group G relative to the standard group G_0 will be given by,

$$\frac{\rho_G}{\rho_{G_0}} = \gamma \qquad (5)$$

where ρ_G and ρ_{G_0} are the reaction constants for reaction series XGY and XG_0Y both of which are undergoing the same reaction under the same conditions. The group chosen as the standard is the *p*-phenylene group. Values of γ for several common groups from the ionization of the carboxylic acids are given in Table III.

TABLE III

TRANSMISSION OF SUBSTITUENT EFFECTS

Group	γ	Ref.[a]	τ
t-Vinylene	2.23	6	6.52
Ethynyl	1.89	—	5.13
4-Phenyl	1.00		2.94[c]
4-Styryl	0.466	3	
4-Phenylethynyl	0.63[b]	10[a]	
4-Diphenyl	0.341	3	
4-Phenylmethyl	0.489	3	
2-(4-Phenyl)ethyl	0.212	3	
Ferrocenyl	0.677	9	2.4
4-Phenylcyclopropyl	0.182	24	
5-Furanyl	1.40	3	
5-Thienyl	1.08	4	

[a] Source of ρ values for γ. [b] From Ref. 10a, values of γ of 0.25 or 0.28 depending upon which of the two ρ values for the ionization of benzoic acids in 50% ethanol given by Jaffé[3] is used. Thus the average value of γ in this case is about 0.44–0.45. [c] Ref. 25.

Hine[25] has recently proposed that the transmission of substituent effect through the *m*- or *p*-phenylene group is given by

$$\tau = \frac{\rho^2}{\log \frac{K_1}{4K_2}} \qquad (6)$$

where ρ is the reaction constant for the ionization of a benzene acid or base reaction series, and K_1 and K_2 are the first and second ionization constants for the member of the series which possesses two identical reaction sites. Examples of such compounds ate isophthalic and terephthalic acids, resorcinol and hydroquinone, and *m*- and *p*-phenylenediamine. This relationship is readily extended to other groups if the reaction constants have been obtained with the same substituent constants. Values of τ for several groups are given in Table III.

It is noteworthy that in both treatments of the transmission of substituent effects the acetylene group is found to be somewhat less effective than the *trans* ethylene group. This is in accord with the observations of Sinn[26] who reports that the carbon-carbon triple bond is less polarizable than the carbon-carbon double bond, and that the electrons in both π bonds of the triple bond are more strongly held than those of the double bond. The energies are 35–36 Kcal./mole for the double bond π electrons, and 44 Kcal./mole for each of the two π bonds of the triple bond.

HOBOKEN, N. J.

---

(24) E. N. Trachtenberg and G. Odian, *J. Am. Chem. Soc.*, **80**, 4018 (1958).

(25) J. Hine, *J. Am. Chem. Soc.*, **81**, 1126 (1959).

(26) H. Sinn, *Z. Elektrochem.*, **61**, 989 (1957).

[CONTRIBUTION FROM MELLON INSTITUTE]

On the Correlation of Hydrogen Bridging Equilibria with Acidity

JOHN E. GORDON

Received April 5, 1960

The relationship $\Delta \log K_{\text{assn.}} = a\Delta \log K_a^{\text{HA}}$ is proposed for correlation of hydrogen bridging equilibria with acidity in the system variable acid-reference base: $\text{HA} + \text{B} \overset{K_{\text{assn}}}{\rightleftharpoons} \text{AH} \cdots \text{B}$. The available chemical and spectroscopic data are found to be largely in accord with this and the analogous expression for variation of the proton acceptor moiety. Analogous expressions are found applicable to formation of the bridged ion pair, $\text{A}^- \cdots \text{HB}^+$, and on inclusion of the Brønsted catalysis law, the formation of each of the species ($\text{AH} \cdots \text{B}$, proton transfer transition state, $\text{A}^- \cdots \text{HB}^+$) intermediate between $\text{AH} + \text{B}$ and $\text{A}^- + \text{BH}^+$ can be described by $\Delta \log K = x\Delta \log K_{\text{ion}}$ with suitable coefficient x. Numerical results of the correlations are compared and related to structure using this model, as are the formation of complex ions of the type $\text{BHB}^\pm$ and the influence of proton acceptor polarizability on hydrogen bridge stability.

The concept of a relationship between the strength of a hydrogen bridge, $\text{AH} \cdots \text{B}$, and the acidity and basicity of the proton donor and acceptor moieties involved is not a new one; indeed, it finds common qualitative employment in the literature.[1] The basis and scope of this generalization, and the possibilities of a quantitative extension thereof, however, have not been explored as fully as existing data permit. Such exploration is the purpose of the present article. Several authors[2–5] have plotted data on association through

---

(1) See, for example, H. Van Looy, and L. Hammett, *J. Am. Chem. Soc.*, **81**, 3872 (1959).

(2) R. Denyer, A. Gilchrist, J. Pegg, J. Smith, T. Tomlinson, and L. Sutton, *J. Chem. Soc.*, 3889 (1955).

TABLE I

ACIDITY DEPENDENCE OF PROTON BRIDGING EQUILIBRIA AND PROTON TRANSFER RATES

	Acceptor	Donor	Solvent	a	b	r^a	Ref.	Method
1	$(C_2H_5)_3N$	ArOH	Cyclohexane	0.58		0.15	2	Vapor-liquid partition
2	$CH_3CO_2CH_3$	ArOH	Heptane	0.36		0.01	10	U.V. spectra
3	$(C_2H_5)_3N$	ROH	CCl_4	0.15		0.025	11, 12	$\Delta\nu_s{}^{OH}$
4	$(C_2H_5)_2O$	ROH	CCl_4	0.065		0.008	11, 12	$\Delta\nu_s{}^{OH}$
5	$(C_2H_5)_2O$	ArOH	CCl_4	0.25		0.02	13b	$\Delta\nu_s{}^{OH}$
6	[c]	CH_3OD	[d]		0.099	0.0065	3	$\Delta\nu_s{}^{OD}$
7	Pyridines	CH_3OD	[d]		0.17	0.01	4	$\Delta\nu_s{}^{OD}$
8	Methylbenzenes[e]	HCl	Heptane		0.044	0.002	14, 15	Vapor pressure
9	[f]	*t*-Butyl alcohol	CCl_4		1.00[g]		11, 12	$\Delta\nu_s{}^{OH}$
10	[f]	*i*-Propyl alcohol	CCl_4		1.14[g]		11, 12	$\Delta\nu_s{}^{OH}$
11	[f]	C_2H_5OH	CCl_4		1.18[g]		11, 12	$\Delta\nu_s{}^{OH}$
12	[f]	CH_3OH	CCl_4		1.20[g]		11, 12	$\Delta\nu_s{}^{OH}$
13	[f]	$C_2H_5O(CH_2)_2OH$	CCl_4		1.27[g]		11, 12	$\Delta\nu_s{}^{OH}$
14	[f]	$Cl(CH_2)_2OH$	CCl_4		1.37[g]		11, 12	$\Delta\nu_s{}^{OH}$
15	Pyridines[h]	$CHCl_3$	—		0.14	0.01	4	Heat of mixing
16	[h, i, j]	$CHCl_3$	—		0.048	0.004	3, 16	Heat of mixing
17	Cyclic ethers[j]	$CHCl_3$	—		0.089	0.008	3, 17	Heat of mixing
18	Various	RCOOH	H_2O	0.3–0.9[k]			18, 19	Brønsted rel.
19	Amines, $RCOO^-$	Various	H_2O		0.4–0.9[k]		18, 19	Brønsted rel.
20	$C_6H_5NBrCOCH_3$	RCOOH, ArOH	C_6H_5Cl	0.30[k]			20	Brønsted rel.
21	$RCOO^-$	Acetone	H_2O		0.88[k]		21	Brønsted rel.
22	$RCOO^-$	Chloroacetone	H_2O		0.82[k]		21	Brønsted rel.
23	$RCOO^-$	2-Carbethoxycyclohexanone	H_2O		0.64[k]		21	Brønsted rel.
24	$RCOO^-$	1-Phenyl-1,3-butanedione	H_2O		0.52[k]		21	Brønsted rel.
25	$RCOO^-$	3-Bromo-2,4-pentanedione	H_2O		0.42[k]		21	Brønsted rel.

[a] Probable error in a or b. [b] Further measurements of ref. 13 were in reasonable agreement with entries 3 and 4; however, data for ROH-tetrahydrofuran correlate very poorly. [c] Amines, ArCOR, $ArNO_2$. [d] Acceptor. [e] −78°. [f] $(C_2H_5)_3N$, $(C_2H_5)_2O$. [g] b (ref. acid = ROH)/b (ref. acid = t-C_4H_9OH) = $[\Delta\nu_s{}^{ROH}$ $(N(C_2H_5)_3$ cplx.) $-\Delta\nu_s{}^{ROH}$ $(O(C_2H_5)_2$ cplx.)]/[$\Delta\nu_s$ t-C_4H_9OH $(N(C_2H_5)_3$ cplx.) $-\Delta\nu_s$ t-C_4H_9OH $(O(C_2H_5)_2$ cplx.)], included to show variation of b with reference acid strength; true only if $(C_2H_5)_3N$ and $(C_2H_5)_2O$ obey the same relation of type (6). [h] Data for amines not included as they appeared to fractionate into separate families but were too few and covered too narrow basicity ranges to establish a separate line. [i] Nitriles, ketones, ethers, *N*,*N*-dialkyl amides, esters, nitrates, nitro compounds. [j] Basicities were estimated from $\Delta\nu_s{}^{CH_3OH}$ [29] [k] The coefficients α and β of Equations (4) and (5).

hydrogen bridges against corresponding aqueous acid or base dissociation constants; however, the data are derived from a wide variety of experimental methods, and no general means for their numerical comparison have evolved. Although two excellent new books[6,7] assemble much of the heretofore scattered quantitative and semiquantitative association data, these remain largely unexamined from this point of view. We have recently had occasion to employ the following relations for this purpose, principally in the hope of making semiquantitative predictions of association constants and to provide a background for stability studies on complex ions of the type BHB±. For the association reaction[8]

$$HA + B \overset{K_{assn.}}{=} AH \cdots B \qquad (1)$$

in the system variable acid + reference base,

$$\Delta\Delta F_{assn.} = a\Delta\Delta F_{ion}^{HA} \text{ or } \Delta \log K_{assn.} = -a\Delta pK_a^{HA} \qquad (2)$$

and in the system variable base + reference acid

$$\Delta\Delta F_{assn.} = -b\Delta\Delta F_{ion}^{BH^+} \text{ or } \Delta \log K_{assn.} = b\Delta pK_a^{BH^+} \qquad (3)$$

What follows tests the utility of (2) and (3). Just as the stable hydrogen bridge is a close structural analog of the proton transfer transition state, this formulation is analogous to the Brønsted catalysis law, which is employed below in the forms

$$\Delta\Delta F\mp = \alpha\Delta\Delta F_{ion}^{HA} \qquad (4)$$

$$\Delta\Delta F\mp = -\beta\Delta\Delta F_{ion}^{BH^+} \qquad (5)$$

RESULTS

The available data[9] are summarized in Table I and plotted in Figs. 1-7. Entries 1-8 of Table I contain all the material which may be said to constitute

---

(3) W. Gordy and S. Stanford, *J. Chem. Phys.*, **9**, 204, 215 (1941).

(4) M. Tamres, S. Searles, E. Leighly, and D. Mohrman, *J. Am. Chem. Soc.*, **76**, 3983 (1954).

(5) G. Allen and E. Caldin, *Quart. Rev.*, **7**, 255 (1953).

(6) G. Pimentel and A. McClellan, *The Hydrogen Bond*, W. H. Freeman and Co., San Francisco, 1960.

(7) D. Hadži, *Hydrogen Bonding*, Pergamon Press, Inc., New York, N. Y., 1959.

(8) Unless otherwise indicated, ΔF_{ion}^{HA} and K_a^{HA} refer to equation (7), and $-\Delta F_{ion}^{BH^+}$ and K_b^B to equation (8), both in water.

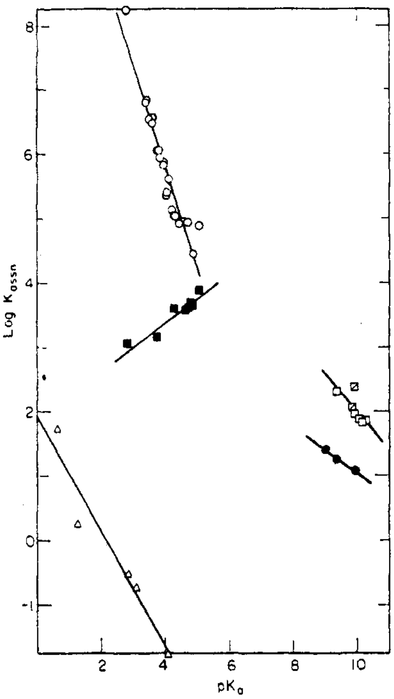


Fig. 1. Equilibria involving hydrogen bridging *vs.* acidity: ○, benzoic acids with 1,3-diphenylguanidine in benzene[32]; △, RCOOH $\cdots$ NC_5H_5 = $RCOO^- \cdots \overset{+}{H}NC_5H_5$ in carbon tetrachloride[33]; □, phenols with triethylamine[2] (▨ = naphthols); ●, phenols with methyl acetate[10]; ■, dimerization of carboxylic acids in benzene[5]

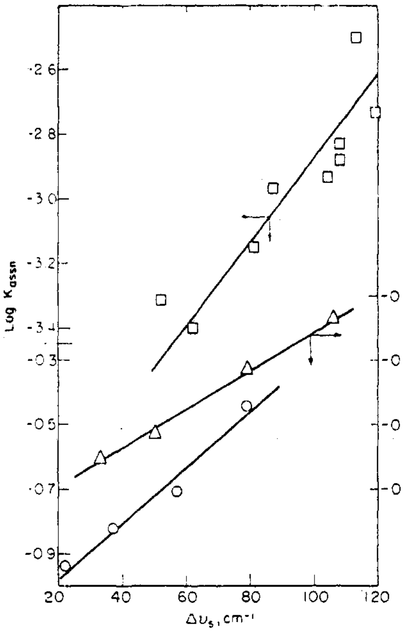


Fig. 2. Association constants *vs.* association shifts, $\Delta\nu_s$, for aromatic bases: ○ pyrrole-ArH[23]; △, phenol-ArH[23]; □, HCl-ArH[14,25]

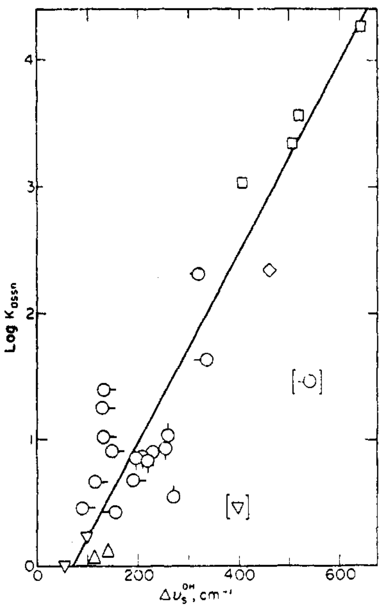


Fig. 3. Association constants *vs* association shifts, $\Delta\nu_s^{OH}$: △, ROH dimerization; ▽, ROH-various; □, RCO_2H dimerization; ◇, RCO_2H-pyridine: ọ, ArOH-ethers; ○-, ArOH-esters; ọ, ArOH-ketones; -○, ArOH-nitrogen compounds; reference 6 (Appendix C); parenthesized points are phenol—hexamethylenetetramine and ethanol—triethylamine

a test of equations (2) and (3), although the quality of these results is not uniformly good; all of these data are shown in the figures. Recorded value of *a* and *b* were calculated by the method of least squares. The remainder of Table 1 contains isolated or indirectly applicable results along with some Brønsted coefficients for comparison.

Direct measurement of K_{assn}. Entries 1, 2, and 8 of Table I represent direct spectrophotometric and dynamic measurements of association equilibria. For the hydrogen chloride complexes, statistical corrections were applied to the association and basicity constants according to the method of Benson,[22] using the structures suggested in ref. (14). Though scanty, the data (Figs. 1, 6) accord satisfactorily with Equations 2 and 3. The very limited data[15,23] for OH and NH acids reacting with aromatic *pi* bases (Fig. 6) are not represented in Table I; the relative probable error in *b* in these cases (0.22 and 0.47) would be considerably larger than the average (0.12) for entries 1, 2, and 8; the same behavior is noted below for the infrared shifts in these systems, and failure of the relation may be indicated.

Association shifts in AH stretching frequencies. The observation by Grunwald and Coburn[24] of a linear relation between the shift in stretching frequency of OH acids on hydrogen bridging,

---

(9) All frequency shifts, $\Delta\nu_s$, are given in cm.$^{-1}$, measured from the free stretching frequency displayed in carbon tetrachloride solution; all association constants refer to concentration units of moles per liter (at 25° in carbon tetrachloride unless otherwise stated).

(10) S. Nagakura, *J. Am. Chem. Soc.*, **76**, 3070 (1954).

(11) G. Barrow, *J. Phys. Chem.*, **59**, 1129 (1955).

(12) J. Hine and M. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952).

(13) L. Henry, ref. (7), p. 163.

(14) H. Brown and J. Brady, *J. Am. Chem. Soc.*, **74**, 3570 (1952).

(15) E. Mackor, A. Hofstra, and J. van der Waals, *Trans. Far. Soc.*, **54**, 186 (1958).

(16) C. Marvel, M. Copley, and E. Ginsburg, *J. Am. Chem. Soc.*, **62**, 3109 (1940).

(17) S. Searles and M. Tamres, *J. Am. Chem. Soc.*, **73**, 3704 (1951).

(18) R. P. Bell, *Acid-Base Catalysis*, Oxford University Press, 1941, pp. 86–91.

(19) L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., New York, N. Y., 1940, p. 226.

(20) Ref. (18), p. 111.

(21) R. P. Bell, *The Proton in Chemistry*, Cornell University Press, Ithaca, N. Y., 1959, p. 172.

(22) S. W. Benson, *J. Am. Chem. Soc.*, **80**, 5151 (1958).

(23) N. Fuson, P. Pinot, and M. Josien, ref. 7, p. 169.

(24) E. Grunwald and W. Coburn, Jr., *J. Am. Chem. Soc.*, **80**, 1322 (1958).

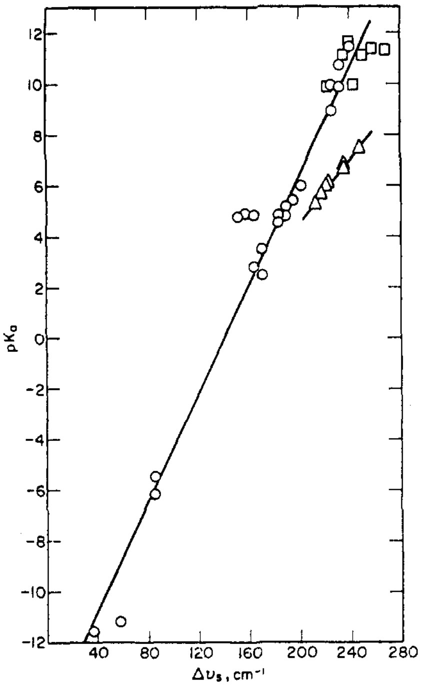


Fig. 4. Association shifts, $\Delta\nu_s^{CH_3OD}$, *vs.* acidity: Δ, methanol-*d* substituted pyridines[4]; ○, methanol-*d*-amines, ArCOR, ArNO$_2$[3]; □, methanol-*d*-aliphatic amines[4]

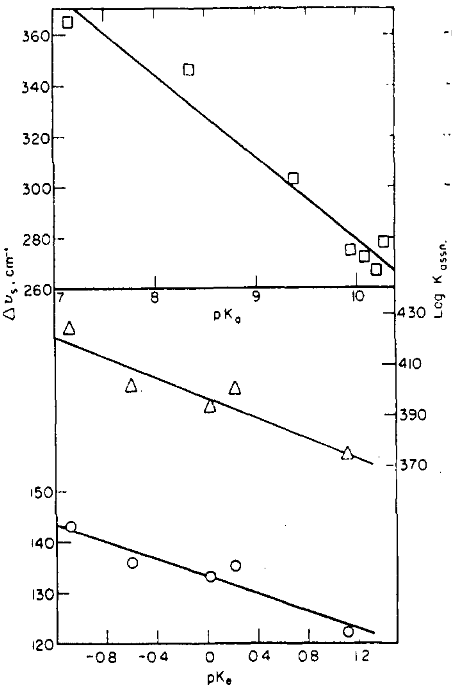


Fig. 5. Association shifts, $\Delta\nu_s^{OH}$, *vs.* acidity: Δ, ROH-N(C$_2$H$_5$)$_3$[11,12] (right ordinate); ○, ROH-O(C$_2$H$_5$)$_2$[11,12] (lower left ordinate); □, ArOH-O(C$_2$H$_5$)$_2$ in carbon tetrachloride[13] (upper left ordinate); $pK_e \equiv$ relative pK_a in 2-propanol solvent[12]

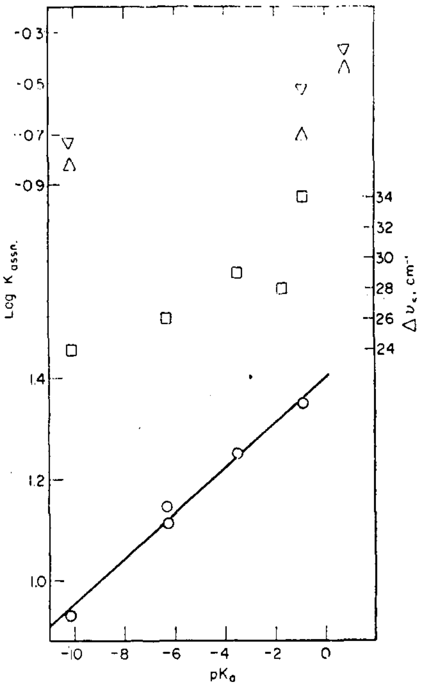


Fig. 6. Association data for aromatic bases *vs.* acidity: ○, log $K_{assn.}$ for HCl-ArH[14,15]; □, $\Delta\nu_s$ for CH$_3$OD-substituted benzenes[15,30]; Δ (∇), log $K_{assn.}$ for pyrrole (phenol)-substituted benzenes[15,23]

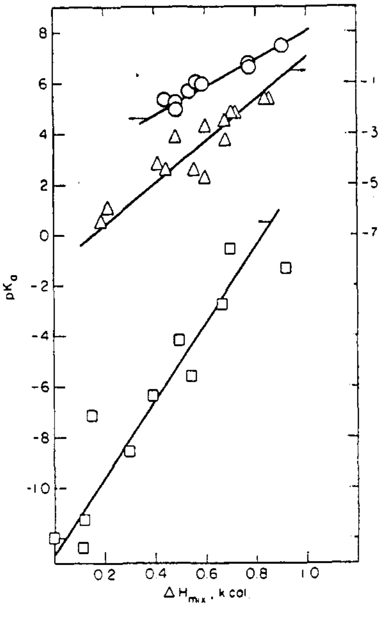


Fig. 7. Heats of mixing with chloroform *vs.* acidity: ○, pyridines[4]; □, various (see Table I, entry 16)[16,29]; Δ, cyclic ethers[17,29]; footnotes *h* and *j* of Table I apply for □ and Δ

$\Delta\nu_s^{OH}$, and log $K_{assn.}$ suggests that the extensive literature of infrared association shifts might be used to supplement the available association constants; the existence of such a relationship would provide support for Equations 2 and 3 since $\Delta\nu_s$ has been observed[3,4,11,13] in a variety of cases to be linearly related to the pK_a of the proton acceptor or donor.

The available data for testing the log $K_{assn.}$–$\Delta\nu_s$ relation are assembled in Figs. 2 and 3; the former contains data for aromatic *pi* bases reacting with phenol,[23] pyrrole,[23] and hydrogen chloride,[15,25] which conform to log $K_{assn.} = d + e\Delta\nu_s$ with the following values of d, e, and r_e, the probable error in e: phenol, −1.02, 0.00615, 0.00028; pyrrole, −1.14, 0.00844, 0.0010; hydrogen chloride, −3.98, 0.0109, 0.0018. The data for 'onium bases refer almost exclusively to OH acids; these are shown in Fig. 3 without attempting separation into structural families, partly because the data are too scant in most cases to do so, and also in order to test the possibility that some correlation remains even when only the identity of the bond under spectroscopic observation remains constant. This proves moderately successful, considering the wide variety of data sources and the generally low precision of both association constant and $\Delta\nu_s$ measurements, and leads, on analysis[26] by least squares, assuming equal relative probable errors[27] in $\Delta\nu_s^{OH}$ and log $K_{assn.}$, to

---

(25) M. Josien and G. Sourisseau, *Bull. Soc. chim France*, 178 (1955).

$$\log K_{\text{assn.}} = -0.541 + 0.00754\ \Delta\nu_s \qquad (6)$$

with a probable error in the slope of 0.00043 and a correlation coefficient of 0.925.

These results are potentially applicable to the present problem in two ways. First, establishing that both the $\Delta\nu_s$–pK_a and $\log K_{\text{assn.}}$–$\Delta\nu_s$ relations hold independently for numerous, though different, structure families (of course, if both sets of information are available for the same set of compounds $\log K_{\text{assn.}}$ and pK_a can be compared without involving $\Delta\nu_s$) would argue for a general applicability of (2) and (3) to cases of limited structure variation. Second, to the extent that the slopes of $\log K_{\text{assn.}}$ –$\Delta\nu_s$ plots are structure independent $K_{\text{assn.}}$ values for more or less analogous systems might be estimated from $\Delta\nu_s$, leading to further numerical tests of (2) and (3). Neither of these possibilities can be very satisfactorily realized at present; although it is apparent that a single $\Delta\nu_s$—$\log K_{\text{assn.}}$ slope does not hold for all of the OH association equilibria, the average value from Fig. 3 has been used to compute very approximate a and b values from all of the available $\Delta\nu_s$ measurements.[3,4,11,13] (entries 3–7, 9–14 of Table I) on compounds of known acidity or basicity, employing $\Delta\nu_s^{\text{OH}} = 1.4\ \Delta\nu_s^{\text{OD}}$ where necessary.[28] In what follows, no conclusions are based on the magnitudes of these coefficients alone; the qualitative structure dependence of $\Delta\nu_s$ within families, however, is considered a safe indication of the qualitative direction of $K_{\text{assn.}}$ variation.

The relevant $\Delta\nu_s^{\text{OD}}$—pK_a plots are shown in Fig. 4 and 5.[29] It is noted that this relation is rather poorly obeyed by OH and NH donors *vs.* aromatic *pi* bases[30]; for methanol-*d* (data shown in Fig. 6; phenol and pyrrole gave very similar results) the relative probable error in b would be about 2.5 times the average (0.10) for entries 3–7 in Table I.

Association equilibria which also involve proton transfer. In dealing with proton transfer processes which involve hydrogen bridged ion pairs rather than free ions, it is essential to take into account the effect of the acidity-dependent association reaction on the position of the over-all equilibrium (see Discussion); conversely, it is possible to gain some information on the association reaction from the over-all process. For the common case of acid-base reactions in nonwater-like solvents the reaction $HA + B = A^- \cdots HB^+$ often applies; in a formal manner this may be approached as the sum of the following:

$$HA = H^+ + A^- \quad K_a \qquad (7)$$

$$B + H^+ = BH^+ \quad K_b \qquad (8)$$

$$A^- + BH^+ = A^- \cdots HB^+ \quad K_{\text{assn.}} \qquad (9)$$

$$HA + B = A^- \cdots HB^+ \quad K_{\text{obs.}} \qquad (10)$$

For variation of one component, say HA, application of (2) leads to

$$\Delta \log K_{\text{obs}} = (1 - b)\Delta \log K_a \qquad (11)$$

except that the first term on the right hand side should refer to the reaction in the solvent in question, not to water as written; here b refers to A^- The best that can happen is that

$$(\Delta \log K_a)_{\text{solvt.}} = c\Delta \log K_a\,(H_2O) \qquad (12)$$

which, for reasonably polar solvents, has a rather approximate validity for acids in general and for limited structure variation may be quite precise.[31] In this case

$$\Delta \log K_{\text{obs}} = (c - b)\Delta \log K_a \qquad (13)$$

and the $\log K_{\text{obs}}$ *vs.* $\log K_a$ plot should still be linear. This is indeed observed for *m*- and *p*-substituted benzoic acids reacting with 1,3-diphenylguanidine in benzene[32]; the data are shown in Fig. 1, from which $(c - b) = 1.59 \pm 0.07$.

Similarly, measurements of Barrow[33] give rise to equilibrium constants for

$$AH \cdots B = A^- \cdots HB^+ \qquad (14)$$

in the reaction of carboxylic acids with pyridine in carbon tetrachloride. In this case

$$\Delta \log K_{\text{obs.}} = (c - a - b)\Delta \log K_a^{\text{RCOOH}} \qquad (15)$$

with a referring to AH and b to A^-; the $\log K_{\text{obs.}}$ *vs.* pK_a plot is shown in Fig. 1; $(c\text{-}a\text{-}b) = 0.90 \pm 0.09$.

Related measurements. Some heat of mixing data for chloroform with various bases are shown in Fig. 7. The simplest interpretation of the heat of mixing in these systems[34] is as a fraction of the heat of association, which fraction increases as a function of

---

[26] This treatment of the data differs in three respects from that of Grunwald and Coburn[24]: cyclic planar structures were assumed for alcohol dimers [M. Van Thiel, E. Becker, and G. Pimentel, *J. Chem. Phys.*, **27**, 95 (1957)], statistical corrections were made according to Benson,[22] and $\log K_{\text{assn.}}$ values for carboxylic acids were not halved, reasoning that formation of both bridges contributes to $\Delta\nu_s$ just as it does to ΔF; in support of this, the frequency shifts for open chain, 1:1 association of RCO_2H with bases [acetic acid-pyridine, 461 cm.$^{-1}$ (reference 6, p. 92) and formic acid-secondary amide, 232 cm.$^{-1}$ (C. Cannon, *Mikrochim. Acta.*, **1955**, 555)] are distinctly smaller than those for dimerization although the basic moieties involved are very much stronger. The widely discrepant points for ethanol-triethylamine and phenol-hexamethylenetetramine were not included.

[27] A. Worthing and J. Geffner, *Treatment of Experimental Data*, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 258*ff*.

[28] Ref. 6, p. 112.

[29] The $\Delta\nu_s^{\text{OD}}$–pK_a relation of Gordy and Stanford[3] was modified by inclusion of statistical corrections[22] and of more modern pK_a values; the equation used was $\Delta\nu_s\ (\text{cm.}^{-1}) = 141 + 9.36\,pK_a$.

[30] M. Josien and N. Fuson, *J. Chem. Phys.*, **22**, 1169 (1954).

[31] Ref. 19, pp. 207, 259.

[32] M. Davis and H. Hetzer, *J. Research Natl. Bur. Standards*, **60**, 569 (1958).

[33] G. Barrow, *J. Am. Chem. Soc.*, **78**, 5802 (1956).

[34] G. Zellhoefer and M. Copley, *J. Am. Chem. Soc.*, **60**, 1343 (1938).

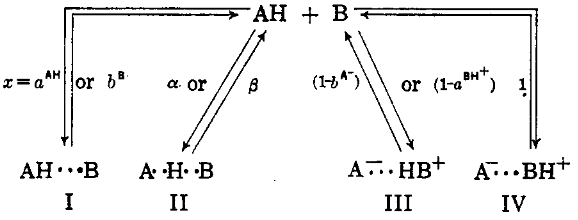
K_{assn}. If one assumes ΔH_{assn} to be a monotonic function[35] of log K_{assn}, then ΔH_{assn} will be more negative and show a more negative slope *vs.* log K_{assn} than ΔF_{assn}, as ΔS becomes more negative as the bridge becomes stronger.[36] The slope of ΔH_{mix} *vs.* log K_{assn} changes from more positive to more negative than that for ΔH_{assn} as log K_{assn} increases, and it is reasonable to expect ΔH_{mix} to parallel ΔF_{assn} somewhere in the range 0–50% of starting molecules associated, though perhaps only over a very limited part of this range. The data of Fig. 7 are consistent with such a picture, and the values of b given in entries 15–17 of Table I were calculated for comparison using ΔH_{mix} in place of ΔF_{assn}.

Dimerization of carboxylic acids is one of the earliest association reactions for which a correlation with acidity was observed,[5] although it is far from the most accurate; data for saturated acids are given in Fig. 1. Even if the requisite basicities for the acids were known, the present analysis cannot describe this type of cyclic complex very well; in the absence of a basicity measure, we can only explore the results of hypothesizing that $\Delta\ pK_b$ will be roughly proportional to $-\Delta\ pK_a$ for the saturated acids. In this event a linear log K_{assn} *vs.* log K_a plot might be expected, and the negative slope displayed in Fig. 1 implies a larger dependence of dimer stability on acceptor basicity than on donor acidity, and/or greater dependence of K_b on structure than obtains for K_a. A preliminary report[37] of Hammett *rho* = 1.47 for $ArCO_2H_2^+$ ionization implies that the latter is indeed the case.

Another interesting but unanalyzable case is the parallelism between association of substituted benzamides[38] and acetophenone oximes[39] and the Hammett *sigma* values.

DISCUSSION

The possible products, excluding for the time being those of other than 1:1 stoichiometry, of interaction of the base B and the acid AH are included in the following diagram[40]:



By II is implied the transition state for the proton transfer from I to III. These species may be viewed as successive stations on the reaction coordinate leading ultimately to the separated ions, IV. In general I and III comprise well-defined minima on the potential energy profile, separated by the transition state II[33,41]; when the total acidity-plus-basicity level of the reactants is low, however, the states beyond I may lie so high energetically as to be negligibly populated under ordinary conditions (*e.g.* alcohol dimers *etc.*).

Evidence has now accumulated for the applicability of the expression $\Delta\Delta F = x\ \Delta\Delta F_{ion}{}^{AHorB}$ to the reactions leading to each of the above states, and the appropriate expressions for x are shown in the diagram.[42] While this relation is firmly established for II[43] and with considerable certainty for III,[44] it cannot be said that the preceding sections constitute an extensive or very precise demonstration on behalf of I; hence, any conclusions regarding this species must be qualitative and somewhat tentative. Certain useful corollaries of the unified view afforded by the above diagram, however, may be developed within these restrictions. In part, these are extensions of the detailed consideration given II in Bell's two books.[18,21]

1. The coefficient x may be considered a rough measure of the degree of charge transfer which has occurred, and identified with the relative importance of the structures $A^- \cdots H - B^+$ in the valence bond description of the bridged species.

2. It may be expected that values of the coefficients x will decrease as the degree of charge transfer decreases, hence $1 > (1\text{-}b) > \alpha > a$. Unfortunately, although many of the a-values listed in Table I are indeed small, no data are available for comparison of a and α for closely analogous structures. With III a considerable solvent effect on

---

(35) Ref. 6, p. 85.

(36) Ref. 6, p. 220.

(37) R. Stewart and K. Yates, Abstracts, 133rd Am. Chem. Soc. Meeting, San Francisco, April, 1958, p. 40 N.

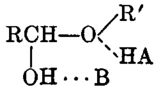
(38) M. Hobbs and R. Bates, *J. Am. Chem. Soc.*, **74**, 746 (1952).

(39) A. Reiser, Ref. 7, p. 446.

(40) Superscripts on a and b indicate the species to which the latter refer; thus, f^{A^-} is defined by $\Delta\Delta F_{assn} = -f^{A^-}\Delta\Delta F_{ion}{}^{AH}$, for the reaction: A^- + reference acid.

(41) C. Bell and G. Barrow, *J. Chem. Phys.*, **31**, 300 (1959).

(42) There are certain difficulties inherent in comparing II with I or III when the discussion becomes more specific regarding the functional groups involved. First, since more or less drastic structure changes may be concerted with the actual proton transfer, the A and B moieties of the transition state II may have no close analogs among more or less stabile bridges. For example, when the hemiacetal complex



decomposes to

$$RCH{=}O \cdots HB^+ \text{ and } R'OH \cdots A^-,$$

the proton acceptor associated with AH at the transition state can only be described as something between an ethereal hemiacetal oxygen and an alkoxide ion. Second, many of the kinetic data concern structures II for which it is questionable that a detectable minimum exists for the analogous structure I, *e.g.* in the deprotonation of carbon acids. Therefore the discussion should be limited to those Brønsted relation data for which these complications are absent.

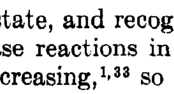
(43) Ref. 18, Chapter 5.

(44) Ref. 21, Chapter 4.

the numerical value of x must be anticipated.[45] In the previous development, less polar solvents were approached by taking $x = a$, α, $(c\text{-}b)$ and c for I–IV respectively, corresponding to the assumption of the validity of equation (12). It is theoretically expected and generally found experimentally that c increases with decreasing solvent polarity[46,47] (for the carboxylic acids with which we are primarily concerned). Values of $x = c\text{-}b$ for III in non-polar solvents are thus not necessarily smaller than unity, and of course do not yield unequivocal values of b; however, if experience allowed reasonable estimation of b, information on the effect of solvent on ionization (to IV) might be obtained for solvents of low dielectric constant. The available data are consistent with the behavior expected from extrapolation from modestly polar solvents; thus, for carboxylic acids in *m*-cresol and chlorobenzene, $x = c - b$ is very close to unity[44] while in the less polar benzene, $x = 1.59$.[32] With b in the vicinity of 0.5, these results would correspond to c-values in the range 1.5 (cresol, chlorobenzene) and 2.1 (benzene).

3. Values of a, α, *etc.* depend not only upon the degree of donor—acceptor interaction but upon the exact chemical structure of the interacting functions as well, because of the formation of structurally different types of bridges, including not only differences in the identity and valence state of the electron donor atom, but possible bi- and trifurcated structures[48] and the involvement of either moiety in a second bridge to solvent[49] or gegenion as well. This fractionation into family groups is well known for the catalytic constants, and such data as are available indicate the same behavior for the association constants.

4. The values of a and α for a set of acids AH depend upon the strength of the reference base employed. Similarly with b, β, and the reference acid. In addition, it is to be expected that none of the relationships under consideration will hold for variation of acid or base strength over extremely wide limits even though the reference substance and the functional group of the variable substance are kept constant. These restrictions arise from the fact that a large change in the acidity-plus-basicity level of the complex effectively changes its structure, shifting it along the proton transfer reaction coordinate, and changing its susceptibility to electronic effects in A and B.[50] These rules were given and illustrated by Bell[51] for species II. The first of these two rules is illustrated in Table I for species I by comparison of the a-values for entries 1 and 2, 3 and 4, where a approximately doubles on passing from ethyl ether or methyl acetate to the stronger reference base triethylamine. Entries 9–14 indicate that b increases steadily with increasing strength of the reference acid. Turning to the second rule, comparison of entries 1 and 3, 4 and 5 is of interest; if we consider the alcohols and phenols as two ends of the same family, differing principally in the level of acidity, then it is apparent that the value of a has suffered considerable change on passing from one end of the scale to the other although it appeared approximately constant within each subgroup; other differences may play a part, however. In this respect, the $\Delta\nu_s^{CH_3OD} - pK_b$ correlation of Gordy and Stanford,[3] entry 6 of Table I, is remarkable in spanning twenty powers of ten in basicity with acceptable precision, using a single value of a.

5. The effects of increasing the strength of the reference acid (base) on the values of b and β (a and α) should be to decrease the difference between the latter, since lowering the product state energy will bring I and II closer together energetically and structurally. As pointed out above, Table I shows that b *increases* with reference acid strength for the ROH complexes. Entries 21–25 reproduce Bell and Lidwell's[21] demonstration that β, for the base-catalyzed prototropy of ketones in water, *decreases* as the acidity of the ketone increases, in harmony with the above expectation. Although there is considerable uncertainty regarding the existence of species I,  $R-CO-\overset{|}{\underset{|}{C}}H\cdots O_2CR'$, bridges in this system, it seems unlikely that this vitiates extrapolation of the direction of shift in β to other systems, including those for which double minima obtain.

On the stability of BHB$^\pm$ ions. The complex ions BHB$^\pm$ arising from bridging of a molecule or ion to its conjugate acid or base have long been known in the solid state, and recognition of their importance in acid-base reactions in nonwater-like solvents is rapidly increasing,[1,33] so that it is now possible to define the conditions of their solution existence fairly well. Here we wish to analyze the formation constants for BHB$^\pm$ in terms of Equations 2 and 3. In the reactions

---

[45] Solvent effects in the less polar species I and II have been neglected; the scant information available in the case of I (*e.g.*, the excellent internal consistency of entry 6 of Table I despite extreme solvent variation) is consistent with this procedure; some indications to the contrary may exist for II, as values of α in excess of unity have been reported for some reactions in benzene, *etc.* [J. Brønsted and R. Bell, *J. Am. Chem. Soc.*, **53,** 2478 (1931); R. Bell, O. Lidwell, and M. Vaughan-Jackson, *J. Chem. Soc.*, 1792 (1936)], although other explanations of this anomaly have been given.

[46] L. Wooten and L. Hammett, *J. Am. Chem. Soc.*, **57,** 2289 (1935).

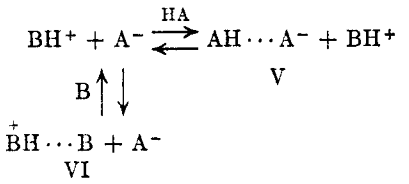
[47] H. H. Jaffé, *Chem. Rev.*, **53,** 191 (1953).

[48] G. Barrow and E. Yerger, *J. Am. Chem. Soc.*, **77,** 4474 (1955).

[49] R. Pearson and D. Vogelsong, *J. Am. Chem. Soc.*, **80,** 1038, 1048 (1958).

[50] One might expect the numerical values of a and b to be related to some measure of the total acidity-plus-basicity level of the complex, say $pK_a^{BH^+} - pK_a^{HA}$. One can obtain an approximate parallelism of this sort from Table I if greater weight is assigned to pK_a^{HA}, and the HCl–ArH complexes are omitted.

[51] Ref. 18, Chapter 8; ref. 21, Chapter 10.



$$\begin{tikzcd} \mathrm{BH^+ + A^-} \arrow[r, shift left, "\mathrm{HA}"] \arrow[d, shift left] & \underset{\mathrm{V}}{\mathrm{AH\cdots A^-}} + \mathrm{BH^+} \arrow[l, shift left] \\ \underset{\mathrm{VI}}{\overset{+}{\mathrm{B}}\mathrm{H\cdots B}} + \mathrm{A^-} \arrow[u, shift left, "\mathrm{B}"] & \end{tikzcd}$$

(16a)

(16b)

the formation of BHB± (V or VI) from BH and B is given by

$$\Delta \log K_{\mathrm{assn}} = (b^{\mathrm{B}} - a^{\mathrm{BH}})\Delta \log K_{\mathrm{b}}{}^{\mathrm{B}} \qquad (17)$$

This is a particularly significant system for discussing whether the stability of the hydrogen bridge is inherently more dependent upon donor acidity or on acceptor basicity. Unfortunately, direct measurements of the stability of BHB± as a function of structure are lacking. Conductimetric titrations of carboxylic acids with triethylamine in acetonitrile[52] provide evidence for increasing stability of $(\mathrm{RCO_2})_2\mathrm{H}^-$ with increasing $\mathrm{RCO_2H}$ acidity, corresponding to $a^{\mathrm{RCOOH}} > b^{\mathrm{RCOO^-}}$ in Equation 17. Spectroscopic results for $(\mathrm{RCO_2})_2\mathrm{H}^-$, $\mathrm{C_6H_5NH^+}$ in carbon tetrachloride[33] and $\mathrm{BHB^+}$ (B = aryl guanidines) in benzene[53] are also consistent with $(b^{\mathrm{B}}\text{-}a^{\mathrm{BH}}) < 0$, however these cases suffer from a variety of other complications.

On the influence of electron donor atom polarizability. If, as current views indicate,[54] electrostatic forces account for as much as 50% of the total hydrogen bridging energies, one might expect to find a dependence of the latter on proton acceptor atom polarizability. This possibility is further suggested by work of Edwards,[55] who found rates of base catalyzed mutarotation of glucose to be considerably better correlated by a two-parameter (basicity, polarizability) equation than by the basicity term alone (Brønsted relation). Thus, although no accurate measure of proton acceptor polarizability is known for most organic bases,[56] it seemed desirable to compare both the association and catalytic data now available with even an approximate polarizability measure; octet refractions at infinite wavelength, R^∞, of the electron donor atom in most of the proton acceptors involved were compiled. No regular relationship of these to either the left-hand quantities of Equations 2 to 5 or the deviations from correlation with basicity *via* these equations was discovered. The range of polarizabilities covered in these oxygen and nitrogen bases, however, is not large.

Recently, Schleyer, and West[57] have presented data which perhaps imply that the hydrogen bridging equilibria do indeed respond to larger polarizability changes in the electron donor moiety. Shifts in the OH stretching frequency of methanol dissolved in the mono-, di-, and tri-*n*-butyl derivatives of fluorine, chlorine, bromine, iodine, oxygen, sulfur, nitrogen, phosphorus, and arsenic were measured (19, 37, 41, 47, 155, 155, 396, 267, and 310 cm.$^{-1}$, respectively) and attributed to the formation of hydrogen bridges. It is apparent that the shifts do not follow the order of basicities; for the halides, $\Delta\nu_s$ indeed increases with the polarizability of the halogen atom. It appears that a double scale equation of the Edwards type should be capable of reproducing the observed shifts, although at present so few of the basicities are known that the numerical fitting using estimated basicities is too arbitrary to be very convincing. However, these results do perhaps suggest that a more comprehensive relationship for correlating relative equilibrium and rate constants for proton transfer involving I–III would be

$$\Delta \log K = x\Delta \log K_{\mathrm{ion}} + y\Delta \log R^\infty$$

which is a special case of the Edwards equation. It is probable that the polarizability of the proton acceptor moiety plays a particularly important role in the formation of bridges to aromatic and olefinic hydrocarbons and to halide ions in crystals.

PITTSBURGH 13, PA.

---

[52] P. Bryant and A. Wardrop, *J. Chem. Soc.*, 895 (1957).

[53] M. Davis and H. Hetzer, *J. Research Natl. Bur. Standards*, **48**, 381 (1952).

[54] C. A. Coulson, *Research*, **10**, 149 (1957).

[55] J. O. Edwards, *J. Am. Chem. Soc.*, **76**, 1540 (1954).

[56] J. O. Edwards, *J. Am. Chem. Soc.*, **78**, 1819 (1956).

[57] P. Schleyer and R. West, *J. Am. Chem. Soc.*, **81**, 3164 (1959).