If equilibration of a classical norbornyl cation IIIa with its enantiomorph IIIb is to account for the >99.95% racemic character[1] of the solvolysis product from IV-OBs, the equilibration rate would need to exceed the rate of collapse of IIIa to solvolysis product by a factor greater than 2×10^3. The rate constant for collapse of the norbornyl cation to product can be estimated in several ways to be at least in the 10^9–10^{10} sec.$^{-1}$ range.[7] This brings the equilibration rate IIIa → IIIb into the 2×10^{12}–2×10^{13} sec.$^{-1}$ range. This is becoming greater than kT/h in absolute rate theory, namely 6×10^{12} sec.$^{-1}$ at 25°, the rate constant predicted for zero ΔF^*. An additional argument, which may be dubbed the "windshield wiper," has been employed by Brown[3a] in accounting for the *exo* nature of the solvolysis product from norbornyl derivatives. Quoting him, "These bicyclic carbonium ions are unusual in that they cannot be fully solvated from both directions. . . The very rapid movement of the ethylene bridge between the two adjacent positions of the cyclopentyl ring system will prevent an accumulation of solvent in the *endo* direction and thereby favor substitution in the *exo* direction." It is rather an astonishing suggestion that a cation, which allegedly prefers a classical structure, nevertheless equilibrates so rapidly that solvent is effectively excluded from the *endo* side. Such "desolvation" should inevitably be associated with a corresponding destabilization, so that the proposal is thermodynamically unsound.

Brown apparently ignores available evidence that a classical norbornyl cation does not uniformly have the properties he attributes to it. From deamination[9] of the norbornyl amines, where it is more likely that a classical cation is produced, the product contains appreciable *endo* epimer and displays considerable optical activity. Further, in solvolysis[1] of *endo*-norbornyl *p*-bromobenzenesulfonate, which leads first to a classical cationic species, the *exo* solvolysis product also displays appreciable optical activity. Thus, Brown needs two varieties of equilibrating classical cations, the one from IV-OBs, very rapidly equilibrating with zero ΔF^*, and another type, *e.g.*, from VI-OBs, not so rapidly equilibrating.

We ourselves have visualized the possible importance of equilibrating classical ions in certain neighboring group situations,[10] and good examples of such are now known.[8b] However, it seems clear to us that equilibrating classical ions III do not and the nonclassical bridged ion I does provide the explanation for *exo*-norbornyl solvolysis. We certainly do not regard a "classical ion" equilibrating with zero ΔF^*, or the "windshield wiper," as a "reasonable alternative to the nonclassical structure."[3a]

Brown has employed a great deal of indirect "evi-

dence" in favor of equilibrating norbornyl classical ions in solvolysis of IV-OBs, based on the behavior of 1- and 2-substituted 2-norbornyl systems as compared to cyclopentyl analogs or unsubstituted norbornyl itself. However, we disagree with most of his treatment of the data.[11] Brown rather assumes, and gives the impression that it is generally agreed, that tertiary norbornyl cations are classical. In his series of communications Brown reports the behavior of a series of tertiary norbornyl systems to be qualitatively similar to the symmetrical secondary ones as regards *exo*/*endo* rate ratios[12] and even stereochemistry. The general conclusion he reaches is that the secondary and tertiary norbornyl cations are either both nonclassical or both classical. He chooses the latter alternative, having already assumed it for the tertiary cations. We have felt for some time[1b] that the older evidence for typical tertiary norbornyl cations is in line with preferred bridged structures. So is Brown's recent evidence and other recent observations on the camphenehydro[13a,b] and 2-phenyl-2-norbornyl types.[13c] Except for possible extreme tertiary norbornyl systems, the available evidence seems to us to favor preferred bridged structures for typical secondary and tertiary norbornyl cations.

(11) For example, Brown incorrectly employs Hammond's postulate [G S. Hammond, *ibid.*, 77, 334 (1955)] to argue that the transition state for ionization of a substrate to a bridged ion should closely resemble the latter. However, there are good reasons to expect carbon bridging to lag behind C–X ionization at the transition state.

(12) The apparent quantitative similarity in these ratios for tertiary and secondary systems is not to be trusted because the necessary corrections have either not been applied or are unknown for the disturbances from *exo*–*endo* ground state free-energy differences, ion-pair return, and nucleophilic solvent participation (for *endo* secondary substrates in a nucleophilic solvent).

(13) (a) P. Beltrame, *et al.*, *J. Chem. Soc.*, 658 (1964); C. A. Bunton, private communication; (b) W. F. Erman, *J. Am. Chem. Soc.*, 86, 2887 (1964); (c) C. J. Collins, *et al.*, Paper at International Symposium on Organic Reaction Mechanisms, Cork, Ireland, July 20–25, 1964, p. 38 of Abstracts; *J. Am. Chem. Soc.*, 86, 4913 (1964).

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The Acidities of Weak Acids in Dimethyl Sulfoxide. II. The Hammett Acidity Function

Sir:

We reported earlier[1] that the apparent acidity of alcohols in dimethyl sulfoxide (DMSO) or tetrahydrofuran is comparable to that of triphenylmethane when alcohol concentrations are low. Further study of this unexpected result led us to extend one Hammett[2] acidity scale into regions of high basicity in the solvent systems DMSO, water–DMSO, methanol–DMSO. The acidity scale is expressed in terms of the acidity function, $H- = -\log (a_H \cdot \gamma_I - / \gamma_{IH}) = pK_{IH} + \log$ [I$^-$]/[IH], which is measured through the use of indicator acids (IH). The function is useful when there are available a series of overlapping indicators of known relative acidities which have activity coefficient ratios, $\gamma_I - / \gamma_{IH} = \Gamma$, which are essentially constant from me-

(7) For example, ion collapse in aqueous acetone is faster than 6,2-hydrogen shift.[2] The rate constant for the latter process may be estimated as 10^9 sec.$^{-1}$ at 25° from the data of Olah, *et al.*, on the direct observation of the norbornyl cation.[8a] The fact that rate of collapse of classical secondary ions to products is quite competitive with rate of rotation about C–C single bonds[8b,c] also leads to a minimal estimate of 10^9–10^{10} sec.$^{-1}$ for rate of collapse.

(8) (a) G. Olah, *et al.*, *J Am. Chem Soc.*, 86, 5679, 5680, 5682 (1964); (b) C. J. Collins and B. M. Benjamin, *ibid.*, 85, 2519 (1963); (c) P. S. Skell, Special Publication No. 16, The Chemical Society, London, 1962, p. 173.

(9) J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, 86, 1749 (1964), and cited references.

(10) S. Winstein, *et al.*, *ibid.*, 70, 835 (1948); 74, 1134 (1952); 77, 1738 (1955).

(1) E. C. Steiner and J. M. Gilbert, *J. Am. Chem. Soc.*, 85, 3054 (1963).

(2) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, p. 269.

Table I

Indicator	H2O-DMSO pKa	[H2O] f M	MeOH-DMSO pKa	[MeOH] f M	DMSO pKa	Anion λmax	ε × 10⁻⁴
(DMSO)					31.3		
Diphenylmethane					28.6	460	7.68
Triphenylmethane	27.2	0.080	27.2	0.003	27.2	500	4.51
9-Phenylxanthene	24.3	0.40	24.2	0.022	24.2	510	1.96
Fluorene	20.5	6.0	20.5	0.811	20.5	485 (457, 518)	0.147
4-Nitroaniline	18.4[a,b]		18.5		18.6	468 (495)	3.48
2-Nitrodiphenylamine	17.6[a]		17.5[c,d]				
4-Nitrodiphenylamine	15.9[a]		15.5[c]				
2,4-Dinitroaniline	15.0[a]		14.5[c]	0.72–6.8	14.7	510	1.31
4,4'-Dinitrodiphenylamine	14.1[a]		13.4[c]				
2,4-Dinitrodiphenylamine	13.8[a]		13.2[c]		e	500	1.61

[a] Ref. 4. [b] Used as standard value. [c] Calculated from data in ref. 5. [d] Corrected. [e] Reproducible results could not be obtained. [f] Concentration used in relating adjacent indicators.

dium to medium. Several workers have studied indicators for basic media,[3] the most extensive work being that of Stewart and O'Donnell.[4] They interrelated many indicators (highest pK_a, 18.37) in four solvent systems of varying composition—water, pyridine-water, sulfolane-water, DMSO-water—and found the relative acidities to be independent of solvent changes. They assigned pK_a values based on the pH scale in water. Later, Stewart, O'Donnell, Cram, and Rickborn[5] published data which permit calculation of relative acidities, but not pK_a values, of some of the same indicators in methanolic DMSO. More O'Ferrall and Ridd,[6] using dilute methanol solution as a reference state, determined pK_a values for a few of the same indicators and found them to average 3.13 units higher than the values determined in water. The relative acidities of the indicators agree well between the three sets of data.

We have extended the indicator series to include triphenylmethane (pK_a 27.2), obtaining relative acidity values in both methanolic and aqueous DMSO. Thus for successive pairs of indicators, a suitable amount of each compound was added to a separate aliquot of a solution containing the required amount of potassium base and the concentration of hydroxylic solvent shown in Table I. Conversion of indicators to their anions was measured spectrophotometrically. We have also interrelated selected indicators from the whole series in pure DMSO by dissolving both indicators of a pair in DMSO, adding a suitable amount of dimsylpotassium solution,[7] and obtaining the combined spectrum which could be analyzed to determine the amount of each anion present. Finally, we have related diphenylmethane and triphenylmethane to DMSO by the method of Stearns and Wheland,[3c] thereby placing the solvent in the over-all acidity scale. Several additional indicators were incidentally related

(3) (a) W. K. McEwen, J. Am. Chem. Soc., 58, 1124 (1936); (b) G. Schwarzenbach and R. Sulzberger, Helv. Chim. Acta, 27, 348 (1944); (c) R. S. Stearns and G. W. Wheland, J. Am. Chem. Soc., 69, 2025 (1947); (d) N. C. Deno, ibid., 74, 2039 (1952); (e) J. Hine and M. Hine, ibid., 74, 5266 (1952); (f) C. H. Langford and R. L. Burwell, ibid., 82, 1503 (1960).

(4) R. Stewart and J. P. O'Donnell, ibid., 84, 493 (1962).

(5) R. Stewart, J. P. O'Donnell, D. J. Cram, and B. Rickborn, Tetrahedron, 18, 917 (1962).

(6) R. A. More O'Ferrall and J. H. Ridd, J. Chem. Soc., 5030 (1963).

(7) Fluorenylpotassium was used with 2,4-dinitroaniline because dimsyl ion appeared to react in such a way as to destroy the desired indicator anion.

to suitable compounds in Table I using DMSO-MeOH-MeOK buffer solutions. Their pK_a values are given in Table II along with spectroscopic data obtained from DMSO solutions containing the indicators and excess dimsylpotassium.

Table II

Indicator		pKa	Anion λmax	ε × 10⁻⁴
9-Methylanthracene	ca.	27.7	470	1.52
4-Benzyldiphenyl		27.2	548	7.69
Xanthene		27.1	500	4.80
Diphenylyldiphenylmethane		25.3	595	5.75
Trisdiphenylylmethane		22.8	635	7.65
2,3-Benzofluorene		<19.5	440	3.09
4,5-Methylenephenanthrene		<19.5	515	.79
Indene		18.2	380	.15

The data obtained with aqueous DMSO allow the new indicators to be assigned pK_a values which are based through the work of Stewart and O'Donnell[4] on the pH scale. The combined data allow pK_a values based on the same absolute scale to be assigned to the indicators in methanolic DMSO and in DMSO. To do this it is necessary to assume that the pK_a of triphenylmethane is the same in the three solvent systems. The assumption is warranted because the solvent changes so little between the measurements involving triphenylmethane (DMSO, 0.11% water in DMSO, 0.02% methanol in DMSO). The resultant pK_a values along with some of the previously reported values and those calculated from published data are listed in Table I.

The pK_a values determined in three solvent systems—two changing and protic, one constant and aprotic—agree within 0.5 unit over a total of 12 pK units. This fact, coupled with an analysis of the calculations involved in the stepwise process of relating two indicators, 1 and n, of very different acidities, suggests (but does not prove) that the indicators behave nearly ideally. Thus, if the thermodynamic relative acidities of each successive pair of indicators are known, the relative acidity of indicators 1 and n can be calculated as $(K_1/K_2)(K_2/K_3) \ldots (K_{n-1}/K_n) = K_1/K_n$. The same formal calculation using experimental relative acidities (known only in terms of concentrations) gives

$$\frac{{}^sK_1{}'}{{}^sK_2{}'} \frac{{}^sK_2{}'}{{}^sK_3{}'} \cdots \frac{{}^sK_{n-1}{}'}{{}^sK_n{}'} = \frac{K_1}{K_2} \frac{{}^sT_2}{{}^sT_1} \cdots \frac{K_{n-1}}{K_n} \frac{{}^sT_n}{{}^sT_{n-1}} = \frac{K_1}{K_n} \frac{{}^sT_n}{{}^sT_1}$$

for a constant solvent system and

$$\frac{{}^1K_1{}'}{{}^1K_2{}'} \frac{{}^2K_2{}'}{{}^2K_3{}'} \cdots \frac{{}^sK_{n-1}{}'}{{}^sK_n{}'} = \frac{K_1}{K_2} \frac{{}^1T_2}{{}^1T_1} \cdots \frac{K_{n-1}}{K_n} \frac{{}^sT_n}{{}^sT_{n-1}} =$$

$$\frac{K_1}{K_n} \frac{{}^sT_n}{{}^1T_1} \frac{{}^1T_2}{{}^2T_2} \cdots \frac{{}^{s-1}T_{n-1}}{{}^sT_{n-1}}$$

for a changing solvent system, where K_n = thermodynamic ionization constant of indicator n, ${}^2K_n{}'$ = concentration ionization constant of indicator n in solvent 2, and ${}^sT_n$ = activity coefficient ratio for indicator n in solvent s (DMSO). In order for the same relative acidity to be obtained in the two types of solvent systems, it is necessary that

$$\frac{{}^sT_n}{{}^sT_1} = \frac{{}^sT_n}{{}^1T_1} \frac{{}^1T_2}{{}^2T_2} \frac{{}^2T_3}{{}^3T_3} \cdots \frac{{}^{s-1}T_{n-1}}{{}^sT_{n-1}}$$

It seems very improbable that this relationship would hold if the individual ratios changed markedly, and this suggests that the ratios are nearly constant and equal to unity by definition. This in turn suggests that an H_- scale based on the indicators will be valid in these solvents of high dielectric constants.

Although the indicators appear to behave ideally in these solvents, it is unlikely that this will be generally true. Due to the highly delocalized charge on the indicator anions and the high dielectric constant of the solvents, the salts are probably highly dissociated.[8,9] There should also be a minimum of difference in specific solvation effects on the anion and neutral molecule. In solvents of low dielectric constant, ion pairing is important and could cause large deviations from ideality. This effect probably accounts for the different relative acidities found by Streitwieser, *et al.*,[10] for some of the indicators studied here.

(8) K. Ziegler and H. Wollschitt, *Ann.* **479**, 123 (1930).
(9) Preliminary conductivity measurements made in this laboratory by Dr. G. J. McDonald support this statement.
(10) A. Streitwieser, Jr., J. I. Brauman, J. H. Hammons, and A. H. Pudjaatmaka, *J. Am. Chem. Soc.*, **87**, 384 (1965).

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Equilibrium Acidities of Hydrocarbon Acids in Cyclohexylamine[1]

Sir:

The importance of acidity measurements on proton acids in the elucidation of molecular properties has long been recognized. Nevertheless, experimental work on equilibrium acidities of hydrocarbon acids too weak to be studied in hydroxylic solvents (*i.e.*, pK's greater than about 20) has been almost nonexistent. In the 1930's, Conant and Wheland[2] and McEwen[3] made semi-

(1) Acidity of Hydrocarbons. XVI. Part XV: A. Streitwieser, Jr., R. A. Caldwell, and M. R. Granger, *J. Am. Chem. Soc.*, **86**, 3578 (1964). This research was supported in part by grants from the Air Force Office of Scientific Research and the Petroleum Research Fund of the American Chemical Society.
(2) J. B. Conant and G. W. Wheland, *ibid.*, **54**, 1212 (1932).
(3) W. K. McEwen, *ibid.*, **58**, 1124 (1936).

quantitative determinations of pK's of some hydrocarbon acids, but no other quantitative work in this area has been reported. We report herein the results of more precise equilibrium acidity measurements in the pK range 18–34.

Equilibrium constants were determined in cyclohexylamine for reactions (1) in which AH and BH are

$$\text{A}^-\text{M}^+ + \text{BH} \rightleftharpoons \text{AH} + \text{B}^-\text{M}^+ \qquad (1)$$
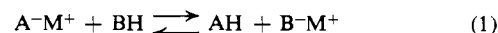
hydrocarbons whose corresponding carbanions show usable spectral differences and M is lithium or cesium. The solutions were made up on a vacuum line with careful exclusion of air and moisture using known amounts of hydrocarbons and solvent and amounts of lithium cyclohexylamide or cesium cyclohexylamide such that measurable amounts of all four components were present. The concentrations of the two anions at equilibrium were determined from visible spectra of the solutions and the spectral data of Streitwieser and Brauman[4] plus the additional results in Table I.

The organocesium compounds studied obeyed Beer's law over a concentration range of at least 10-fold, showing that reaction 2 goes to completion. The

$$\text{C}_6\text{H}_{11}\text{NH}^-\text{Cs}^+ + \text{RH} \longrightarrow \text{R}^-\text{Cs}^+ + \text{C}_6\text{H}_{11}\text{NH}_2 \qquad (2)$$
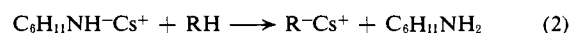
lithium salts of all compounds more acidic than *p*-biphenylyldiphenylmethane also obeyed Beer's law, but Beer's law correlations could not be obtained for solutions of *p*-biphenylyldiphenylmethane, triphenylmethane, or diphenylmethane in lithium cyclohexylamide–cyclohexylamine. These compounds are clearly not much more acidic than cyclohexylamine and are not completely converted to the lithium salts. It is clear from the differences between the cesium and lithium salts of these hydrocarbons that the acidity of cyclohexylamine relative to hydrocarbons depends on the metal used. This result is undoubtedly a manifestation of the concentrated charge in cyclohexylamide ion compared to the charge delocalization in the carbanion.

The absorbances of the equilibrium solutions decreased slowly with time, presumably from reaction of base with water in the glass or with the silicone stopcock grease, but the calculated equilibrium constant for any pair of hydrocarbons did not vary significantly over the observed range of anion concentrations. Our procedure establishes relative equilibrium acidities; however, it is convenient to record the results as absolute pK values. This was done by arbitrary reference to 9-phenylfluorene, which Langford and Burwell[5] found to have pK = 18.5 ± 0.1 in aqueous sulfolane. The results are summarized in Table II. Although we plan to extend the present methods to additional hydrocarbons of interest and to provide cross-checks within the present series, most of the important equilibria in Table II have been reproduced by two independent workers[6] and we do not expect the present numbers to change by more than ~0.2 pK unit.

One of the important aspects of the present results is their confirmation of McEwen's approximate assignments. Our earlier suggestion[7] that the McEwen scale

(4) A. Streitwieser, Jr., and J. I. Brauman, *ibid.*, **85**, 2633 (1963).
(5) C. H. Langford and R. L. Burwell, Jr., *ibid.*, **82**, 1503 (1960).
(6) Unpublished results of Dr. E. Ciuffarin.
(7) A. Streitwieser, Jr., W. C. Langworthy, and J. I. Brauman, *J. Am. Chem. Soc.*, **85**, 1761 (1963).