magnesium turnings in 5 mL of THF was added a crystal of iodine together with a few drops of a neat nopyl bromide. After initiation of a reaction, an additional 15 mL of THF was added. Then a solution of 21.4 g (93.5 mmol) of nopyl bromide in 30 mL of THF was added dropwise, at a rate to maintain a mild reflux. The whole mixture was refluxed for 1 h and cooled, and a stream of gaseous formaldehyde formed from 8.4 g of paraformaldehyde was passed into the solution. Finally the reaction was quenched with about 11 mL of saturated NH_4Cl solution and left overnight. The organic layer was removed from a solid cake by filtration and dried ($MgSO_4$). After evaporation of solvent, the residue was distilled under reduced pressure to give 11.59 g (69%) of homonopol (bp 66–69 °C at 0.25 Torr): $[\alpha]^{25}_D$ −40.7° (*c* 5.135, $CHCl_3$); ^1H NMR δ 0.83 (s, 3 H), 1.27 (s, 3 H), 1.15 (d, *J* = 9 Hz, 1 H), 3.64 (t, *J* = 6 Hz, 2 H), 5.22 (br s, 1 H); ^{13}C NMR δ 20.94, 26.10, 29.93, 31.03, 31.39, 32.85, 37.66, 40.64, 45.56, 62.10, 115.74, 147.60; exact mass calcd for $C_{12}H_{20}O$ 180.1514, found 180.1511.

6,6-Dimethylbicyclo[3.1.1]hept-2-ene-2-(3′-propanol) Benzyl Ether. A solution of 5.34 g (29.6 mmol) of homonopol in 10 mL of THF was added dropwise to a vigorously stirred suspension of 1.185 g (39.5 mmol) of 80% NaH in 40 mL of dry THF. The mixture was then refluxed overnight, cooled to room temperature, treated with 6.32 g (37 mmol, 4.4 mL) of benzyl bromide, and refluxed for an additional 5 h. After cooling, the unreacted NaH was destroyed with 3 mL of methanol and the THF was removed under reduced pressure. The residue was diluted with water and extracted with ether. The combined organic extracts were washed with saturated NaCl solution and dried (K_2CO_3). After evaporation of ether, the residue was distilled in vacuo to give 3.55 g (44%) of homonopyl benzyl ether (bp 102–104 °C at 0.025 mmHg): $[\alpha]^{25}_D$ −26.3° (*c* 4.12, $CHCl_3$); ^1H NMR δ 0.81 (s, 3 H), 1.12 (d, *J* = 8 Hz, 1 H), 1.26 (s, 3 H), 3.46 (t, *J* = 7 Hz, 2 H), 4.49 (s, 2 H), 5.18 (br s, 1 H), 7.33 (m, 5 H); ^{13}C NMR δ 21.06, 26.22, 27.32, 31.15, 31.51, 33.22, 37.72, 40.76, 45.62, 69.95, 72.68, 115.92, 127.23, 127.35, 128.08, 138.54, 147.66; exact mass calcd for $C_{19}H_{26}O$ 270.1983, found 270.1991.

Reduction of Acetophenone with Homo-NB-Enantride. A solution of 1.688 g (6.24 mmol) of homonopyl benzyl ether was refluxed for 60 h with 11.2 mL (5.58 mmol) of 0.499 M 9-BBN solution in THF. Formation of the trialkylborohydride and workup followed the standard procedure.

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Carbon Acidity. 78. Extended Cesium Ion Pair Indicator Scale in Tetrahydrofuran

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A revised cesium ion pair acidity scale relative to fluorene at pK_a = 22.90 is presented. The range of the scale is extended 3 p*K* units by including more acidic indicators and now encompasses pK_as from 15.62 to 38.73. The accuracy of the scale has been improved by multiple equilibria among indicators. Uncertainties between close lying indicators is generally less than ±0.01 p*K* unit. Brønsted plots are constructed for series of fluorenyl and arylmethyl hydrocarbons. From these plots, the acidity value for toluene in THF was extrapolated (pK_a = 40.9). Comparisons are drawn to ionic acidities in dimethyl sulfoxide.

Introduction

We have recently presented a scale of cesium ion pair p*K*s in tetrahydrofuran (THF) for various indicators.[1] This scale was a revision of earlier scales[2] with updated values and with the reference system chosen as the p*K* of fluorene in dimethyl sulfoxide (DMSO).[3] This type of reference is required because absolute acidities in THF are not available. The cesium ion pair p*K*s of other compounds are defined by the equilibrium constant of eq 1, where R = 9-fluorenyl.

$$R^-Cs^+ + R'H \rightleftharpoons RH + R'^-Cs^+ \qquad (1)$$

In the present work we have added new indicators to provide independent determinations of individual p*K*s and to fill large gaps in the previous scale. We have also improved methods for determining the content of any interfering impurities in the indicators. The lower end of the scale has been extended by 3 p*K* units.

Results and Discussion

Equilibrium Measurements. Several new indicators have been added to the scale at the lower pK_as and to fill in between adjacent indicators on the ion pair scale that have large differences in acidity. These new indicators are 7-phenyl-7*H*-benzo[*c*]fluorene (Ph-3,4-BF),[4,5] 9-*p*-biphenylylfluorene (9-BpFl),[6] 11-phenyl-11*H*-benzo[*a*]fluorene (Ph-1,2-BF),[7] 9-(*p*-(dimethylamino)phenyl)fluorene (*p*-DMAPhFl),[5] 11-phenyl-11*H*-benzo[*b*]fluorene (Ph-2,3-BF), 9-isopropylidenefluorene (IPF),[8] 1,3-di-

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phenylpropene (DP3),[9] 1,5-diphenyl-1,3-pentadiene (DP5),[9] and phenyl *p*-tolyl sulfide (PpTS).[10]

Compounds were synthesized to fill in large gaps between the adjacent compounds to improve the accuracy of the cesium ion pair acidity scale. An example of such a gap in the previous scale was between 9-*tert*-butylfluorene (9-*t*-BuFl) and 1,1,3-triphenylpropene (TTP). The acidity difference between these two indicators was 2.3 p*K* units, too large a difference in acidity for accurate measurement. 1,5-Diphenyl-1,3-pentadiene was introduced to fill this gap, which has a p*K* about half way between 9-*t*-BuFl and TPP. Eliminating such large acidity differences between indicators allows for overlap of measurements and a check of internal consistency in the acidity scale. In all cases, such multiple determinations gave excellent agreement, less than the combined experimental errors of the measurements. The consistency is such that p*K* differences between nearby compounds on the scale are known with a precision of better than ±0.01 pK unit.

Another problem discovered was the presence of interfering trace impurities in three indicators, 11*H*-benzo[*a*]fluorene, 11*H*-benzo[*b*]fluorene, and 7*H*-benzo[*c*]fluorene. The interference occurs when the impurity is more acidic than the indicator and has an absorbance band in the same region as the anion of the indicator. Detection is by a change in the band shape of the indicator with a change in the percent deprotonation. A method for detecting this change in band shape from impurities is described in the Experimental Section. Besides the normal determinations of purity (e.g., melting point, spectroscopy, etc.), all indicators were checked for these trace impurities, as well as by remeasuring the extinction coefficients before they were used to prepare the revisions in the acidity scale.

The resulting scale is summarized in Table I. The differences from the previous version[1] are about 0–0.1 p*K* unit below 25 but the new scale is generally 0.2–0.3 p*K* unit lower for less acidic indicators. The scale now covers a range of 23 p*K* units. This scale may be compared with that for cesium ion pairs in cyclohexylamine, pK_{CsCHA}.[11] Twenty-one indicators are on both lists. Despite the fact that the pK_{CsCHA} scale uses a different reference standard—the pK_{CsCHA} of 9-phenylfluorene was set to 18.49—the two scales are remarkably similar. The average deviation in absolute p*K* values is 0.18. A linear correlation between the two scales is even more precise, eq 2.

$$pK_{CsCHA} = 1.0084pK_{Cs/THF} - 0.13 \ (r^2 = 0.999) \quad (2)$$

This comparison means that the dissociation constants of the cesium carbanide ion pairs to free ions must vary with structure to essentially the same degree in both solvents. The similarity of the relative ion pair p*K*s to the ionic p*K*s in DMSO was remarked on previously,[1] and this comparison is not significantly altered by the new results. Up to the highest p*K*s measured in DMSO,[3] the dissociation constants of the cesium ion pairs in THF are of comparable magnitude, $K_d = (1\text{–}20) \times 10^{-8}$ M.[1] A further argument extends this generalization to toluene.

Since the CsCHA and Cs/THF scales are so similar, previous Brønsted correlations[12,13] established between kinetic acidities and CsCHA p*K*s will apply with no significant change to the present THF results. The correlation with rates of tritium exchange of polyarylmethanes with lithium cyclohexylamide (LiCHA)[14] is of particular significance. The rate constants for triphenylmethanes, diphenylmethanes, etc., gave a linear log correlation with CsCHA p*K* values that was used to extrapolate to a CsCHA p*K* value for toluene of 41.2.[11] A similar correlation between log *k*(LiCHA) and $pK_{Cs/THF}$ is equally good (Figure 1) and extrapolates to a p*K* of toluene on the THF scale of 40.9. The linearity of the plot in Figure 1 shows

Table I. Cesium Ion Pair Equilibrium Acidity Constants and Spectral Data for Compounds in Tetrahydrofuran at 25.0 °C[a]

symbol	compound	p*K*[b]	λ_{max} (ϵ)[c]
Ph-3,4-BF	7-phenyl-7*H*-benzo[*c*]fluorene	15.62[d]	379 (24 700)
9-BpFl	9-biphenylylfluorene	17.72[d]	455 (29 400)
Ph-1,2-BF	11-phenyl-11*H*-benzo[*a*]fluorene	17.94[d]	452 (10 400)
9-PhFl	9-phenylfluorene	18.15[d]	359 (20 200) 397 (24 000)
Ph-2,3-BP	11-phenyl-11*H*-benzo[*b*]fluorene	18.92[d]	428 (41 800)
p-DMAPhFl	9-(*p*-(dimethylamino)phenyl)fluorene	19.23[d]	376 (28 700)
3,4-BF	7*H*-benzo[*c*]fluorene	19.47[d]	374 (7580) 394 (1530)
1,2-BF	11*H*-benzo[*a*]fluorene	20.13[d]	433 (9710)
9-BzFl	9-benzylfluorene	21.30[d]	371 (13 300) 467 (1120) 494 (1530) 528 (1160)
IPF	9-isopropylidenefluorene	22.08[e]	370 (24 500)
9-MeFl	9-methylfluorene	22.32[f]	376 (12 350) 478 (980) 503 (1250) 539 (890)
Fl	fluorene	(22.90)[a]	363 (12 700) 450 (890) 474 (1160) 504 (1020)
4,5-MP	9*H*-benzo[*def*]fluorene	22.91[f]	500 (6850)
2,3-BF	11*H*-benzo[*b*]fluorene	23.63[d]	415 (23 900)
9-*t*-BuFl	9-*tert*-butylfluorene	24.39[g]	376 (13 700) 469 (900) 495 (1150) 528 (810)
DP5	1,5-diphenyl-1,3-pentadiene	25.62[g]	572 (117 000)
TPP	1,1,3-triphenylpropene	26.76[f]	545 (45 200)
DP3	1,3-diphenylpropene	27.85[g]	538 (57 800)
PDDA	9-phenyl-10,10-dimethyl-9,10-dihydroanthracene	28.11[g]	439 (35 000)
9-PX	9-phenylxanthene	28.73[f]	491 (17 600)
BDPM	*p*-biphenylyldiphenylmethane	30.07[f]	568 (44 500)
TPM	triphenylmethane	31.26[f]	488 (29 900)
p-BB	*p*-benzylbiphenyl	31.70[f]	529 (64 600)
TpTM	tri-*p*-tolylmethane	33.10[f]	494 (30 200)
DPM	diphenylmethane	33.25[f]	443 (50 600)
DoTM	di-*o*-tolylmethane	34.22[h]	447 (40 300)
BzMS	benzyl methyl sulfide	34.68[h]	389 (17 600)
DmXM	bis(2,4-dimethylphenyl)methane	35.96[h]	446 (35 100)
PpTS	phenyl *p*-tolyl sulfide	37.69[h]	378 (36 400)
p-MB	*p*-methylbiphenyl	38.73[h]	472 (35 700)

[a] The acidity scale is referenced to 22.90 for fluorene at 25.0 °C (ref 3). [b] On a per hydrogen basis. [c] nm. [d] This work. [e] Work of J. T. Petty. [f] Reference 2b. [g] Reference 9. [h] Reference 17.

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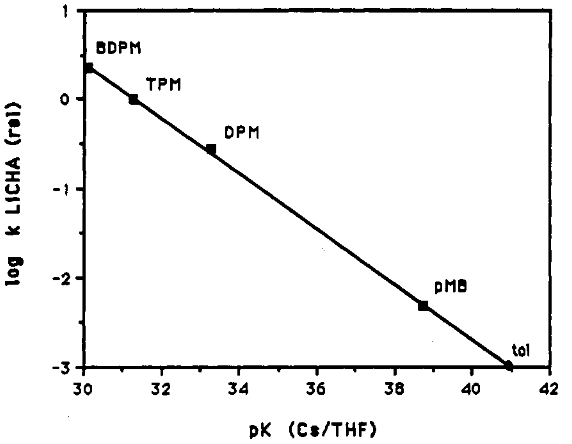

Figure 1. Brønsted plot of relative rate of protodetritiation of arylmethane hydrocarbons in lithium cyclohexylamide/cyclohexylamine and the cesium ion pair p*K*s in THF. The point for toluene is extrapolated from the least-squares line: log *k*(LiCHA) = 9.703 - 0.310p*K*.

that the ion pair dissociation constants of the cesium salts cannot be changing much over this range. The further comparison is with DMSO. Bordwell et al.[15] showed that the p*K*s of a group of para-substituted toluenes in DMSO correlate linearly with the p*K*s of correspondingly substituted anilines in DMSO, and using the p*K* of aniline itself estimated the p*K* of toluene in DMSO as about 42. This value again is remarkably close to the present estimate for the relative ion pair p*K* in THF. One might have expected that the less delocalized charge of the simple benzyl anion would bind the cesium cation more strongly than, say, di- or triphenylmethyl anion. The resulting smaller ion pair dissociation constant would then result in a lower value for the p*K*. The actual results show that any such effect is relatively small and that, in general, the relative ion pair p*K*s of cesium salts in THF are numerically similar to ionic p*K*s in DMSO. This generalization extends the applicability of Bordwell's extensive set of DMSO p*K* values[3h] to cesium ion pair acidities as well.

Conclusion. In this paper we have presented a refined and extended cesium ion pair acidity scale in THF. Comparison with ionic acidities in DMSO shows an excellent correspondence between the two scales extending up to toluene with an extrapolated cesium ion pair p*K* in THF of 40.9.

Experimental Section

The syntheses of the aromatic hydrocarbons have been reported elsewhere[4-8,10] or were available from previous studies. In general, the aromatic hydrocarbons were recrystallized from hexane or an ethanol/hexane mixture and then vacuum sublimed. Purity was assessed by spectroscopic methods, melting point, and/or elemental analysis as necessary. The diphenylpolyenes, DP3, and DP5, will be reported separately.[9]

Spectroscopic Test for Impurities. Interference in the equilibrium acidity measurements could arise from an impurity that is more acidic than the indicator that is to be used and has a UV-vis absorbance in the same region. Impurities of this nature were detected in the following manner: 3 mL of a THF solution containing 1-2 mg of the indicator to be tested was placed in one UV-vis cell, and enough cesium diphenylmethide was added to deprotonate approximately 50% of the indicator. The UV-vis spectrum of this solution was then recorded. In another cell was placed about 30 mg of the same indicator in 3 mL of THF. Cesium diphenylmethide was added to produce an absorbance of approximately 0.2. The UV-vis spectrum of this solution was then compared with that of the previous solution. The peak shape of the two should be identical if no impurity is present. If the indicator does contain an impurity, the spectra will not match completely because a greater amount of impurity will be deprotonated in the second case, causing a larger percentage of the absorbance to be from the impurity instead of the indicator.

11-Phenyl-11*H*-benzo[*b*]fluorene. To a solution of phenyllithium in dry THF (7.6 mmol in 20 mL) was added a solution of 11*H*-benzo[*b*]fluorenone[16] (1.15 g in 10 mL of THF) dropwise under N_2 with stirring. After the addition was complete, the solution was stirred for 16 h and poured into a solution of 2 g of NH_4Cl in 50 mL of water. This mixture was extracted with diethyl ether, the organic phase was washed with saturated NaCl solution and dried over Na_2SO_4, and the solvent was removed to give 1.73 g of crude product. TLC showed no 11*H*-benzo[*b*]fluorenone present. The crude product, 11-hydroxy-11-phenyl-11*H*-benzo[*b*]fluorene, was dissolved in 60 mL of glacial acetic acid, and 9 mL of 57% hydriodic acid was added. The mixture was heated at 80 °C for 1 h, diluted with water, and extracted with ether. The organic extracts were washed with 10% $Na_2S_2O_4$ until the dark color of dissolved I_2 was removed, followed by addition of a saturated $NaHCO_3$ solution, and then drying over Na_2SO_4. Removal of solvent gave 1.2 g of a pale yellow solid, which was recrystallized from hexane/CH_2Cl_2 twice and then sublimed (120 °C, 0.5 mm) to give a white solid, mp 205-206 °C. NMR: δ 5.26 (1 H, s, H_{11}), 7.1-8.2 (15 H, m, aromatic). Anal. Calcd for $C_{23}H_{16}$: C, 94.48; H, 5.52. Found C, 94.31; H, 5.48.

Note that HI reduction of the ketone was used instead of catalytic hydrogenation because the latter gave small amounts of ring hydrogenation products that were difficult to remove.

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Supplementary Material Available: Table of equilibrium constants of 39 pairs of indicators with their cesium salts in THF at 25 °C (2 pages). Ordering information is given on any current masthead page.

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