

greater driving force for the reaction.

Often in chemistry nearly identical reactivities have nearly identical underlying explanations. This apparently is not true for the reactions of alkenes with Cu^+ and with other transition-metal ions (Fe^+ , Co^+ , Ni^+). Research is under way to understand the unusual reactivity of Cu^+ .

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Equilibrium Ion Pair Acidities in Tetrahydrofuran of Benzylic Carbon Acids Stabilized by an Adjacent Cyano, Carboalkoxy, and Sulfonyl Substituent. Delocalization and Aggregation of Ion Pairs¹

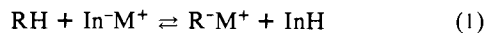
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Carbon acids containing stabilizing groups at the α -position constitute an important class of synthetically useful reagents. Equilibrium ionic acidities are known for many of these compounds, especially in dimethyl sulfoxide solution, in large part through the work of Bordwell and his research group.² Nevertheless, many synthetic applications make use of ether, and particularly tetrahydrofuran (THF), solutions in which the carbanions are present wholly as ion pairs. Moreover, a number of lithium salts of such carbanions have been shown to be aggregated in THF solution.³ Accordingly, important questions concern the relevance of ionic acidities to the effective acidities in THF solution and of the role of ion pair aggregation in such compounds. In this paper, we present results concerning equilibrium acidities and thermodynamic parameters for transmetalation reactions in THF for a related group of *benzylic carbon acids* containing a cyano, carboalkoxy, or sulfonyl substituent and draw significant conclusions regarding the state of aggregation and type of ion pairing of these carbanion systems.

The positions of transmetalation equilibria (eq 1) were deter-



mined spectroscopically by using hydrogen indicators InH of known^{4,5} pK_a values in THF. The experimental procedure followed those published previously from this laboratory.⁴⁻⁶ Results are summarized in Table I. Note that in most cases it was possible to use more than one indicator to measure the acidity of each carbonyl derivative RH. The data in Table I reveal that the pK_a assignments are independent of the indicator used, and this internal

Table I. Acidity Data for Phenylacetonitrile (1), (*p*-Methoxyphenyl)acetonitrile (2), *tert*-Butyl Phenylacetate (3), and Benzyl Phenyl Sulfone (4), 25.0 °C in THF

cmpd	indicator ^a	<i>N</i> ^b	$10^4[\text{R}^-\text{M}^+]^c$	pK_a
Lithium Cation				
1	9-PhFl	5	1.05-6.40	18.60 ± 0.03
	1,2-BF	4	6.30-22.2	18.66 ± 0.04
2	9-PhFl	4	1.34-3.04	20.16 ± 0.05
	1,2-BF	5	4.90-17.4	20.17 ± 0.03
3	9-PhFl	10	0.634-9.96	19.61 ± 0.10
4	Bza	4	1.35-6.49	20.45 ± 0.03
	1,2-BF	3	5.95-14.0	20.41 ± 0.02
Cesium Ion ^d				
1	4,5-MP	6	1.02-24.0	22.99 ± 0.06
	Fl	3	11.5-14.0	23.02 ± 0.04
2	DBF	5	0.449-2.54	24.82 ± 0.04
	2,3-BF	5	1.71-7.74	24.85 ± 0.03
3	9-MeFl	3	1.25-4.36	24.15 ± 0.08
	2,3-BF	5	2.76-6.59	24.14 ± 0.05
4	Fl	8	4.62-38.5	24.12 ± 0.08
	4,5-MP	3	6.43-14.8	23.33 ± 0.05
4	2,3-BF	6	3.05-7.94	23.34 ± 0.03

^aIndicator anion for measurement: 9-PhFl, 9-phenylfluorene; 1,2-BF, 1,2-benzofluorene; Bza, benzanthracene; 4,5-MP, 4,5-methylene-phenanthrene; Fl, fluorene; DBF, 2,3:6,7-dibenzofluorene; 2,3-BF, 2,3-benzofluorene; 9-MeFl, 9-methylfluorene. Spectral data and equilibrium acidity assignments for these indicators are contained in ref 4 and 5. pK_a values are relative to an assigned value of 18.49 for 9-phenylfluorene. ^bNumber of measurements. ^cEquilibrium carbanion concentration in M. ^dResults include an upward correction of 0.8 unit in the pK_a 's of these indicators from previously published values (ref 4); Kaufman, M. J., Gronert, S., results to be published.

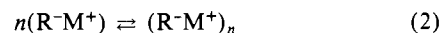
Table II. Thermodynamic Values for Equilibrium 1^a

cmpd	egeion			
	Li ⁺		Cs ⁺	
	ΔH°	ΔS°	ΔH°	ΔS°
1	-4.1	8.6	-2.7	-4.0
2	-1.0	11.3	0.0	-3.2
3	-6.1	-2.9	-1.6	-5.3
4	0.2	15.0	1.5	7.8

^aUnits are kcal mol⁻¹ for ΔH° and eu for ΔS° . Estimated errors are ± 0.5 kcal mol⁻¹ for ΔH° and ± 1 eu for ΔS° .

consistency constitutes our best evidence that the equilibria 1 are not being perturbed by side reactions involving addition of the carbanions to substrates.

It is particularly important that the substrate carbanion concentrations could be varied by factors of 10-40 without affecting the pK_a values. When aggregation occurs, the additional associative equilibrium 2 has the effect of "pulling" equilibrium 1 to



the right, which results in pK_a values that show a concentration dependence. It can be readily shown that K_{expl} is proportional to $[\text{R}^-\text{M}^+]_{\text{expl}}^{(n-1)/n}$. For example, if the equilibrium actually involves dimers, a 4-fold concentration change in $[\text{R}^-\text{M}^+]_{\text{expl}}$ will give a 2-fold change in K_{expl} or a change in apparent pK of 0.3. The lack of a concentration dependence in the present examples unambiguously demonstrates that these benzylic carbanions exist exclusively as monomeric ion pairs in dilute THF solution. This result is in contrast to the behavior of more localized non-benzylic carbanion derivatives which form aggregated ion pairs in ethereal solutions.^{3,6} Note particularly that the lithium salts of phenylacetonitrile⁷ and benzyl phenyl sulfone⁸ are dimeric in the crystal state. The present results provide a useful demonstration that the structures of organolithium compounds in solution are not necessarily the same as structures in the crystal.

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We conclude that the degree of association of carbanion ion pairs in nonpolar solvents is highly dependent upon the extent of charge delocalization; the anionic charge in benzylic carbanion ion pairs is sufficiently delocalized that the electrostatic stabilization provided by aggregate formation is insufficient to overcome the resultant unfavorable entropy of association. It is notable that the substitution of a strongly electron donating *p*-methoxy group into phenylacetonitrile has the expected acid-weakening effect but did not lessen the degree of charge delocalization to an extent where aggregate formation could be observed.⁹

Standard enthalpies and entropies of reactions obtained by studying eq 1 as a function of temperature are summarized in Table II. The indicator used in this study was 2,3:6,7-dibenzo-fluorene (DBF). DBF was chosen because its lithium and cesium salts are known to exist exclusively as solvent-separated and contact ion pairs, respectively, in THF.^{4,5} Table II shows that the formation of the lithium salts is generally accompanied by a net entropy increase of 9–15 eu, whereas for the cesium benzylates an entropy decrease of ca. 4 eu is usually observed; exceptions to this generalization are exhibited by the lithium enolate of *tert*-butyl phenylacetate and the cesium salt of benzyl phenyl sulfone. The data for the remaining compounds are consistent with both the lithium and cesium salts existing as contact ion pairs. The large positive entropy changes exhibited by the lithium salts are then a consequence of the releasing of solvating THF molecules as the solvent-separated indicator anion is protonated and the carbanion contact ion pair is formed.¹⁰ Highly delocalized carbanions tend to form solvent-separated ion pairs with lithium as gegenion in THF.¹¹ Thus, the formation of monomeric contact lithium benzylate ion pairs demonstrates that *contact-solvent separated and monomer-aggregate equilibria have different dependencies on the degree of carbanion delocalization*.

The reactions with cesium cation involve only contact ion pairs and are expected to show entropy changes near zero. However, formation of a benzylic carbanion is accompanied by the restricted rotation of a conjugating aryl group, resulting in a small net decrease in entropy.¹² Note that this factor also makes the lithium ΔS° values less positive than they would otherwise be. The small negative entropy change observed in the reaction of *tert*-butyl lithiophenylacetate probably results from additional restrictions on the motions of the conjugating ester group in the carbanion. The large positive entropy change for the formation of the cesium salt of benzyl phenyl sulfone is particularly striking and suggests a reduced solvation of the cation because of the chelating effect of the negative sulfone oxygen atoms. Note that the same effect seems manifest with the lithium salt and is also suggested by recent molecular orbital calculations.¹³

Finally, note that the THF ion pair pK_a values are relative values based for convenience on an assigned value of 18.49 to 9-phenylfluorene. With this assignment, the cesium ion pair pK_a values are numerically in close agreement with acidity measurements under free ion conditions in dimethyl sulfoxide solution:² phenylacetonitrile, 22.2; *tert*-butyl phenylacetate, 23.9; benzyl phenyl sulfone, 23.4. However, contact ion pairs with lithium cation are less dissociating than those with the larger cesium cation, and, accordingly, lithium ion pair pK_a 's of these benzylic systems are 3–5 pK_a units more acidic (relative to the 9-phenylfluorenyllithium solvent-separated ion pair standard) than the cesium pK_a or ionic pK_a values.

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Variable-Pressure Study of a Molybdenum(III) Reaction: First Definitive Evidence for the Associative Nature of Complex Formation on Hexaaquamolybdenum(III)

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Kinetic studies of substitution reactions on transition-metal aqua cations have been subject to a renewed interest especially since kinetic evidence was found for a changeover in the mechanisms of water exchange along the first-row transition-metal series.³ This gradual trend was also subsequently seen for monocomplex formation reactions of divalent cations of the same series.⁴ For the second-row transition-metal series, Mo³⁺ (d³) is, at present, the only monomeric aqua ion of an early element available for such a kinetic study. Unfortunately, the water exchange rate on Mo(H₂O)₆³⁺ is not accessible (it appears too slow to be followed using the Swift–Connick ¹⁷O NMR line-broadening approach and too fast for isotopic labeling techniques) and one is forced to turn toward complex formation reactions.

Rate constants for 1:1 anation on Mo(H₂O)₆³⁺ highly depend upon the incoming ligand.^{5–7} The values, including recent results on an inner sphere reaction with molecular oxygen,⁸ cover almost 5 orders of magnitude (Table I), implying an associative mode of activation. The preparation of several seven-coordinate Mo³⁺ complexes has been reported.^{9–11}

We now report the results from a variable-temperature and pressure study of the 1:1 NCS[−] anation reaction on Mo(H₂O)₆³⁺, a well-characterized reaction, proceeding to completion.⁵ Solutions of Mo(H₂O)₆³⁺ in triflic (trifluoromethanesulfonic) acid were prepared and characterized as described previously.⁷ A 10-fold excess of Mo³⁺ over NCS[−] concentration ensured pseudo-first-order conditions and monocomplex formation. The acid concentration was fixed at 0.98 M with triflic acid (no acid dependence is observed) and the ionic strength at 1.00 M (lithium triflate). The UV spectrum of the 1:1 thiocyanato complex shows a well-resolved charge-transfer band at 303 nm (ϵ 2170 M^{−1} cm^{−1}). This band suggests N bonding of the NCS[−] group.⁵ The reaction was studied at 320 nm. The temperature range covered in the previously reported study (298.1–313.5 K)⁵ was extended downward to 283.0 K, to include the temperature at which the variable-pressure experiments would be performed. A double-beam Perkin-Elmer 340 spectrophotometer equipped with thermostated cells was used. The variable-pressure work was carried out up to 140 MPa at 285 K, a temperature at which the time required for the preparation of samples, their introduction into the pressure vessel, and thermostating at the desired pressure (ca. 15 min) limited the loss to only one-half of the starting material at most. The high-pressure optical cell was designed and built in Lausanne.¹² It is small enough to fit into the sample compartment

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