The H_0 Function in Tetrahydrothiophen 1,1-Dioxide (Sulpholane)

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WE have commented[1–4] on the high level of acidity attainable in dilute solutions of strong acids (*e.g.*, HBF_4) in sulpholane; several aspects justify interim publication of our quantitative measurements of acidity functions. Nine standard Hammett bases[5] were examined in moderately dilute (0·1—2·0 M) solutions of seven acids in sulpholane When the convention of van Looy and Hammett[6] is adopted of setting the p*K* of 4-chloro-2-nitroaniline at its value in water, our results lead to an indicator basicity scale (Table) and a set of H_0 *versus* log [AH] plots (Figure) which show interesting features.

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TABLE

Indicator basicity scales

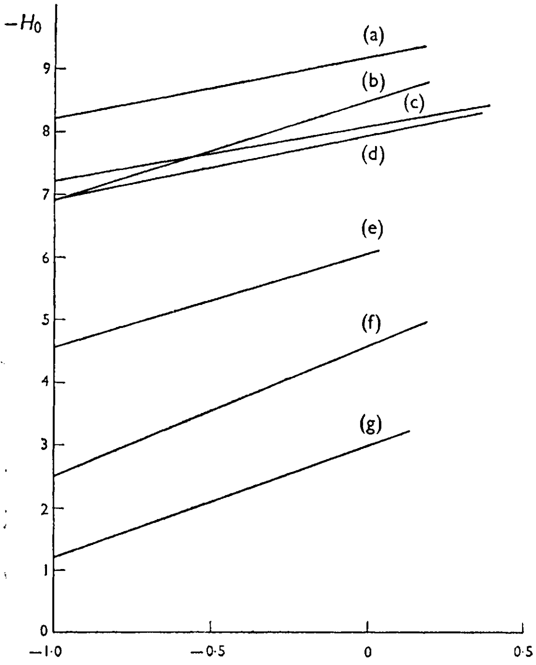
	pK_{BH^+}		
	In sulpholane (present work)	In sulpholane–sulphuric acid[10]	In aqueous sulphuric acid
4-Chloro-2-nitroaniline	−1·03[a]	−1·03[a]	−1·03[b]
2-Chloro-6-nitroaniline	−2·42 ± 0·08[e]		−2·43[c]
2,4-Dichloro-6-nitroaniline	−3·14 ± 0·11	−3·37	−3·32[b]
2,4-Dinitroaniline	−3·74 ± 0·15	−4·36	−4·53[b]
2,6-Dinitroaniline	−4·50 ± 0·21		−5·54[c]
2-Bromo-4,6-dinitroaniline	−6·06 ± 0·22	−6·55	−6·68[c]
2-Benzoylnaphthalene	−6·40 ± 0·24		−6·0[d]
2,4,6-Trinitroaniline	−8·21 ± 0·30	−8·22	−10·10[c]
Anthraquinone	−8·87 ± 0·31	−8·64	−8·4[d]

[a] Arbitrary
[b] Reference 5
[c] Reference 13
[d] Estimated from references 5 and 13
[e] 95% Confidence limits; uncertainty rises as acidity increases because results are dependent on an increasing number of ΔpK values.

The scale covers a range in which most functional groups act as bases, and allows for the first time a comparative study of their basicity in an essentially constant medium. In the aqueous sulphuric acid system the changing composition of the solvent causes large changes in the activity coefficients of bases and their conjugate acids,[7] undoubtedly connected with the ability of these solvents to form hydrogen bonds, notably to nitro-groups;[8] these are probably responsible for the very large differences in values of ΔpK for bases of different types between our system and water–sulphuric acid. Such phenomena are also probably responsible for the fact that *in mixtures of mineral acids and water* (which may be particularly unfavourable) compounds with different types of basic group increase in degree of protonation at different rates as acid concentration is increased.[9] Simpler behaviour might be expected in systems consisting mostly of an aprotic solvent such as sulpholane.

As would be expected, results reported for the sulpholane–sulphuric acid system[10] are intermediate between ours and the water–sulphuric acid system, and agree in the region of overlap.

The slope of the H_0 *versus* log [AH] plot should give the ratio of the mean molecular complexity (apart from solvation) of the free acid and its anion,[6] since conductivity results[11] suggest (and insensitivity of our results to indicator concentration confirms) that indicator salts are essentially ion-paired in sulpholane. Values near unity for HSO_3F, $HClO_4$ and HPF_6 indicate a simple anion and a simple free acid, probably $SH^+ \cdots PF_6^-$ (S=sulpholane) in the last case. (Cryoscopic experiments indicate a monomeric state for HSO_3F and H_2SO_4 in sulpholane). The values near two for HCl, HBr and HSO_4H suggest anions



FIGURE

Acidity function for seven acids in sulpholane. Gradients are given in parenthesis (a) HPF_6 (1·06 ± 0·06); (b) HBF_4 (1·58 ± 0·12); (c) $HClO_4$ (0·92 ± 0·08); (d) HSO_3F (1·06 ± 0·12); (e) HBr (1·98 ± 0·09); (f) H_2SO_4 (2·07 ± 0·15); (g) HCl (1·78 ± 0·11).

Lines a—g *rationalize, within the precision limits indicated,* 10—41 *measured indicator ratios of widely varying accuracy per line.*

of the type HA_2^-. The value of *ca.* 1·58 for HBF_4 is more probably due to partial dissociation of the acid, to HF and BF_3, than to association of the anion; the H_0 *versus* log [AH] plot shows a slight *downward* curvature (probably significant) at increasing concentrations, and while both HF and BF_3 dissolve exothermically in sulpholane, little if any heat is evolved when the solutions are mixed. If the "HPF_6" solution is assumed to be $SH^+ \cdots PF_6^-$ the data for HBF_4 give an equilibrium constant for the dissociation of $SH^+ \cdots BF_4^-$ of 0·41 ± 0·02 l. mole^{-1}.

New methods of handling data were used (a) to assure objectivity, (b) to minimise errors, and (c) to estimate precision. For each indicator/acid/concentration combination, measurements were made at 5 or 6 wavelengths symmetrically across the absorption maximum of the chromophore;[12] from each, a value of the indicator ratio was calculated:—

$$P_\lambda \equiv \frac{\epsilon_B - \epsilon_{obs}}{\epsilon_{obs} - \epsilon_{BH^+}} \approx \log \frac{[BH^+]}{[B]}$$

and a mean (P) and variance (V_1) were obtained. For a given wavelength—usually near the maximum—a second variance V_2 was calculated on the assumption that the standard deviation of the measured optical density, E, is given by $\alpha + \beta E$, where α and β were estimated by many replicate measurements of the spectra in neutral or very acidic solutions of the indicators employed; normally medium effects were small, and, $V_2 \gg V_1$. In a linear least-squares plot of P against log [AH] each point was assigned a weight of $1/(V_1 + V_2)$. This procedure automatically reduces the weight of points at very low or very high values of P (such points, though very inaccurate, tend to determine slopes in unweighted least-squares calculations, or in the subjective graphical methods that have been used for most Hammett acidity function measurements, even recently[10,13]). When regression lines for different indicators with the same acid indicated slopes within computed 95% confidence limits (which they always did), the weighted points were fitted to a set of parallel lines, differences in vertical intercept providing objective values for basicity differences and 95% confidence limits, relative to the acid used. When pairs of bases gave insignificantly different basicity differences for two different acids (which they always did), the points were fitted to five parameters defining two pairs of parallel lines having the same intercept difference. In principle, given adequate computer storage, the entire set of measurements, at several wavelengths, on the solutions of several bases in several acids, each at several concentrations, can be fitted to a single set of parameters, and an estimate can be made of their precision. The advantages of such a method of handling data are of course limited to systems where P is linearly related (within experimental error) to a convenient concentration variable; some published[10] non-linear plots may have been due to experimental errors at extreme values of P.

The simple behaviour observed with the acids and bases discussed is not found for solutions containing simple un-nitrated anilines and carboxylic acids. Attempts to extend the scale into regions of low acidity and, on the other hand, to other very strong acids, and to examine the behaviour of bases that do not follow H_0 in water–sulphuric acid, are now in progress.

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