round-bottom flask equipped with a magnetic stirring bar and a reflux condenser. The solution was stirred at 60–65 °C for 17 h and poured into 50 mL of ice water. The solid was collected by filtration to give 0.85 g (87% yield) of product: NMR (CDCl$_3$) δ 3.01 (s, 6 H), 4.12 (s, 2 H), 7.33 (d, 4 H, J = 8 Hz), 7.87 (d, 4 H, J = 8 Hz). Recrystallization from 95% ethanol and sublimation at 190 °C to gave a colorless powder); mp 197–198 °C; IR (CHCL$_3$) 1600, 1410, 1320, 1150, 1090 cm^{-1}; mass spectrum 324, 165; Anal. C, H, S.

Carbon Acidity. 67. The Indicator Scale of Cesium Ion Pairs in Tetrahydrofuran

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Abstract: An equilibrium cesium ion-pair indicator scale relative to 9-phenylfluorene at pK$_a$ = 18.49 has been established for 22 hydrocarbons in tetrahydrofuran. Comparison of this scale to those developed in Me$_2$SO and DME shows the scale to be independent of solvent. Visible absorbance spectral characteristics of the indicator anions are also reported and discussed in relation to other solvents. Thermodynamic studies of the equilibrium reactions were carried out over a temperature range of –20 to 25 °C and reveal the importance of internal rotation on the entropy of reactions. Thermodynamic constants found for reaction between fluorenes show a complex behavior and are generally not interpretable at this time.

Quantitative and semiquantitative equilibrium acidity data for a wide variety of carbon acids have been presented by several investigators. Since the pioneering work of Conant, Wheland, and McEwen in the 1930's,[1] acidity scales have been proposed for weak carbon acids in many solvents, including dimethyl sulfoxide (Me$_2$SO),[2] dimethoxyethane (DME)[3] and *N*-methylpyrrolidin-2-one (NMP).[4] For over two decades, research in our own laboratories has focused on the determination of the relative acidity of carbon acids in cyclohexylamine (CHA) solvent. Cyclohexylamine is a relatively nonpolar solvent, and the anions present in this solvent exist almost entirely as ion pairs. By assuming a pK$_a$ value of 18.49 for 9-phenylfluorene, relative equilibrium ion-pair indicator scales have been developed for both lithium and cesium gegenions.[5] Much additional data have been

made available by application of the H$_-$ technique to aqueous and alcoholic organic solvent mixtures.[6] Collectively, this body of data has provided valuable insight into the various factors which determine the ease of ionization of a carbon acid.

Unfortunately, relatively few carbanion-forming reactions are performed in these solvents. Instead, metalation reactions conducted in ethereal solvents, especially tetrahydrofuran (THF), have increased enormously in both scope and usage in recent years.[7] However, despite the widespread use of this solvent in synthetically useful transformations, relatively little quantitative ion-pair acidity data are currently available in THF.[8] Therefore,

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we have recently established a comprehensive relative equilibrium indicator scale in tetrahydrofuran with cesium as the counterion.[9]

In addition to the importance of the pK scale, the solvent properties of THF allow more extensive analysis of the ion-pair equilibrium reactions. The lower melting point of THF allows the determination of equilibrium constants over a much larger temperature range than in CHA or Me$_2$SO thus permitting measurement of the enthalpy and entropy of the equilibria. Such data permit additional assessment of the effects of substituents, solvent, ion pairing, and ion aggregation of carbanions. Some work of this type has already been accomplished in CHA[10] and DME,[3,11] and comparisons can be made to these solvents.

Also, the use of a relatively aprotic solvent should permit the extension of our pK_a scale to higher values. Upper limits of measurements in CHA and Me$_2$SO are imposed by the acidities of the solvents; in practice, this corresponds to maximum determinable pK_a's of 39 and 32, respectively. In DME, no such upper limit is imposed by "solvent levelling"; however, DME is decomposed by strong bases and a practical upper limit of 33 pK units has been established at room temperature.[3] Existing literature data suggest that the anion of cumene (pK_{CHA} estimated at 40.7),[5] but not that of toluene (pK_{THF} estimated at 41.2),[12] is stable in THF at room temperature.[13] Thus, a practical limit of about 40 pK units should be obtainable in THF at 25 °C. However, at lower temperatures, solvent decomposition may be slowed so that the pK_a scale could be extended to even less acidic compounds. Work of this nature is being actively pursued. The indicator scale was established in a manner similar to that used for the development of the indicator scales in CHA. Spectroscopic data for the cesium salts of fluorene and polyarylmethane derivatives are reported and discussed in relation to ion-pairing and solvent effects. The equilibrium reactions involving this series of overlapping indicators were measured by visible spectroscopy, and the equilibrium constants were used to construct a scale of pK_{THF} indicator values. Thermodynamic parameters obtained from studying equilibria as a function of temperature are also presented and discussed in relation to solvation of ion pairs and substituent effects.

Results

Deprotonation Agents. In contrast to work in CHA and Me$_2$SO, it is not possible to use the lyate anion of the solvent as a base for generating cesium salts in THF; THF anion is unstable and readily decomposes to give ethylene and acetaldehyde enolate.[14] The choice of a suitable base was made on the basis of the following considerations: (1) ease of preparation and handling, (2) stability in THF, (3) absence of side reactions with substrate molecules, (4) absence of other cesium salts that could lead to complicating aggregations. Of course, the base must also be sufficiently strong to completely deprotonate the substrate compounds chosen for study. These factors led to the investigation of cesium hydride as a possible base.

Prior to our studies, and in contrast to the other alkali-metal hydrides, no data concerning the reactivity of cesium hydride toward acidic organic compounds were available. However, consideration of the physical properties of the alkali-metal hydrides suggests that the effective basicity should increase proceeding down the alkali group. Potassium hydride is known to metalate dimethyl sulfoxide (Me$_2$SO) but not triphenylmethane in THF solution.[15] In the presence of 18-crown-6-ether, potassium hydride is capable of metalating di-p-tolylmethane.[16] It therefore appeared likely

that cesium hydride would react readily with all of the relatively acidic fluorene derivatives and at least some of the polyarylmethane derivatives contemplated in our study.

Cesium hydride was prepared by the direct reaction of cesium metal with hydrogen at 400–500 °C,[17] using a slight modification of the procedure of Gunn.[17b] The hydride was obtained in 72% yield as a white crystalline solid. Some contamination by free metal was apparent but was not extensive.

Deprotonation reactions with cesium hydride proceed to completion or near completion with hydrocarbons having an acidity as low as triphenylmethane. However, the reaction of cesium hydride with hydrocarbon acids is a kinetically slow process. Cesium hydride is insoluble in THF, and the long reaction times needed to completely deprotonate the carbon acids are undoubtedly caused by the heterogeneous nature of the reactions. In none of the reactions discussed above was provision made for efficient stirring of the hydride/hydrocarbon mixture. It is likely that stirring would markedly accelerate the reaction rate. Nevertheless, the slow reaction rates obtained in our initial studies seriously detract from the usefulness of cesium hydride as a standard base.

To effect rapid deprotonation, it was necessary to use a base that is soluble in THF. Therefore, cesium hydride was used to prepare a stock solution of tritylcesium. Tritylcesium is soluble in THF at the concentration levels employed (0.1 M), is stable indefinitely in THF, and reacts rapidly with all of the fluorene hydrocarbons studied. Consequently, tritylcesium was used to completely deprotonate the corresponding fluorene acids.

In order to measure the acidity of the remaining polyarylmethanes, a much stronger base was required. Szwarc et al.[13a] have reported that the benzyl anion (pK_{CHA} estimated at 41.2)[12] decomposes quickly in THF at room temperature but that the anion formed from cumene (pK_{CHA} estimated at 40.7)[5] is stable for at least a week. We found comparable behavior for the cesium salts. This large difference in rates suggests that attack on the solvent by cumyl anion is inhibited by the steric bulk of the methyl groups. Indeed, the anion formed from p-methylbiphenyl (pK_{CHA} = 39.0),[12] which is more thermodynamically stable than cumyl anion, quenched at a much faster rate under similar reaction conditions. Furthermore, the cesium salt of p-isopropylbiphenyl (pK_{CHA} = 38.4), which is about as basic as the anion of p-methylbiphenyl,[12] was found to be comparatively stable in THF. Thus, although cumylcesium is sufficiently basic to decompose THF, the steric hindrance of the methyl groups of the anion markedly slows the rate of such decomposition.

Cumylcesium was prepared by the addition of cesium metal to a solution of 2,3-dimethyl-2,3-diphenylbutane (bicumyl). The reaction to form the anion goes to completion in less than 2 h at room temperature. At the concentration levels employed (0.1 M), cumylcesium is soluble in THF. Because of eventual decomposition, freshly prepared solutions of the anion were used to completely deprotonate all of the polyarylmethane derivatives used in this study. In most cases the deprotonation occurred within seconds; however, TpTM and DoTM (see Table I for an explanation of the abbreviations) required several minutes for complete reaction.

Finally, a convenient preparation of dicesium tetraphenylethylene has been developed.[18] This compound exhibits good stability in the solid state and is particularly useful when it is desired to deliver accurately a precisely known amount of base.

Anion Spectra. Spectroscopic data for the cesium salts of 22 hydrocarbon acids are recorded in Table I along with corresponding values in some other solvents. Replicate measurements of the extinction coefficients show that the values are accurate to within ±5%. In all of the cases studied, adherence to Beer's law was found over a concentration range comparable to those employed in the acidity determinations (five- to tenfold) without

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Table I. Spectral Data for the Indicators

indicator[c,d]	THF $\lambda_{max}{}^e$ (ϵ)	CHA[a] λ_{max} (ϵ)	DME[b] λ_{max} (ϵ)
9-PhFl	359 (20200)		
	397 (24000)	398 (22300)	395 (23500)
3,4-BF	374 (7580)		
	394 (5240)	394 (5070)	
1,2-BF	433 (9710)	426 (8780)	
9-BzFl	371 (13300)		373 (15600)
	467 (1120)	476 (1060)	471 (1510)
	494 (1530)	500 (1430)	500 (1900)
	528 (1160)	536 (1080)	534 (1270)
9-MeFl	376 (12350)		377.5 (12700)
	478 (980)	477 (950)	474 (1050)
	503 (1250)	505 (1170)	506 (1290)
	539 (890)	541 (820)	539 (890)
4,5-MP	500 (6850)	505 (7100)	
Fl	363 (12700)		364 (14500)
	450 (890)	457 (980)	
	474 (1160)	472 (1200)	
	504 (1020)	504 (870)	
2,3-BF	415 (22000)	418 (19300)	
9-t-BuFl	376 (13700)		378 (15300)
	469 (900)	471 (925)	471 (930)
	495 (1150)	496 (1160)	498 (1090)
	528 (810)	532 (800)	532 (690)
TPP	545 (45200)	556 (46500)	
9-PX	491 (17600)	490 (17100)	490 (16000)
PDDA	439 (35000)	445 (33600)	
BDPM	568 (44500)	573 (44300)	580
TPM	482 (29900)	487 (30300)	495 (28500)
		423 (15100)	
TpTM	491 (30200)	496 (27500)	
		445 (19300)	
p-BB	528 (64600)	525 (65000)	
DPM	441 (50600)	443 (50200)	
DoTM	445 (40300)	449 (50500)	
DXM	444 (35100)	445 (37700)	
PTX	378 (36400)		
p-MB	471 (35700)		

[a] Reference 5. [b] References 11 and 19. [c] Abreviations are as follows: 9-PhFl, 9-phenylfluorene; 3,4-BF, 3,4-benzfluorene; 1,2-BF, 1,2-benzfluorene; 9-BzFl, 9-benzylfluorene; 9-MeFl, 9-methylfluorene; 4,5-MP, 4,5-methylenephenanthrene; Fl, fluorene; 2,3-BF, 2,3-benzfluorene; 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. [d] 2-Phenylindene (2-PI) exhibited only an end absorbance in the 350–550 nm range. [e] In nm.

Table II. Equilibrium Acidity Data (25 °C)

entry	RH[a]	R'H	K	ΔpK^b
1	9-PhFl	2-PI	3.98	0.61 ± 0.02
2	9-PhFl	1,2-BF	52.5	2.02 ± 0.07
3	2-PI	1,2-BF	29.5	1.47 ± 0.08
4	3,4-BF	1,2-BF	4.32	0.64 ± 0.03
5	1,2-BF	9-BzFl	5.06	0.38 ± 0.09
6	1,2-BF	9-MeFl	41.0	1.30 ± 0.07
7	1,2-BF	4,5-MP	123	2.09 ± 0.07
8	9-MeFl	4,5-MP	1.96	0.59 ± 0.01
9	9-MeFl	2,3-BF	10.0	1.30 ± 0.02
10	Fl	4,5-MP	1.03	0.01 ± 0.01
11	Fl	2,3-BF	5.72	0.76 ± 0.01
12	4,5-MP	2,3-BF	5.01	0.70 ± 0.05
13	2,3-BF	9-t-BuFl	25.3	1.07 ± 0.03
14	9-t-BuFl	TPP	200	2.30 ± 0.07
15	TPP	9-PX	100	2.00 ± 0.04
16	TPP	PDDA	21.9	1.34 ± 0.06
17	PDDA	9-PX	4.17	0.62 ± 0.03
18	PDDA	BDPM	93.3	1.97 ± 0.05
19	9-PX	BDPM	21.4	1.33 ± 0.01
20	BDPM	TPM	15.5	1.19 ± 0.01
21	BDPM	p-BB	41.7	1.62 ± 0.01
22	TPM	DPM	100	2.00 ± 0.03
23	TPM	p-BB	2.45	0.39 ± 0.03
24	p-BB	TpTM	25.7	1.41 ± 0.06
25	p-BB	DPM	37.2	1.57 ± 0.01
26	TpTM	DPM	1.41	0.15 ± 0.01
27	TpTM	DoTM	9.33	0.97 ± 0.04
28	DoTM	DXM	6.17	0.79 ± 0.04
29	DXM	PTS	36.3	1.56 ± 0.08
30	DXM	p-MB	380	2.58 ± 0.04
31	PTS	p-MB	11.0	1.04 ± 0.12

[a] RH is the more acidic hydrocarbon. [b] On a per-hydrogen basis.

centrations. When other sources of error are also included, the accuracy of the pK_a values listed in the last column of Table II is estimated as ±0.1 pK unit. The precision of these values is somewhat better. The errors shown in the last column of Table II are standard deviations based on at least three determinations for each entry. The reproducibility of the ΔpK_a values is routinely better than ±0.1 pK unit. The validity of the results is also strongly reinforced by the internal consistency of the ΔpK_a values. In all cases where overlapping measurements occur, agreement between observed and calculated values is excellent. Any differences are within the combined experimental errors of the measurements.

To exclude the possibility of aggregation effects, equilibrium constants for several runs were determined over a five- to tenfold range of anion concentrations. In all cases, the equilibrium constants are essentially equivalent within experimental error. Thus, at these low concentrations, interpretation of the equilibrium constants is uncomplicated by possible aggregation effects,

Thermodynamic Constants. Several of the equilibria were studied as a function of temperature. The carbanion solutions were stable over the period of the measurements and repeated cycles of raising and lowering the temperature caused no significant change in the equilibrium constant at any one temperature. Measurements were made over a temperature range of about 45 °C, and the calculated equilibrium constants were corrected for the variation in the extinction coefficients of the carbanions with temperature. The results have also been adjusted to account for the changes in concentrations due to solvent contraction and expansion. The density of THF as a function of temperature was calculated from the equation[20]

$$d_{THF} = 0.880(1 + 0.001085[25 - T])$$

The corrected data were treated with DeTar's ACTENG computer program,[21] and the results were converted to the appropriate thermodynamic parameters. In all cases, satisfactory linear van't Hoff plots (log K vs. $1/T$) were obtained from a least-squares fit of the corrected data.

change in the position of maximum absorbance. Furthermore, in conjunction with the thermodynamic studies, the molar extinction coefficient was measured as a function of temperature. For each of the compounds listed, there is a small but significant increase in the molar extinction coefficient of the hydrocarbon anions as the temperature is lowered.

Equilibrium Measurements. Equilibrium constants were determined spectroscopically for reactions of the general type

$$RH + R'^-Cs^+ \rightleftharpoons R^-Cs^+ + R'H$$
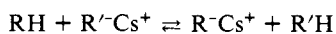
The results of these determinations are presented in Table II. Note that the equilibrium constants were calculated on the basis of concentrations rather than activities. This involves the simplifying assumption that the activity coefficient ratio for RH and R'H, and for their respective ion pairs, is unity. In view of the close structural similarity of the compounds studied, and the low concentrations employed (about 10^{-4} M), this assumption seems warranted.

In general, anion decomposition over the course of an acidity measurement was not a serious problem when air and moisture were rigorously excluded and when due regard was taken of solvent purity. The carbanion solutions were stable for at least several hours. The major source of error is most likely the extinction coefficient values used to convert absorbance readings to con-

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Table III. Thermodynamic Data for the Equilibria

$$RH + R'^-Cs^+ \rightleftarrows R^-Cs^+ + R'H$$

entry	RH[a]	R'H	ΔpK[b]	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, eu	$\Delta S°$,[c] eu
1	9-PhFl	2-PI	0.61	-1.7	-2.8	-1.4
2	3,4-BF	1,2-BF	0.64	-0.3	1.8	1.8
3	1,2-BF	9-BzFl	0.38	0.01	4.2	2.8
4	1,2-BF	9-MeFl	1.30	-0.5	5.3	3.9
5	9-MeFl	4,5-MP	0.59	0.25	2.2	3.6
6	9-MeFl	2,3-BF	1.30	-0.7	2.2	3.6
7	Fl	4,5-MP	0.01	-0.3	-1.8	-1.8
8	Fl	2,3-BF	0.76	-1.7	-2.7	-2.7
9	4,5-MP	2,3-BF	0.70	-1.2	-0.7	-0.7
10	2,3-BF	9-*t*-BuFl	1.07	-3.9	-6.8	-8.2
11	9-*t*-BuFl	TPP	2.30	0.5	10.9	12.3
12	TPP	9-PX	2.00	-5.8	-8.8	-10.2
13	TPP	PDDA	1.34	-5.4	-10.6	-12.0
14	PDDA	9-PX	0.62	-0.3	1.8	1.8
15	PDDA	BDPM	1.97	-0.1	8.5	8.5
16	9-PX	BDPM	1.33	0.15	6.6	6.6
17	BDPM	TPM	1.19	-1.5	-0.2	-0.2
18	BDPM	*p*-BB	1.62	-2.9	-3.9	-2.7
19	TPM	DPM	2.00	-3.4	-3.7	-2.3
20	TPM	*p*-BB	0.39	-1.1	-3.3	-1.9
21	*p*-BB	TpTM	1.41	-1.2	3.8	2.4
22	*p*-BB	DPM	1.57	-2.1	0.2	0.2
23	TpTM	DPM	0.15	-0.8	-3.4	-2.0
24	TpTM	DoTM	0.97	-1.7	-2.6	-1.2

[a] RH is the more acidic hydrocarbon. [b] On a per-hydrogen basis. [c] Value after the symmetry component is removed, in eu.[31]

The thermodynamic data recorded in Table III are in all cases the average obtained from 2–4 separate runs for each entry. Replicate measurements indicate a precision of about ±0.4 kcal mol^{-1} in the enthalpy and ±0.5 eu in the entropy. On the basis of several overlapping measurements of the thermodynamic parameters, we estimate the accuracy of the results to be generally better than ±0.6 kcal mol^{-1} in the enthalpy and ±1 eu in the entropy. The satisfactory agreement between observed and calculated values indicates that the data are of sufficient quality to allow a detailed interpretation of the results.

Discussion

It has been proposed by several investigators that the spectral shift in alkali-metal salts of organic compounds caused by a variation in solvent is related to the solvating power of that solvent,[22] Moreover, much evidence has accumulated to suggest that cation solvation effects greatly dominate anion solvation effects.[23] Since this should be particularly true for the extensively charge-delocalized anions listed in Table I, it is of interest to see what conclusions can be drawn regarding the relative solvating powers of THF, CHA, and DME.

From conductivity measurements and Stokes radii calculations on cesium tetraphenylborate, Smid and co-workers have presented evidence to suggest that DME is an effectively more polar solvent than THF.[23b] Other investigators have presented supporting data and have generally interpreted the results as being caused by the bidentate nature of DME.[24] The increase in solvent polarity on changing from THF to DME should result in a bathochromic shift

in the position of λ_{max} due to the enhanced stabilization of the more polar excited state of the ion pair. The results in Table I tend to support this expectation, but DME is also less basic than THF and the λ_{max} comparisons on the two solvents show considerable variations.

The positions of the absorption maxima in CHA and THF are also found to be similar in most cases. Significant hypsochromic shifts are found for several of the hydrocarbons. Most of the remaining compounds, except for 1,2-BF and *p*-BB, have maxima at the same or at slightly shorter wavelengths in THF. For 1,2-BF and *p*-BB bathochromic shifts of 7 and 3 nm, respectively, are observed on going from CHA to THF. On the whole, the data strongly suggest that CHA is effectively more polar than THF for electronic excitation of the cesium salts. Note that this is in the opposite order from that expected by consideration of molecular dipole moments and dielectric constants (THF: $\mu = 1.63$ D, $\epsilon = 7.39$; CHA: $\mu = 1.32$ D, $\epsilon = 4.5$) but is consistent with the concept that solvation by specific cation solvent interaction is of prime importance. Specifically, CHA is more basic but less polar than THF. Accordingly, variations in solvent effects are expected in the competition of solvent with delocalized carbanions or association with the cation.

The important work of Hogen-Esch and Smid has demonstrated the existence of two discrete types of ion pairs, termed solvent-separated (SSIP) or "loose" and contact (CIP) or "tight" ion pairs.[25] The relative proportions of these species is a function of such factors as substrate, gegenion, solvent, and temperature. Previous research showed that fluorenylcesium exists exclusively as a contact ion pair (CIP) in THF over the temperature range of 25 to −70 °C.[25a] Similarly, both fluorenylcesium and indenylcesium exist as CIP's in CHA and in a 2:1 CHA–diethylamine mixture.[26] Spectroscopic and NMR studies of triphenylmethylcesium and diphenylmethylcesium show that these salts exist as contact ion pairs in THF over a temperature range of 25

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Table IV. pK_a of Organic Indicator Acids[a]

indicator[b]	THF[c]	CHA[c]	Me$_2$SO[d]	DME[e]
9-PhFl	(18.49)	(18.49)	17.9	17.55
2-PI	19.10		19.4	
3,4-BF	19.90	19.75		
1,2-BF	20.54	20.35		
9-BzFl	20.92	21.27	21.4	20.95
9-MeFl	21.85	22.30	22.3	
Fl	22.41	23.04	22.9	22.3
4,5-MP	22.42	22.93	22.4	
2,3-BF	23.15	23.47	23.4	
9-*t*-BuFl	24.22	24.25	24.3	23.75
TPP	26.52	26.59	25.9	25.85
PDDA	27.86	28.01		
9-PX	28.50	28.49	27.7	
BDPM	29.83	30.17	29.4	27.7
TPM	31.02	31.45	30.60	29.3
p-BB	31.46	31.82		30.75
TpTM	32.86	33.04		
DPM	33.01	33.41		
DoTM	33.98	34.8		
DXM	35.80	36.3		
PTS	37.53			
p-MB	38.57	39.0		

[a] All pK values on a per-hydrogen basis. [b] See Table I for explanation of abbreviations. [c] pK_a values referenced to 9-PhFl at pK_a = 18.49 (ref 5). [d] pK_a values referenced to 9-PhFl at pK_a = 17.9 (ref 2). [e] pK_a values referenced to 1,1,3,3-tetraphenylpropene at pK_a = 25.25 (ref 3).

Table V. Solvent Effects on Relative pK Values

$$pK_{solvent} = slope \times pK_{THF} + intercept$$

solvent	slope	intercept	r^2
CHA	1.02	−0.265	0.999
Me$_2$SO	0.934	1.52	0.995
DME	0.999	−0.411	0.997

to −50 °C.[27] Conductometric studies in DME show that the cesium salts of 9-PX, TPM, 9-BzFl, 9-PhFl, and Fl are also contact ion pairs in this ether solvent.[3,11] All of these studies suggest that the cesium salts of extensively delocalized carbanions exist as CIP's in THF. Indeed, this was the primary reason for initiating our acidity studies with cesium ion rather than lithium, which tends to form complex mixtures of CIP's and SSIP's.[25,26]

Variable-temperature spectral studies in the temperature range of 25 to −20 °C confirmed that only contact ion pairs exist in THF. These studies were undertaken primarily in connection with the evaluation of thermodynamic quantities (vide supra), but the results have intrinsic interest. For each of the compounds listed, there is a small but significant change in the molar extinction coefficient as the temperature is changed. The possibility of a change in the nature of the ion pair as the temperature changes is precluded on the basis of the following evidence. In no case was there a change in the position of λ_{max} or of the appearance of any new peaks at low temperature. For spectra containing shoulders or several peaks, no isosbestic point appeared as the temperature was changed and only monotonic increases in all peak heights were observed. For example, the spectrum of fluorenylcesium was obtained at 15 °C intervals over the range 25 to −20 °C. At 25 °C, fluorenylcesium has an absorption maximum at 363 nm, ϵ = 12 700. These values are in good agreement with those previously reported: λ_{max} = 364 nm, ϵ = 12 000.[25a] As the temperature is lowered, the peak narrows and grows larger and the molar extinction coefficient increases. However, neither a shift in the position of λ_{max} nor the appearance of any new maximum is apparent over the entire temperature range. The weaker absorption bands in the visible region of the spectrum exhibit similar behavior. These observations are in complete accord with those reported by Hogen-Esch and Smid[25a] and verify that only one type of ion pair is present for fluorenylcesium in THF. The results are also in accord with changes in band envelopes expected from a change in occupation of vibrational and rotational levels.

The equilibrium constants shown in Table II were found not to change appreciably on varying the anion concentrations. In

favorable situations, an almost tenfold variation in the anion concentrations could be studied by our spectroscopic techniques. The independence of the ΔpK values to changes in anion concentrations constitutes additional strong evidence that ion-pair aggregation is not important at the concentration levels used in this work.

To facilitate discussion of the acidity data, it is convenient to construct a pK_{THF} scale from the relative measurements. Following our previous practice,[28] absolute acidities are assigned on the basis of a reference pK_{THF} for 9-phenylfluorene taken as 18.49.[29] The resulting pK_{THF} scale is shown in Table IV along with the corresponding values in several other solvents. Prior to this work, it was known that the acidity of the hydrocarbon acids which give highly delocalized anions shows a remarkable insensitivity to solvent effects.[2,3] The correlation between pK_{THF} and pK_A values in other solvents is summarized in Table V. Although the choices of the pK_{THF} reference is arbitrary, the value adopted has the unexpected but useful property that pK_{THF} and pK_{Me_2SO} values for these reference hydrocarbons differ generally by no more than 0.2–0.3 pK units. THF, DME, and CHA are nonpolar solvents in which the dissociation constants of hydrocarbon acid salts are uniformly small.[11,20,30] In contrast, Me$_2$SO is a polar organic solvent in which the carbanion salts are generally dissociated. In view of the marked difference in solvent properties, the correspondence of pK_a values shown in Table V is remarkable but fortunate. Structural change in highly delocalized carbanions clearly involves comparable effects toward ions in ion pairs as toward solvent dipoles. As a result, these compounds provide a valuable reference system for other types of carbanions.

Attention is now directed toward the thermodynamic constants obtained in this study. Prior to this work, little data regarding the thermodynamics of the transmetalation reaction have been available. Shatenshtein has presented some results in DME,[11] and our laboratory has contributed some data for solvent CHA.[10] These studies will be compared to our own results where appropriate.

First of all, it is interesting to compare the magnitudes of the enthalpy and entropy changes for the transmetalation reactions. With few exceptions, the enthalpy changes recorded in Table III are all rather small. Consequently, the entropy changes make an important contribution to overall free energy changes. In some cases, the TΔS is large enough to overcome an unfavorable enthalpy change. The enthalpy and entropy terms oppose each other in several other reactions such that the relative acidities of some pairs of acids reverse as a function of temperature. For example, at temperatures below −37 °C, DPM is more acidic than TpTM. At temperatures above 56 °C, *p*-BB becomes more acidic than TPM. For most cases, however, the acid pairs reverse strength only at temperature extremes.

Another interesting feature of the entropy values is the relatively large magnitude of the entropy term in several of the reactions that are presumably between contact ion pairs with little or no change in the solvation of the anion or cation. Because the correlation of the pK_a scales in different solvents shows excellent linearity with slopes near unity (Table V), solvation effects are considered to be negligible for reactions involving extensively delocalized contact ion pairs. On the basis of this hypothesis, one

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Table VI. Acidity Data for the Polyarylmethanes

$$RH + TPM^-Cs^+ \rightleftharpoons R^-Cs^+ + TPM$$

RH	ΔpK	$\Delta H°$, kcal/mol	$\Delta S°$, eu
TPP	-4.50	-7.1	-2.0
PDDA	-3.16	-1.6	8.7
9-PX	-2.52	-1.3	6.8
BDPM	-1.19	-1.5	0.2
p-BB	0.39	1.1	3.3
TpTM	1.84	2.4	0.4
DPM	2.00	3.4	3.7
DoTM	2.93	4.1	3.0

Table VII. Acidity Data for the Fluorenes

$$RH + Fl^-Cs^+ \rightleftharpoons R^-Cs^+ + Fl$$

RH	ΔpK	$\Delta H°$, kcal/mol	$\Delta S°$, eu
3,4-BF	-2.51	0.0	11.6
1,2-BF	-1.87	0.3	9.8
9-BzFl	-1.49	0.2	5.6
9-MeFl	-0.56	0.8	4.5
4,5-MP	0.01	0.4	1.9
2,3-BF	0.76	1.7	2.7
9-*t*-BuFl	1.81	5.6	9.5
TPP	4.11	5.1	-1.4

would initially expect rather small entropy differences. Indeed, thermodynamic studies for equilibrium among contact ion pairs in DME[11] and in CHA[10] have shown that the absolute magnitudes of the entropy values fall in the range of 0 to 6 eu. With a few exceptions, all of the entropy values for the reactions in THF fall within this range indicative of equilibrium involving similar types of ion pairing; that is, none of the entropy values approach the 20–30 eu range found for $\Delta S°$ between contact and solvent-separated ion pairs.[11,25] However, the presence of several equilibria with relatively high entropy values suggest that other effects may contribute importantly.

Examination of specific reactions shown in Table III suggests that some substituent effects are particularly significant. Consider the reaction of BDPM with PDDA (entry 15) and 9-PX (entry 16). NMR analysis of PDDA[31] and 9-PX[32] suggests that both molecules exist in a flattened boat conformation with the phenyl group occupying the pseudoaxial position. Thus, relatively free rotation of the phenyl group is possible because steric interactions of the ortho hydrogens of the phenyl ring with the adjacent peri hydrogens of the parent system are eliminated. However, upon formation of the respective anions, the central ring should become more planar to enhance conjugation of the anionic center; steric interactions are then increased, and the rotational barrier for the phenyl group becomes substantial. Thus, an overall lowering of the entropy of this system is exhibited upon formation of the anion. BDPM also displays a similar type of behavior except that in this case the rotational barrier increases for all three aryl substituents upon formation of the anion thus causing an even greater loss in entropy. That is, a significant portion of the overall entropy of reaction of BDPM with PDDA and 9-PX is probably caused by the differences in the loss of rotational entropy upon formation of the anions of the respective compounds.

That this result is general among polyarylmethanes is shown in Table VI in which some results are summarized in relation to TPM. When a diarylmethylcesium is allowed to equilibrate with a triarylmethane, the entropy generally decreases by 3–4 eu because of the restriction of rotation of the third aryl substituent of the triarylmethane derivatives. Entries 18–21 and 23 (Table III) confirm this hypothesis; the magnitude of this change in all cases is between 2 and 3 eu when the contribution caused by symmetry is removed from the experimental value for the entropies.[33] This rotational entropy effect has been used previously to explain why the methyl groups in DoTM are less acid weakening than the methyl groups in di-*p*-tolylmethane.[34] With use of several approximations, an entropy change of approximately 3 eu per aryl substituent was suggested. Indeed, the rotational barrier of lithium salt of diphenylmethane has been measured by ^{1}H NMR temperature studies in THF to be 10.9 kcal mol^{-1}.[35] Assuming that no phenyl rotation occurs in the anion, the tables of Pitzer and Gwinn[36] can be used to generate a maximum entropy value for

this reaction of about 3.0 eu. The magnitude of this value is in agreement with the results presented above. Finally, one would expect, based on this hypothesis, that the entropy of reaction between methane derivatives with the same number of aryl substituents would be close to zero. The equilibria among BDPM, TpTM, and TPM show this to be the case. Similarly, the reactions among *p*-BB, DoTM, and DPM, three diaryl-substituted methanes, also cause almost no change in the entropy.

More complicated is the interpretation of the large $\Delta S°$ values in the reactions involving TPP (entries 11–13). Internal restriction of rotation upon the formation of the anions cannot be supported in these reactions. Two of the phenyl groups in TPP are conjugated to the double bond of the propene unit thus causing a significant barrier to rotation of these phenyl groups. The third phenyl group is relatively free to rotate. However, upon formation of the anion, the third phenyl is now conjugated to the allyl anion causing a restriction of rotation. Thus, in TPP, the rotation of one phenyl group is restricted in the anion. If this were the only effect operating in the reactions of TPP with PDDA or 9-PX, the entropy of the reaction would be near zero because of the cancellation of the restricted internal rotation effect that occurs in both compounds in the reaction. However, the magnitude of the entropy for these equilibrium reactions is the highest in the table.

To account for this behavior, we can invoke the possibility that TPP is an externally solvated contact ion pair, a discrete species distinct from unsolvated contact ion pairs. Experimental evidence for this third type of ion pair is limited, but spectroscopic studies of the potassium salt of 1,3-diphenyl-1-butene show that this ion pair exists as an externally solvated contact ion pair at temperatures from -50 to 25 °C.[37] Conductivity studies in DME of the cesium salts of 1,1,3,3-tetraphenylpropane by Shatenstein show behavior that is intermediate between unsolvated contact ion pair and solvent-separated ion pairs.[11] TPP, a structurally similar molecule to the above-mentioned compounds, may also exhibit the same type of behavior. Indeed, the magnitude of the entropy for reaction involving TPP is intermediate between reaction involving only contact ion pairs and reactions involving a contact ion pair going to a solvent-separated ion pair.

Thus, measurement of the entropy of reaction between ion pairs may be a useful method to detect the existence of externally solvated contact ion pairs. Buncel et al. have previously concluded, based on the position of λ_{max} in various solvents, that diphenylmethylcesium exists as an externally solvated contact ion pair in THF while triphenylmethylcesium exists solely as an unsolvated contact ion pair over a temperature range of -50 to 25 °C.[38] Therefore, as in the case of reactions involving TPP, one would expect a large entropy value for the equilibrium reaction of TPM and DPM. However, the entropy for this reaction is -2.3 eu, too small to account for a change in ion pairing in the reaction. Our results show that the cesium salt of diphenylmethane exists solely as a contact ion pair in THF with no special solvation.

The fluorenyl systems show a more complex entropy behavior; entropies relative to fluorene itself are summarized in Table VII. It is interesting to note that all 9-substituted fluorenes show an increase in entropy upon formation of the anion. Furthermore, the entropy values measured for the reaction of the benzfluorenes

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with fluorene are inexplicably large. Obviously, rotational entropy is not important for these planar systems. Anion aggregation was also found not to be important for these reactions, and this conclusion is supported by kinetic studies.[39]

Another anomalous reaction is the equilibrium between 2,3-BF and 9-*t*-BuFl (entry 10 in Table III). A rotational entropy effect is one possible explanation for the large entropy value. The sign of the entropy term is such that a decrease in entropy is attendant with the protonation of the 9-*t*-BuFl anion. That is, the bulky *tert*-butyl group appears to undergo freer rotation in the absence of the 9-hydrogen. However, this analysis is complicated by the presence of the ring peri-hydrogens, which may inhibit rotation of the *tert*-butyl group in both the hydrocarbon and anion. Indeed, measurements of the equilibrium between 2,3-BF and 9-*t*-BuFl in CHA yield a $\Delta S°$ value of -0.6 ± 0.2 eu,[10a] a value a full order of magnitude lower than that obtained in THF. For comparison, the reaction between 2,3-BF and 9-MeFl gives $\Delta H° = 0.70$ kcal mol^{-1} and $\Delta S° = 2.2$ eu in THF and $\Delta H° = 0.74$ kcal mol^{-1} and $\Delta S° = 0.7$ eu in CHA. Apparently, some type of solvent effect is operative in the case of the *tert*-butyl compound, although the nature of this effect is unclear at present.[40]

Another aspect of the thermodynamic data deserves attention. Studies in both ionizing and non-ionizing solvents consistently reveal that 9-methylfluorene is a stronger acid than fluorene. This result is not expected on the basis of solution-phase inductive effects, and several explanations have been proposed to account for the anomaly.[41] In particular, we had earlier interpreted the result in terms of the difference in σ bond strengths resulting from the hybridization changes $C_{sp3}-C_{sp3}$ to $C_{sp3}-C_{sp2}$ for 9-MeFl compared to $C_{sp3}-H$ to $C_{sp2}-H$ for Fl.[34] For the reaction

$$Fl^-Cs^+ + 9\text{-MeFl} \rightleftharpoons Fl + 9\text{-MeFl}^-Cs^+$$
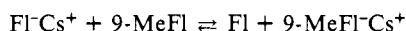
the values in Table VII show that $\Delta H° = 0.8$ kcal mol^{-1} and $\Delta S° = 4.5$ eu. At 25 °C the entropy contribution $T\Delta S$ is then 1.3 kcal mol^{-1}; that is, the greater acidity of 9-MeFl is not a consequence of the enthalpy of reaction (which should be indicative of changes in bond strength) but rather the entropy of reaction. This example clearly demonstrates the value of thermodynamic measurements in the elucidation of the factors determining relative acidities and will hopefully encourage more work in this area.

Experimental Section

General. Starting materials for syntheses were obtained from commercial suppliers and were purified by recrystallization or distillation prior to use. Melting points (Pyrex capillary) were determined on a Buchi melting point apparatus and are uncorrected. Proton nuclear magnetic resonance (¹H NMR) spectra were determined with either a Varian EM-390 spectrometer or the UCB-250 (a superconducting 250-MHz instrument) operating in the FT mode. Chemical shifts are expressed as parts per million downfield from tetramethylsilane (internal standard). Vapor-phase chromatography (VPC) was performed on a Hewlett-Packard 5880 gas chromatograph with a 6 ft × ¹/₈ in. OV-101 column. All anion spectra were recorded on a Cary 118 UV–visible spectrometer fitted with a thermostated cuvette holder designed to accommodate cells of 1 mm path length. Variable-temperature studies made use of a Neslab RTE-4 refrigerated recirculating bath.

Carbon Acids. Most of the hydrocarbon acids used in this work were already available from our previous studies in CHA; those that were not were synthesized according to published procedures. When warranted, the compounds were further purified by multiple recrystallizations followed by vacuum sublimation. The purity of the indicator acids was ascertained by one or more of the following techniques: melting point, TLC, ¹H NMR, VPC, and elemental analysis.

2-Indanone.[42] In a three-necked flask equipped with an addition funnel, mechanical stirrer, and thermometer, 160 mL of 97% formic acid and 35 mL (0.34 mol) of 30% hydrogen peroxide were combined. The flask was immersed in a water bath and heated to 35 °C. The addition
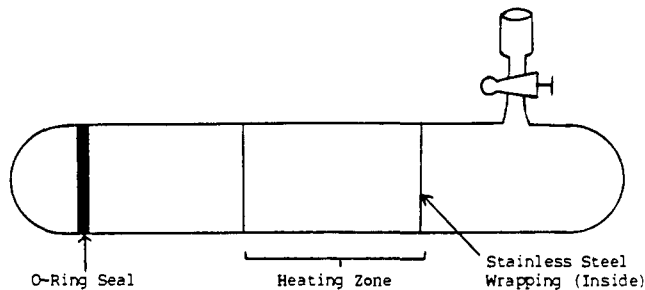

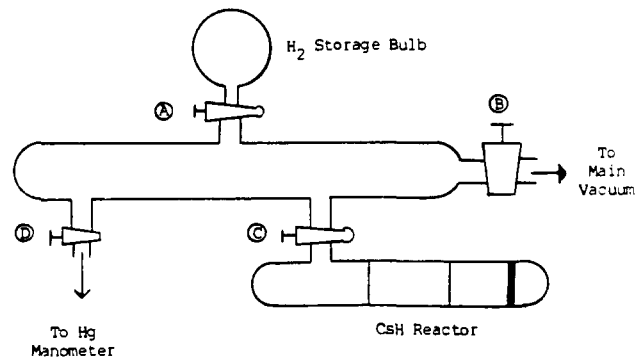Figure 1. Cesium hydride reactor.

Figure 2. Cesium hydride reaction apparatus.

funnel was charged with 29.4 mL (0.25 mol) of indene, and the indene was slowly added over a 0.5-h period with the reaction being kept in the 35-40 °C range. On complete addition, the reaction was vigorously stirred an additional 7 h. The formic acid was removed by vacuum distillation, and the pasty, brown residue was added to 500 mL of boiling 7% aqueous sulfuric acid. The mixture was steam distilled, and the product was collected in a Buchner funnel and dried overnight in a vacuum oven. Recrystallization from alcohol gave 13.72 g (42%) of a white, crystalline solid: mp 52-53 °C (lit.[43] mp 57-58 °C); ¹H NMR (CDCl₃) δ 7.2 (d, $J = 4$ Hz, 4 H), 3.6 (2,4 H).

2-Phenylindene. 2-Indanone (0.690 g, 5.20 mmol) in 25 mL of THF was added slowly to a solution of phenylmagnesium bromide (from 1.74 g of bromobenzene and 0.265 g of Mg metal) in 20 mL of THF. The solution was stirred overnight and hydrolyzed with 30 mL of saturated aqueous ammonium chloride. The reaction was diluted with 100 mL of water, and the product was extracted with ether. After workup, the crude product consisted of a viscous oil which was added directly to 50 mL of 20% aqueous sulfuric acid. The solution was refluxed for 3 h, cooled to room temperature, and taken up in ether. The ethereal extract was washed with water, 10% NaHCO₃, water, and brine. After the mixture was dried (MgSO₄), the ether was removed by rotary evaporation and the residue was chromatographed on silica gel (CH₂Cl₂ eluent). The first component to come off the column was collected and recrystallized from acetone, yielding 0.378 g (38%) of 2-phenylindene as a white, lustrous solid: mp 161.5-162 °C (lit.[44] mp 167.5-168 °C); ¹H NMR (CDCl₃) δ 7.2-7.8 (m, 10 H), 3.8 (s, 2 H).

Bases and Solvent. Cesium Hydride. The method and apparatus employed in the synthesis of cesium hydride was a slight modification of that given by Gunn.[17b] The cesium hydride reactor is shown in Figure 1, and the experiental setup is illustrated in Figure 2. The reactor was constructed of Pyrex glass and was equipped with an O-ring joint on one end through which reagents could be introduced and the product removed. The other joint was a standard taper 24/40 female joint equipped with a vacuum stopcock and was used to mount the reactor onto the vacuum system. A thin sheet of stainless steel was wrapped around the inside of the reactor; the area covered by the steel wrap is referred to as the heating zone. The outside of the heating zone was tightly wrapped with nichrome wire, and the measurement arm of a Cu–constantin thermocouple wire was placed flush against the outside of the glass in the middle of the heating zone. The entire length of the heating zone was insulated with several layers of asbestos paper, glass wool, and aluminum foil.

In an argon-filled glovebox, 5.27 g (39.7 mmol) of cesium metal (Atomergic Chemetal, 99.97% pure) was placed in a small, rectangular

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(40) One referee suggests that the results may be rationalized by perturbation of the cesium solvation sphere by the *tert*-butyl group in the ion pair.

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stainless steel dish and the dish was placed in the reactor in the middle of the heating zone. The reactor was tightly sealed at the O-ring joint, removed from the glovebox, and mounted on the vacuum system. The entire system was evacuated to a pressure of ca. 10^{-3} mm and flushed with an atmosphere of hydrogen gas. After the system was reevacuated, stopcock B was closed and hydrogen gas (Matheson, 99.99%) was admitted until the manometer registered a pressure of about 600 mm. From the previously calibrated volume of the reactor and vacuum system, the amount of H_2 in the reactor was calculated to be 32.3 mmol (1.6 equiv). Stopcock C was then closed, and stopcock B was opened to remove the residual hydrogen. The ends of the nichrome wire were connected to a variac, and heating was initated. The reaction was kept in the temperature range 450–500 °C (the temperature should be carefully monitiored as it is dangerous to heat too much above 500 °C). After 44 h, stopcock B was closed and C was opened. The final manometer reading (79 mm) corresponded to an H_2 uptake of 22.4 mmol (1.1 equiv). The entire system was then evacuated by opening stopcocks B and C. With stopcock C closed, the reactor was removed from the vacuum line and brought back into the glovebox. The product was removed through the O-ring joint and consisted of a white crystalline solid which tended to clump together in cotton-like balls. Some of the clumps were slightly discolored grey, indicating the presence of free cesium metal. The clumps which were most discolored were discarded. The remainder of the material (3.85 g, 72%) was transferred to a vial and stored in the glovebox.

Triphenylmethylcesium. (Note: the following preparation was conducted in a glovebox.) To a solution of 0.756 g (3.09 mmol) of triphenylmethane in 21.83 mL of THF was added in one portion 0.501 g (3.74 mmol, 1.2 equiv) of CsH. The addition was accomplished by a vigorous gas evolution which subsided after several minutes. After 7 days, the dark red solution was decanted onto a fresh portion of hydride. This procedure was repeated twice more at 7-day intervals. The solution was filtered and assayed by visible spectroscopy and by titration with 9-phenylfluorene and fluorene.

α-Cumyl Alcohol.[45] Into a three-necked, round-bottomed flask fitted with a reflux condenser, dropping funnel, and a mechanical stirrer all flamed out under a nitrogen purge and kept under nitrogen was placed 5.31 g (0.221 mol) of crushed Mg turnings that were oven-dried for at least 24 h. About 50 mL of dry ether and 2.10 g (0.0194 mol) of 1,2-dibromoethane were added. After the reaction had begun, about 650 mL of ether was quickly added and the solution was brought to reflux. Bromobenzene (31.3 g, 0.199 mol) in 150 mL of ether was slowly added over a period of 4 h. The resulting solution was refluxed and stirred overnight. Dry acetone (12.2 g, 0.210 mol) in 50 mL of ether was then added over 30 min. The resulting mixture was refluxed and stirred for 3 h. The reaction mixture was cooled to room temperature and quenched with 100 mL of a saturated aqueous solution of ammonium chloride. The ether layer was washed with water and then brine and dried over $MgSO_4$. The solvent was removed by roto-evaporator to give a viscous yellow liquid which was vacuum distilled (bp 66 °C (1 mmHg)) and recrystallized in methanol to give a low-melting white solid (16.5 g, 61%): mp 30–31 °C; ^1H NMR (CDCl$_3$) δ 1.52 (s, 6), 2.08 (s, 1), 7.31 (m, 5). Anal. C, H.

2,3-Dimethyl-2,3-diphenylbutane.[46] Titanium trichloride (9.24 g, 0.061 mol) was weighed in a glovebag filled with nitrogen and placed in a 300-mL, three-necked, round-bottomed flask containing 250 mL of dry, degassed THF. Lithium aluminum hydride (LAH, 0.763 g, 0.021 mol) was quickly added to the vigorously stirred TiCl$_3$ slurry in THF. Some gas evolution was evident as the solution turned black. The mixture was stirred for 10 min and then removed from the glovebag, fitted with a reflux condenser and dropping funnel, and kept under positive nitrogen pressure. α-Cumyl alcohol (2.72 g, 0.020 mol) in 20 mL of THF was added over 20 min, and the resulting mixture was refluxed overnight. After the reaction mixture was cooled to room temperature, it was

carefully quenched with several drops of 5% aqueous HCl (some gas evolution occurred). The mixture was extracted with ether, washed with water and brine, and dried over $MgSO_4$. The solvent was removed by roto-evaporator to give a yellow solid which was washed with cold acetone, recrystallized in benzene/hexane, and sublimed (70 °C (10 μmHg)) to yield 2.09 g (92%) of a white solid: mp 118–119 °C (lit.[46] mp 118–119 °C); ^1H NMR (CDCl$_3$) δ 1.25 (s, 12), 7.10 (m, 10). Anal. C, H.

Cumylcesium. Stock solutions of cumylcesium were prepared by dissolving the appropriate amount of 2,3-dimethyl-2,3-diphenylbutane (bicumyl) in THF and adding a stoichiometric amount of cesium metal. A red color formed immediately on the surface of the metal. Occasional shaking over 2 h yielded a dark red solution which gave a visible spectrum (λ_{max} = 344 nm) consistent with literature (λ_{max} = 338 nm for cumylpotassium[14a]). Also, the reaction of cumene with cesium hydride gives the same visible spectrum. These solutions decompose over time to give a yellow solution of unknown composition with λ_{max} = 398 nm.

Dicesium Tetraphenylethylene. This compound was prepared by J. Swanson from cesium metal and tetraphenylethylene in THF.[18] The sparingly soluble cesium salt was obtained by filtration of the reaction mixture.

Tetrahydrofuran. Several methods were explored for the purification of THF. Optimum results were obtained by using the following procedure:

A commercial sample of reagent grade solvent was predried by refluxing over CaH$_2$ for 24 h. The solvent was distilled under an inert atmosphere into a long-necked flask containing several grams of lithium aluminum hydride. The flask was connected to a vacuum system via an O-ring seal, and the contents were degassed by the freeze–thaw method. The flask was then closed off from the vacuum and the contents were stirred for 24 h. The solvent was then vacuum transferred onto a small portion of Na–K alloy, and this mixture was stirred until a blue color developed. A final vacuum transfer of the solvent into a clean flask which had previously been flamed out under vacuum was performed, and the solvent was thoroughly degassed by several freeze–thaw cycles. The dried solvent was stored in a glovebox.

Equilibrium Measurements. The procedures used in the present study have been adequately described elsewhere.[26,47] Thermodynamic parameters were obtained by using these procedures at 5–10 °C intervals over a temperature range of −20 to 25 °C. At each temperature, the ion-pair concentrations were determined directly from the absorbance readings by application of Beer's law, and an equilibrium constant was calculated. A linear least-squares plot of log K vs. $1/T$ was obtained by using a modified version of DeTar's ACTENG computer program.[21] The thermodynamic parameters were subsequently determined.

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