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Comparisons of Ion Pair Acidities of Some Acidic Carbon Acids[1]

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In the course of determining proton transfer equilibria of a number of ketones and amines, we determined the ion pair acidities of several relatively acidic carbon acids in THF. Some of these acidic indicators have been found recently to form proton transfer ion pairs with some amines in THF and have led to the corresponding relative ion pair amine basicities that differ significantly from the ionic basicities in polar solvents.[2] Ion pair acidity is defined in terms of the equilibrium (1) where M^+ is generally either Li^+ solvent-separated ion pairs (SSIP) or Cs^+ contact ion pairs (CIP) in our work, and the equilibrium constants are converted to absolute numbers by eq 2 where the standard is taken as 22.90, the ionic p*K* of fluorene per hydrogen in DMSO.[3] Tables of such p*K*'s have been published previously for the Cs[4] and Li[5] scales. A corresponding list was published recently by the Antipin group for a range of [2.2.1]encryptated lithium ion pairs.[6]

$$R^- M^+ + R'H \overset{K}{\rightleftharpoons} RH + R'^- M^+ \qquad (1)$$

$$pK(R'H) = pK(RH) - \log K \qquad (2)$$

The new p*K*'s show several interesting features. The compounds studied are shown as **1**−**5**. The results are summarized in Table 1 with the details given in the Supporting Information.

Table 1 shows some significant differences between the lithium and cesium ion pair p*K*'s. Such differences are unusual because for other delocalized carbon acids the SSIP lithium and CIP cesium scales generally agree to within a few tenths p*K* unit and also agree well with Bordwell's ionic p*K*'s in DMSO. Table 1 shows that for the lithium salt of **1**, the p*K* agrees reasonably well with the ionic value in DMSO. The value for 1,3-diphenylindene, **1**, is a direct measurement on Bordwell's absolute DMSO scale[7] corrected for statistical effects: **1** has one acidic proton but the anion has two equivalent positions for the proton to return; the compound is therefore intrinsically more acidic than is indicated by the observed p*K* with a Δp*K* of log(1/2) or −0.3. The same correction applies to **2** and **4**. The structure of **4** was assigned by Kuhn et al.[8] on the basis of UV spectra.

The p*K* of **3** is a direct measurement by Ritchie of its acidity using the glass electrode.[9] Ritchie originally divided up the acidity into contributions of the two tautomers **3** and **3a**, based on earlier work of Kuhn and Rewicki who reported that the tautomer **3a** dominates.[10] More recently, however, the NMR spectrum of the ring-deuterated analogue showed only the structure **3**.[11] Accordingly, we use Ritchie's value corrected only for the statistical effect of +0.3; it has two equivalent protons that can be lost and one position to which the proton can return. The acidities of compounds **2**−**4** were determined by Kuhn and Rewicki[12] in DMSO with varying bases and assigned as pseudoaqueous acidities based on the H_- method.[13] Compounds **1** and **2** were also determined in a DMSO−*t*-BuOK mixture and assigned p*K*s on the same H_- basis.[14] Bordwell and Drucker[7] have shown that subtraction of about 3 units corrects these H_- values approximately to the absolute DMSO scale. We use a correction of −3.6 units for this acidity region to adjust the Kuhn and Rewicki value for **3**, 12.3,[12] to Ritchie's direct value of 8.7. This correction was also applied to derive the DMSO values for **2** and **4** in Table 1.

Relative ionic acidities, pK_0, in THF have been shown to parallel corresponding acidities in DMSO;[15] relative ion pair acidities, pK_{ip}, require consideration of the ionization constant, K_i, to the free ions as in eq 3.

$$pK_{ip} = pK_0 + \log K_i \qquad (3)$$

Thus, if an ion pair is more strongly bound, K_i becomes relatively smaller and so does pK_{ip}. In a SSIP, a lithium cation coordinated to four THF molecules is a large cation and K_i is expected to change slowly with a change in size of the anion. Indeed, for a number of SSIP lithium ion pairs K_i has been found to be relatively constant at 10^{-5} M.[15] Accordingly, the Li ion pair p*K*'s for **1**−**4** in Table 1 should all be similar to the ionic DMSO values. The differences for **2**−**4** probably indicate the combined experimental uncertainties although the greater differences for **3** and **4** may indicate a K_i somewhat larger than 1×10^{-5} M for these large delocalized carbanion salts. Note that these acidities are symbolized as p*K* and not pK_a; consideration of the K_i values can give ΔpK_a values, but to our knowledge no absolute pK_a values are known for any compound in THF.

The cesium p*K*'s in Table 1 for **1**−**4** show much greater changes in K_i. The Cs pK_{ip} value for **1** is only 0.35 units higher than for Li, but for **2**−**4** the differences are 1.4−2.1 units. These anions have negative charge concentrated at the fluorenyl units at the ends of a joining chain.

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(1) Carbon Acidity. 112.

(2) Streitwieser, A.; Kim, Y.-J. *J. Am. Chem. Soc.*, submitted.

(3) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456−63.

(4) Streitwieser, A.; Ciula, J. C.; Krom, J. A.; Thiele, G. *J. Org. Chem.* **1991**, *56*, 1074−6.

(5) Streitwieser, A.; Wang, D. Z.; Stratakis, M.; Facchetti, A.; Gareyev, R.; Abbotto, A.; Krom, J. A.; Kilway, K. V. *Canad. J. Chem.* **1998**, *76*, 765−9.

(6) Antipin, I. S.; Gareyev, R. F.; Vedernikov, A. N.; Konovalov, A. I. *J. Phys. Org. Chem.* **1994**, *7*, 181−91.

(7) Bordwell, F. G.; Drucker, G. E. *J. Org. Chem.* **1980**, *45*, 3325−8.

(8) Kuhn, R.; Fischer, H.; Rewicki, D.; Fischer, H. *Liebigs Ann. Chem.* **1965**, *689*, 1−20.

(9) Ritchie, C. D. *J. Am. Chem. Soc.* **1969**, *91*, 6749−53.

(10) Kuhn, R.; Rewicki, D. *Tetrahedron Lett.* **1965**, *39*, 3513.

(11) Neugebauer, F. A.; Fischer, H. Z. *Z. Naturforsch. B. Anorg. Org. Chem.* **1977**, 904−7.

(12) Kuhn, R.; Rewicki, D. *Liebigs Ann Chem* **1967**, *706*, 250−261.

(13) Rochester, C. H. *Acidity Functions*; Academic Press: New York, 1970.

(14) Streitwieser, A., Jr.; Chang, C. J.; Hollyhead, W. B. *J. Am. Chem. Soc.* **1972**, *94*, 5292−6.

(15) Kaufman, M. J.; Gronert, S.; Streitwieser, A., Jr. *J. Am. Chem. Soc* **1988**, *110*, 2829−35.

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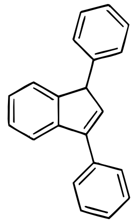
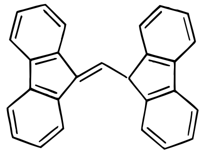
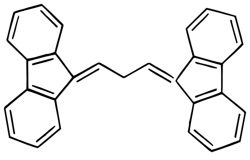
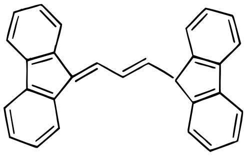
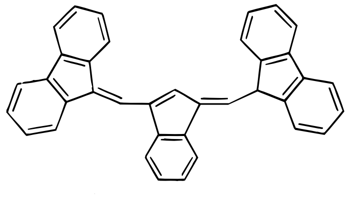
Table 1. Spectroscopic Data and Ion Pair Acidities for Lithium[a] and Cesium Anions of 1−5 in THF at 25 °C Compared to the Ionic Acidities in DMSO (The p*K*s Listed Are Corrected to Be on a Per-Hydrogen Basis)

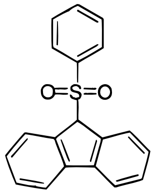

1 DPI


2 BBP


3 BBP-5


3a


4 DFB


5 PhSO$_2$Fl

compd	cation	λ_{max} (nm)	ϵ (cm^{-1} M^{-1})	p*K* (THF)[a]	p*K* (DMSO)
1	Li	450	32 900	12.32	12.47[b]
	Cs	422	23 300	12.66	
2	Li	557[c]	112 500	10.38[d]	10.2[e]
	Cs	554[c]	107 600	12.29	
3	Li	635[f]	193 000	8.16	9.0[g]
	Cs	629[f]	169 000	10.46	
4	Li	699[h]	79 600	5.61	6.1[i]
	Cs	670[h]	53 300	7.47	
5	Li	384	8630	8.95	11.55[j]
	Cs	367	7960	11.80	

[a] For compounds **1** and **2** from ref 5; otherwise this work. [b] References 7 and 14. [c] λ_{max} of potassium salt in DMSO, 559 nm; ref 27. [d] p*K* for the Li[2.2.1]cryptate ion pair is 11.4, statistically corrected from 11.7.[6] [e] Extrapolated from refs 12 and 14: 14.1 using a correction of −3.6 (see text) to obtain the pK_a in DMSO −0.3 (statistical correction). [f] λ_{max} of potassium salt in DMSO, 634 nm; ref 27. [g] Extrapolated as 12.3 (ref 12) − 3.6 (see text) + 0.3 (statistical correction). [h] λ_{max} of potassium salt in DMF, 694 nm; ref 27. [i] Extrapolated as 10.0 (ref. 12) − 3.6 (see text) − 0.3 (statistical correction). [j] Reference 17.

The electrostatic attraction to the smaller cesium cation is lower than for other indicator anion salts in which the charge is concentrated closer to the metal cation center and $K_{\rm i}$ is then relatively greater as is p$K_{\rm ip}$. This type of effect has been noted before,[14] and was also found for the relative dissociation constants of cesium salts of α,ω-diphenylpolyenes in THF.[16] It appears to occur also in the lithium [2.2.1]cryptate scale of Antipin et al.[6] The cryptated lithium cation appears to be somewhat smaller than a SSIP lithium cation because dissociation constants to free ions in THF are about 2−10-fold smaller than the SSIPs, but they are effectively larger than cesium cation. On their scale, the value for BBP, **2**, 11.4 (statistically corrected from their published value of 11.7), is somewhat larger than the SSIP value given in Table 1, but the difference is less than for the cesium CIP.

Different considerations apply to the sulfone **5**. Here, the p*K* on the Cs ion pair scale compares well with the DMSO value[17] but the Li value is much lower. The dissociation of the cesium salt of **5** to free ions is thus comparable to that of the other indicators making up the cesium p*K* scale in THF[4] but the lithium ion pair is more firmly bound. More basic lithium salts of sulfone carbanions were found previously to be contact ion pairs and to have p*K*'s in THF 3.5 units lower than the corresponding Cs values.[18] Coordination of lithium cation to the sulfone oxygens is dominating in these cases as shown also in crystal structures[19−24] and ab initio calculations[25] of lithium salts of sulfones. For **5** the lithium salt has a longer λ_{max} wavelength than the cesium salt indicative of a SSIP and Δp*K* is slightly less at 2.9 but coordination to the sulfone oxygens is still clearly important.

These observations emphasize that subtle structural effects even for highly delocalized carbanions can significantly affect relative ion pair acidities.

Experimental Section

Materials. 1,3-Diphenylindene, **1**, and 1,3-bis(biphenylene)propene, **2**, were available from our previous studies. They were

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[16] Thiele, G.; Streitwieser, A. *J. Am. Chem. Soc.* **1994**, *116*, 446−454.

[17] Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1980**, *45*, 3314−20.

[18] Streitwieser, A.; Wang, G. P.; Bors, D. A. *Tetrahedron* **1997**, *53*, 10103−10112.

[19] Gais, H.-J.; Lindner, H. J.; Vollhardt, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 859.

[20] Gais, H.-J.; Vollhardt, J.; Lindner, H. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 939.

[21] Gais, H.-J.; Vollhardt, J.; Hellmann, G.; Paulus, H.; Lindner, H. J. *Tetrahedron Lett.* **1988**, *29*, 1259.

[22] Boche, G.; Marsch, K.; Harms, G.; Sheldrick, M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 573.

[23] Boche, G. *Angew. Chem.* **1989**, *101*, 286−306.

[24] *Carbon acidity resulting from sulfur substituents*; Boche, G., Lohrenz, J. C. W., Ciolowski, J., Koch, W., Eds.; J. Wiley & Sons: New York, 1993.

[25] Bors, D. A.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 1397−404.

further purified by sublimation before the use. The other compounds are known and were prepared by literature procedures.

1,5-Bis(biphenylene)-1,4-pentadiene (**3**, BBP-5): sublimed, mp 183 °C (lit.[11] mp 181 °C.

3-(Dibenzofulvenyl)-6-(9-fluorenyl)-1,2-benzofulvene (**4**, DFB): crystals from benzene, mp 237−9 °C (lit.[8] mp 239−241 °C.)

9-(Phenylsulfonyl)fluorene: sublimed, mp = 183−4 °C (lit.[26,] mp 182−3 °C).

Purity of all of the materials used in this study was checked by H NMR, GC, and elemental analysis.

Acidity Measurements. The λ_{max} and extinction coefficients were measured by UV−vis spectra taken on known concentrations of Li or Cs salts of the carbanions in THF at 25 °C using the glovebox-spectrometer system described previously. These solutions were diluted several times with known amounts of solvent. The absorbances followed Beer's Law in all cases (Figures S1−S8, Supporting Information) and the extinction coefficients were determined from the slope of plots of absorbance vs concentration.

Acidity measurements were made by adding a base (solid LiTMS or solution of diphenylmethylcesium) to known mixtures of substrate and indicator. For the cesium runs equilibrium was established within a few minutes but the lithium runs required 1−2 days to reach equilibrium. The actual acidity runs are summarized in Table S1 (Supporting Information). In all cases the experimental pK values are independent of the carbanion salt concentration indicating that all of these indicator salts are monomeric at the concentrations used (Figures S9−S16, Supporting Information).

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Supporting Information Available: Experimental details presented in Figures S1−S16 and Table S1. This information is available free of charge via the Internet at http://pubs.acs.org.

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[26] Bavin, P. M. G. *Can. J. Chem.* **1960**, *38*, 917−22.

[27] Kuhn, R.; Rewicki, D. *Liebigs Ann. Chem.* **1965**, *690*, 50−78.