Hydrogen Bonding. Part 7. A Scale of Solute Hydrogen-bond Acidity based on log *K* Values for Complexation in Tetrachloromethane

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A scale of solute hydrogen-bond acidity has been constructed using equilibrium constants (as log K values) for complexation of series of acids (i) against a given base in dilute solution in tetrachloromethane, equation (A). Forty-five such equations have been solved to yield L_B and D_B

$$\log K^i = L_B \log K_A^{Hi} + D_B \qquad (A)$$

values characterising the base, and log K_A^H values that characterise the acid. In this analysis, use has been made of the novel observation that all the lines in equation (A) intersect at a given point where $\log K = \log K_A^H = -1.1$ with K on the molar scale. Some 190 log K_A^H values that constitute a reasonably general scale of solute hydrogen-bond acidity have been obtained. It is shown that there is no general connection between log K_A^H and any proton-transfer quantities, although certain family dependences are obtained. A number of acid–base combinations are excluded from equation (A), and alternative log K_A^{HE} values have been determined for such cases. The general log K_A^H values may be transformed into α_2^H values suitable for use in multiple linear-regression analysis through the equation $\alpha_2^H = (\log K_A^H + 1.1)/4.636$.

There is voluminous literature on hydrogen-bonding. Earlier reviews on hydrogen-bond complexation in solution listed 615 references (in 1968),[1] and 2 703 references (in 1974),[2] whilst Green[3] gave no fewer than 409 references to hydrogen-bonding by C–H groups, again in 1974. Since, then, much additional work on complexation constants and on enthalpies of complexation has been reported, notably by Abboud *et al.*,[4,5] Hadzi *et al.*,[6,7] Huyskens *et al.*,[8,9] Jarva,[10] Kivinen and Kuopio,[11,12] Luck *et al.*,[13] Taniewska-Osinska *et al.*,[14] Roussel *et al.*,[15–19] Ruostesuo *et al.*,[20–26] Spencer *et al.*,[27,28] Virtanen *et al.*,[29] Buchet and Sandorfy,[30] and Zeegers-Huyskens *et al.*,[31–35] as well as our own previous work.[36–38] Drago *et al.*,[39] and also Purcell *et al.*[40] have analysed enthalpies of complexation, but there are important reasons why analyses of complexation constants, as log $K°$ values or the equivalent $\Delta G°$ values, are more useful. First of all, it has been shown that numerous processes can be rationalised in terms of solute hydrogen-bond acidity and basicity.[41,42] Examples are octanol–water partition coefficients,[43] solubilities of non-electrolyes in water[44] and in blood,[45] the adsorption of solutes from water onto carbon,[46] h.p.l.c. retention indexes,[47] the toxicity of aqueous solutes to Photobacterium phosphoreum,[48] and the solubility of gases and vapours in polymers.[49] All these examples are equilibrium or free-energy-related processes, and hence it is the Gibbs energy of hydrogen-bond formation (or log $K°$) and not the enthalpy of hydrogen-bond formation that is the relevant thermodynamic parameter to use. Secondly, we have already shown[38] that in cases where enthalpies of complexation are perturbed through involvement of the solvent, the corresponding $\Delta G°$ or log $K°$ values are quite normal.

In the event, there have been very few discussions on general hydrogen-bond acidity and basicity in terms of $\Delta G°$ or log $K°$,[50–53] and only one realistic attempt to account for such properties over a wide range of solutes. Zeegers-Huyskens[53] was able to relate $\Delta G°$ values for hydrogen-bond complexation in solution to gas-phase proton-transfer acidities and basicities, but only by considering various classes of bases separately, *c.f.* also her work on enthalpies of complexation.[54] The only scales of solute hydrogen-bond acidity that have been used generally are those of Karger, Snyder, and Eon,[55,56] and of Kamlet and co-workers.[41–49] The former is based on enthalpy measurements and, for reasons already set out, is not directly relevant to the present work. The latter, denoted as α_m, will be discussed when we set out our own scale, see later. Indeed, the main purpose of the present work is to establish a scale of solute hydrogen-bond acidity, based on log K values for hydrogen-bond complexation.

Data Analysis.—The data we use refer to log K values for the 1:1 hydrogen-bond complexation reaction, equation (1), in

$$\text{A–H} + \text{B} \overset{K}{\rightleftharpoons} \text{A–H} \cdots \text{B} \qquad (1)$$

which a series of hydrogen-bond acids complex with a given reference base in an inert solvent. Both the acid and the base must be present at low concentration in order for both to be in solution as monomeric, unassociated solutes, otherwise some suitable correction for association must be applied.[35] Although several rather inert solvents have been used in studies of complexation, by far the largest number of investigations have used tetrachloromethane as the solvent. In order to simplify the analysis, we restrict the present work to this particular solvent (with one or two exceptions, as explained); we hope to extend our studies to other solvents later. We used both review,[1–3] and more recent papers[4–38,40] as sources of data, but invariably checked the original papers cited in reviews. The data is assembled as a series of log K values for acids against a given reference base in CCl_4 at a constant temperature with equilibrium constants expressed on the usual molar concentration scale. We refer to such a series of log K values as a 'set'. There were 45 such sets collected—i.e. series of log K values against 45 reference bases. In order for a general scale of

Table 1. Known combinations of acid and base excluded from the general scheme.[a]

Acids in CCl_4	Bases in CCl_4
Diphenylamine	Pyridine
4-Bromoaniline	4-Methylpyridine
N-Methylaniline	2,6-Dimethylpyridine
Indole	2,4,6-Trimethylpyridine
$CHCl_3$	Diethyl ether
Pyrrole	Dioxane
5-Fluoroindole	THF
$CDCl_3$	
Hept-l-yne	
$CHBr_3$	
N-Phenylurethane	
N-Methylacetamide	
Alkyl thiols	

[a] That is combinations of any of the acids listed with any of the bases listed. Results from ref. 57 and this work.

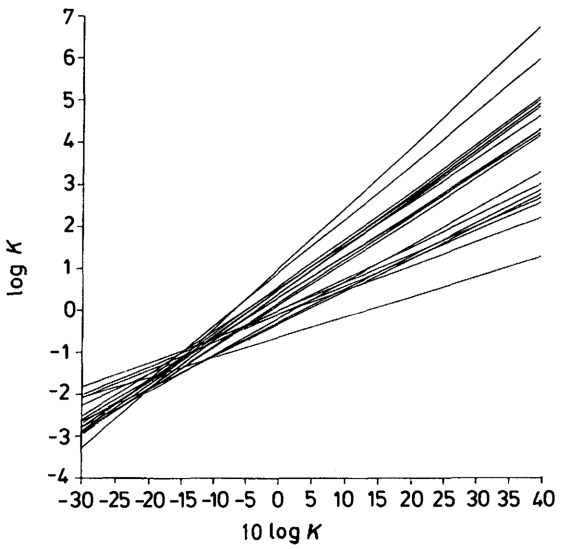

Figure 1. Plots of log *K* for series of acids against given reference bases *vs.* plots against any other reference base.

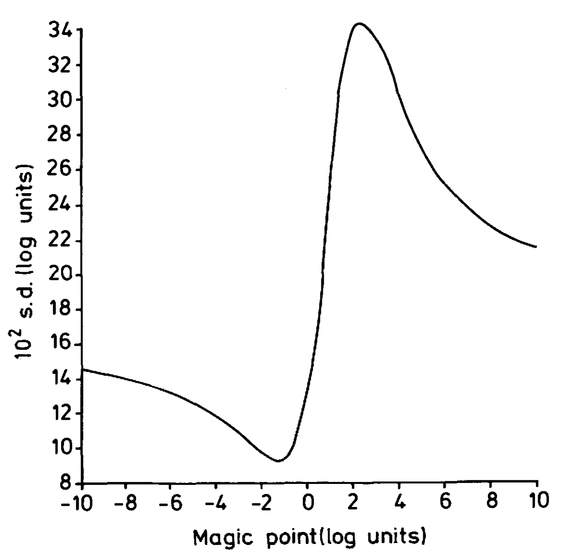

Figure 2. Plot of the standard deviation of 589 observed and calculated log *K* values against the chosen magic point.

hydrogen-bond acidity to be set up, it is necessary for a plot of log *K* (against reference base *x*) *vs.* log *K* (against reference base *y*) to yield a single straight line. That is, the various log *K* plots must show family-independent behaviour. Should such plots yield a number of lines for different families of acid (family-dependent behaviour) no completely general acidity scale can be constructed.

We have investigated family-independent or -dependent behaviour in hydrogen bonding in some detail,[57] using the methodology of Maria and Gal *et al.*[58] These workers defined an angle θ, experimentally obtainable, characteristic of the electrostatic:covalent ratio in complexes between a given acid and a series of bases. Family-independent behaviour will only be exhibited between log *K* values for acids with the same, or nearly the same θ value. It turns out that, for a large number of acids, including alcohols, phenols, and strong nitrogen acids, the variation in the characteristic θ value is in the range 64–73 degrees. Hence for these acids, a 'reasonably general' acidity scale can be constructed. However, for a number of rather weak acids the characteristic θ value rises to around 82 ± 5 and such acids will then show family-dependent behaviour in conjunction with certain classes of base. We therefore have to exclude a number of acid–base combinations, so that our scale is not completely general, but is 'reasonably general.' In Table 1 are given the acids and bases that in combination must be excluded: the list of acids contains those that we have previously identified,[57] together with a few that we have identified during preliminary calculations. It must be stressed that the acids in Table 1 are excluded only when in combination with the bases in Table 1, but are included in our general scheme in combination with any other base.

Having excluded the combinations shown in Table 1, we selected the first 28 sets given in Table 2 for analysis. These particular sets were chosen because they contained a large number of data points or because the data points spanned a large range of log *K* values. Having plotted log *K* for one set *vs.* log *K* for another set, it became clear that a series of lines could be generated that all intersected at some given 'magic point,' as shown in Figure 1. We then forced the first 28 sets through various intersection points, and determined the standard deviation (s.d.) of the 589 observed and calculated log *K* values. Results are shown in Figure 2 as a plot of s.d. *vs.* the magic point chosen. It is quite clear that the best point of intersection is *ca.* −1.1 on the log *K* scale: for the total of 589 data points the standard deviation, when restricted in this way is 0.093 log units, as compared with an s.d. of 0.085 for the completely unrestricted plots. Furthermore, Figure 2 shows unambiguously that the first 28 sets in Table 2 do not define a series of parallel lines, since the standard deviation rises considerably as the lines are forced to be parallel. We shall discuss the significance of the magic point later, but refer now to work in progress on the construction of a hydrogen-bond basicity scale,[59] where we have found that sets of bases against reference acids in CCl_4 also intersect at exactly the same point, −1.1 on the log *K* scale.

We felt, beyond any doubt, that a magic point certainly exists for hydrogen-bond acid–base complexation in CCl_4, and we then analysed the entire 45 sets in Table 2 as follows. A system of 45 linear equations (2) was constructed: log K^i refers to log *K* values for a series of acids against a given reference base. The

$$\begin{aligned} \log K^i \text{ (series of acids against base 1)} &= L_1 \log K_A^H + D_1 \\ \log K^i \text{ (series of acids against base } B\text{)} &= L_B \log K_A^H + D_B \end{aligned} \qquad (2)$$

constants L_1 to L_B and D_1 to D_B characterise the reference bases (1 to *B*, where *B* = 45). The log K_A^{Hi} values then serve to characterise the hydrogen-bond acids, and hence represent the hydrogen-bond acidity of the acids over all the equations (1 to

Table 2. Bases in tetrachloromethane used in the correlations through equations (2).[a]

	Base[b]	L_B	D_B	S.d.	r	n
1	Pyridine	1.0151	0.0139	0.1127	0.9897	33
2	Triethylamine	1.0486	0.0517	0.0854	0.9956	23
3	Tetramethylurea	1.1836	0.2011	0.0459	0.9988	16
4	Tetramethylthiourea	0.8196	−0.1978	0.0465	0.9967	12
5	Dimethylacetamide	1.1706	0.1865	0.0748	0.9964	35
6	Dimethylformamide	1.0719	0.0800	0.0944	0.9953	32
7	*N*,*N*-Dimethylbenzenesulphinamide	1.0873	0.0953	0.0439	0.9980	18
8	*N*,*N*-Dimethylmethanesulphinamide	1.1661	0.1832	0.0614	0.9955	17
9	HMPT	1.5693	0.6287	0.1546	0.9912	50
10	Acetone	0.7758	−0.2420	0.1009	0.9884	35
11	Cyclohexanone	0.8212	−0.1963	0.0654	0.9931	24
12	Benzophenone	0.7371	−0.2879	0.1008	0.9758	19
13	DMSO	1.2399	0.2656	0.0956	0.9947	51
14	Diphenyl sulphoxide	1.0622	0.0679	0.0447	0.9975	19
15	Ethyl acetate	0.7428	−0.2861	0.1171	0.9936	13
16	Dioxane	0.7477	−0.2750	0.0918	0.9895	17
17	THF	0.8248	−0.1970	0.0888	0.9960	23
18	Diethyl ether	0.7129	−0.3206	0.1261	0.9832	25
19	Acetonitrile	0.6878	−0.3396	0.1430	0.9694	23
20	Diethyl sulphide	0.4491	−0.6063	0.0720	0.9518	11
21	Trimethyl phosphate	1.2089	0.2298	0.0423	0.9969	11
22	Triphenylphosphine oxide	1.4480	0.4943	0.1010	0.9955	12
23	*N*-Methylacetamide	1.1002	0.1074	0.1519	0.9934	7
24	NMP	1.2145	0.2359	0.0775	0.9952	15
25	Pyridazine	1.0136	0.0148	0.0428	0.9943	12
26	Pyrimidine	0.8417	−0.1742	0.0388	0.9911	12
27	2-Aminopyrimidine	0.9689	−0.0338	0.0429	0.9980	12
28	Pyrazine	0.7643	−0.2591	0.0349	0.9914	12
29	Aniline	0.5946	−0.4461	0.0530	0.9767	13
30	1-Methylimidazole	1.2864	0.3145	0.1093	0.9818	10
31	2,2-Dimethyl-3-methylamino-2*H*-azirine	1.2192	0.2410	0.0530	0.9929	9
32	*N*,*N*-Diethylnicotinamide	1.1450	0.1594	0.0440	0.9962	7
33	*N*,*N*-Dimethyltoluene-4-sulphinamide	1.1040	0.1137	0.0625	0.9982	9
34	*N*,*N*-Dimethylbenzenesulphonamide	0.8341	−0.1815	0.1155	0.9491	9
35	*N*,*N*-Dimethyltoluene-4-sulphonamide	0.8556	−0.1576	0.1277	0.9446	9
36	Hexamethylthiophosphoric triamide	0.8250	−0.1924	0.0167	0.9988	9
37	Diethyl selenide	0.4173	−0.6410	0.0394	0.9761	6
38	Triethyl phosphate	1.2726	0.3001	0.0601	0.9986	5
39	Triphenyl phosphate	1.0008	0.0008	0.0421	0.9892	6
40	Pyridine *N*-oxide	1.2854	0.3150	0.0985	0.9974	6
41	Pentanonitrile	0.6894	−0.3422	0.0614	0.9955	9
42	*N*,*N*-Dimethylmethanesulphonamide	0.8099	−0.2089	0.0319	0.9964	9
43	Nicotine	1.0931	0.1023	0.0247	0.9981	7
44	1,3-Dimethyluracil	0.9802	−0.0214	0.0458	0.9956	13
45	3-Methylpyrimidin-4-one	1.0112	0.0129	0.0448	0.9979	13

[a] The constants in equation (2) are L_B and D_B. S.d. and r are the standard deviation and correlation constant, and n is the number of data points. [b] All values at 298 K except for set 20 (302), 29 (300), 31 (300), 32 (295), 37 (302), and 40 (293).

B, where $B = 45$). These log K_A^H values thus constitute a scale of solute hydrogen-bond acidity.* A computer program was devised to carry out the computations. It is necessary to input not only all the log K^i values, but also arbitrary log K_A^H values for any two acids in order to define the log K_A^H scale. However, the goodness-of-fit, and the relative log K_A^H values are quite independent of the two input log K_A^H values. The system of 45 equations contained 738 data points, as log K^i values, and reproduced these data points with a standard deviation of 0.089 log units. The system of equations is given in Table 2 in terms of L_B and D_B, and the resulting log K_A^H for the 89 acids included in the system are given in Table 3. Only acids that occurred in two or more equations were allowed in this primary list. As mentioned above, the combinations in Table 1 were excluded, and a few other acids were also left out. For example, we chose not to include carboxylic acids, which have less certain log K_A^H values, in order not to weight some of the equations unduly. Given the L_B and D_B values in Table 2, it is then possible to calculate by hand numerous secondary log K_A^H values for acids excluded from the primary set: these secondary values are in Table 4, giving a total of 186 log K_A^H values in Tables 3 and 4. Some of these secondary values were obtained from results by Buchet and Sandorfy[30] who used *N*-ethylacetamide in CCl_4 as the reference base, although this set was too restricted to be included in the system, equation (2). Similarly, values for a number of alkynes were calculated from results of Paugam and Lauransan,[60] not included in the general system.

A very interesting set of heterocyclic compounds has been studied by Roussel *et al.*,[15–19] who used the reference bases dimethyl sulphoxide (DMSO) and hexamethylphosphoric triamide (HMPT) in tetrachloromethane. From the recorded log K values and the constants in Table 2, it is possible to

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* These K_A^H values are formally equivalent to equilibrium constants for the series of acids against a particular base with $L_B = 1$ and $D_B = 0$.

calculate log K^H_A values in the usual way. Unfortunately, for the hydrogen-bond acids studied against each of the reference bases, there are systematic differences in the calculated log K^H_A values. The latter are given separately in Table 5, but clearly further work is needed on these systems.

Although our analysis is based on log K values in CCl_4, we have used otherwise unavailable results obtained by us against *N*-methylpyrrolidone (NMP) with 1,1,1-trichloroethane (TCE) as the solvent.[36,37] For acids, excluding those in Table 1, we find a reasonable correlation:

Table 3. Primary values[a] of log K^H_A.

Solute	log K^H_A	S.d.	*n*	pK_a[b]
Water	0.5359	0.0680	11	
Methanol	0.6027	0.0625	15	15.09
Ethanol	0.4424	0.0793	13	15.93
Propan-1-ol	0.3630	0.1089	4	16.1
Butan-1-ol	0.4299	0.1466	6	16.1
Propan-2-ol	0.4048	0.1714	5	17.1
t-Butyl alcohol	0.3833	0.1950	10	19.0
3-Ethyl-2,4-dimethylpentan-3-ol	0.0413	0.1493	3	
Di-t-butylmethanol	0.1452	0.1333	2	
3-Isopropyl-2,2,4,4-tetramethylpentan-3-ol	−0.1931	0.1842	3	
Me_3SiOH	0.7222	0.3972	4	
2,2,2-Trifluoroethanol	1.5305	0.0823	25	12.39
2,2,2-Trichloroethanol	1.2176	0.0299	11	12.25
2,2,2-Tribromoethanol	1.1154	0.0287	11	
2,2,3,3-Tetrafluoropropan-1-ol	1.3681	0.1543	3	12.74
Hexafluoropropan-2-ol	2.4737	0.1246	15	9.3
2,2,2-Trifluoro-1,1-bis(trifluoromethyl)ethanol	2.8959	0.1886	6	5.4
Phenol	1.6649	0.0717	45	10.00
Thiophenol	−0.7564	0.1752	2	
2-Methoxyphenol	0.1093	0.1010	4	
2-Methylphenol	1.3041	0.1557	3	
2-Isopropylphenol	1.3843	0.0152	5	
2-t-Butylphenol	1.2193	0.1306	6	
3-Methylphenol	1.5504	0.0636	6	10.09
3-Fluorophenol	2.0354	0.0491	10	9.21
3-Chlorophenol	2.1116	0.0760	14	9.13
3-Bromophenol	2.1387	0.0377	14	9.03
3-Trifluoromethylphenol	2.2436	0.1173	2	8.95
3-Nitrophenol	2.5410	0.1126	14	8.39
4-Methoxyphenol	1.5573	0.0427	25	10.21
4-Methylphenol	1.5377	0.0452	20	10.26
4-s-Butylphenol	1.5520	0.0437	11	
4-t-Butylphenol	1.4879	0.0544	4	
4-Fluorophenol	1.8177	0.0631	27	9.91
4-Chlorophenol	2.0069	0.0642	32	9.42
4-Bromophenol	2.0227	0.0433	27	9.36
4-Iodophenol	2.0484	0.0518	15	9.31
4-Acetylphenol	2.2513	0.0815	9	8.05
4-Cyanophenol	2.5468	0.0703	5	7.95
4-Nitrophenol	2.7184	0.0558	15	7.15
2,6-Dimethylphenol	0.7102	0.3170	4	
3,4-Dimethylphenol	1.4915	0.0563	11	
2-Methyl-6-t-butylphenol	0.5948	0.2297	4	
3,4-Dichlorophenol	2.3467	0.0818	16	
3,5-Dichlorophenol	2.4867	0.0863	14	
2,4,6-Trimethylphenol	0.6316	0.1722	3	
3,4,5-Trichlorophenol	2.6853	0.1244	8	
Pentafluorophenol	2.4414	0.2045	4	
Pentachlorophenol	1.4635	0.0965	9	
Pentabromophenol	1.2135	0.0820	2	
1-Naphthol	1.7201	0.0823	14	
2-Naphthol	1.7386	0.0620	7	
N,*N*-Dibenzylhydroxylamine	1.0005	0.0609	2	
4-Chloroperoxybenzoic acid	0.6538	0.0227	3	
Hept-l-yne	−0.5102	0.1761	3	
Chloroform	−0.1848	0.0862	8	24[c]
1,1-Dinitroethane	0.7267	0.1737	5	3.57[d]
Ammonia	0.9102	0.1538	3	
Cyanic acid	1.4892	0.0862	4	
Thiocyanic acid	2.3812	0.2569	5	
N-Nitromethylamine	1.6495	0.0818	6	
N-Nitropropylamine	1.5396	0.0902	6	
N-Nitrobutylamine	1.5322	0.0990	6	
N-Nitrocyclohexylamine	1.3984	0.1214	5	

Table 3 (*continued*)

Solute	$\log K_A^H$	S.d.	n	pK_a[b]
2-Cyano-*N*-nitroethylamine	2.3226	0.1237	5	
N,3,3,3-Tetranitropropylamine	2.4936	0.1047	6	
Ethyl *N*-Nitrocarbamate	1.7490	0.1415	6	
Aniline	0.1223	0.0219	2	
2-Nitroaniline	0.6043	0.0298	2	
3-Nitroaniline	0.7445	0.0144	2	
4-Nitroaniline	0.8524	0.0337	2	
4-Bromoaniline	0.3258	0.0902	6	
2-Chloro-4-nitroaniline	0.9990	0.0454	2	
4-Chloro-2-nitroaniline	0.9618	0.0216	2	
2-Aminopyridine	0.3743	0.0351	2	
3-Aminopyridine	0.5152	0.0016	2	
4-Aminopyridine	0.7949	0.0569	2	
Diphenylamine	0.4013	0.2176	10	17.7[e]
N,*O*-Dibenzylhydroxylamine	0.6356	0.1418	2	
N-Methylacetamide	0.6779	0.0818	4	
Pyrrole	0.7934	0.1067	10	17.51
Tetrachloropyrrole	2.2495	0.0770	5	
Tetrabromopyrrole	2.1166	0.1116	5	
Tetraiodopyrrole	1.6893	0.1309	5	
Indole	0.9194	0.0955	12	16.97
5-Fluoroindole	1.068	0.0456	9	16.30
Carbazole	1.0745	0.1155	7	
Maleimide	1.2037	0.1005	7	
Succinimide	1.1834	0.2084	7	9.62

[a] These values generate the L_B and D_B values for the sets given in Table 2. [b] From a number of standard sources, chiefly E. P. Serjeant and B. Dempsey, 'Ionisation Constants of Organic Acids in Aqueous Solution,' Pergamon, Oxford, 1979; for alkanols: J. Murto in 'The Chemistry of the Hydroxyl Group,' ed. S. Patai, Interscience, New York, 1971, Part 2, p. 1087; for phenols, especially: A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 1961, 388; and in general, from what appear to the authors to be the best-attested sources. [c] A. J. Kresge, *Acc. Chem. Res.*, 1975, **8**, 354. [d] pK_a of dinitromethane; A. T. Nielsen in 'The Chemistry of the Nitro and Nitroso Groups,' ed. H. Feuer, Interscience, New York, 1969. [e] Extrapolated from 4-nitrophenyl(phenyl)amine, pK_a 15.90; bis(4-nitrophenyl)amine, pK_a 14.08 (R. Stewart and J. P. O'Donnell, *Can. J. Chem.*, 1964, **42**, 1681).

$$\log \mathrm{K}\ (\text{against NMP in TCE}) = 0.883 \log K_A^H + 0.636 \quad (3)$$
$$r = 0.983 \quad \text{s.d.} = 0.129 \quad n = 24$$

where r is the correlation constant and n is the number of data points. From the above correlation, we were able to deduce $\log K_A^H$ values for a number of carboxylic acids as shown in Table 6. For the overlapping acid, trichloroacetic acid, there is excellent agreement between the NMP/TCE value, and values obtained from results of Hadzi and Rajnvajn[6] using the equations in Table 2. We can therefore, include $\log K_A^H$ values for ten carboxylic acids in Table 4.

Combinations of acid and base shown in Table 1 were excluded when the equations given in Table 2 were set up. Specifically, $\log K$ values for the acids listed were not used in set 1 (pyridine), set 2 (triethylamine), set 16 (dioxane), set 17 (THF), and set 18 (ether). Of course, there are other sets that actually contained no $\log K$ values for these acids, such as set 29 (aniline), where we suspect the acids in Table 1 will also be anomalous, but further information is needed in these cases. We can bring acids with high θ values into our general system, provided that we define amended $\log K_A^H$ values to be used in sets 1, 2, 16, 17, and 18. We have therefore calculated a Δ-value for those acids, defined by equation (4):

$$\Delta = \log K_A^H, \text{ calculated from equations in Table 2 (sets 1, 2, 16, 17, and 18)} - \log K_A^H, \text{ given in Tables 3 and 4} \quad (4)$$

The Δ value thus provides an estimate of the deviation from general behaviour of the acid–base combinations given in Table 1. There is not a great deal of information, but, as expected, all the Δ values are negative. Within the rather considerable error limits of Δ, we can only say that on average Δ is -0.318 log units for the acids listed, other than for the alkylthiols. We can now bring these acids into the general scheme by defining a hydrogen-bond acidity parameter, $\log K_A^{HE}$, for use with acids where there is a higher electrostatic:covalent ratio in complexes than usual:

$$\log K_A^{HE} = \log K_A^H + \Delta \quad (5)$$

These $\log K_A^{HE}$ values are also in Table 7. It must be stressed that only for complexation of these acids with certain bases (1, 2, 16, 17, and 18, as known to date) is it necessary to use the $\log K_A^{HE}$ values. For complexation with ketones, esters, amides, *etc.*, the normal $\log K_A^H$ values in Tables 3 and 4 can be used.

Finally, it must be noted that we give $\log K_A^H$ values in Table 3 to four decimal places, only to avoid rounding-off errors in the generation of equations listed in Table 2. Our estimate of inter-laboratory errors in the determination of $\log K$ values in equation (1) is *ca.* 0.05 units, so that the average error in the $\log K_A^H$ values obtained must be at least this value. Indeed, the standard deviations given in Table 3, and our overall standard deviations of 0.085 or 0.093 log units (above) confirm our estimate. The corresponding error in the derived α_2^H values (see later) will be *ca.* 0.02 units, and here again we give some values to three decimal places merely to distinguish primary values from less reliable secondary values.

Discussion

One of the key features of the present work is the discovery that when $\log K$ for one set in Table 1 is plotted *vs.* $\log K$ for any other set, there results a series of lines, Figure 1, that intersect near a given point. Whether or not there is an exact point of intersection is crucial to the construction of a scale of hydrogen-bond basicity on the same lines as the construction of the present scale of acidity. A simple geometrical figure shows that a general scale of hydrogen-bond basicity can be generated if, and only if, (*a*) all the lines in Figure 1 are parallel or (*b*) all the lines in Figure 1 intersect at a given point. Should the lines in Figure 1 be randomly orientated, then no general scale of hydrogen-bond basicity is possible. It is quite clear, both by inspection,

Table 4. Additional values of log $K^{\mathrm{H}}_{\mathrm{A}}$.

Solute	log $K^{\mathrm{H}}_{\mathrm{A}}$[a]	pK_a[b]
Isobutyl alcohol	0.343(1)	16.1
Neopentyl alcohol	0.406(1)	
t-Pentyl alcohol	0.365(1)	
2-Chloroethanol	0.502(1)	14.31
2-Fluoroethanol	0.734(1)	
Hexachloropropan-2-ol	1.892(1)	
Benzyl alcohol	0.715(1)	15.4
Pentafluorobenzyl alcohol	1.060(1)	
1,1,1-Trichloro-2-methylpropan-2-ol	0.754(1)	
1,1,1-Trifluoro-2-methylpropan-2-ol	1.064(1)	
1,1,1,3,3,3-Hexafluoro-2-methylpropan-2-ol	1.936(1)	
1,1,1,3,3,3-Hexafluoro-2-trichloromethylpropan-2-ol	2.344(1)	
[*O*-^{2}H]Phenol	1.435(2)	
2-Chlorophenol	1.914(1)	
2-Cyanophenol	2.323(1)	
3-Ethylphenol	1.442(1)	9.9
3-Dimethylaminophenol	1.309(1)	10.22
3-Methoxyphenol	1.641(1)	9.65
3-Cyanophenol	2.480(2)	8.61
4-Ethylphenol	1.433(1)	
4-Propylphenol	1.433(1)	10.47
4-Isopropylphenol	1.453(1)	10.24
4-Octylphenol	1.435(1)	
4-Phenylphenol	1.657(1)	9.55
4-Trifluoromethylphenol	2.253(2)	8.68
2,3-Dimethylphenol	1.370(1)	
2,4-Dimethylphenol	1.365(1)	
2,5-Dimethylphenol	1.395(1)	
3,5-Dimethylphenol	1.530(1)	
4-Methyl-2-t-butylphenol	1.518(1)	
3-Methyl-6-t-butylphenol	1.467(1)	
2,4-di-t-butylphenol	1.426(1)	
4-Nitro-3-trifluoromethylphenol	3.326(2)	
2,6-Dichlorophenol	0.387(1)	
3,5-Di(trifluoromethyl)phenol	2.680(2)	
2,3,5-Trimethylphenol	1.311(1)	
3,4,5-Trimethylphenol	1.431(1)	
4-Bromo-2,6-dimethylphenol	1.046(2)	
2,6-Dichloro-4-nitrophenol	2.165(1)	
3-Chloroperbenzoic acid	0.692(1)	
4-t-Butylperbenzoic acid	0.355(1)	
Trifluoroacetic acid	3.307(1)	0.52
Trichloroacetic acid	3.291 ± 0.232(4)	0.51
Dichloroacetic acid	3.068 ± 0.207(3)	1.35
Pentafluorobenzoic acid	3.018(1)	1.75
2-Bromobenzoic acid	1.875(1)	2.88
Chloroacetic acid	2.690 ± 0.326(3)	2.87
Benzoic acid	1.626(1)	4.21
Acetic acid	1.587(1)	4.76
Hexanoic acid	1.082(1)	4.85
Trimethylacetic acid	1.285(1)	5.04
1,2-Dichloroethane	−0.66(1)	
1,1,1-Trichloroethane	−1.05(1)	
Dichloromethane	−0.50(1)	
Deuteriochloroform	−0.18(1)	
Bromoform	−0.31(1)	
Bromodichloromethane	−0.53(1)	
1,1,2-Dichloroethene	−0.55(1)	
1,2-Dibromo-1,1-difluoroethane	−0.45(1)	
1,2-Dichloro-1-fluoroethane	−0.29(1)	
1-Chloro-1,1,2-trifluoro-2-iodoethane	−0.24(1)	
1,2-Dichloro-1,2-difluoroethane	−0.17(1)	
1,1,2-Trichloro-2, 2-difluoroethane	−0.14(1)	
1-Bromo-2-chloro-1,1,2-trifluoroethane	−0.13(1)	
1-Bromo-1-chloro-2,2,2-trifluoroethane	−0.06(1)	

Table 4 (*continued*)

Solute	log K_A^H [a]	pK_a [b]
2,2-Dichloro-1,1-difluoroethyl methyl ether	−0.33(1)	
2-Chloro-1,1,2-difluoroethyl difluoromethyl ether	−0.20(1)	
3-Chloro-3-methylbut-1-yne	−0.40(1)[c]	
Trimethylsilylethyne	−0.49(1)[c]	
Triethylsilylethyne	−0.49(1)[c]	
3-Chloropropyne	−0.24(1)[c]	
3-Bromopropyne	−0.24(1)[c]	
t-Butylethyne	−0.51(1)[c]	
Benzoylethyne	−0.20(1)[d]	
Phenylethyne	−0.56(1)[d]	21[e]
Pentamethyl(prop-2-ynyl)phosphoric triamide	−0.53(1)[f]	
N,N,N'N'-Tetramethyl-*N''*-benzyl-*N''*-prop-2-ynylphosphoric triamide	−0.53(1)[f]	
Prop-2-ynyl bis(piperidino)phosphinate	−0.46(1)[f]	
Prop-2-ynyl bis(diethylamido)phosphinate	−0.47(1)[f]	
Prop-2-ynyl bis(dimethylamido)phosphinate	−0.39(1)[f]	
But-3-ynyl bis(dimethylamido)phosphinate	−0.50(1)[f]	
Prop-2-ynyl bis(dibutylamido)phosphinate	−0.39(1)[f]	
N''-Ethyl-*N,N,N',N'*-tetramethyl-*N''*-prop-2-ynyl-phosphoric triamide	−0.58(1)[f]	
Prop-2-ynyl bis(piperidino)phosphinate	−0.29(1)[f]	
Prop-ynyl bis(morpholino)phosphinate	−0.27(1)[f]	
S-Prop-2-ynyl bis(dimethylamido)thiophosphinate	−0.26(1)[f]	
Diethyl prop-2-ynyl phosphate	−0.15(1)[f]	
O-Prop-2-ynyl bis(dimethylamido)thiophosphinate	−0.40(1)[f]	
Butyl sulphide	−1.182 ± 0.169(8)[g]	
Isopropyl sulphide		
t-Butyl sulphide		
Thioacetamide	1.570(1)	
N-Methylaniline	−0.296(1)	27[h]
N-Phenylurethane	0.555(1)	
Propynonitrile	0.471 ± 0.080(3)[i]	
2-Aminopyrimidine	0.16(1)	
4-Aminopyrimidine	0.62(1)	
5-Aminopyrimidine	0.68(1)	
α-Naphthylamine	0.35(1)	
β-Naphthylamine	0.51(1)	
α-Heptafluoronaphthol	2.047 ± 0.118(6)[j]	
β-Heptafluoronaphthol	2.483 ± 0.144(6)[j]	

[a] Values for carboxylic acids taken from Table 5. [b] See footnotes to Table 3. [c] From results by R. Queignec and B. Wojtkowiak, *Bull. Soc. Chim. Fr.*, 1970, 860. [d] By comparison with log K_A^H for neopentyl CH against pyridine or diethyl ether in CCl_4. [e] Footnote *c*, Table 3. [f] From results in ref. 60 against Me_2SO in CCl_4. [g] Average value for the three thiols. [h] J. B. Conant and G. W. Wheland, *J. Am. Chem. Soc.*, 1932, **54**, 1212. [i] From results by G. Cornu, Thèse 3e cycle, Nantes. [j] From results by G. S. Denisov, L. A. Kuzina, and L. A. Smolyanskii, *Zh. Obshch. Khim*, 1987, **58**, 196 (*Engl. translation* p. 170).

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and by consideration of the standard deviation shown in Figure 2, that the lines in Figure 1 are certainly not parallel, whilst both Figures 1 and 2 indicate that the set of lines does intersect at or near a given point. Indeed, if all the lines are forced through this magic point, then the s.d. of all the 589 points in sets 1–28 rises from 0.085 to only 0.093 log units. We know also that an exactly similar plot to that shown in Figure 1 arises in the construction of a hydrogen-bond basicity scale, and that the magic point, −1.1 log units, is exactly the same as found in this work.[59]

At first sight, such a magic point as in Figure 1 appears rather odd since it implies a situation in which acids with a log *K* value of −1.1 against one base have the same log *K* value against any other base that gives rise to such intersecting lines. It must be remembered, however, that although the log K_A^H constants refer specifically to hydrogen bonding, a quite variable electrostatic : covalent ratio in the complexes is allowed. As the log *K* (or log K_A^H) value becomes more and more negative, so the extent of electrostatic bonding of the dipole–dipole type (or even dispersion interaction) becomes dominant. Hence at around log $K = -1.1$, with *K* on the molar scale, the complex can no longer be regarded as a hydrogen-bond complex at all. A number of very small equilibrium constants have been recorded in the literature, often by application of a g.l.c. method. Thus against dioctyl ether,[61] log *K* values are −0.55 (CH_2Cl_2), −0.98 (CH_3CCl_3), −0.92 (CBr_4), and −1.18 (CCl_4). Clearly, the last two values must correspond to molecular complexes, probably of the dipole–dipole type, but also the complexes with CH_3CCl_3 or CH_2Cl_2 must include a large element of dipole–dipole interaction, rather than simple hydrogen-bonding. Hence if the extent of hydrogen-bonding is very small in complexes as log $K \longrightarrow -1.1$, it is not surprising that all hydrogen-bond acids appear equally strong (or equally weak) towards a given base.

The identification of the magic point leads to an important practical consideration, in that it is now comparatively easy to define the constants L_B and D_B in equation (2) for a set of acids against a new base. Instead of a rather large number of acids covering a wide range of log *K* values being required, the line can now be identified easily using the magic point of intersection plus log *K* values for but a few acids against the given base. Thus we are able to include in our general system, sets such as 31–43, where there are only a restricted number of log *K* values. Another practically useful consideration is in the setting up of a hydrogen-bond acidity scale with a lower limit of zero, since all that is needed is an adjustment of 1.1 units to log K_A^H, as explained below.

Table 5. Values of log K_A^H for some heterocyclic compounds.[a]

Compound	log K_A^H	
Thiazole-2(3*H*)-thione	2.205	1.927[b]
4-Methylthiazole-2(3*H*)-thione	2.238	1.786[b]
4-Ethylthioazole-2(3*H*)-thione	2.222	1.781[b]
4-Isopropylthiazole-2(3*H*)-thione	2.127	1.674[b]
4-t-Butylthiazole-2(3*H*)-thione	2.255	1.658[b]
4-Ethyl-5-methylthiazole-2(3*H*)-thione	2.080	1.623[b]
4-Isopropyl-5-methylthiazole-2(3*H*)-thione	2.127	1.392[b]
5-Methyl-4-t-butylthiazole-2(3*H*)-one	1.595	1.029[b]
1-Methylimidazolidin-2-one	1.031	
1-Methylimidazolidine-2-selone	1.298	
Oxazolidine-2-thione	1.963	
Thiazolidine-2-thione	1.642	
1-Methylimidazolidine-2-thione	1.095	
4,5-Dimethyloxazole-2(3*H*)-thione	2.269	
4,5-Dimethylthiazole-2(3*H*)-thione	2.238	
1,4,5-Trimethylimidazole-2(1*H*)-thione	1.783	
Benzo[*d*]oxazole-2(3*H*)-thione	2.590	
Benzo[*d*]thiazole-2(3*H*)-thione	2.448	
Benzo[*d*]imidazole-2(1*H*)-thione	1.884	
Thiazolidin-2-one	1.432	
Thiazolidine-2-selone	1.771	
1-Methyl-3,4,5,6-tetrahydrodiazine-2(1*H*)-thione	0.798	
Oxazolidin-2-one	1.220	
4,5-Dimethyloxazol-2(3*H*)-one	1.847	
4-Methylthiazol-2(3*H*)-one	2.038	
Benzo[*d*]oxazol-2(3*H*)-one	2.391	
Benzo[*d*]thiazol-2(3*H*)-one	2.205	
1-Methylbenzo[*d*]imidazol-2(1*H*)-one	1.827	
5-Methyl-1,4,5-oxadiazole-2(3*H*)-thione	2.323	
5-Methyl-1,4,5-thiadiazole-2(3*H*)-thione	1.901	
3-Methyl-1,2,4-thiadiazole-5(4*H*)-thione	2.934	
3-Phenyl-1,2,4-thiadiazole-5(4*H*)-thione	2.861	
1,3-Dimethyl-1,2,4-triazole-5(4*H*)-thione	2.411	
4-Phenylthiazole-2(3*H*)-thione	2.196	

[a] All calculated from log *K* values against DMSO in tetrachloromethane, except where indicated. [b] From log *K* values against HMPT in tetrachloromethane.

In Part 2 of this series,[37] we compared log *K* values for hydrogen bonding against NMP in TCE with various parameters characteristic of proton transfer, *viz.* pK_a values in water, ionisation constants in DMSO, and gas-phase proton transfer ΔG° (or ΔH°) values. We found no general connection between the log *K* values and any measure of proton transfer. There is little point in repeating the various plots shown in Part 2, but we can now state that the more extensive results in the present work confirm entirely our previous conclusion on the lack of a general connection between hydrogen-bonding (as log K_A^H) and proton transfer. However, there are a number of family-dependent correlations that might be valuable in the conversion of pK_a into log K_A^H, or *vice versa*. We give some of the more extensive correlations of log K_A^H against pK_a, or σ values.

$$\log K_A^H(\text{carboxylic acids})^* = 3.69 - 0.47\,\mathrm{p}K_a \qquad (6)$$
$$r = -0.976 \quad \text{s.d.} = 0.22 \quad n = 9$$

$$\log K_A^H(m\text{-phenols}) = 8.13 - 0.66\,\mathrm{p}K_a \qquad (7)$$
$$r = -0.980 \quad \text{s.d.} = 0.09 \quad n = 11$$

$$\log K_A^H(m\text{-phenols}) = 1.63 + 1.35\,\sigma_I + 0.63\,\sigma_R \qquad (8)$$
$$r = 0.995 \quad \text{s.d.} = 0.05 \quad n = 11$$

$$\log K_A^H(p\text{-phenols}) = 5.56 - 0.39\,\mathrm{p}K_a \qquad (9)$$
$$r = -0.965 \quad \text{s.d.} = 0.11 \quad n = 14$$

$$\log K_A^H(p\text{-phenols}) = 1.64 + 1.38\,\sigma_I + 1.01\,\sigma_R \qquad (10)$$
$$r = 0.992 \quad \text{s.d.} = 0.06 \quad n = 14$$

$$\log K_A^H(\text{alkanols})^\dagger = 4.42 - 0.25\,\mathrm{p}K_a \qquad (11)$$
$$r = -0.973 \quad \text{s.d.} = 0.20 \quad n = 13$$

It is of interest to note that the overall spread of log K_A^H values, from -1.1 up to 3.3 for 4-nitro-3-trifluoromethylphenol, is very much less than that of pK_a values (*ca.* 58 log units from 48 for methane to -10 log units for perchloric acid). Since the proton is only partially transferred during hydrogen-bond formation, it is not surprising that the spread of log K_A^H values is much less than the spread of pK_a values. However, another factor that will tend to introduce an upper limit to log K_A^H is the propensity of strong hydrogen-bond acids to act also as proton-transfer agents, so that it becomes almost impossible to measure hydrogen-bond complexation constants, for these acids.

Equations (6)–(11) set out a number of general relationships. We now discuss a few important individual solutes. Water is not a particularly strong hydrogen-bond acid in its monomeric state: the log K_A^H value of 0.536 is only of the same order as that for methanol (0.603) or ethanol (0.442), and less than many NH acids.‡ Bulk water, of course, is a powerful hydrogen-bond acid (*i.e.* by comparison with dilute aqueous solutions of other acids) but how much of the bulk water/monomer water difference is due to a mass-law effect and how much to any intrinsic effect is not known. Chloroform is another well known hydrogen-bond acid in the bulk form that is only a very weak acid as a monomeric solute (log $K_A^H = -0.185$). Indeed, carbon acids generally are very much weaker hydrogen-bond acids than their pK_a values would suggest. The nitrogen acids cover a wide range of hydrogen-bond acidity. Although we have no values for simple aliphatic primary or secondary amines, their log K_A^H values must be quite negative. It has very recently been suggested, on various grounds, that ammonia possesses virtually no proton-donating properties.[62] We think it reasonable to regard hydrogen bonding in liquid amines as lying on the border with non-specific dipolar stabilisation. As proton donors, simple amines join alkyl thiols at the limit of detectability. However, electron-withdrawing substituents can transform NH acids into strong hydrogen-bond acids: thus tetrachloropyrrole is stronger than acetic acid or most phenols. On the other hand, SH acids seem to be considerably weaker than expected. Even thiophenol (pK_a = 6.5) is a very poor hydrogen-bond acid, whilst the calculated log K_A^H values for simple thiols (-1.18) suggest that these solutes have almost no true hydrogen-bond acidity.

The coefficients of pK_a in equations (6), (7), (9), and (11) may be regarded as pseudo-Brønsted coefficients; pseudo, in that hydrogen-bonding in tetrachloromethane is being compared with full proton transfer in water. Hence, while they cannot quantify the extent of proton transfer on hydrogen-bond formation, they can be used accurately to compare its relative extent between classes. In addition to values for carboxylic acids (0.47), *m*-phenols (0.66), *p*-phenols (0.39), and alkanols (0.25), we also have approximate values for unactivated nitrogen acids

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* Omitting 2-bromobenzoic acid, where internal hydrogen-bonding leads to a lower log *K* value than calculated.

† Omitting t-butyl alcohol.

‡ Note that the log *K* value for water refers only to 1:1 water base complexes.

Table 6. Determination of log K_A^H values for carboxylic acids.

Acid	Reference Base				Average
	Me_2SO[6]	Ph_2SO[6]	Ph_3PO[6]	NMP/TCE[37]	
Trifluoroacetic				3.307	3.307
Trichloroacetic	3.541	3.400	3.005	3.217	3.291 ± 0.233
Dichloroacetic	3.248	3.114	2.842		3.068 ± 0.207
Pentafluorobenzoic				3.018	3.018
2-Bromobenzoic				1.875	1.875
Chloroacetic	2.811	2.939	2.321		2.690 ± 0.326
Benzoic				1.626	1.626
Acetic				1.587	1.587
Hexanoic				1.082	1.082
Trimethylacetic				1.285	1.285

Table 7. Deviations from general behaviour, and log K_A^{HE} values[a] for the acids in Table 1 in combination with bases in sets 1, 2, 16, 17, and 18.

Acid	Δ	n	log K_A^{HE}
Diphenylamine	−0.312 ± 0.066	3	0.083
4-Bromoaniline	−0.339 ± 0.051	2	0.008
Indole	−0.251 ± 0.203	3	0.601
Chloroform	−0.300 ± 0.184	4	−0.503
Pyrrole	−0.419 ± 0.096	3	0.475
5-Fluoroindole	−0.419 ± 0.144	4	0.750
Deuteriochloroform	−0.234 ± 0.088	2	−0.495
Hept-1-yne	−0.260 ± 0.127	2	−0.828
Bromoform	−0.178	1	−0.627
N-Phenylurethane	−0.165	1	0.237
N-Methylacetamide	−0.429	1	0.360
average	−0.318 ± 0.136	26	
Alkyl thiols	−0.119 ± 0.080	3	−1.301[b]

[a] $\log K_A^{HE} = \log K_A^H - 0.318$. [b] $\log K_A^{HE} = \log K_A^H - 0.119$.

(0.11), and for carbon acids (0.054).* These pseudo-Brønsted coefficients turn out to be remarkably variable, ranging from 0.66 for *m*-phenols to less than a tenth of this value for carbon acids. Qualitatively, their magnitude appears to reflect the extent to which the developing anionic charge is immediately able to delocalise; carboxylic acids and carbon acids represent the extremes in this respect. In between lie the alkanols, the oxygen atoms of which are well able to support an isolated negative charge, and the nitrogen acids, the nitrogen atoms of which are much less capable of this. The high pseudo-Brønsted coefficients for phenols is particularly interesting. Some light is thrown on this by the dual-substituent parameter analysis given in equations (8) and (10), where σ_I and σ_R are the Hammett inductive and resonance substituent constants, respectively. The relative importance of the resonance component is very surprising, 32% for *m*-phenols and 42% for *p*-phenols, indicating a degree of resonance involvement not far short of that for full proton transfer. At the other extreme, the very low pseudo-Brønsted coefficient for carbon acids represents a minimal degree of proton transfer in which no resonance component is conceivable.

We have used the equations mentioned above, together with results in Tables 3 and 4 to identify a hitherto unsuspected stereoelectronic effect. Succinimide is a considerably poorer proton donor than expected; this is plausibly due to lone-pair repulsion between the incoming proton acceptor and the carbonyl groups on succinimide itself. We have previously noted that carboxylic acids are no stronger as proton donors than simple phenols, and have attributed this to resonance stabilisation in the carboxylate anion, which will disproportionately favour full proton transfer over hydrogen-bonding.[37] The present results suggest an additional cause: carboxylic acids are weaker than expected as proton donors through the identical repulsive effect that operates in succinimide. Another class of anomalously weak proton donor[37] for which a similar explanation can be adduced is the sulphonamides. The resonance theory as the sole explanation of the relative carboxylic acid/phenol hydrogen-bond strengths is further weakened by the similar pseudo-Brønsted coefficients for these solutes, and by the large resonance component in the phenol hydrogen bonding as revealed by our analysis of equations (8) and (10). Whilst resonance must play some part, we now attribute to stereoelectronic repulsion much or most of the anomalous weakness as hydrogen-bond donors of carboxylic acids, sulphonamides, cyclic amides and possibly other classes of a similar sort yet to be examined. This conclusion may have considerable consequences, *e.g.* in discussion of the binding of such compounds to biological receptor sites.

Classical steric effects play only a small role in influencing hydrogen-bond acidity. Thus all primary alcohols, even neopentyl alcohol, have almost the same log K_A^H value. Introduction of a 2-isopropyl or 2-t-butyl group into phenol lowers log K_A^H, but not by very much.† However 2,6-dimethylphenol or 2-methyl-6-t-butylphenol are weaker than phenol by *ca.* one log unit, and 2,6-di-isopropylphenol and 2,6-di-t-butylphenol are so weak that we had to exclude them from our general analysis.

We can conclude by stating that we have been able to set up a reasonably general scale of solute hydrogen-bond acidity, and that such a scale has little overall connection with solute proton-transfer ability. Within certain families it is possible to estimate log K_A^H values from, *e.g.*, pK_a values, see equations (6)–(11), but outside these families proton-transfer quantities are not reliable indicators of hydrogen-bond acidity. Finally, we note that the log K_A^H scale is based on log K values in tetrachloromethane. In a later publication we hope to extend the scale to cover other inert solvents.

Construction of an α_2^H *Scale.*—It is now well-established[41,42] that a large number of physicochemical and biochemical processes involving a series of solutes can be interpreted using a multiple linear-regression equation that contains terms reflecting solute hydrogen-bonding. Two general equations have been put forward, equations (12) and (13). The former

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* We do not give the full equation for these two classes because they are based on only four and three points, respectively. However, the pK_a coefficients, we feel, are worthy of discussion.

† Note that the very low log K value for 2-methoxyphenol (0.109) is probably due to internal hydrogen-bonding in the phenol.

Table 8. Some values of the hydrogen-bond parameters α_2^H and α_2^{HE}.

Solute	α_2^H	α_2^{HE}
Water	0.353	
Methanol	0.367	
Simple primary alcohols	0.328	
Simple secondary alcohols	0.324	
Simple tertiary alcohols	0.319	
2-Fluoroethanol	0.396	
2-Chloroethanol	0.346	
2,2,2-Trifluoroethanol	0.567	
2,2,2-Trichloroethanol	0.500	
2,2,2-Tribromoethanol	0.478	
Hexafluoropropan-2-ol	0.771	
2,2,2-Trifluoro-1,1-bis(trifluoromethyl)ethanol	0.862	
Phenol	0.596	
3-Fluorophenol	0.676	
3-Chlorophenol	0.693	
3-Bromophenol	0.699	
3-Iodophenol	0.701[a]	
3-Cyanophenol	0.772	
3-Nitrophenol	0.785	
4-Fluorophenol	0.629	
4-Chlorophenol	0.670	
4-Bromophenol	0.674	
4-Iodophenol	0.679	
4-Cyanophenol	0.787	
4-Nitrophenol	0.824	
Formic acid	?	
Acetic acid	0.550	
Other alkanoic acids	0.542	
Fluoroacetic acid	0.77[a]	
Chloroacetic acid	0.74[a]	
Bromoacetic acid	0.74[a]	
Iodoacetic acid	0.71[a]	
Cyanoacetic acid	0.78[a]	
Dichloroacetic acid	0.899	
Trichloroacetic acid	0.947	
Trifluoroacetic acid	0.951	
Benzoic acid	0.588	
3-Chlorobenzoic acid	0.64[a]	
3-Nitrobenzoic acid	0.68[a]	
4-Chlorobenzoic acid	0.63[a]	
4-Nitrobenzoic acid	0.68[a]	
5-Fluoroindole	0.468	0.399
Indole	0.436	0.367
Pyrrole	0.408	0.340
Maleimide	0.497	
Carbazole	0.469	0.400
Diphenylamine	0.324	0.255
N-Methylacetamide	0.383	0.314
Aniline	0.264	0.195[b]
3-Chloroaniline	0.33[a]	0.26[b]
3-Bromoaniline	0.33[a]	0.26[b]
3-Nitroaniline	0.398	0.329[b]
4-Chloroaniline	0.30[a]	0.23[b]
4-Bromoaniline	0.308	0.239
4-Nitroaniline	0.421	0.352[b]
Alkylamines	0.00[a]	0.00
Dialkylamines	0.00[a]	0.00
Trichloromethane	0.197	0.129
Dichloromethane	0.129	0.060[b]
Halogenoalkanes	0.00[a]	0.00
1,1-Dinitroethane	0.394	?
Propynonitrile	0.339	0.270
Phenylethyne	0.12	0.05
Alkyl ethynes	0.13	0.06
Nitromethane	0.12[a]	0.05[b]
Methanonitrile	0.09[a]	0.02[b]
Acetone	0.04[a]	0.00
Other ketones	0.00[a]	0.00
Phenyl hydrosulphide	0.116[c]	0.47[b]
Alkyl hydrosulphide	0.00	0.00

[a] Estimated values, see text. [b] Assuming $\Delta = -0.318$, see Table 7. [c] A recent value.

seems adequate for the description of processes in condensed phases,[41–48] whilst the latter is the more satisfactory in dealing with processes of the gas ⟶ liquid or gas ⟶ solid type.[49]

$$SP = SP_0 + s\pi_2^* + a\alpha_2 + b\beta_2 + mV_2 \qquad (12)$$

$$SP = SP_0 + s\pi_2^* + a\alpha_2 + b\beta_2 + l\log L^{16} \qquad (13)$$

In equations (12) and (13), SP is some solubility or solubility-related property, SP_0 is a constant, π_2^* is the solute dipolarity, α_2 the solute hydrogen-bond acidity, β_2 the solute hydrogen-bond basicity, V_2 a solute volume parameter, and $\log L^{16}$ the solute Ostwald absorption coefficient on hexadecane.

The parameters π_2^*, α_2, and β_2 are most conveniently defined such that as the particular solute property becomes very small, the parameter approaches zero. We can quite simply arrange this for hydrogen-bond acidity by adjusting the $\log K_A^H$ scale by exactly the magic point value of -1.1 units. Since the α_2 scale is merely a scale of relative solute hydrogen-bond acidity, the range of scale is unimportant. In order to have a convenient range, and in order that the range should be compatible with that for the β_2 scale, we have used the same factor of 4.636 to

$$\alpha_2^H = (\log K_A^H + 1.1)/4.636 \qquad (14)$$

obtain an α_2 scale that we denote as α_2^H. Since $\log K_A^H$ is so easily transformed into α_2^H, there is little point in giving separate α_2^H values for all 186 solutes in Tables 3 and 4. However, we can make a number of simplifications in constructing an α_2^H scale; for example, within experimental error $\log K_A^H$ for all simple primary alcohols is the same, and hence but one α_2^H value will suffice for these solutes. In Table 8 are listed α_2^H values for a few selected solutes including cases where some simplification is possible. From Tables 3 and 4 it is possible to obtain α_2^H values for some 186 solutes, and further α_2^H values can be deduced *via* the correlations given in equations (6)–(11). Also in Table 8 are α_2^{HE} values derived from the $\log K_A^{HE}$ values in Table 7.* Because the particular acids concerned are all rather weak, there are not very large differences between α_2^H and α_2^{HE} and it is possible that in multiple correlations these differences would hardly be significant.

In addition to all the above results, there are available values of $\log K$ for the complexation of a large number of carbon acids with various bases in tetrachloromethane, obtained by Lorand *et al.*[64] using an n.m.r. method. We have not been able to include these results in Tables 3 and 4 because they have been obtained at 308 K rather than at 298 K. However, it is possible to correct the $\log K$ values to 298 K using $\Delta H°$ values that we have estimated by comparison with other literature values.[1–3] In Table 9 we give details of these corrections as well as our calculated $\log K_A^H$ and α_2^H values for these carbon acids. For a number of acids, there is quite good agreement between values of α_2^H in Table 9 and those we have obtained before (*e.g.* $CHCl_3$, $CHBr_3$, and $ClHC{=}CCl_2$), but for the solute $PhC{\equiv}CH$, the value of 0.04 for α_2^H in Table 9 seems much too low, and that of 0.12 (Tables 4 and 8) is preferred.

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* Ruostesuo *et al.*[63] have recently determined $\log K$ values for the complexation of some phenols and alcohols, carbazole, indole, and pyrrole with a number of bases in tetrachloromethane. For the bases Ph_3PO, $(MeO)_3PO$, and $(PhO)_3PO$ there result excellent plots of $\log K$ *vs.* $\log K_A^H$. However for the bases Ph_3PS and Ph_3PSe, the $\log K$ values for carbazole, indole, and pyrrole are larger than expected. This may result from a lower electrostatic component in the complexes than usual, and suggests that another set of complexation constants (between the acids in Table 1 and bases Ph_3PS, Ph_3PSe, *etc.*) are excluded from our general scheme.

Table 9. Calculation of log K_A^H and α_2^H values from results by Lorand *et al.*[64]

		log *K*				
Solute	Base	308 K[a]	298 K[b]	$-\Delta H°$	log K_A^H	α_2^H
$HCCl_3$	HMPT	0.371	0.431	2.5	−0.126	0.20
$HCCl_3$	DMSO	−0.027	0.021	2.0	−0.197	
$HCBr_3$	HMPT	0.301	0.361	2.5	−0.171	0.20
Br_3CCHBr_2	HMPT	0.049	0.097	2.0	−0.339	0.16
CH_2Br_2	HMPT	−0.167	−0.132	1.5	−0.485	0.13
$PhCHBr_2$	HMPT	−0.167	−0.132	1.5	−0.485	0.13
4-$NO_2C_6H_4CHBr_2$	HMPT	0.744	0.827	3.5	0.126	0.26
F_2CHCN	HMPT	1.029	1.125	4.0	0.316	0.30
Cl_2CHCN	HMPT	1.314	1.433	5.0	0.513	0.35
Br_2CHCN	HMPT	1.217	1.336	5.0	0.451	0.34
Br_2CHCN	DMSO	0.747	0.830	3.5	0.455	
Br_2CHCN	DMF	0.555	0.638	3.5	0.521	
$ClCH_2CN$	HMPT	0.663	0.746	3.5	0.075	0.25
$PhCH(CN)CO_2Et$	HMPT	0.114	0.162	2.0	−0.297	0.17
$CH_2(CH)_2$	HMPT	1.778	1.993	6.5	0.831	0.45
$CH_2(CN)_2$	DMF	1.056	1.176	4.0	1.022	
$CH_2(CN)_2$	Acetone	0.530	0.613	3.5	1.102	
$BrCH(CN)_2$	HMPT	2.312	2.490	7.5	1.186	0.49
Br_2CHNO_2	HMPT	1.013	1.108	4.0	0.305	0.30
$PhCH(NO_2)_2$	HMPT	1.459	1.590	5.5	0.613	0.38
$PhCH(NO_2)_2$	Acetone	0.228	0.288	2.5	0.683	
$PhCH(CN)_2$	DMF	0.723	0.806	3.5	0.677	0.38
$PhCH(CN)_2$	Acetone	0.230	0.290	2.5	0.685	
$Cl_2CHCONMe_2$	HMPT	0.158	0.206	2.0	−0.269	0.18
Cl_2CHCO_2Me	HMPT	−0.167	−0.132	1.5	−0.484	0.13
Cy-C_3HCl_5	HMPT	−0.229	−0.194	1.5	−0.524	0.12
$Br_2C=CHBr$	HMPT	−0.638	−0.614	1.0	−0.792	0.07
$Cl_2C=CHCl$	HMPT	−0.589	−0.545	1.0	−0.748	0.08
(*E*)-NCCH=CHCN	HMPT	1.161	1.280	5.0	0.415	0.33
$EtOC=C(CN)_2$	HMPT	1.258	1.377	5.0	0.477	0.34
$Me_2C=CHCN$	HMPT	−0.585	−0.561	1.0	−0.758	0.07
(*E*)PhCH=CHCN(α)	HMPT	0.072	0.119	2.0	−0.325	0.17
(*E*)PhCH=CHCN(β)	HMPT	−0.020	0.028	2.0	−0.383	0.15
(*E*)$PhCH=CHNO_2$(α)	HMPT	0.025	0.073	2.0	−0.354	0.16
(*E*)$PhCH=CHNO_2$(β)	HMPT	0.093	0.141	2.0	−0.311	0.17
1,2,4,5-$Cl_4C_6H_2$	HMPT	−1.137	−0.113	1.0	−1.110	0
C_6HCl_5	HMPT	−1.053	−1.029	1.0	−1.056	0.01
3-NO_2-1,2,4,5-Cl_4C_6H	HMPT	−0.310	−0.274	1.5	−0.575	0.11
1,2,4,5-$F_4C_6H_2$	HMPT	−0.347	−0.311	1.5	−0.599	0.11
$PhC\equiv CH$	HMPT	−0.824	−0.800	1.0	−0.910	(0.04)[c]
$BrCH_2C\equiv CH$	HMPT	−0.276	−0.240	1.5	−0.554	0.12
$EtO_2C\equiv CH$	HMPT	0.220	0.268	2.0	−0.230	0.19
$NCC\equiv CH$	HMPT	1.083	1.178	4.0	0.350	0.31

[a] Observed[64] values of log *K*. [b] Calculated values of log *K* using the $\Delta H°$ values in kcal mol^{-1} given. [c] This value seems too low, and that calculated from log $K_A^H = -0.56$ in Table 4, $\alpha_2^H = 0.12$ is preferred.

We have found it quite impossible to correlate the log K_A^H or α_2^H values for the total set of carbon acids in Tables 3, 4, and 9. We suspect also that the small, but finite, α_2^H values calculated for the aromatic carbon acids in Table 9 possibly reflect dipole–dipole interactions rather than hydrogen-bond complexation. For two groups of carbon acids, however, we have been able to set up correlations of α_2^H against σ_1 that may be of use in the prediction of further α_2^H values. The halogenated compounds shown in Table 10 lead to the correlation

$$\alpha_2^H = -0.114 + 0.922\sigma_1 \qquad (15)$$
$$r = 0.910 \quad \text{s.d.} = 0.02 \quad n = 18$$

but it should be noted that the correlation collapses if compounds containing CN or NO_2 groups are included.

The substituted alkynes listed in Table 11 can be examined as a group, the resulting correlation with σ_1 being

$$\alpha_2^H(RC\equiv CH) = 0.110 + 0.348\sigma_1 \qquad (16)$$
$$r = 0.926 \quad \text{s.d.} = 0.03 \quad n = 9$$

A solute hydrogen-bond acidity scale, α_m, has been constructed by Kamlet and co-workers,[41–49] based on log *K* values for complexation with pyridine *N*-oxide in cyclohexane,[4] and extended through various back-calculations involving equation (12). Although the origins of the α_m and α_2^H scales are different, there is a fair measure of agreement between them especially for solutes with moderate or low values, see Table 12. At the higher end of the scales, α_m tends always to be larger than α_2^H. We have carried out a number of regressions using equations (12) or (13)

Table 10. Values of α_2^H for some halogenated carbon acids.[a]

Solute	σ_1	α_2^H
$CHCl_3$	0.34	0.20
CH_2ClCH_2Cl	0.21	0.09
CH_3CCl_3	0.14	0.01
CH_2Cl_2	0.28	0.13
$CHBr_3$	0.34	0.17
$CHCl_2Br$	0.34	(0.12)[b]
CH_2BrCF_2Br	0.25	0.14
$CHClFCH_2Cl$	0.31	0.17
$CHIFCClF_2$	0.32	0.19
$CHClFCHClF$	0.33	0.20
$CHCl_2CClF_2$	0.32	0.21
$CHClFCBrF_2$	0.34	0.21
$CHBrClCF_3$	0.32	0.22
$CHBr_2CBr_3$	0.31	0.16[c]
CH_2Br_2	0.28	0.13[c]
$PhCHBr_2$	0.30	0.13[c]
$CHCl_2CONMe_2$	0.30	0.18[c]
$CHCl_2CO_2Me$	0.31	0.13[c]
c-C_3HCl_5	0.26	0.12[c]

[a] Values of α_2^H from Tables 3 and 4 except where shown. [b] Excluded as an obvious outlier. By comparison with $CHCl_3$ and $CHBr_3$ α_2^H should be *ca.* 0.19, and from equation (15) a value of 0.20 is calculated. [c] From Table 9.

Table 11. Values of α_2^H for some alkynes.[a]

R in RC≡CH	σ_1	α_2^H
n-Pe	−0.01	0.13
Me_3C	−0.01	0.13
Ph	0.12	0.12
$ClCH_2$	0.20	0.19
$BrCH_2$	0.20	0.19
$ClMe_2$	0.18	0.15
PhCO	0.30	0.19
NC	0.57	0.34
EtOCO	0.30	0.19[b]

[a] From Tables 3 and 4 except where shown. [b] Table 9.

Table 12. Some comparisons of the α_m and α_2^H scales.[a]

Solute	α_m	α_2^H
Benzoic acid	0.75	0.59
Acetic acid	0.71	0.55
Hexanoic acid	0.55	0.54
4-Nitrophenol	0.93	0.82
4-Fluorophenol	0.65	0.63
Phenol	0.61	0.60
Methanol	0.35	0.37
Ethanol	0.33	0.33
Propan-2-ol	0.31	0.32
t-Butyl alcohol	0.29	0.32
Aniline	0.16	0.26
Alkyl thiols	0.10	0.00
Alkylamines	0.00	0.00

[a] Values of α_m from refs. 41–49 and M. J. Kamlet, unpublished work.

and have confirmed that essentially the same correlation equation is obtained using either α_m or α_2^H. It seems therefore that replacement of the α_m scale with the more extensive α_2^H scale could be undertaken quite simply.

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