Teller distortion is equal to approximately half the spin-orbit coupling constant and approximately half the contribution from a single imidazole ligand. There is a reasonable correspondence between the magnitude of the porphyrin distortion deduced from the spectroscopic data and the distortions observed crystallographically. It appears that the simple model developed in this investigation could be profitably applied to the analysis of EPR data for other porphyrin and heme systems and that it could also be used to predict crystal field energies and spin distributions in low-spin ferric porphyrin systems for which EPR data are not available.

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Carbon Acidity. 73. Conductimetric Study of Lithium and Cesium Salts of Hydrocarbon Acids. A Scale of Free Ion Acidities in Tetrahydrofuran. Revision of the Ion Pair Scales

Michael J. Kaufman, Scott Gronert, and Andrew Streitwieser, Jr.*

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received April 28, 1987*

Abstract: Equilibrium constants for the dissociation of the lithium and cesium salts of eleven hydrocarbons have been determined in tetrahydrofuran solution by a conductimetric technique. The dissociation constants for the fluorenyllithium derivatives are found to be remarkably insensitive to the structure of the carbanion; this is consistent with these compounds existing as solvent separated ion pairs. The K_d's of these lithium salts may be approximated by the primitive Bjerrum model of dissociation. The dissociation constants of the organocesium compounds are generally 10^2–10^3 times lower than those of the corresponding lithium salts, and are consistent with the cesium compounds forming contact ion pairs. The variation of dissociation constants with molecular structure for organocesium compounds is complex, and apparently it is dependent on the charge distribution and steric bulk of the carbanion. The conductimetric dissociation constants can be used to construct a scale of relative free ion acidities in tetrahydrofuran. Comparison of the resulting ionic pK values with those measured in the ion pairing solvent dimethoxyethane and the ionizing solvent dimethyl sulfoxide reveals that the relative acidities of hydrocarbons yielding delocalized anions are almost identical in each solvent. The present data are used to revise the previously published cesium ion pair scale in THF.

Alkali metal salts of carbanions exist predominantly as ion pairs in low polarity solvents such as ethers. Through the classic work of Hogen-Esch and Schmid, it is now known that two types of thermodynamically distinct ion pairs can be identified.[1-12] The first type, denoted "tight" or contact ion pairs (CIP's), are characterized by relatively strong carbanion-metal interactions. Contact ion pairing is promoted by large metal ions such as cesium and by localized carbanionic charge. The second type, denoted "loose" or solvent separated ion pairs (SSIP's), have weaker carbanion-metal interactions. Solvent separated ion pairs are formed by many lithium salts of delocalized hydrocarbons in ethereal solvents. Along with ion pairs, significant concentrations of free ions are observed in ethers if the carbanion is sufficiently delocalized, and the cation is strongly coordinated to solvent (i.e., lithium salts).[3,13-16] Although usually less abundant, the free ions are important in the dilute solution reactions of delocalized carbanions because they are generally more reactive.[3,14,16b] Solov'yanov et al.[14] have affirmed these conclusions with several studies comparing the abundance and reactivity of free vs ion paired lithium carbanion salts in dimethoxyethane (DME). A study from this laboratory in the following paper[3a] further implicates the importance of free carbanion reactions in ethereal solutions. Obviously, to fully understand the reactivity of delocalized organometallic reagents in ethers, both ion pairs and free ions must be considered and, consequently, the dissociative equilibrium that links them, eq 1.

$$R^-M^+ \overset{K_d}{\rightleftharpoons} R^- + M^+ \qquad (1)$$

In previous publications, we have presented scales of ion pair pK values in tetrahydrofuran (THF) for hydrocarbons of the fluorene and polyarylmethane type using both lithium[17] and

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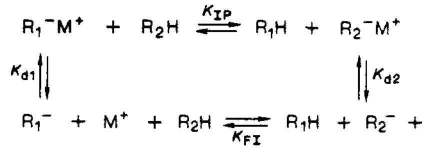
Scheme I



cesium[18] counterions. THF is a relatively nonpolar solvent ($\epsilon = 7.58$),[19] and in the concentration range employed in these studies (ca. 10^{-3} M) the carbanions exist almost exclusively as ion pairs. Consequently, our studies provide equilibrium constants for the transmetalation reaction shown in eq 2. The THF ion pair acidity

$$R_1H + R_2^-M^+ \rightleftarrows R_1^-M^+ + R_2H \qquad (2)$$

scales should provide a valuable reference for applications in synthetic organic chemistry because the concentrations employed generally favor ion pairing. However, it is important to realize that ion pair acidities as defined by eq 2 differ in several respects from free ion acidities (eq 3). The crucial difference is that the

$$R_1H + R_2^- \rightleftarrows R_1^- + R_2H \qquad (3)$$

stabilities of the ion pairs are cation dependent; consequently, the relative ion pair acidities of R_1H and R_2H are also dependent upon the identity of the cation. We have recently shown that the relative ion pair acidities of some ketones, esters, sulfones, and nitriles typically differ by 3–5 pK units when the lithium and cesium derivatives are compared.[20] In the case of *o*-methoxyacetophenone, the change from cesium to lithium gegenion increases the observed acidity by more than 8 pK units.[21] In addition, the pK values of several ketones that are present as dimers or higher aggregates in THF solution are found to vary not only with the identity of the cation but also with the concentration of the enolate present in the equilibrium mixture.[21] These examples clearly underscore the essential point that ion pair acidities may be dominated by metal–anion interactions and therefore may differ significantly from the corresponding free ion acidities.

Despite the principles and examples described in the preceding paragraph, previous work has shown that the relative ion pair acidities of carbon acids that yield highly delocalized anions are often similar to the relative ionic acidities.[22] Two experimental findings are important. First, the relative THF ion pair acidities of a series of fluorene-type hydrocarbons are observed to differ by less than one pK unit on changing the counterion from lithium to cesium.[17] Second, a comparison between cesium relative ion pair acidities in THF and absolute ionic acidities measured in dimethyl sulfoxide reveals only minor differences.[18] Both facts suggest that for a fixed counterion, the nature of ion pairing in THF solution is similar for all of these fluorenyl compounds and that the ion pair pK values can be interpreted primarily on the basis of intrinsic differences in anion stabilities. To provide a rigorous comparison of free ion and ion pair acidities, it is necessary to obtain the equilibrium constants for eq 2 and 3 in the same solvent at the same temperature. Unfortunately, the concentrations of free ions in THF solution are too low for a direct experimental measurement of equilibrium 3. However, if the dissociation constants, K_d, of the ion pairs (eq 1) can be measured, then the free ion acidities can be derived from the ion pair pK assignments by the thermodynamic cycle shown in Scheme I. Due to the low extent of dissociation (see below), the best technique to determine reliable dissociation constants is electrical conductivity. In this paper, we present a conductimetric investigation of equilibria 1 for the lithium and cesium salts of a series of eleven hydrocarbons in THF, and these results are used to construct a scale of relative ionic pK values.

Experimental Section

Carbon Acids. The hydrocarbons employed in this work were available from our previous studies on ion pair acidities in THF.[17,18] When warranted, the compounds were repurified by multiple recrystallizations followed by sublimation under high vacuum. All of the compounds gave satisfactory elemental analyses.

Tetrahydrofuran. Commercial THF (Aldrich) was predried over calcium hydride and then processed in the manner previously described.[18] The dried solvent was stored in a glass container with an O-ring seal cap and was kept in an argon filled glovebox. The specific conductance of the purified solvent was generally 10^{-9}–10^{-10} Ω^{-1} cm^{-1}. This value is low enough such that corrections due to solvent conductance were limited to a few percent or less of the total measured conductance at the lowest ion pair concentrations employed in our study.

Apparatus. Conductance was measured with an ESI Model 2110 video bridge operating in the parallel equivalent circuit mode. Visible spectra were measured with an IBM Model 9430 spectrometer.

The conductivity cell consisted of a closed cylindrical tube constructed from Pyrex glass with an internal diameter of 3 cm. Two parallel platinum wires that extended to within 1.5 cm of the bottom of the tube were sealed into the top of the cylinder; these wires supported two shiny platinum electrodes of approximately 2-cm square. A hollow arm sealed to the top of the cell served as an inlet for solvent and reagents. Also sealed near the top of the cell was a 1-cm quartz cuvette that was used to spectrophotometrically assay carbanion concentrations. The overall dimensions of the conductivity cell were such that about 20 mL of THF were required to completely cover the electrodes with solution.

The cell constant was measured with aqueous potassium chloride according to the procedure of Jones and Bradshaw[23] and was found to be 0.1016 cm^{-1}.

In preliminary experiments with the cell and bridge described above, measurements at each ion pair concentration were performed at frequencies of 0.5, 1.0, 2.0, and 4.0 kHz, and the resulting data were extrapolated to infinite frequency. The small changes in conductance as a function of frequency are indicative of errors associated with electrode polarization.[24] However, dissociation constants calculated from the extrapolated data differed by less than 5% from those calculated from conductance data obtained at a fixed bridge frequency of 1.0 kHz. Consequently, all subsequent work was performed with the bridge operating at 1.0 kHz.

Conductance Measurements. The major experimental difficulty associated with conductance measurements on carbanions is the necessity of maintaining a stable solution of these air and moisture sensitive reagents for relatively long periods of time. Compounding these difficulties is the fact that quite low carbanion concentrations (10^{-5}–10^{-4} M) are normally employed, so that trace atmospheric impurities have a profound effect upon the measurements. In our experience, the most reliable way to circumvent these problems was to modify standard conductimetric techniques[25] so that each experiment could be performed entirely within the confines of an argon-filled recirculating glovebox. The following procedure is typical and illustrative of the method.

The clean, dried conductivity cell was brought into the glovebox, and to the cell was added 3.46 mg (2.08×10^{-5} mol) of fluorene and 17.2 g (19.6 mL) of THF. The solution was immersed in a 25.00 ± 0.02 °C constant temperature bath and was magnetically stirred overnight. This prolonged stirring of the "blank" solution was found to greatly reduce the amount of drift in the solvent conductance measurements. After the solvent conductance had been recorded, the cell was removed from the temerature bath and transferred to the thermostated cuvette holder of an IBM UV–vis spectrometer. The cell compartment was built into the floor of the glovebox.[17] The spectrum of the solution was recorded to provide a base line for subsequent measurements. To generate the fluorenyl anion, a small amount of stock base (diphenylmethyllithium or diphenylmethylcesium) was added to the fluorene solution via microsyringe, and the conductivity cell was then placed back in the constant temperature bath. After ca. 30 min, conductance readings of the solution were made at timed intervals. Thermal equilibration was considered complete when the conductance measurements showed no appreciable

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Table I. Conductance of Lithium and Cesium Salts of Fluorene and Triphenylmethane in THF, 25.0 °C

lithium			cesium		
10^5c^a	10^6C^b	Λ^c	10^5c^a	10^6C^b	Λ^c
		Fluorene			
2.14	8.13	38.7	1.50	0.594	4.01
4.16	12.57	30.7	3.41	0.896	2.66
9.27	20.62	22.6	5.26	1.120	2.16
18.0	30.55	17.2	7.40	1.333	1.83
24.8	36.65	15.0	12.6	1.760	1.42
			15.4	1.956	1.29
			18.2	2.125	1.18
		Triphenylmethane			
0.73	5.37	74.7	0.62	1.212	19.6
1.39	9.08	66.0	1.03	1.594	15.7
2.29	13.20	58.4	1.60	2.058	13.1
2.73	14.96	55.5	2.09	2.384	11.6
4.23	20.31	48.8	3.11	2.965	9.67
5.10	23.03	45.9	4.76	3.683	7.85
6.49	27.07	42.3			

[a] Stoichiometric ion pair concentration in M. [b] Measured conductance in Ω^{-1}. [c] Equivalent conductance in Ω^{-1} cm^2 mol^{-1}.

changes with time. The cell was then transferred back to the spectrometer and the spectrum was recorded. The concentration of fluorenyl anion was calculated from Beer's law with use of the recorded absorbance value and the known[17,18] extinction coefficient of the salt in THF. For the lithium salts, free ion absorbances make a significant contribution to the observed spectra. It was assumed that the extinction coefficients and λ_{max}'s of the free carbanions and lithium SSIP's are identical. Previous work indicates that the extinction coefficient of delocalized carbanions are relatively insensitive to the form of ion pairing and that the λ_{max}'s of SSIP's are similar to those of the corresponding free carbanions.[2,17,18] For fluorenyllithium, the concentration dependence of the extinction coefficient was taken into account. The appearance of free ions increased the SSIP absorbance relative to the CIP absorbance. This effect was resolved by assuming that the SSIP and CIP have similar extinction coefficients (13 500) and deriving a λ_{max} extinction coefficient that reflected the observed short wavelength (CIP) to long wavelength (SSIP) absorbance ratio.[3] Another aliquot of stock base was added, and the entire cycle of measurements was repeated. Typically, each run consisted of 5–7 (concentration, conductance) data points. At the completion of a run the cell was removed from the glovebox, thoroughly cleaned with water, acetone, and 2-propanol, and dried overnight in a 160 °C oven before the next experiment.

Results

The conductimetric behavior of the lithium and cesium salts of triphenylmethane, fluorene, and several related hydrocarbons was studied in the concentration range of 10^{-5}–10^{-4} M at 25.00 ± 0.02 °C. Representative data for two of the compounds are shown in Table I. Note that at similar carbanion concentrations, the equivalent conductances (Λ) of the lithium salts are much larger than those of the cesium salts. This was true for all of the compounds employed in this study.

When the extent of dissociation of ion pairs into free ions is low ($K_d <$ ca. 10^{-2} M), then the conductivity data can be treated by using an equation derived by Fuoss et al.[26]

$$F/\Lambda = 1/\Lambda_0 + f^2 c\Lambda / F K_d \Lambda_0^2 \qquad (4)$$

In eq 4, the variables have the following meanings: Λ, equivalent conductance; Λ_0, equivalent conductance at infinite dilution; f, mean activity coefficient; K_d, dissociation constant. The variable F is a complex function of solvent properties, temperature, concentration, and conductance; it was calculated according to Fuoss.[26] For the lithium runs F varied from 0.91 to 0.96 and for the cesium runs F was close to unity. The mean activity coefficients were obtained from the Debye–Hückel equation; they were close to unity for cesium and about 0.8–0.9 for lithium.[31] Equation 4 is essentially a restatement of the Oswald dilution law[27] modified by the f and F terms to account for nonideal electrolyte behavior. Ionic association higher than ion pairing (e.g., triplet ions, etc.) is neglected in the derivation of eq 4.

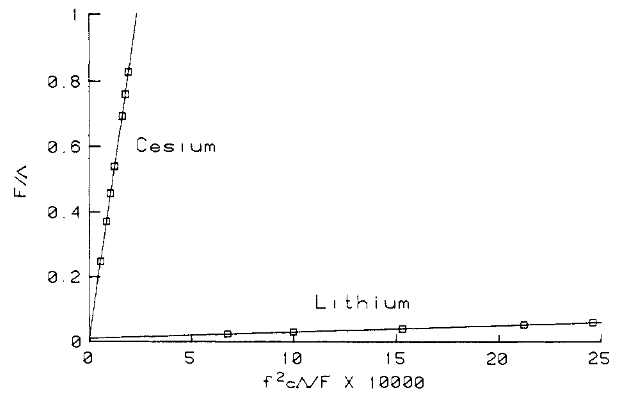

Figure 1. Fuoss plot for cesium and lithium salts of fluorene at 25 °C in THF.

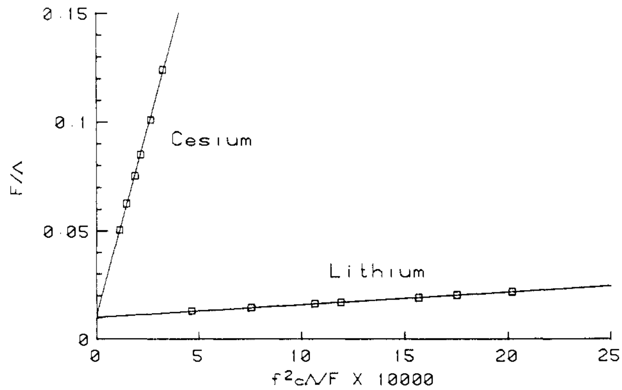

Figure 2. Fuoss plot for cesium and lithium salts of triphenylmethane at 25 °C in THF.

Equation 4 is a two-parameter equation that can be solved for K_d and Λ_0 from the experimental conductance data. A more recent conductivity equation makes use of a third parameter that can be interpreted as a cation–anion distance term.[28] However, in systems where ion association is extensive, the form of the conductivity curve is dominated by the K_d and Λ_0 parameters.[28-30] In our work, anion–cation distances ranging from about 0 to 50 Å all gave essentially the same fit to the experimental data. Consequently, we used the simpler two-parameter eq 4 exclusively.[31]

Figures 1 and 2 show the data from Table I plotted as F/Λ versus $f^2c\Lambda/F$. The excellent linearity of these plots demonstrates that the data are satisfactorily accounted for by the Fuoss two-parameter equation; in particular, the lack of curvature even at the highest ion pair concentrations is evidence that ion triplets and/or higher aggregates are not present in these systems.

In principle, least-squares analysis of the Fuoss plots gives the limiting conductance Λ_0 from the intercept; however, it has been noted by several workers that in systems where ion association is extensive, Λ_0 values are often difficult to obtain with a high degree of precision.[13,32] This situation arises because the intercept of the Fuoss plot is essentially an extrapolation to complete dissociation. We have also found the determination of Λ_0 values to be difficult, particularly for the cesium salts for which free ions account for only 1–3% of the total stoichiometric ion concentration. The lithium salts are more dissociated, and the limiting con-

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Table II. Conductimetric Dissociation Constants for Lithium and Cesium Salts of Carbon Acids in THF, 25.0 °C

	$10^8 K_d$ (M)	
compd[a]	lithium	cesium
9-PhFl	1000	6.43
3,4-BF	1000	2.92
1,2-BF	910	3.49
BA	990	21.3
9-BnFl	1020	1.73
9-MeFl		1.58[b]
4,5-MP		3.33
Fl	690	1.49
DiBF	1090	21.4
2,3-BF	720	5.14
TPM	2340	20.3

[a] Abbreviations: 9-PhFl, 9-phenylfluorene; 3,4-BF, benzo[*c*]fluorene; 1,2-BF, benzo[*a*]fluorene; BA, benzanthrene; 9-BnFl, 9-benzylfluorene; 9-MeFl, 9-methylfluorene; 4,5-MP, 4,5-methylenephenanthrene; Fl, fluorene; DiBF, 2,3:6,7-dibenzofluorene; TPM, triphenylmethane. [b] Derived from single conductivity run.

Table III. Comparison of Free Ion pK_a's Derived from the Lithium and Cesium Ion Pair Acidity Scales

	pK(FI)[a]		
compd[b]	THF/Li	THF/Cs	av (δ)[c]
9-PhFl	17.6		17.6
3,4-BF	19.3	19.3	19.3 (0.0)
1,2-BF	19.7	19.8	19.8 (+0.1)
BA	20.0	20.1	20.0 (+0.1)
9-BnFl	21.4	21.3	21.3 (−0.1)
9-MeFl		22.3	22.3
4,5-MP		22.6	22.6
DiBF	22.7	22.7	22.7 (0.0)
Fl[d]	(22.9)	(22.9)	22.9
2,3-BF	23.1	23.1	23.1 (0.0)
TPM		30.4	30.4

[a] On per hydrogen basis. Defined as pK(FI) = pK(IP) − log K_d/K_d° where K_d° is the dissociation constant of the standard, fluorene. [b] See Table II for key to abbreviations. [c] Average of values derived from lithium and cesium scales is used to define the THF pK(FI). δ is the difference in lithium and cesium derived values. [d] Reference value.

ductance obtained by averaging the experimental values for all the fluorenes gave $\Lambda_0 = 83 \pm 8$ cm^2 Ω^{-1} mol^{-1}. This is quite close to the value $\Lambda_0 = 88.4$ cm^2 Ω^{-1} mol^{-1} that has been estimated previously for fluorenyllithium in THF.[13] For convenience, we have assumed a value of $\Lambda_0 = 85$ cm^2 Ω^{-1} mol^{-1} for all of the lithium salts. To derive the limiting conductance of the cesium salts, we used the law of independent migration, eq 5. The single

$$\Lambda_0 = \lambda_0^+ + \lambda_0^- \qquad (5)$$

ion limiting conductance λ_0^+ of lithium cation in THF has been reported as 36.6 cm^2 Ω^{-1} mol^{-1};[33] with $\Lambda_0 = 85$ cm^2 Ω^{-1} mol^{-1} for the lithium salts, this would put the limiting conductance of these anions at about $\lambda_0^- = 48$ cm^2 Ω^{-1} mol^{-1}. For cesium ion in THF, λ_0^+ values of 68[33] and 79[34] cm^2 Ω^{-1} mol^{-1} have been reported in the literature. The average of these values would give a limiting conductance of 122 cm^2 Ω^{-1} mol^{-1} for the cesium salts; in view of the uncertainty in this estimate, we have simply taken $\Lambda_0 = 120$ cm^2 Ω^{-1} mol^{-1} for the cesium salts.

Although previous studies also have assigned a single λ_0^- to a series of related anions,[13,14] the validity of this assumption should be discussed. Szwarc has used extrapolations to zero concentration to determine the λ_0^-'s of some radical anions in THF, and the range of values is rather small.[32] Furthermore, Szwarc has pointed out the relationship between the diffusion coefficients of the neutral hydrocarbons and the λ_0^-'s of the corresponding anions. Since THF is not expected to specifically solvate the anions, the hydrocarbon diffusion coefficients should parallel the relative anionic mobilities, λ_0^-. Diffusion coefficients are known for a number of aromatic hydrocarbons, and these values may be used to estimate the range of expected λ_0^-'s.[35] The product of solution viscosity and diffusion coefficient (assumed to be a constant for a particular species by the Walden rule) for triphenylmethane, benzo[*a*]pyrene, perylene, and diphenylanthracene give an average value of 7.2×10^{-8} g cm s^{-2} with a standard deviation of only 0.5×10^{-8}; consequently, within a certain size range, the mobilities do not vary greatly. Therefore, assuming a single λ_0^- for a series of similar anions is valid within the constraints of our estimated errors in K_d (see below). It should be noted that the relative errors in Λ_0 are smaller than those in λ_0^- because a constant, λ_0^+, is included in the limiting conductance.

The dissociation constants for the lithium and cesium salts of eleven hydrocarbon acids are presented in Table II. These dissociation constants were calculated from the slope of Fuoss plots such as those shown in Figures 1 and 2 and the limiting conductances discussed above. The values given in Table II are averages obtained from two independent runs with each compound. Deviations in the K_d's derived from separate runs were generally ≤5%. The absolute accuracy of the dissociation constants is limited principally by the uncertainty in the Λ_0 values used in the calculations; we estimate that the values in Table II are within 25% of the true values, but relative errors are expected to be smaller.

The accuracy of the measurements can also be assessed by the thermodynamic cycle shown in Scheme I. This cycle shows that the dissociation constants can be used in conjunction with the previously reported[17,18] ion pair pK assignments to construct a scale of free ion pK values in THF. Obviously, the same relative ionic acidity should result by applying Scheme I to either the lithium or the cesium data. Table III shows the free ion pK values calculated by eq 6, and referenced to an assumed standard of pK_a(fluorene) = 22.90.[36] Although these free ion acidities are directly related to the true THF pK_a's, absolute values may not be given without a compound of known pK_a in THF. As a result, only relative values referenced to an arbitrary standard can be reported now.

$$pK_{FI}(RH) = pK_{IP}(RH) - \log\,[K_d(R^-M^+)/K_d(Fl^-M^+)] \qquad (6)$$

Note that the reference to fluorene differs from our previous practice of using 9-phenylfluorene, pK = 18.49.[17,18] The 9-phenylfluorene standard is based on an H_- value,[37] but a reference based on Bordwell's[38] widely accepted dimethyl sulfoxide (Me$_2$SO) absolute acidity scale seems more appropriate now. Therefore, this free ion scale and the previously published THF ion pair acidity scales have been offset to reflect a fluorene standard using its Me$_2$SO pK_a of 22.90. Additionally, an error has been detected in the original cesium ion pair acidity scale (see below).[18] As a result, the ion pair pK's given in this paper will differ somewhat from our previously reported values.[17,18]

The free ion acidities presented in Table III show that pK values calculated from the lithium and cesium acidity scales are in excellent agreement; the average difference for six compounds is only 0.1 pK unit. In view of the various experimental uncertainties, this agreement is most satisfactory.

Discussion

The results in Table II indicate that the dissociation constants of lithium ion pairs are 10^2–10^3 times greater than those of the cesium salts. These large differences are indicative of a difference

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in the type of ion pairing. In general, the lithium derivatives of these delocalized carbanions exist as solvent separated ion pairs for which dissociation is favored by the relatively weak metal anion interactions and long interionic separations.[17] In contrast, the cesium salts exist as contact ion pairs;[18] the stronger metal–anion interactions and shorter interionic separations make dissociation much less favorable. Note that these conductivity data are completely consistent with prior conclusions regarding the nature of ion pairing in these compounds based on the analysis of spectroscopic data.[2,3,17,18]

The range of K_d values determined for the lithium salts is remarkably small, and within the limits of experimental error, a value of $K_d = 1.0 \times 10^{-5}$ M appears appropriate for almost all of the lithium salts. The smallest dissociation constant among the lithium salts is found for fluorene. However, we note that in THF solution at 25 °C, fluorenyllithium exists as an equilibrium mixture of about 70% solvent separated and 30% contact ion pairs.[3] Assuming that the conductance of a lithium contact ion pair is smaller compared to that of the corresponding solvent separated species, the fluorene results are then consistent with the value cited above. The dissociation constant for benzo[*b*]fluorene is somewhat lower, and that of triphenylmethane is significantly higher, than the values found for the remaining compounds. It should be noted that measurements involving benzo[*b*]fluorenyllithium consistently resulted in unusually small Fuoss plot intercepts leading to large or negative extrapolated Λ_0 values. The reason for this behavior is not understood, but these findings are independent of the base used for deprotonation and the source of the benzo[*b*]fluorene sample. The larger dissociation constant for triphenylmethyllithium can be explained by its nonplanar geometry because steric effects may increase the interionic distance and, consequently, the K_d. On the basis of work by Chan and Smid,[16b] K_d of this magnitude is expected for triphenylmethyllithium. They found $K_d = 7.6 \times 10^{-6}$ M for triphenylmethylsodium in THF, but since the sodium salt is a mixture of SSIP's and CIP's (estimated as 60 to 90% CIP) and the lithium salt is almost exclusively SSIP's,[9,10] the K_d for triphenylmethyllithium should be considerably larger than this value. On the whole, the dissociation constants of the organolithium compounds are surprisingly similar, indicating that the cation–anion interactions in these salts do not vary much. Apparently, the long interionic distance in the SSIP results in an electrostatic potential at the cation that is nearly independent of the carbanion charge distribution. Comparisons to previously determined K_d's may be made for fluorenyllithium (3.89×10^{-6} M)[13] and triphenylmethyllithium (12.4×10^{-6} M).[14b] These values are in general agreement and the deviations may be explained in part by differences in data analysis (i.e., choice of Λ_0 and distance parameter for f calculation).

The experimental results may be compared with a theoretical approach based on the primitive Bjerrum model for dissociation.[39] Here, dissociation is simply described as the separation of charged spheres in a medium of constant dielectric. Although this model does not account for either dissociation-related solvation changes or variations in the dielectric near the charged species, it has been successful in systems employing low-polarity solvents.[40] The Bjerrum equation

$$1/K_d = 4\pi N/1000 \int_a^q r^2 e^{2q/r}\,dr$$
$$\text{with } q = e_z^2/2\epsilon\kappa T \qquad (7)$$

relates the dissociation constant (K_d) to the solvent dielectric (ϵ), the electrostatic unit charge (e_z), Avogadro's number (N), the Boltzmann constant (κ), the temperature (T), and the interionic distance at closest approach (a). A number of important aspects of the present results are remarkably consistent with the Bjerrum model.

Table IV. Calculated Cation Affinities of Delocalized Carbanions[a]

compd[b]	cation affinity (kcal mol^{-1})	compd[b]	cation affinity (kcal mol^{-1})
BA$^-$	82.3	3,4-BF$^-$	87.2
2,3-BF$^-$	85.3	4,5-MP$^-$	88.3
1,2-BF$^-$	86.5	Fl$^-$	89.5

[a] Calculated by the SCF-π method with an interionic distance of 3.1 Å; see ref 42. [b] See Table II for key to abbreviations.

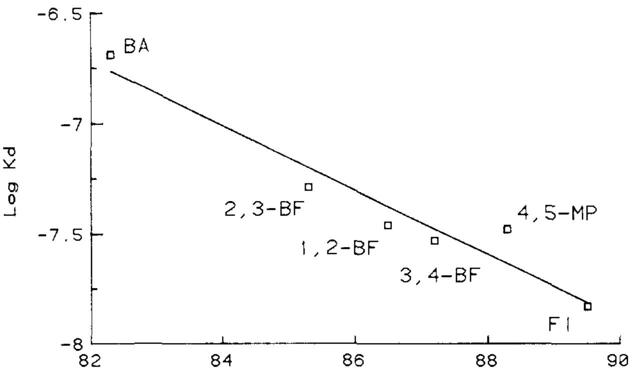

Figure 3. Plot of log K_d versus calculated cation affinity for various carbanions. The calculated values are derived by using an SCF-π method with standard geometries and an interionic distance of 3.1 Å; see ref 42.

The dissociation constants for the lithium salts of about 1×10^{-5} M^{-1} correspond to an a value of 5.5 Å in the integrated Bjerrum equation. Previous conductimetric studies combined with molecular modeling indicate a radius of about 4–5 Å for the THF solvated lithium cation.[13,40] Fluorenyl-type anions are certainly not spherical, but for this analysis an approach radius of about 1.5 Å is not inappropriate.[41] These numbers are of the right approximate magnitude to account for the observed dissociation in terms of SSIP's. Note that a needs to be somewhat larger (6.1 Å) for triphenylmethyllithium to conform with its greater K_d, but this is not unreasonable considering its twisted rings.

The smaller K_d values for the cesium salts require a range of a values of 3.3–3.9 Å. With a cation radius of 1.66 Å,[2] we then require a range of effective anion radii of 1.6–2.2 Å. These distances are of the right magnitude for CIP's but the variation suggests that in such ion pairs the appropriate ion pair distance is not a simple "contact" distance but a weighted average distance that accounts for the charge distribution in the delocalized carbanion. That is, the effective distance is greater for carbanions with charge distributed to farther regions. This effect would be less important for ion pairs with greater interionic distances as in SSIP's. Since the interionic distance is shorter in the contact ion pairs, the dissociation constants of the cesium contact ion pairs are more sensitive to the carbanion charge distribution than those of the corresponding lithium solvent separated ion pairs. The results of another approach are instructive in this connection. Murdoch and Streitwieser[42] used an SCF-π method to obtain the charge distributions of a series of planar hydrocarbon carbanions and used the distances of the individual carbons to the cation to estimate the total electrostatic energies. The resulting cation affinities for the carbanions from benzanthrene, fluorene, and the four benzo-substituted fluorenes (1,2-BF, 2,3-BF, 3,4-BF, and 4,5-MP) parallel the experimentally observed dissociation constants (Table IV and Figure 3). With a single exception, the calculations predict the correct relative order of K_d's; the deviation of 4,5-MP may result from the strain in this molecule or the assumed geometry used in the SCF-π approach. The validity of this type

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(39) For discussions of the Bjerrum equation see ref 26 and Justice and Justice in ref 31.

(40) Salomon, M. *Electrochim. Acta* **1985**, *30*, 1021.

(41) This value is based on the ionic radii determined for the cyclopentadienyl ligand in various metal complexes: Raymond, K. N.; Eigenbrot, C. W., Jr. *Acc. Chem. Res.* **1980**, *13*, 276. For the fluorenyl anion, an ionic radius of about 1.7 Å can be derived from an X-ray diffraction study of fluorenyllithium, but the lithium is only η^3 coordinated in the crystal structure; see: Brooks, J. J.; Rhine, W.; Stucky, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 7339.

(42) Murdoch, J. R.; Streitwieser, A., Jr. *Intra-Sci. Chem. Rep.* **1973**, *7*, 45.

Table V. Ion Pair Dissociation Constants in Dimethoxyethane

	10^8K_d (M)	
compd[a]	lithium	cesium
9-PhFl	790,[b] 560[c]	40,[b] 47[c]
1,2-BF	770[c]	43[c]
BA	920[b]	260[b]
9-BNFl	820,[b] 440[c]	50,[b] 48[c]
9-MeFl	380[c]	22[c]
Fl	740,[b] 470,[c] 620[d]	35,[c] 25[d]
TPM	900[b]	170[b]

[a] See Table II for abbreviations. [b] Reference 15. [c] Reference 14a. [d] Reference 16.

Table VI. Revised Ion Pair Acidity Scales[a]

compd[b]	$pK_{Li/THF}$[c]	$pK_{Cs/THF}$[d]	compd[b]	$pK_{Li/THF}$[c]	$pK_{Cs/THF}$[d]
9-PhFl	17.60		9-*t*-BuFl		24.71
3,4-BF	19.29	19.6	TPP		27.01
1,2-BF	19.70	20.2	PDDA		28.35
BA	20.13	21.3	9-PX		28.99
BnMP	21.35		BDPM		30.32
9-BnMP	21.35		TPM	31.0[g]	31.51
9-BnFl	21.36	21.4	*p*-BB		31.95
9-MeFl		22.34	TpTM		32.35
DiBF	22.68	23.84	DPM		33.50
Fl	(22.90)[e]	(22.90)[f]	DoTM		34.47
4,5-MP		22.91			
2,3-BF	22.95	23.64			

[a] On per hydrogen basis. [b] Abbreviations: BnMP, 9-benzyl-9-*H*-benzo[*def*]fluorene; 9-*t*-BuFl, 9-*tert*-butylfluorene; TPP, 1,1,3-triphenylpropene; 9-PX, 9-phenylxanthene; PDDA, 9-phenyl-10,10-dimethyldihydroanthracene; BDPM, biphenylyldiphenylmethane; TPM, triphenylmethane; TpTM, tri-*p*-tolylmethane; *p*-BB, *p*-benzylbiphenyl; DPM, diphenylmethane; DoTM, di-*o*-tolylmethane; DXM, di-*m*-xylylmethane; PTS, phenyl *p*-tolyl sulfide; *p*-MB, *p*-methylbiphenyl. See Table II for other abbreviations. [c] Revised to fluorene standard. [d] Revised to fluorene standard and corrected for error in 1,2-BF to 9-MeFl relative to p*K*'s. [e] Referenced to the SSIP of fluorene at 22.90 or composite p*K*(SSIP + CIP) = 22.75. [f] referenced to the CIP of fluorene at 22.90. [g] Determined indirectly from cesium ion pair acidity.

of approach is better shown by its success in reflecting the exceptionally large dissociation constant for benzanthrenyl. Note that these cation affinities are not directly related to the basicity of the anions (e.g., benzo[*b*]fluorenyl anion is more basic than benzo[*c*]fluorenyl anion, but its calculated cation affinity is lower). As with the benzanthrenyl anion, a similarly weak electrostatic potential must be involved with the highly delocalized 2,3:6,7-dibenzofluorenyl anion. The cesium derivative of triphenylmethyl anion is also significantly more dissociated than would be expected on the basis of anion basicity. This is probably a joint result of the charge distribution in the anion and steric interactions between the bulky, propeller-shaped triphenylmethyl anion and the cesium cation as in the lithium case above. On the whole, the dissociation constants of these organocesium compounds vary in a complex way and are much less dependent upon anion basicity than might have been expected a priori.

It is instructive to compare the magnitude of the dissociation constants determined in THF with the corresponding values in dimethoxyethane (DME). Relevant published data for DME solution are collected in Table V.[14-16] The differences in the reported values for some of the lithium salts (9-PhFl, 9-BnFl, and Fl) are evidence of the inherent uncertainty in determining dissociation constants. The most notable aspect of the comparison is the larger solvent effect on the dissociation constants of cesium ion pairs with K_d values being approximately an order of magnitude larger in DME compared to THF. A solvent effect of similar magnitude has been recorded for the dissociation of cesium tetraphenylborate.[34] These differences are not due to a change in the type of ion pairing since all of these salts have been shown to exist as contact ion pairs in both solvents.[18,43] Also, the dielectric constants of THF and DME are similar ($\epsilon = 7.58$ and 7.2 respectively for THF and DME).[19] In contrast, the solvent separated lithium ion pairs have similar K_d's in both DME and THF. The most reasonable explanation is that the majority of the specific cation–anion interactions are realized in the contact ion pair (CIP) $\rightleftarrows$ solvent separated ion pair (SSIP) equilibria. The bidentate nature of DME is important in promoting further cation solvation and in favoring SSIP's over CIP's. Since dissociation of a cesium contact ion pair involves increasing cation solvation (possibly forming a cesium SSIP initially), it will be favored by the better coordinating solvent, DME. Since the lithium is already fully solvated in the solvent separated ion pair, the advantage of bidentate DME chelation is not as important in the dissociation process; consequently, the solvent separated ion pairs have similar K_d's in both DME and THF.

On the basis of the assumption that contact ion pair ionization involves first formation of a solvent separated ion pair and then dissociation, the observed K_d's may be used to estimate the percent SSIP for the cesium salts. The K_d for a solvent separated cesium ion pair may be approximated by using the Bjerrum model. By using a slightly larger ionic radius for the solvated cesium than for the solvated lithium cation (1 Å larger), K_d's on the order of $3.5–7.5 \times 10^{-5}$ M may be expected for solvent separated cesium ion pairs. The percent SSIP is calculated by dividing the observed K_d by this hypothetical SSIP K_d. The estimated percent SSIP's vary from about 0.03% for fluorenylcesium to 0.4% for benzanthrenyl, 2,3:6,7-dibenzofluorenyl, and triphenylmethylcesium, fractions that are too small for direct spectroscopic detection. It should be noted that this type of analysis has been successful in systems where the SSIP fraction could be verified spectroscopically.[3]

Acidity Scales

Ion pair p*K* assignments for the hydrocarbon acids used in this study have been given previously,[17,18] but some changes are reported here. The absolute values for the lithium scale have been offset to adopt the new fluorene reference, p*K* = 22.90 (Table VI); the relative values are unchanged. More extensive changes have been made to the cesium ion pair scale. Beyond shifting to a fluorene standard, changes have been made in the relative values to account for an earlier error. We have found that the sample of benzo[*a*]fluorene used previously in the development of the cesium ion pair scale contains a slight impurity that, however, significantly affected the equilibrium measurements and resulted in inaccurate relative ion pair p*K* determinations for 9-phenylfluorene, benzo[*c*]fluorene, benzo[*a*]fluorene, and 9-benzylfluorene. These errors, the largest being about 0.8 unit, were detected first by a comparison of the ionic p*K*'s derived from the lithium and cesium based measurements and were subsequently confirmed by direct cesium ion pair p*K* measurements with a pure sample of benzo[*a*]fluorene. At this point, new preliminary values are available for benzo[*a*]fluorene, benzo[*c*]fluorene, 9-benzylfluorene, and benzanthrene, a new indicator on the cesium scale. These values are presented in Table VI to a single decimal place. After further measurements have been completed, a revised cesium ion pair acidity scale including 9-phenylfluorene will be presented with precision to two decimal places. Nevertheless, the present interrelation of the lithium and cesium scales through the free ions shows that there are no significant systematic errors and that both scales are firmly grounded. Moreover, the present results confirm that only monomeric ion pairs are important in the concentration ranges used. If dimers or higher aggregates were involved, they would have to be similarly involved for all of these compounds together with a fortuitous cancellation of dissociation constants.

Note that we have chosen a reference value of p*K* = 22.90 (per hydrogen) for both the fluorenyl CIP cesium salt and SSIP lithium salt in THF. Since fluorenyllithium is a mixture of SSIP and CIP the actual experimental p*K* is 22.75. This choice of reference is for convenience because the resulting numbers have the same numerical value as the ionic pK_a's in dimethyl sulfoxide. In practice, any of several fluorene derivatives could have been chosen as the reference with virtually no change in the resulting numbers,

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(43) Petrov, E. S.; Terekhova, M. I.; Shatenshtein, A. I. *Zh. Obshch. Khim.* **1974**, *44*, 1118 (Engl. Transl. p 1075).

Table VII. Comparison of Free Ion Acidity Scales

	pK(FI)[a]		
compd[b]	THF	DME[c]	Me_2SO[d]
9-PhFl	17.6	17.7	17.9
BA	20.0	20.1	
9-BnFl	21.3	21.2	21.4
9-MeFl	22.3		22.3
4,5-MP	22.6		22.4
Fl[e]	(22.9)	(22.9)	22.9
2,3-BF	23.1		23.4
TPM	30.4	30.2	30.6

[a] On per hydrogen basis. These are related to true pK_a's; the (FI) notation is used to distinguish clearly from the ion pair pK's. In THF and DME, since arbitrary references are used, only relative values are important. In Me_2SO, absolute pK_a values are given. [b] See Table II for key to abbreviations. [c] Derived in the same way as THF values; see ref 15, 43, and 44 for necessary information. [d] Reference 38. [e] Reference for THF and DME scales.

but it seems more reasonable to choose the parent ring system as the reference. Note that it would now have been possible to assign a reference value only to the *ionic* acidity in THF and to base the numerical relative ion pair acidities to it using the now known dissociation constants, but the result would be a complete distortion of the numerical scale without providing any compensating benefits. There is in any event a difference in units involved. Acid dissociation constants usually have units of M^{-1} whereas ion pair acidities are unit-less. To avoid possible misunderstanding we strongly recommend that any use of these scales make explicit mention of the reference used.

Comparison of the data in Tables III and VI clearly reveals that relative ion pair acidities in THF are quite similar to the ionic acidities derived from conductivity measurements. In particular, the lithium scale is virtually identical with the free ion scale; this is, of course, a consequence of the dissociation constants for all of these solvent separated ion pairs being nearly identical. The close correspondence of the lithium and cesium acidity scales with the free ion acidities in THF provides another example of the now well established phenomenon that relative acidities of compounds with extensively delocalized carbanions are not highly sensitive to solvent or ion pairing. However, for more localized anions such as enolates and acetylides, ion pairing interactions are undoubtedly more important and a close correspondence between ion pair and free ion acidities would not be expected.[38a,44]

Since Shatenshtein et al.[15,43,45] have determined both ion pair acidities and dissociation constants in DME, a comparison to an analogous DME pK(FI) scale can be made. Given that DME and THF have similar properties (i.e., dielectric constants), similar relative ionic pK's are expected. In Table VII, an ionic acidity scale derived from Shatenstein's DME data is presented. Comparison of this scale to the THF scale indicates only minor differences; the largest deviation on the scale from 9-phenylfluorene to triphenylmethane, a pK range of about 13 units, is only 0.2 unit. Clearly, small changes in the nature of the solvent do not affect the relative stabilities of these carbanions.

The THF free ion acidities also may be compared to Bordwell's acidity scale in Me_2SO.[38] Here, the values are true pK_a's because the carbanion salts are fully dissociated in Me_2SO and the relative values are anchored to a compound of known self-ionization constant in Me_2SO. With use of fluorene as a reference, six independent comparisons can be made between the two ionic pK scales. All of the deviations are small with the largest being only 0.3 unit. Furthermore, the ΔpK's between 9-phenylfluorene and triphenylmethane are similar, 12.8 units in THF and 12.7 units in Me_2SO. Since the consistency in these values is good, it appears that solvent has little effect on the relative stabilities of these delocalized carbanions. Me_2SO and THF have vastly different dielectric properties ($\epsilon(Me_2SO) = 46.7$ and $\epsilon(THF) = 7.6$),[19] yet the relative ionic pK's are similar in both solvents. The assumption of solvent independence on carbanion stability should break down, however, in cases where specific anion solvation is important (i.e., hydrogen bonding).

Finally, we note that the conductimetric method described herein provides a method for extending the lithium ion pair scale in THF to higher pK values. In previous work, it was observed that equilibria between lithium salts of highly basic carbanions such as triphenylmethyl are attained so slowly that anion decomposition can preclude an accurate pK assignment. The corresponding equilibria with cesium salts are attained much more rapidly; hence, the cesium pK scale and the experimental dissociation constants can be used to deduce a pK value on the lithium scale. For example, the pK of triphenylmethane on the cesium ion pair scale is 31.51. The data in Table II indicate that the pK on the lithium scale is about 31.0.

Conclusions. Ionic dissociation constants, K_d, derived from conductivity studies in THF show that the lithium salts of benzanthrene, fluorene and 9-substituted fluorenes, benzofluorenes, and triphenylmethane are present predominantly as solvent separated ion pairs whereas the corresponding cesium salts are contact ion pairs. The simple Bjerrum model is remarkably successful in accounting for the various K_d values found. The relative ionic acidities derived from both series are identical and are also the same as relative ionic acidities in the more polar solvent dimethyl sulfoxide. The results have led to some revisions in the ion pair scales; these scales in THF are now firmly based and contain no apparent systematic errors in this pK region.

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Registry No. 9-PhFl, 789-24-2; 3,4-BF, 205-12-9; 1,2-BF, 238-84-6; BA, 56-55-3; 9-BnFl, 1572-46-9; 9-MeFl, 2523-37-7; 4,5-MP, 203-64-5; Fl, 86-73-7; DiBF, 242-47-7; 2,3-BF, 30777-19-6; TMP, 519-73-3.

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