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HYDROGEN-BONDING. PART 6. A THERMODYNAMICALLY-BASED SCALE OF SOLUTE HYDROGEN-BOND BASICITY

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A scale of solute hydrogen-bond basicity has been constructed for over 500 solutes, based on logK values for the hydrogen-bond complexation of solutes against reference acids in CCl_4.

The first scale of solute hydrogen-bond basicity was set up by Taft and co-workers,[1] who defined pK_{HB} as logK for the 1:1 complexation of bases with 4-fluorophenol in carbon tetrachloride at 25° C, equation (1; HA = 4-fluorophenol). It was shown[1] that the pK_{HB} scale yielded good linear free energy relationships (LFER) with logK values for bases against six other oxygen acids in CCl_4. Later work[2] revealed systematic deviations from LFER's when more polar solvents were used, and, even more significantly, when logK values for bases against 5-fluoroindole in CCl_4 were compared to pK_{HB} values.[3]

$$B + H\text{-}A \overset{CCl_4}{\rightleftharpoons} B\bullet\bullet\bullet H\text{-}A \qquad (1)$$

Possibly because of these observations, little further work on the pK_{HB} scale has been reported, and a number of other solute hydrogen-bond basicity scales have been put forward, based either on spectroscopic measurements,[4] or on ΔH^{o} values for complexation.[5-8] Since we believe the pK_{HB} scale to be the most satisfactory of these scales, and since we have already established a solute hydrogen-bond acidity scale based on equation (1),[9] we now report on a solute hydrogen-bond basicity scale also constructed using logK values for equation (1). We already know[10] that a completely general scale cannot be set up even with the standard solvent CCl_4 and that certain acid-base combinations must be excluded, specifically those giving rise to Maria-Gal[10,11] θ-values larger than about 75 degrees. Thus ethers, pyridines and trialkylamines in conjunction with acids such as pyrrole, indole, 5-fluoroindole, Ph_2NH, $CHCl_3$, *etc* are excluded. But note that the above bases in combination with other acids are retained in the general scheme.

We now set up a series of equations (2), where K^i is the complexation constant for a series of bases (i) against a given reference acid in CCl_4. The constants L_A and D_A characterise the reference acid, whilst the $\log K_B^{Hi}$ values characterise the bases, and thus represent a reasonably general scale of solute hydrogen-bond basicity. As pointed out above, the scale is not completely general because of the exclusion of certain acid-base combinations.

$$\log K^i = L_A . \log K_B^{Hi} + D_A \qquad (2)$$

Using literature data on logK values for equation (1), that we shall detail in a full paper, we set up a system of 34 equations containing 1040 $\log K^i$ values pertaining to 215 bases (only bases that appeared in two or more equations were allowed in this primary set). As found for the corresponding equations leading to an acidity scale,[9] all the 34 generated equations (2) intersect at a given point with logK = -1.1 units. On forcing (slightly), all the equations through this magic point where log K = -1.1, the 1040 $\log K^i$ values could be reproduced with a standard deviation of only 0.082 log units. The constants in equation (2) can be scaled in any arbitrary way without affecting the goodness of fit. However, since 4-fluorophenol is exceptionally useful as a reference acid, and since we are currently engaged in a programme to measure futher logK values against this reference,[12] we have arranged for the L_A and D_A values to be scaled such that $L_A = 1$ and $D_A = 0$ for 4-fluorophenol. Hence any further determined logK values for bases against 4-fluorophenol in CCl_4 will automatically be on the $\log K_B^H$ scale. A selection of derived $\log K_B^H$ values is in Table 1, and an example of one of the equations (2) is given as equation (3), where n is the number of bases and sd is the standard deviation; we do not give the correlation constant because this has little meaning for a forced line.

$$\log K^i \text{ (against phenol)} = 0.9462 \log K_B^H - 0.0567 \qquad (3)$$
$$n = 189, \quad sd = 0.088$$

From the set of 34 equations (2), it is possible to obtain a large number of secondary $\log K_B^H$ values for bases that appear in only one equation, giving a total of over 500 $\log K_B^H$ values. Together with the constants L_A and D_A for the 34 equations, it is now possible to predict some 17,000 logK values in CCl_4 to around 0.1 log units. The 500 $\log K_B^H$ values represent the first scale of solute hydrogen-bond basicity for which the generality is well defined. But note that the pK_{HB} scale of 1969 could be generalised to cover a total of seven reference oxygen acids.[1-3]

For many purposes,[13,14] it is very convenient to express the relative hydrogen-bond basicity of solutes on a scale with a zero reference point. But for logarithmic scales such as pK_{HB}, there is no method of selection of a zero reference point, since in principle the logK values can extend down to any large negative number. We have now indicated, both in this paper and in the preceding paper on hydrogen-bond acidity,[9] that there is a magic point of intersection when logK = -1.1 with K defined in concentration units of mol dm^{-3}. Further work is needed to refine the position of the magic point, since there are available only few reliable complexation constants with K less than about 1 mol dm^{-3}. However, once it is accepted that there is no inversion in basicity order for bases that follow equation (2), the existence of a magic point follows automatically. Either the lines defined by equation (2) must be parallel, or they must be convergent. Our analysis shows that they are convergent and, very clearly, that they are not parallel. We may then take $\log K_B^H$ = -1.1 as a zero reference point, and introduce a scaling factor of 4.636 so that hexamethylphosphortriamide with a $\log K_B^H$ value of 3.536 defines a new solute hydrogen-bond basicity scale, β_2^H, with β_2^H = 1 when $\log K_B^H$ = 3.536, eqn (4).

$$\beta_2^H = (\log K_B^H + 1.1)/4.636 \qquad (4)$$

We give in Table 1 a selection of β_2^H values, and in a full paper we shall list the 500 or so bases for which we can now derive β_2^H values. However, we wish strongly to point out now that across families there is very little connection between our scale of hydrogen-bond basicity, and any scale of full proton transfer basicity.

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TABLE 1. Hydrogen-bond basicities of some monomeric solutes[a]

Solute	$\log K_B^H$	β_2^H
water	0.65	0.38
methanol		0.41[b]
ethanol		0.44[b]
primary alcohols		0.45[b]
secondary alcohols		0.47[b]
tertiary alcohols		0.49[b]
HMPA	3.536	1.000
Me_3PO	3.444	0.980
DMSO	2.492	0.775
$(MeO)_3PO$	2.431	0.762
NMP	2.445	0.765
DMA	2.283	0.730
$MeSONMe_2$	2.313	0.736
DMF	1.973	0.663
cyclohexanone	1.325	0.523
$MeSO_2NMe_2$	1.296	0.517
acetone	1.206	0.497
THF	1.264	0.510
diethylether	0.988	0.450
ethyl acetate	0.968	0.446
benzaldehyde	0.826	0.415
Et_3N	2.001	0.669
Bu_3N	1.667	0.597
pyridine	1.797	0.625
acetonitrile	0.933	0.439
aniline	0.651	0.378
diethyl sulphide	0.220	0.285
benzene	-0.441	0.142
chlorobenzene	-0.589	0.110

[a] Values are given to three decimal places only to distinguish them from secondary values that we give to two decimal places. Since the error in $\log K_B^H$ is around 0.08, the corresponding error in β_2^H is about 0.02 units. [b] Secondary values using logK against 1-naphthol and 3,5-dichlorophenol in cyclohexane (R. Benizri and L. Bellon, Bull. Soc. Chim. France, 1978, I-378, and this work), logK against 3,4-dinitrophenol in cyclohexane (J.-L.M. Abboud, K. Straidi, G. Guiheneuf, A. Negro, M.J. Kamlet, and R.W. Taft, J. Org. Chem., 1985, 50, 2870), and logK against 4-nitrophenol in 1,1,1-trichloroethane, this work).

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