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STRONGLY BASIC SYSTEMS—V

H-ACIDITY SCALE BASED ON THE IONIZATION OF CARBON ACIDS

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Abstract—An investigation of the ionization of a number of carbon acids in strongly basic systems has been made. An H-acidity scale for ethanol–dimethyl sulfoxide solutions containing sodium ethoxide has been constructed and the p*Ka* values of the acids have been measured. The values found range from 11·14 (malononitrile) to 21·0 (fluorene). The relation of the acidity scale to acid type and the effect of substituents on acidity are discussed.

INTRODUCTION

Hammett H– and $H_=$ scales based on the ionization of substituted anilines have been reported.[1,2] The acidity function H– has recently received much attention in connection with kinetic investigations and the determination of the acidity of very weak acids.[3–5] This function measures the ability of a system to ionize an acid, HA, to form the anion, A^-, and is defined as:[6]

$$H- = pKa - \log\frac{[HA]}{[A^-]} = -\log\frac{a_{H^+}f_{A^-}}{f_{HA}} \qquad (1)$$

In dilute aqueous solution H– becomes identical with pH.

The existing H– scales have been determined by using substituted anilines as indicators whereas most kinetic investigations using strongly basic systems have been made on reactions involving carbon reaction sites. It is known that acidity functions can be dependent on the type of acid employed in setting up the scale.[7] The present work, then, reports the formation of an acidity function based solely on the ionization of carbon acids.

EXPERIMENTAL

Preparation of indicators. Malononitrile was fractionally distilled twice under red. press. and had b.p. 98–99°/11 mm (lit.[8] b.p. 92–94°/8 mm). 9-Cyanofluorene was prepared by Wislicenus' method[9] and, after recrystallization from ethanol twice, had m.p. 151–152° (lit.[9] m.p. 151–152°). Methyl

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fluorene-9-carboxylate (Eastman Kodak Co.) was recrystallized thrice from methanol, m.p. 64–65° (lit.[10] m.p. 64–65°). Nitration of triphenylmethane gave 4,4′,4″-trinitrotriphenylmethane which was recystallized from toluene, m.p. 212–213° (lit.[11] m.p. 214·5°). 4,4′-Dinitrodiphenylmethane and 2,4′-dinitrodiphenylmethane were prepared by the nitration of diphenylmethane[12] and, after repeated recrystallization from benzene, had m.p. 181–182° (lit.[12] m.p. 183°) and m.p. 118–119° (lit.[12] m.p. 118°). 3,4′-Dinitrodiphenylmethane was prepared by condensing *p*-nitrobenzylalcohol with nitrobenzene and was recrystallized twice from ethanol, m.p. 105–106° (lit.[12] 103–104°). The reduction of 9-phenylfluoren-9-ol gave 9-phenylfluorene[13] which was recrystallized from ethanol, m.p. 84–85° (lit.[13] 85°). Fluorene was recrystallized repeatedly from benzene–light petroleum (b.p. 80–100°), m.p. 116–117°.

Deuterium exchange. Samples of the three compounds, 2,4,6-trinitrotoluene, 4,4′-dinitrodiphenylmethane, and 4,4′,4″-trinitrotriphenylmethane, were added to a solution of NaOD in D_2O under N_2 with the minimum volume of dimethylsulphoxide added to fully dissolve the compounds. After 5 to 15 min the coloured solutions were neutralized with DCl solution. After isolation, the samples were recrystallized from benzene.

The three compounds were examined by PMR in $CHCl_3$ solution. Exchanged and unexchanged material in the same concentration and conditions were assayed using a Varian A60 spectrometer and the results are shown in Table 1.

TABLE 1. ASSAY OF DEUTERIUM EXCHANGE BY PROTON MAGNETIC RESONANCE

Compound	Aliphatic proton chemical shift (τ) (chloroform).	Extent of exchange
4,4′,4″-Trinitrotriphenylmethane	5·85	Nearly complete (90–100%)
4,4′-Dinitrodiphenylmethane	4·20	Extensive (75–85%)
2,4,6-Trinitrotoluene	*	Negligible (0–10%)

* *TMS* was not added because of precipitation of compound.

Indicator measurements. The p*Ka* value of the acids were established in a stepwise manner as previously described,[1,2] and are shown in Table 2 together with the spectral details. All indicators used showed instantaneous or *very* rapid, completely reversible, spectral changes in basic solution. A number of compounds were discarded because of irreversible, slow, or complex spectral changes.†

The p*Ka* value of malononitrile was measured in NaOHaq, the pH of which was measured immediately before the optical measurement. The value found was in good agreement with that reported by Hashimoto *et al.* (Table 2). The latter indicator was then used to transfer the measurements to a non-aqueous system; sodium ethoxide in ethanol. In these dil. basic solutions the anion concentration, $[A^-]$, was comparable to the free base concentration, $[OEt^-]$, and corrections were necessary to the base concentration. The measurements were then extended in ethanolic and ethanolic–dimethylsulphoxide solutions containing sodium ethoxide and the acidity scale formed is shown in Table 3.

In the present work it was found particularly important to rigorously exclude air from the system. Measurements were made under N_2 using the technique previously described.[1] The nitrophenylmethane indicators were difficult to redissolve in the cell, and to ensure complete solution, the indicators were added directly to the basic system in a small volume of dimethylsulphoxide. Corrections were applied to the solvent compositions for this addition and that of the added sodium ethoxide in ethanol.

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† These indicators included indene, 2-nitrofluorene, 2,5- and 2,7-dinitrofluorene, 3,3-dinitrodiphenylmethane, and diphenylacetonitrile.

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TABLE 2. THE p*Ka* VALUES OF THE CARBON ACIDS

Acid	p*Ka*	lit.p*Ka*	λ_{max}(mμ)	ε^{d}	Solvent
1. Malononitrile	11·14	11·16[a]	225	18,600	Water[c]
			226	20,800	Ethanol
2. 9-Cyanofluorene	11·41	—	410	2,220	Ethanol
3. Methyl fluorene-9-carboxylate	12·88	—	389	4,690	Ethanol
4. 4,4′,4″-Trinitrotriphenylmethane	14·32	—	707	19,300	Ethanolic Dimethylsulphoxide
5. 4,4′-Dinitrodiphenylmethane	15·85	15·82[b]	704	40,600	Ethanolic Dimethylsulphoxide
6. 2,4′-Dinitrodiphenylmethane	17·38	—	555	15,700	Ethanolic Dimethylsulphoxide
7. 3,4′-Dinitrodiphenylmethane	17·62	—	550	31,700	Ethanolic Dimethylsulphoxide
8. 9-Phenylfluorene	18·59	18·49[b]	409	11,300	Ethanolic Dimethylsulphoxide
			375	9,780	
9. Fluorene	21·0	—	517	3,670	Ethanolic Dimethylsulphoxide
			483	4,940	
			455	3,800	

[a] see Ref. 8. [b] see Ref. 18. [c] lit.[8] λ_{max} = 224 mμ, ε = 17,960.
[d] Acids do not absorb at these wavelengths.

TABLE 3. H_- FUNCTION FOR ETHANOL AND ETHANOLIC DIMETHYLSULPHOXIDE CONTAINING SODIUM ETHOXIDE

Dimethylsulphoxide (Mole %)	Sodium ethoxide (M)	H_-	H_- for corresponding soln. using methanol[a]
0	1×10^{-4}	11·97	—
0	1×10^{-3}	12·97	—
0	1×10^{-2}	13·99	12·23
1	1×10^{-2}	14·07	12·32
5	1×10^{-2}	14·25	12·63
10	1×10^{-2}	14·45	12·97
20	1×10^{-2}	14·92	13·67
30	1×10^{-2}	15·40	14·30
35	1×10^{-2}	15·68	14·56
40	1×10^{-2}	16·11	14·84
45	1×10^{-2}	16·61	15·15
50	1×10^{-2}	17·03	15·43
55	1×10^{-2}	17·37	15·77
60	1×10^{-2}	17·75	16·16
65	1×10^{-2}	18·13	16·47
70	1×10^{-2}	18·45	16·80
75	1×10^{-2}	18·69	17·21
80	1×10^{-2}	18·97	17·64
85	1×10^{-2}	19·28	18·06
90	1×10^{-2}	19·68	18·51
92·5	1×10^{-2}	20·05	18·85
95	1×10^{-2}	20·68	19·37

[a] methanolic dimethylsulphoxide containing sodium methoxide (0·025 M), (the aniline H_- scale[20], see text).

Some of the nitrophenylmethanes showed variation in the anion spectra with solvent composition. This was marked for 4,4′,4″-trinitrotriphenylmethane where the λ_{max} changed from 582 mμ (ethanol) to 703 mμ (40 mole % ethanolic dimethylsulphoxide) although there was little change in the extinction coefficients. The dinitrodiphenylmethanes on the other hand had a shift of less than 20 mμ.

In setting up an acidity scale, it is desirable that the differences in p*Ka* values for consecutive indicators be less than 1·0 unit and never greater than 2·0 units. This ideal has been attained in the present work with the exception of the gap before the weakest acid, fluorene. The difference in p*Ka* between fluorene and 9-phenylfluorene is about 2·4 units and it is not completely certain that fluorene is fully ionized in the most basic system used, potassium t-butoxide in dimethylsulphoxide. The p*Ka* value of fluorene is thus less certain than those of the other acids.

DISCUSSION AND RESULTS

Neither dimethylsulphoxide aq nor the methanolic dimethylsulphoxide scales previously used were suitable for the investigation of the ionization of carbon acids because of indicator insolubility in the former system. The latter system was discarded because of the rapid formation of species strongly absorbing in the region of 200 to 230 mμ, after the addition of sodium methoxide to both blank and sample, which precluded measurements using malononitrile.

The acidity scale. When setting up an acidity scale it is very important to employ only indicators the behaviour of which in basic systems can be unequivocably interpreted as a simple proton loss.

$$\mathbf{HA} + \mathbf{B}^- \rightleftharpoons \mathbf{A}^- + \mathbf{HB} \tag{2}$$

It has already been shown that *p*-nitrobenzyl cyanide has an anomalous behaviour in basic systems.[14] For acids whose ionization process requires confirmation, two criteria are available. If an acid is partially ionized in a medium containing deuterium oxide, it must exchange its acidic hydrogen estensively and rapidly for deuterium. This test will exclude many anomalous indicators. However, a compound could still be exchanging quite rapidly when the observed coloured anionic species is not the simple anion.[15]

The results of the deuterium exchange experiments indicate that 2,4,6-trinitrotoluene does not appear to lose a proton in our system; while they suggest that 4,4′,4″-trinitrotriphenylmethane and 4,4′-dinitrodiphenymethane ionize normally.

The most probable alternative to proton loss is the production of either a "Meisenheimer" complex or a π-complex between the compound and the basic species present*, as below:

$$\mathbf{HA} + \mathbf{B}^- \rightleftharpoons [\mathbf{HA.B}]^- \tag{3}$$

The relative stability of the complex will depend on the nucleophile, **B**$^-$, as well as the acid, **HA**. If identical p*Ka* values were found for an indicator using different solvent systems containing different basic ions, this would tend to confirm the occurrence of simple ionization by proton loss.

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* The possibility remains that a charge transfer or "Meisenheimer" complex is formed between the carbanion initially formed and a neutral molecule.[15,16] This seems unlikely in the present case since the base concentration is so much greater than that of the indicators.

[14] R. Stewart and J. P. O'Donnell, Unpublished studies.

[15] R. Foster and R. K. Mackie, *Tetrahedron* **19**, 691 (1963).

[16a] G. A. Russell and E. G. Janzen, *J. Amer. Chem. Soc.* **84**, 4153 (1962); [b] J. M. Miller and H. Pobiner, *Analyt. Chem.* **36**, 238 (1964).

The p*Ka* of 4,4′,4″-trinitrotriphenylmethane was 14·26 by stepwise comparison against methyl fluorene-9-carboxylate (p*Ka* = 12·88) in methanolic dimethylsulphoxide containing 0·025 M sodium methoxide. This value is in excellent agreement with that found in ethanolic solution, containing ethoxide ion (p*Ka* = 14·32.)

Furthermore measurements on 4,4′-dinitrodiphylmethane and 9-phenylfluorene using *aqueous* dimethylsulphoxide containing 0·011 M tetramethylammonium hydroxide (the aniline **H**–scale) gave values of 15·64 and 18·38, respectively. Langford and Burwell[17] had previously determined these values, in the same way, in aqueous sulpholane with added base and found for 4,4′-dinitrodiphenylmethane the p*Ka* to be 15·82 and for 9-phenylfluorene the p*Ka* to be 18·49. All these values are in good agreement with our values determined in ethanolic dimethylsulphoxide as shown in Table 2.

It appears that in the basic systems, phenylmethanes which have only a mono-nitro group in any one aromatic ring ionize normally.* This is not the case, however, for di- and tri-nitro derivatives.

A comparison of the **H**– scale based on carbon acids and nitrogen acids is not completely straightforward because the scales have not been determined under the same conditions. However, the relation (3) holds for dilute alcoholic alkoxide solutions (up to 0·1 M) and relates the alkoxide concentration, $[\mathbf{OR}^-]$, to the acidity, **H**–, by a constant, **B**, dependent on the nature of the alcohol.

$$\mathbf{H}- = \mathbf{B} + \log[\mathbf{OR}^-] \qquad (4)$$

The constant **B**, for ethanol, has been found by using substituted anilines[18,19] to be 15·74 whereas the present study using a carbon acid (malononitrile) gives 15·97. The results in Table 3 show that the increase in basicity of the ethanolic dimethylsulphoxide containing base (determined using carbon acids) parallels that of methanolic dimethylsulphoxide containing base (determined using substituted anilines[20]). The approximately constant separation is ascribable to the greater basicity of the ethanolic system.

An important cause of deviations in acidity functions determined in strong acid is the variation in the hydrogen bonding capacity of the cationic species (e.g. RNH_3^+, $R_2NH_2^+$, and R_3C^+).[21–23] Since the **H**– acidity scale appears to be general for both carbon and nitrogen acids (i.e. the ratio of indicator activity coefficients, f_{A^-}/f_{HA}, for carbon and nitrogen acids is approximately equal for the same solution) it seems probable that the anionic indicator species present in the basic systems considered here all have similar solvation patterns.

Substituent effects on the acidity. As would be expected electron-withdrawing groups greatly strengthens carbon acids. Thus the acid strengthening effect of the

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* Recently it has been found that, in very basic systems, *o*- and *p*-nitrotoluenes give rise to radical ions probably via the carbanion.[16]

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[21] R. W. Taft, Jr., *J. Amer. Chem. Soc.* **82**, 2965 (1960).

[22] M. J. Jorgenson and D. R. Harlter, *J. Amer. Chem. Soc.* **85**, 878 (1963).

[23] R. H. Boyd, R. W. Taft, Jr., A. P. Wolf and D. R. Christman, *J. Amer. Chem. Soc.* **82**, 4729 (1960).

9-substituents of fluorene (ΔpKa) is in the following order: 9-cyano (−9·6), 9-methoxycarbonyl (−8·1), 9-phenyl (−2·4). However, the degree of inhibition of resonance in the anions must be considered. The fluorene molecule is rigid and planar. Models suggest that steric inhibition is absent in the 9-cyano anion, is minimal for the 9-methoxycarbonyl anion, and is large for the 9-phenyl anion.

The small difference in acidity between 4,4′-dinitrodiphenylmethane and 4,4′4″-trinitrotriphenylmethane ($\Delta pKa = 1{\cdot}5$) must be due to the steric hindrance to resonance in the crowded anion of the latter. A *para*-nitro group is very much more acid strengthening than an *ortho*- or *meta*-nitro group; an *ortho*-nitro group appears to be only slightly more effective than a *meta*-nitro group. This must be due to the increased steric interactions inhibiting resonance in the "crowded" anion of the *ortho*-nitrodiphenylmethane. This effect has been previously observed when comparing the effect of an *ortho*- and a *para*-nitro group on the acidity of aniline and diphenylamine.[1] Similarly, an *ortho*-nitro group in diphenylamine is less effective than a *para*-nitro group. The reverse is true for the aniline, since steric interactions in the anion (of *o*-nitroaniline) will be less important.