The Effect of Substituents on the Acidity of Fluorene

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SEVERAL reports have been made recently on the acidity of carbon acids.[1-3] This has prompted us to report some of the salient features of our results. An acidity function,[4] H_-, has been established for the range 40—95 mole % aqueous dimethyl sulphoxide using a series of carbon acid indicators. The indicators, listed in the Table were chosen to enable a systematic study of the effect of both 9- and 2- substituents on the acidity of fluorene. The present acidity function is based on a pK_a value of 18·59 for 9-phenylfluorene.[5] This value has the advantage of being entirely dependent on a scale of carbon-acid indicators and has been measured by successive overlap of indicators in ethanolic dimethyl sulphoxide. However, this scale was anchored in aqueous solution by malononitrile and the pK_a of 9-phenylfluorene may be in some error due to deviations in pK_a scales in different protic solutions. Other values by Langford and Burwell[6] (18·49), Bowden and Stewart[5] (18·38), and the present workers[7] (18·42) are based on acidity scales generated by aniline indicators. The value of Steiner and Starkey[3b] (18·1) was obtained from a comparison with the dubious indicator,[8] 4-nitroaniline. Ritchie's measurements (16·4) in pure dimethyl sulphoxide[2b] will not be applicable to correlations in the presence of protic solvents and are based on a non-Hammett indicator technique. In the present studies, the acidity scale has been generated by closely overlapped Hammett-type indicators which give slopes of approximately unity and are completely reversible. The values relative to 9-phenylfluorene are thus considered reliable.

TABLE

The pK_a values of the carbon-acid indicators for the acidity function (H_-) of aqueous dimethyl sulphoxide containing tetramethylammonium hydroxide

Acid	pK_a‡
2-Nitrofluorene	17·96
9-(*p*-Biphenyl)fluorene	18·21
9-Phenylfluorene	(18·59)[a]
2-Cyanofluorene	18·96
3,4-Benzofluorene	19·62[b]
2-Bromofluorene	20·56
2-Chlorofluorene	20·59
9-Benzylfluorene	21·20
4,5-Methylenephenanthrene	21·19[c]
9-Methylfluorene	21·80[d]
Fluorene	22·10[e]
9-Ethylfluorene	22·22
2-Methoxyfluorene	22·36
9-Isopropylfluorene	22·70
9-t-Butylfluorene	23·41

‡ pK_a of acids relative to a value of 18·59 for 9-phenylfluorene.[5] Literature values are: [a] 18·49 (aqueous sulpholan);[6] 18·38 and 18·42 (aqueous dimethyl sulphoxide);[5,7] 18·1 (dimethyl sulphoxide);[3b] 16·4 (dimethyl sulphoxide).[2b]

[b] 19·45 (Cæsium cyclohexylamide in cyclohexylamine); 19·38 (lithium cyclohexylamide in cyclohexylamine).[1b]

[c] 22·63 (Cæsium cyclohexylamide in cyclohexylamine);[1a] 22·60 (lithium cyclohexylamide in cyclohexylamine);[1b] 20·0 (dimethyl sulphoxide).[2a]

[d] 19·7 (Dimethyl sulphoxide).[2b]

[e] 22·74 (Cæsium cyclohexylamide in cyclohexylamine);[1a] 22·83 (cæsium cyclohexylamide in cyclohexylamine);[1b] 21·0 (ethanolic dimethyl sulphoxide);[5] 20·5 (dimethyl sulphoxide);[3a] 20·5 (dimethyl sulphoxide);[2b] 21·1 (dimethyl sulphoxide).[3b]

A number of interesting points are evident from our acidity measurements. By treating the 2-substituents as equivalent to *meta*-benzene substitution,[9] a Hammett correlation gives a ρ value of 7·1; *N.B.* the parent compound, fluorene, alone deviates from this plot. This very high reaction constant can be compared to that for phenols[10] (2·23) and anilines[8] (4·07) and attributed to the increased charge delocalisation. The 9-alkylfluorenes follow the order of acidity attributable to the expected inductive effect and are well correlated by Taft σ^* values; except that fluorene is less acidic than 9-methylfluorene (as reported previously[2a]). This unexpected acid strengthening effect of the methyl group may arise from two effects. The first is that 9-alkyl substituents with α-hydrogen atoms may stabilise the anion by an "anti-hyperconjugation" effect, *i.e.*, the contribution of structures involving H^-. The second is that the same substituents could give rise to fulvene character, again caused by the contribution of structures involving H^-.

The present acidity function increases slightly more rapidly with increasing mole % dimethyl sulphoxide than does the scale recently established using aniline indicators.[8] Some part of this discrepancy can be attributed to the different base concentrations used (0·0471M in the present study and 0·0111M by the previous workers) in establishing the scales, which causes a more rapid onset of the shortage of base-solvating water molecules.[4] However, it possibly results from a different behaviour of the activity coefficients of the conjugate bases of the two indicator systems. A comparison of the behaviour of aniline and carbon-acid indicators in our system shows a slower response of 4-nitroaniline compared to the carbon acids and 4-chloro-2-nitroaniline.[7] Recent investigations indicate that the ionisation of 4-nitroaniline is very solvent dependent.[11] This aniline may not be a Hammett indicator.[8]

Studies are in progress to correlate the pK_a values of the fluorene indicators with LCAO–MO calculations. The full implications and details of these and related results will be discussed in the full publication.

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