Equilibrium Caesium Ion Pair Acidities in Tetrahydrofuran

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Equilibrium acidities for contact ion pair caesium salts of delocalized carbanions are reported for tetrahydrofuran and are similar to values in other solvents.

Quantitative and semi-quantitative equilibrium acidity scales have been established for weak carbon acids in several solvents, including cyclohexylamine (CHA),[1] dimethoxyethane (DME),[2] and dimethyl sulphoxide (DMSO).[3] In contrast, relatively few data are available concerning equilibrium acidities in tetrahydrofuran (THF) solution, despite the common use of this solvent for carbanion reactions.[4] We report a scale of hydrocarbon acidities in THF spanning a range of over 16 pK_a units.

The relative acidities of hydrocarbon acid pairs have been evaluated by spectroscopic determination of the equilibrium constant for the reaction (1). Spectral studies were conducted

$$XH + Y^-Cs^+ \rightleftharpoons X^-Cs^+ + YH \qquad (1)$$

in the visible and near-u.v. region at equilibrium carbanion concentrations of the order of 10^{-3}—10^{-4} M. Studies with varying concentrations and data from other laboratories[5] show that at these low concentrations alkali metal salts of highly delocalized carbanions exist predominantly in the form of monomeric contact ion-pairs. The caesium salts were prepared generally by reaction of the hydrocarbons with caesium hydride[6] or by reaction with cumylcaesium. The results are, therefore, free of complications arising from ion-pair aggregation and/or subsidiary equilibria involving solvent-separated ion-pairs or other caesium salts, and provide an accurate measure of intrinsic relative acidity in THF solution.

The relative hydrocarbon acidities have been placed on an absolute basis by assigning a pK_a to 9-phenylfluorene of 18.49.[7] The resulting scale is given in Table 1 together with values determined in CHA, DMSO, and DME. Note that for

Table 1. pK_a of organic indicator acids.[a]

Compound[b]	THF[c]	CHA (ref. 1)	DMSO (ref. 3)	DME[e] (ref. 2)
9PhFl	(18.49)[d]	(18.49)[d]	17.9	17.55
2PI	19.10		19.4	
3,4BF	19.90	19.75		
1,2BF	20.54	20.35		
9BzFl	20.92	21.27	21.4	20.95
9MeFl	21.85	22.33	22.3	
Fl	22.41	23.04	22.9	22.3
4,5MP	22.42	22.93	22.7	
2,3BF	23.15	23.47	23.5	
9tBuFl	24.22	24.25	24.3	23.75
TPP	26.52	26.59	26.2	
PDDA	27.86	28.01		
9PX	28.50	28.49	27.7	27.7
BDPM	29.83	30.17	29.4	29.3
TPM	31.02	31.45	30.6	30.75
pBB	31.43	31.82		
TpTM	32.86	33.04		
DPM	33.01	33.41	32.6	
DoTM	33.95	34.80		

[a] The pK values are estimated to be accurate to ±0.1 pK units and are statistically corrected to refer to a per-H basis (ref. 1c). [b] Abbreviations are: 9PhFl, 9-phenylfluorene; 2PI, 2-phenylindene; 3,4BF, benzo[*c*]fluorene; 1,2BF, benzo[*a*]fluorene; 9BzFl, 9-benzylfluorene; 9MeFl, 9-methylfluorene; 4,5MP, 4,5-methylenephenanthrene (4*H*-cyclopenta[*def*]phenanthrene); Fl, fluorene; 2,3BF, benzo[*b*]fluorene; 9tBuFl, 9-t-butylfluorene; TPP, 1,1,3-triphenylpropene; PDDA, 9-phenyl-10,10-dimethyldihydroanthracene; 9PX, 9-phenylxanthene; BDPM, *p*-biphenylyldiphenylmethane; TPM, triphenylmethane; pBB, *p*-benzylbiphenyl; TpTM, tri-*p*-tolylmethane; DPM, diphenylmethane; DoTM, di-*o*-tolylmethane. [c] At 25 °C. [d] Assumed value to set the scale in absolute terms related to aqueous conditions (ref. 1c). [e] Referred to 1,1,3,3-tetraphenylpropene with an assumed value of 25.25 (statistically corrected).

Table 2. Correlation of pK scales.

pK(solvent) = (slope) × pK_{THF} + (intercept)

Solvent	Slope	Intercept	r^2
CHA	1.02	−0.307	0.999
DMSO	0.941	1.42	0.996
DME	0.999	−0.412	0.997

these hydrocarbon acids that yield highly delocalized anions, an excellent correlation exists between the relative pK_a values in THF and in the other solvents (Table 2). Of particular interest is the close correspondence between ionic acidities in DMSO and ion-pair acidities in the ether and amine solvents.

The remarkable independence of the acidities shown in Table 1 to solvent changes has been noted in the past.[1c,8] These delocalized carbanions form an ideal background reference to which other types of carbon acids can be compared in different solvents for the identification of specific solvent ion pairing and aggregation effects.

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