence of a small fraction of solvent-separated ion pairs.[30] This fraction should of course be much lower than for the fluorenyl salts because of decreased delocalization of the charge in the polystyryl salts.

Alkali salts of radical ions exhibit the same phenomena. The shifts, however, appear to be much smaller. An example is shown in Figure 10, where the spectrum of sodium naphthalene mononegative ion is shown at three different temperatures. At −48°, two peaks are clearly visible, one at 323 and one at 326 mμ. The relative heights of the two bands at this temperature are not affected by dilution or by addition of sodium ions, and the peaks may therefore again be assigned to the two ion pairs. At room temperature, N^-,Na^+ in THF is essentially a contact ion pair, whereas the corresponding lithium salt has about 60 to 80% solvent-separated ion pairs, the respective absorption maxima being 322 and 326 mμ. The effect of temperature, counterion, and solvating power of the solvent on the spectra of these radical ions is very similar to that found for the fluorenyl salts.

Reactivities. The reactivity of the free polystyryl ion on addition of styrene in THF was found to be about a thousand times higher than that for the ion pair of the sodium salt.[15] It may be anticipated that the reactivity of the solvent-separated ion pair will approach that of the free ion. Our preliminary experiments so far seem to indicate that this is the case. For example, fluorenyllithium adds to α-pyridylstyrene in THF at 25° about 50 times faster than does fluorenylsodium. Under these conditions the concentration of free ions is small for both salts, but the fraction of solvent-separated ion pairs is about 0.75 for the lithium salt and only 0.05 for the sodium salt.

The rate of hydrogen abstraction from 3,4-benzofluorene by fluorenyllithium in dioxane to yield the 3,4-benzofluorenyllithium was also found to be enhanced by a large factor when minute quantities of DMSO were added to convert the contact fluorenyl ion pair to its solvent-separated state. Studies are in progress to determine the reactivities of both types of ion pairs in a number of solvents.

General Discussion

Evidence for the existence of two chemically distinct ion pairs has chiefly come from investigations of the mechanism of organic reactions. Winstein, *et al.*,[31] were the first to visualize the two kinds of ion pairs in order to rationalize the mechanism and stereochemistry of solvolysis of arene sulfonates. Three varieties of carbonium ions, representing different stages of ionization–dissociation, were postulated, *i.e.*

$$\begin{tikzcd}
RX \arrow[r, shift left] & R^+X^- \arrow[l, shift left] \arrow[r, shift left] \arrow[d, "k_i"] & R^+\|X^- \arrow[l, shift left] \arrow[r, shift left] \arrow[d, "k_s"] & R^+ + X^- \arrow[l, shift left] \arrow[d, "k_f"] \\
 & \; & \text{products} & \;
\end{tikzcd}$$

The products of solvolysis could arise either from the free R^- ion, the solvent separated ion pair $R^+\|X^-$ or the intimate or contact ion pair R^+X^-. This mechanism

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(28) G. Spach, H. Monteiro, M. Levy, and M. Szwarc, *Trans. Faraday Soc.*, **58**, 1809 (1962).

(29) A. Streitwieser, Jr., J. I. Brauman, J. H. Hammons, and A. H. Pudjaatmaka, *J. Am. Chem. Soc.*, **87**, 384 (1965).

(30) K. J. Toelle, J. Smid, and M. Szwarc, to be published.

(31) 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 S. Winstein, *et al.*

could account satisfactorily for the stereochemical course in these reactions and the peculiar salt effects observed in these processes.

The concept of the two ion pairs has also been successfully applied by Cram, *et al.*,[32] in their extensive investigations of the steric course of electrophilic substitution at saturated carbon. In these reactions, carbanions were shown to be the intermediates, and retention, inversion, or racemization was observed depending, among other things, on the dissociative power and solvating properties of the solvent. It is precisely in those solvents (*e.g.*, benzene, dioxane) where the spectra of the fluorenylcarbanions show only intimate ion pairs, that stereospecificity (*i.e.*, retention of configuration) is observed. On the other hand, solvent-separated ion pairs, leading to racemization, were postulated by Cram, *et al.*, in the same solvents (*e.g.*, mixtures with dimethyl sulfoxide) where our spectra show extensive solvent separation.

Grunwald[33] has pointed out that the concept of two ion pairs may be more general and should also apply to stable ions. It is instructive to consider the physical basis of the ion-pairing process in order to appreciate the factors determining the stability of the two ion pairs. Following Grunwald's description, Figure 11 represents the potential energy diagram for a univalent electrolyte in a medium of dielectric constant about 20. As the two ions approach each other, the potential energy drops. However, one or both ions may carry a solvation shell. To bring, therefore, the two ions into contact, one must remove this last layer of solvent molecules and this process may require a considerable amount of energy. Hence, the potential energy may rise again as the interionic distance, *r*, decreases, but will eventually drop to a low value at short distances where bonding forces become strong. The potential energy diagram shows, therefore, two minima, representing two distinct and chemically different entities, *i.e.*, the contact or intimate ion pair and the solvent-separated ion pair, with equilibrium distances of about 3 and 6 Å., respectively, depending of course on the ionic radii.

The stability of the solvent-separated ion pair is largely determined by the strength of the forces acting between the ions and the solvating molecules. Specific interactions like those between small alkali ions and certain ether-type molecules greatly facilitate solvent-separated ion-pair formation due to the large gain in solvation enthalpy. Molecules endowed with more than one coordination site, *e.g.*, 1,2-dimethoxyethane, are very effective if both sites can simultaneously solvate the cation resulting in a smaller loss in entropy. It is obvious that the solvating properties of the solvent rather than its dielectric constant are of prime importance. DME has a lower dielectric constant than THF, yet it is much more effective in forming solvent-separated ion pairs.

Very stable solvent-separated ion pairs may be realized when the solvating molecules possess exposed coordination sites for both cation and anion. Such may be the case in dimethyl sulfoxide or even more in a molecule like triisopropanolamine borate (see above). In the latter case, the alkali ion would be coordinated with the nitrogen, while the boron can accommodate the pair of electrons in the fluorenyl carbanion.

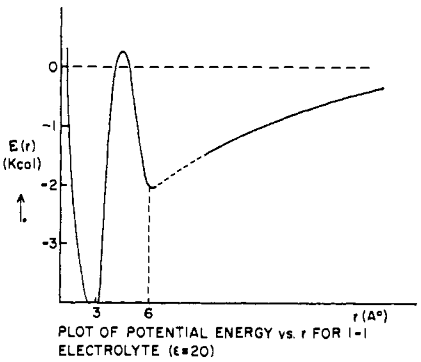

Figure 11. Plot of potential energy *vs.* interionic distance for a univalent electrolyte.

As was pointed out in the introduction, spectral changes in carbanion and radical-ion solutions have been observed recently by many investigators. The shifts, which did not clearly reveal two separate species as in the fluorenyl salts, due to broadness of the absorption bands, have been explained in terms of solvent interactions with the anion or the cation. Increased polarity of the solvent would then lead to a red shift either because of enhanced solvation of the more polar excited state of the carbanion, or because of dispersion of cationic charge by cation–solvent interactions.

It is our belief that both these factors are not the main contributors to the shifts observed in the carbanion spectra. One of the striking observations is that the absorption maximum of the solvent-separated ion pair of the fluorenyl salts is not affected by a change of solvent in spite of the widely different polarities and solvating properties of the solvents employed (Table III). This may not be too surprising, since specific interactions between ethereal solvents and carbanions are weak. Dimethyl sulfoxide with its positive sulfur may be an exception, but also here the absorption maximum does not seem to be different. On the other hand, specific interactions between ethereal solvents (or solvents like pyridine and dimethyl sulfoxide) and small alkali cations are strong. In spite of this, Table III and Figure 8 show that the position of the contact ion pair is only slightly affected by the solvent. The contact ion pairs are probably complexed with one or two ether molecules. For example, in mixtures of toluene and DME, the fluorenyllithium contact ion pair is very likely present in the form of F^-,Li^+,DME. But apparently, the dispersion of cationic charge in such complexes is too little to cause large changes in the spectrum, although a small red shift is likely to occur.

On the other hand, charge separation by insertion of a solvent molecule will very effectively reduce the influence of cationic charge on the molecular energy levels of the carbanion. We believe, therefore, that most of the observed spectral shifts should be interpreted in terms of two distinct ion pairs rather than in terms of a cationic charge dispersion through solvent interactions. The latter interpretation would make the magnitude of the shift strongly dependent on solvent polarity, contrary to what is observed with the fluorenyl salts.

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(32) D. J. Cram, J. L. Mateos, F. Hauck, A. Langemann, K. R. Kopecky, W. D. Nielsen, and J. Allinger, *J. Am. Chem. Soc.*, **81**, 5774 (1959); see also related papers by D. J. Cram, *et al.*

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

Some observations which were reported as being inconsistent with the existing theories dealing with the effect of solvent and cationic radius on carbanion spectra may now be better understood. Streitwieser and Brauman[6] found a blue shift in the spectra of the fluorenyl and 3,4-benzofluorenyl carbanion in changing from Li to Cs, contrary to the common observation that increasing the radius of the cation causes a red shift. However, the observations were made in cyclohexylamine and DME, two good solvents for solvating small cations. Our observations show that the lithium salts of both carbanions must be solvent separated in DME, causing the blue shift in changing to the Cs contact ion pair. The slightly lower absorption maxima reported for the lithium salts in cyclohexylamine may indicate a mixture of the two ion pairs in this solvent.[34] If this is the case, then an interpretation of the differences in the relative magnitudes of the spectral shifts of the fluorenyl and 3,4-benzofluorenyl anion in changing from Li to Cs in cyclohexylamine is not justified if solely based on differences in solvation of excited states.[6] A larger shift from Li to Cs in the 3,4-benzofluorenyl anion may simply be caused by the presence of a larger fraction of solvent-separated ion pairs in solutions of this carbanion, due to increased charge delocalization.

Waack and Doran[5] have suggested a linear relationship between solvent dielectric constant and the position of the absorption maximum (in cm.$^{-1}$), based on the observed spectral shifts in 1,1-diphenyl-*n*-hexyllithium. A closer inspection of their data, however, reveals that the linear relationship is essentially based on the observed shift in THF. The similarity between the structure of this carbanion and that of the dianion of 1,1,4,4-tetraphenylbutane (see above) strongly suggests that the Li salt of the 1,1-diphenyl-*n*-hexyl anion is predominantly a solvent-separated ion pair. In fact, the reported absorption maxima for this salt in THF and DME, *i.e.*, 496 and 495 mμ, respectively, are very close to our value of 500 mμ found for the solvent-separated ion pairs of the tetraphenylbutyl dianion (see also ref. 22).

The reported[35] absorption maximum for the sodium dianion of tetraphenylethylene in THF (*i.e.*, 485 mμ at 25° and 510 mμ at $-70°$) indicates the Na ion pair to be essentially a contact ion pair at room temperature. Garst, *et al.*,[36] have determined the thermodynamic quantities associated with the disproportionation equilibrium of the tetraphenylethylene monoanion into its dianion and monomer, *i.e.*

$$2\text{TPE}^-, \text{M}^+ \rightleftarrows \text{TPE} + \text{TPE}^{2-}, 2\text{M}^+$$

In THF the enthalpy change $\Delta H°$ for this equilibrium is about 19 kcal./mole for $\text{M}^+ = \text{Na}$ and only 7.4 kcal./mole for $\text{M}^+ = \text{Li}^+$, the ΔS values being 68 and 25 e.u., respectively. This strongly suggests that TPE^{2-},2Li^+ is present as a solvent-separated ion pair, probably as $\text{Li}^+,\text{TPE}^{2-},\text{THF},\text{Li}^+$ while the Na salt is essentially a contact ion pair, at least in the temperature range of their measurements (+20 to $-20°$). This is consistent with results found for 1,1-diphenylhexyllithium and the dianion of 1,1,4,4-tetraphenylbutane. Conductance measurements carried out by Roberts and Szwarc[35] on the Na salt strongly favor this assumption. They also found the sodium monoanion of tetraphenylethylene to be solvent separated even at room temperature and have proposed models for both dianion and monoanion explaining the difference in behavior.

The absorption spectra of the investigated radical ions reveal the same phenomena as observed for carbanion solutions. Buschow, Dieleman, and Hoijtink[9] have reported similar spectral shifts on cooling THF or MeTHF solutions of radical ions of aromatic hydrocarbons. They concluded from conductivity measurements of these solutions that the shifts resulted from free ion formation at low temperature. A similar conclusion[9b] was reached for carbanions of the type RH^-, *i.e.*, the primary proton adducts of the dinegative ions of aromatic hydrocarbons.

Their reasoning, however, seems to be based on a questionable interpretation of their conductivity data, namely, that complete ionization can be assumed when the decrease in molar conductance with temperature at a particular salt concentration is in agreement with the temperature coefficient of the solvent viscosity. The same behavior, however, would be observed for partially dissociated ion pairs with an enthalpy of dissociation equal or close to zero. Such a situation is found for the dissociation of solvent-separated ion pairs.[16] More accurate conductivity data[16,37] show indeed that most radical-ion salts are only partially ionized in THF in the concentration range of 10^{-3} to 10^{-4} *M*. The dissociation constants are, of course, much lower in MeTHF, and even at very low temperatures, the percentage of free ions may be rather low. We believe, therefore, that the spectral shifts must be attributed to the change from contact into solvent-separated ion pairs. This conclusion is supported by recent work of Shatenshtein, *et al.*,[37b] whose study on the conductivity behavior of ethereal solutions of the sodium adducts of naphthalene and biphenyl led them to postulate also two kinds of ion pairs. The dissociation into free ions was reported to be low, even in THF and DME.

An inspection of the conductivity data reported by Buschow, *et al.*,[9] indicates that the sodium salts of the mononegative ions of anthracene, tetracene, and pentacene are predominantly contact ion pairs in MeTHF at room temperature. The Λ–T curves show distinct maxima, due to the relatively high exothermicity of dissociation of a sodium contact ion pair.[16] On the other hand, the lithium salts appear to be solvent separated, the Λ *vs.* T curves being in close agreement with the viscosity–temperature coefficient. Similar conclusions can be drawn for the sodium and lithium salts of biphenyl, terphenyl, and quarterphenyl in THF at room temperature.

The lithium and sodium salts of the dianions of anthracene, tetracene, and pentacene seem to be contact ion pairs in MeTHF down to at least $-70°$,

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[34] Unfortunately, the fraction of solvent-separated ion pairs is difficult to determine because the absorption measurements were carried out in the region between 400 and 600 mμ.[6] Extensive peak overlap of the two ion pairs in this region makes interpretation of solvent shifts more difficult. A change in the fractions of the two ion pairs is then often observed as a shift in the maxima rather than as a change in peak height ratio of two distinct species as in our fluorenyl spectra.

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

[36] J. F. Garst and E. R. Zabolotny, *J. Am. Chem. Soc.*, **87**, 495 (1965).

[37] (a) R. V. Slates and M. Szwarc, *J. Phys. Chem.*, **69**, 4124 (1965); (b) A. I. Shatenshtein, E. S. Petrov, and E. A. Yakovleva, International Symposium on Macromolecular Chemistry, Prague, 1965; Preprints, p. 163.

and all of them are poorly ionized. The observed spectral shift for these salts in MeTHF at liquid nitrogen temperature is probably caused by the formation of solvent-separated ion pairs such as M^+,R^{2-},MeTHF,M^+, since the second counterion would be more difficult to remove.

The e.s.r. spectra of naphthalene$^-$,Na^+ also point to the presence of two kinds of ion pairs. In THF, MeTHF, tetrahydropyran, and dioxane, the Na^+ ion was shown to cause an additional splitting in the spectrum of N^-, arising from the close proximity of the Na nucleus.[38] In all of these solvents, Na^+N^- should be a contact ion pair, a conclusion based on our results found for this radical ion in THF. The splitting disappears at low temperatures (−70°), due to formation of the solvent-separated ion pair (or a mixture of free ions and solvent-separated ion pairs). In DME, no splitting is observed at room temperature, indicating Na^+N^- is solvent separated in this solvent (as was found for F^-,Na^+ in DME). The dissociation constant in this solvent is still not high and must be in the order of 10^{-5} mole/l. at 25° for a solvent-separated ion pair with a center-to-center distance of 5.5 Å.[16] The values for the thermodynamic quantities obtained from the temperature dependence of the e.s.r. spectrum of Na^-N^+ in THF[38] also strongly suggest that one measures the change from a contact ion pair into a solvent-separated ion pair or a mixture of solvent-separated ion pairs and free ions, depending on the radical-ion concentration. It is therefore not justified to calculate the dissociation constant of free ion formation from the relative intensities of the split and unsplit spectra.

Our observations are also consistent with the reported differences in the rate constants of the reaction $N^- + N \rightarrow N + N^-$ in THF and DME.[39] Its value was found to be about 100 times higher in DME than in THF, and this is to be expected, since the contact ion pair Na^+,N^- (in THF) would be much less reactive than a mixture of solvent separated ion pairs, $Na^+||N^-$, and free N^- ions.

Reactivities. The experimental evidence so far indicates that the solvent-separated ion pair is much more reactive than the contact ion pair. Its reactivity may approach that of the free ion, although strong coordination of the carbanion with the solvent molecule in some cases may decrease the reactivity substantially.

The anionic homopolymerization of styrene in THF was shown to proceed through ion pairs and free ions, the latter species being about a thousand times more reactive than the ion pairs.[15] It is interesting to observe that in dioxane the ion-pair rate constant for this reaction increases in the order Li < Na < K < Rb < Cs.[40] In THF, the order is reversed. This may indicate the presence of a small fraction of very reactive solvent-separated ion pairs, which would rapidly decrease in the order Li > Na > K > Rb > Cs. In dioxane, the reactivity follows the expected order for contact ion pairs.

The presence of two kinds of ion pairs would also lead to abnormal activation energies. The Arrhenius plot of the apparent rate constant would then result in a sigmoidal type of curve as depicted in Figure 12, the straight portions representing temperature regions where either the contact or the solvent-separated ion pair exists.

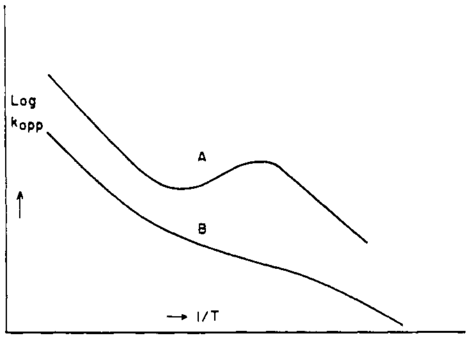

Figure 12. Temperature dependence of the apparent rate constant for a reaction in which both contact and solvent-separated ion pairs participate.

Let us consider the anionic homopolymerization of a monomer in a solvent in which both ion pairs may exist (free ion propagation can be virtually eliminated by addition of an ionizable salt)

$$\begin{aligned} &\sim\!\sim C_n^-, M^+ + C \longrightarrow \sim\!\sim C_{n+1}^-, M^+ && k_c \\ &\sim\!\sim C_n^- \,||\, M^+ + C \longrightarrow \sim\!\sim C_{n+1} \,||\, M^+ && k_s \\ &\sim\!\sim C_n^-, M^+ \rightleftarrows \sim\!\sim C_n^- \,||\, M^+ && K_i \end{aligned}$$

In this notation, C, $\sim\!\sim C^-$, and M^+ are the monomer, the propagating carbanion, and the counterion, respectively.

The apparent rate constant of propagation is given by

$$k_{app} = k_c(1 - x) + k_s x \qquad (6)$$

x being the fraction of solvent-separated ion pairs. Since $x/(1 - x) = K_i$, one finds on substitution

$$k_{app} = (k_c + k_s K_i)/(1 + K_i) \qquad (7)$$

For $k_c \ll k_s K_i$, eq. 7 may be approximated as follows

$$k_{app} \approx k_s K_i/(1 + K_i).$$

The apparent activation energy ΔE_{app} is then given by

$$\Delta E_{app} = \Delta E_s + \Delta H_i^\circ - \Delta H_i^\circ K_i/(1 + K_i) \qquad (8)$$

In this expression, ΔE_s is the activation energy of propagation for the solvent-separated ion pair and ΔH_i° the enthalpy change on formation of the solvent-separated ion pair from the contact ion pair.

Equation 8 shows that a negative apparent activation energy is obtained in the temperature range where

$$-\Delta H_i^\circ/\Delta E_s > 1 + K_i \qquad (9)$$

This may be the case for the propagation of polystyrylsodium in THF. The activation energy ΔE_s will not be much different from that found for the free ion,[41] *i.e.*, about 6 kcal./mole, while $-\Delta H_i^\circ$ is of the order of 7 to 8 kcal./mole (see above). For example, if we take the value of 8 kcal./mole, ΔE_{app} will be negative in the temperature range where $K_i < 0.3$. Of course, when $K_i \rightarrow 0$, the ΔE_{app} must again go through zero and eventually approach the value for ΔE_c. The conclusion therefore is that in polar solvents which strongly

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coordinate with the counterion (*i.e.*, $-\Delta H_{\mathrm{i}}^\circ$ large), the Arrhenius plot will behave as depicted in curve A, Figure 11. In less polar solvents, or when large counterions are involved (*e.g.*, Cs$^+$), the exothermicity of solvent-separated ion-pair formation is too low to cause the ΔE_{app} to assume a negative value (curve B).

The presence of two propagating ion pairs will tend to broaden the molecular weight distribution of the resulting polymer. This phenomenon has previously been observed when free ions are present.[42] When caused by two different ion pairs, however, the broadening cannot be eliminated by salt addition. The broadening itself will depend on the rate of solvent exchange, and would become important in cases where the carbanion tends to coordinate rather strongly with an added component of the solvent medium.

Finally, we would like to point out that formation of solvent-separated ion pairs (and free ions) will make anionic copolymerization studies rather complicated. The two propagating carbanions will contain different fractions of solvent-separated ion pairs, and the copolymer composition will therefore be a sensitive function of solvent composition, counterion, and temperature. It seems to us not realistic at this stage to attempt to develop a coherent mechanism for anionic copolymerization as has recently been proposed.[43] The number of propagating species can be numerous (solvated and nonsolvated contact ion pairs, associated ion pairs, solvent-separated ion pairs, triple ions,[44] free ions, etc.), while association between the ion pairs of the two propagating carbanions[45] may be a serious problem. The situation would be even more complex in mixtures of solvents. The conditions under which these species are stable, and their individual reactivities still need continued investigation, and any copolymer mechanism which could explain the behavior of a particular system may completely fail when conditions are changed.

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Studies of Contact and Solvent-Separated Ion Pairs of Carbanions. II. Conductivities and Thermodynamics of Dissociation of Fluorenyllithium, -sodium, and -cesium

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Abstract: The conductance behavior of the lithium, sodium, and cesium salts of the fluorenyl carbanion has been studied in tetrahydrofuran over a temperature range of +25 to −70°. The dissociation constants have been calculated from the slopes of the plots of the Fuoss conductance equation for associated electrolytes. The dissociation of the cesium salt can be described by the "sphere in continuum" model, the center-to-center distance between the ions being 3.76 Å., leading to an electrostatic radius of 2.1 Å. for the fluorenyl carbanion. The data for the lithium and sodium salts clearly reveal the presence of two ion pairs, *viz.*, contact and solvent-separated ion pairs for which spectrophotometric evidence was given in the preceding paper. The dissociation of the solvent-separated ion pairs is fairly well represented by the sphere in continuum model. At −70°, an interionic distance of 6.3 Å. is found for the lithium salt and 7 Å. for the sodium salt. The conventional model, however, is completely inadequate to describe the dissociation of the respective contact ion pairs, due to strong specific solvation of the cation. The enthalpy of dissociation for the contact ion pair of the sodium salt at 25° is found to be −9.5 kcal./mole, or about 7.5 kcal. lower than for the solvent-separated ion pair. The entropy of dissociation at this temperature is −60 e.u., or about 30 e.u. lower than for the solvent-separated ion pair.

In the preceding paper[2a] evidence was presented supporting the existence of two chemically distinct ion pairs in solutions of carbanions and radical ions. The contact and solvent-separated ion pairs were shown to exhibit different absorption maxima. The relative amounts of the two species were found to depend on the type of carbanion, the counterion, the nature of the solvent, and the temperature. In ethereal solvents, the ion pairs are dissociated into free ions to such an extent that reasonably accurate conductivity data can be obtained, allowing us to calculate the dissociation constants of free ion formation. The two kinds of ion pairs obviously have different interionic distances and solvation states. Hence, one may expect substantial differences both in the absolute values of the dissociation constants and their temperature dependence. In this paper we report the results of conductivity studies of lithium, sodium, and cesium fluorenyls carried out in tetrahydrofuran in the temperature range 25

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