

A Two-Parameter Model for Estimating Hydrogen Bond Enthalpies of Reaction

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Synopsis

A two-parameter equation is developed that allows for the estimation of the enthalpies of hydrogen formation between two compounds. The compound acting as a proton donor is assigned a donating parameter, and the compound acting as a proton acceptor is assigned an accepting parameter. The compounds described can be assigned both a donating and an accepting parameter. These parameters are derived either from the observed linear relationship between measured hydrogen bond enthalpies and the shift in the OH stretching frequency of alcohols or from the estimated contribution of hydrogen bonding to the cohesive energy density of liquids. The donating parameters correlate well with observed autoprotolysis constants for several compounds, and the accepting parameters correlate well with observed equilibrium constants for the protonation reaction in which a compound (base) gains a proton. The ability to estimate enthalpies is important in predicting polymeric resin solubilities in solvents.

INTRODUCTION

This article concerns a two-parameter model that can estimate hydrogen bond enthalpies for reactions between compounds acting as proton donors and proton acceptors. A second article will concern an extension of this model to the problem of predicting the solubility of polymeric resins in solvents and involves another model utilizing the parameters developed in this article. While the model described here may lack strict rigor, its extension to the very practical problem of solubility prediction makes it very useful.

The problem with attempting parametric modeling to estimate bond energies has received considerable attention recently. Most approaches, such as the one described here, rely on an empirical treatment of experimental data. Drago and Wayland¹ have developed a two-parameter equation involving electrostatic parameters (E) and covalent parameters (C) for the hydrogen bonding interaction. Each compound is assigned both an E and a C parameter which can be combined in the form of eq. (1) to yield estimated enthalpies with a high degree of accuracy when compared to experimental results:

$$-\Delta H \text{ (kcal/mole)} = E_a E_b + C_a C_b \quad (1)$$

Drago et al.² have expanded upon the details of this model, and in a recent article Drago and Marks³ have given theoretical justification for such an approach based upon charge-transfer theory. This latter article attempts to generalize the approach to all acid-base reactions, although the original intention of the model was to treat only hydrogen bonding reactions. They show that a summation of electrostatic and covalent contribution to an energy of bond formation is a reasonable model to describe interactions. Klopman⁴ also demonstrated that this was reasonable using first-order perturbation theory. Small⁵ developed a do-

nating-accepting parametric model for hydrogen bonding interactions as they relate to heats of mixing.

Two-parameter empirical models have been suggested by Sherry and Purcell⁶ using experimental data and by Kollman and co-workers^{7,8} from results of theoretical calculations using appropriate wave functions for small molecules. Drago et al.² discussed the limitations of two-parameter models and indicated that only under certain circumstances would they be expected to yield reasonable result. The two-parameter model in this report was developed using data for systems in which a two-parameter model might be expected to yield fairly accurate results.

Pearson⁹ described the hydrogen bonding interaction as an example of a "hard-acid hard-base" reaction in his theory on the hard and soft behavior of acids and bases. Such interactions are dominated by electrostatic forces. This has also been discussed by Kollman et al.⁷ in terms of their theoretical calculations on small molecular dimer formation using a basis set of wave functions that accentuated electrostatic contributions. Kollman⁸ also mentioned the dominance of electrostatic forces in weak molecular interactions and how this leads to a two-parameter model for predicting energies of such interactions.

THE TWO-PARAMETER MODEL

The mathematical form of the model is given in eq. (2):

$$-\Delta H \text{ (kcal/mole)} = b \times C \quad (2)$$

expressed as the product of a parameter (b) associated with the proton-donating tendency of a hydrogen bonding acid and a parameter (C) associated with the proton-accepting tendency of a hydrogen-bonding base. The way in which parameters may be assigned is described below.

The basis for the two-parameter model is the linear relationship first observed by Badger and Bauer¹⁰ between the enthalpy of hydrogen bond formation of one alcohol with several bases and the observed shift in the infrared OH stretching frequency brought about because of the bonding. This is given in eq. (3),

$$-\Delta H = m\Delta V_{\text{OH}} + b \quad (3)$$

where m and b refer to the slope and intercept of the relationship and depend upon the particular alcohol used as a donor. This relationship has been of some controversy as to its generality, as was recently discussed by Arnett and co-workers,^{11,12} who indicated that it has limited validity. However, several investigators (refs. in Table I) have reported it to be valid for a number of different alcohols when bonded to a variety of bases.

Since the intercept b of eq. (3) is characteristic of the alcohol and independent of the base, it can be used as the b parameter in eq. (2). Table I gives the slopes and intercepts for a number of alcohols for eq. (3). It is apparent that b increases as the alcohol becomes a stronger proton donor but that the slopes are quite similar for all the alcohols.

To convert eq. (3) into the form of eq. (2), it may be rearranged as is shown in eq. (4),

$$-\Delta H = b \left(\frac{m\Delta V_{\text{OH}}}{b} + 1 \right) \quad (4)$$

TABLE I
Slope and Intercept Values for Linear Relationship^a between Hydrogen Bond Enthalpy and Alcohol OH Frequency Shift for Alcohols Bonded to Several Bases

Alcohol	Slope <i>m</i>	Intercept <i>b</i>	Reference
Di- <i>t</i> -butyl carbinol (DTBC)	0.0008	1.24	13
<i>t</i> -Butyl alcohol (TBA)	0.0106	1.65	14
2,2,2-Trifluoroethanol (TFE)	0.0121	2.70	6
<i>p</i> -Fluorophenol (PFP) ^b	0.0100	2.80	12
Phenol	0.0105	3.00	2
1,1,1,3,3,3-Hexafluoroisopropanol (HFIP)	0.0115	3.60	15

^a The linear relationship is $-\Delta H$ (kcal/mole) = $m \Delta V_{OH}$ (cm⁻¹) + b (kcal/mole).

^b The values for PFP were calculated by least-squares fitting from data in the reference.

with the term in brackets defined as *C*. For the model to be useful, *C* should reflect the accepting tendency of the base.

Table II contains measured enthalpies of hydrogen bond formation and frequency shifts (OH) for the six alcohols in Table I, with eight bases selected for their variety. Using the *m* and *b* values for a given alcohol in conjunction with the observed frequency shift, the ratio $m\Delta V_{OH}/b$ for a given base with all six alcohols appears to be fairly constant, i.e., the ratio is characteristic of the base and independent of the alcohol. This is shown in Table III along with the average

TABLE II
Measured Enthalpies of Hydrogen Bond Formation and Alcohol OH Frequency Shifts for Alcohols Bonded to Several Bases

Base	DTBC	TBA	TFE	PFP	Phenol	HFIP
Acetonitrile	—	2.30; 77 ^a	4.35; 130	4.30; 184	4.70; 150	5.90; 208
Ethyl acetate	—	2.40; 73	4.45; 150	4.80; 199	4.80; 164	6.50; 224
Acetone	2.20; 109	2.70; 98	5.05; 201	5.20; 232	4.90; 193	6.70; 280
Diethyl ether	2.20; 126	3.00; 126	5.10; 232	5.50; 285	—	7.20; 357
Tetrahydrofuran	2.50; 156	3.20; 142	—	6.00; 292	6.00; 285	—
<i>N,N</i> -Dimethylacetamide	2.90; 192	3.40; 160	6.37; 283	6.70; 356	6.80; 345	8.50; 428
Dimethyl sulfoxide	3.00; 224	3.60; 183	6.25; 303	6.90; 367	6.90; 366	8.70; 449
Pyridine	3.50; 277	4.30; 247	7.82; 428	7.70; 485	7.50; 467	—

^a The first value listed is the enthalpy (kcal/mole), and the second value after the semicolon is the frequency shift (cm⁻¹).

TABLE III
Ratio Values of Slope-Frequency Shift Term to Intercept Term from Linear Enthalpy Versus Frequency Shift Relationship for Alcohols with Bases

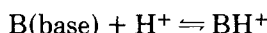
Base	DTBC	TBA	TFE	PFP	Phenol	HFIP	Average Ratio
Acetonitrile	—	0.50	0.58	0.65	0.53	0.66	0.58
Ethyl Acetate	—	0.47	0.67	0.71	0.57	0.71	0.63
Acetone	0.70	0.63	0.90	0.83	0.68	0.89	0.77
Diethyl ether	0.81	0.81	1.04	1.02	—	1.14	0.96
Tetrahydrofuran	1.01	0.91	—	1.04	1.00	—	0.99
<i>N,N</i> -Dimethylacetamide	1.23	1.03	1.27	1.27	1.20	1.37	1.23
Dimethyl Sulfoxide	1.45	1.18	1.35	1.32	1.28	1.43	1.34
Pyridine	1.79	1.59	1.92	1.72	1.64	—	1.73

of the ratios for each base. For any base, the tendency for this ratio to be constant is sufficient to let C (the ratio plus 1) represent the accepting tendency of that base.

To test eq. (2), the b parameters for the alcohols can be combined with the C parameters for the bases to yield predicted enthalpies of bond formation. The results are given in Table IV. It is apparent that these parameters predict the observed enthalpies with a reasonable degree of accuracy. Uncertainties in measured values tend to be of the order of 0.1 to 0.2 kcal/mole, which places the predicted values within the limits of uncertainty for most cases.

Nozari and Drago¹⁶ report the same linear enthalpy-frequency shift relationship for pyrrole with several bases. Since this compound is an amine, the frequency shift refers to the NH stretching frequency. They give an intercept value b of 1.8 kcal/mole. When this is used with the C parameters for the bases (derived from alcohol data) in eq. (2), the resulting predicted enthalpies agree very well with those reported by the authors. These results are shown in Table V. This is an indication that the C values for the bases do reflect a general tendency toward proton acceptance.

In order to further substantiate the correlation between C parameters and proton accepting tendency, the following reaction may be considered:



Unlike the hydrogen bonding reaction, this reaction involves complete proton transfer to the base. However, values of the equilibrium constant for the reaction for the bases used in developing the model have been reported by Arnett et al.¹² These are listed as $\log K$ values along with the C values in Table VI ($\log K$ is given

TABLE IV
Predicted and Experimental Enthalpies of Hydrogen Bond Formation^a

Base	DTBC $b = 1.24$	TBA ^b 1.65	TFE 2.70	PFP 2.80	Phenol 3.00	HFIP 3.60
Acetonitrile ($C = 1.58$)	1.96 (—)	2.61 (2.30)	4.27 (4.35)	4.42 (4.30)	4.74 (4.70)	5.69 (5.90)
Ethyl acetate ($C = 1.63$)	2.02 (—)	2.70 (2.40)	4.40 (4.45)	4.56 (4.80)	4.89 (4.80)	5.87 (6.50)
Acetone ($C = 1.77$)	2.19 (2.20)	2.92 (2.70)	4.79 (5.05)	4.96 (5.20)	5.31 (4.90)	6.37 (6.70)
Diethyl ether ($C = 1.96$)	2.43 (2.20)	3.23 (3.00)	5.29 (5.10)	5.49 (5.50)	5.88 (—)	7.06 (7.20)
Tetrahydrofuran ($C = 1.99$)	2.47 (2.50)	3.28 (3.20)	5.37 (—)	5.57 (6.00)	5.97 (6.00)	7.16 (—)
<i>N,N</i> -Dimethylacetamide ($C = 2.23$)	2.77 (2.90)	3.68 (3.40)	6.02 (6.37)	6.24 (6.70)	6.69 (6.80)	8.03 (8.50)
Dimethyl sulfoxide ($C = 2.34$)	2.90 (3.00)	3.86 (3.60)	6.32 (6.25)	6.55 (6.90)	7.02 (6.90)	8.42 (8.70)
Pyridine ($C = 2.73$)	3.39 (3.50)	4.50 (4.30)	7.37 (7.82)	7.64 (7.70)	8.19 (7.50)	9.83 (—)

^a Experimental values are in brackets. Alcohols and literature references are di-*t*-butyl carbinol (DTBC),¹³ *t*-butyl alcohol (TBA),¹⁴ trifluoroethanol (TFE),⁶ parafluorophenol (PFP),¹² phenol,² and hexafluoroisopropanol (HFIP).¹⁵ Units for alcohol b values and enthalpies are kcal/mole.

^b Some of the TBA enthalpies in brackets are estimated from Drago's E and C values as discussed in the article referenced.

TABLE V
 Predicted Enthalpies of Hydrogen Bond Formation of Pyrrole with Bases Compared to Values from Nozari and Drago¹⁶

Base	$-\Delta H^a$ kcal/mole	$-\Delta H^b$ kcal/mole	Base	$-\Delta H^a$ kcal/mole	$-\Delta H^b$ kcal/mole
Acetonitrile	2.84	2.6	Tetrahydrofuran	3.58	3.7
Ethyl acetate	2.93	2.9	<i>N,N</i> -Dimethylacetamide	4.01	4.0
Acetone	3.19	3.2	Dimethyl sulfoxide	4.21	4.2
Diethyl ether	3.53	3.5	Pyridine	4.91	5.0

^a Values predicted using a *b* value of 1.8 for pyrrole from linear enthalpy vs. NH frequency shift reported in reference and using *C* values for bases from Table

^b Values for enthalpies reported in reference, pyridine and dimethyl sulfoxide values measured calorimetrically, the others were estimated from E and C equation.

because it is directly related to energy of reaction). While there is some scatter, there does appear to be a reasonably direct correlation between increasing *C* value and increasing log *K* value for these bases. Thus, these *C* values do reflect the base strength of the compounds as judged from the protonation reaction.

ALCOHOLS AND WATER AS HYDROGEN-BONDING BASES

The usual situation in which eq. (3) is found to apply is one in which alcohols act as strictly proton donors. However, it is well known that alcohols and water self-associate through hydrogen bonding and that when this occurs they are also acting as proton acceptors (bases). Since there is no reason not to expect them to follow the linear enthalpy–frequency shift relationship, it should be possible to derive *C* parameters for them which should measure their proton accepting tendency.

In the infrared spectrum of alcohols, the absorption frequency occurring at approximately 3600 cm^{-1} is assigned to monomeric OH stretching. Another band, usually observed at about 3500 cm^{-1} , has been identified with an OH stretching on a self-associated dimer. Pimentel and McClellan¹⁷ discuss this band as such, and Hammaker et al.¹⁸ offer experimental evidence for several alcohols which is consistent with such an assignment. This has been disputed by Tucker et al.,¹⁹ and Tucker and Christian²⁰ question the existence of a dimer in most alcohols and suggest that a trimer might be a more common species formed during self-association. They further indicate that the state of agglomeration in alcohols may be very complicated and not as well defined as many investigators have assumed.

TABLE VI
 Comparison of Base *C* Values with log *K* Values for the Protonation Reaction of the Base from Arnett et al.¹²

Base	<i>C</i>	log <i>K</i> ^a	Base	<i>C</i>	log <i>K</i> ^a
Acetonitrile	1.58	-10.0	Tetrahydrofuran	1.99	-2.0
Ethyl acetate	1.63	-4.5	<i>N,N</i> -Dimethylacetamide	2.23	-0.4
Acetone	1.77	-7.2	Dimethyl sulfoxide	2.34	-1.8
Diethyl ether	1.96	-2.4	Pyridine	2.73	+5.2

^a This refers to the equilibrium constant for the reaction $B(\text{base}) + H^+ \rightleftharpoons BH^+$.

There are two reasonable explanations for the 3500 cm^{-1} band. One is that it may be a "free" OH stretching frequency for an OH in a complex (i.e., it is an endgroup OH not involved in the bonding). The second is that it is an OH involved in a bonded complex. Assuming the second explanation to be true, data are available for the frequency shifts between monomer stretching and this band that can be used along with b values for alcohols in eq. (3) to calculate the enthalpy of formation of one hydrogen bond between two alcohol molecules.

The results are given in Table VII for three of the alcohols used in developing the two-parameter model and other alcohols and water. The b value for methanol was determined from the observed²⁷ frequency shift of its OH group when bonded to acetone, and the $m\Delta V_{\text{OH}}/b$ ratio for acetone, assuming the m value for methanol to be 0.0105 (the average of the six b values for alcohols in Table I). The result, 1.8 kcal/mole, is slightly larger than that for *t*-butyl alcohol, which is consistent with the slightly greater acidity of methanol. Ethanol was assigned a b value of 1.7 kcal/mole to indicate its relative acidity. It was assumed that other aliphatic alcohols, ROH, would have b values more similar to that of *t*-butyl alcohol, and these were assigned b values of 1.6 kcal/mole.

To arrive at a b value for water, it was assumed that its m value would be the same (0.0105) as that for alcohols. This along with the measured frequency shift was combined with a reported self-association energy¹⁷ of 3.4 kcal/mole to yield a value of 2.0 kcal/mole.

In Table VII, the predicted values from the linear relationship using the indicated frequency shifts and b values are given along with reported values from

TABLE VII
Self-Association of Alcohols and Water, Predicted Hydrogen Bond Enthalpies for the Formation of One Bond, Literature Values, C Values for Alcohols and Water

Compound	$\Delta V_{\text{OH}},^a$ cm^{-1}	$b,^b$ kcal/mole	Predicted $-\Delta H,$ kcal/mole ^c	Measured $-\Delta H,^d$ kcal/mole	C
Phenol	128	3.08	4.3	4.3	1.43
TBA	120	1.65	2.9	2.4-5.8	1.76
DTBC	121	1.24	2.2	2.2-4.2	1.56
Methanol	117	1.80	3.0	3.7-5.8	1.68
Ethanol	120	1.70	3.0	3.6-5.4	1.74
ROH	120-130	1.60	3.0	3.0-6.0	1.80-1.85
Water	135	2.00	(3.4)	3.4, 5.1	1.71

^a Values are from the following references: phenol²¹; TBA was measured by the author; DTBC²²; methanol, ethanol and ROH²⁷; water¹⁷, p. 120, calculated from monomer frequency and ratio of frequency shift to monomer frequency.

^b Values are from the following references: phenol² TBA¹⁴; DTBC¹³; methanol was calculated from OH frequency shift when bonded to acetone²⁷ and acetone ratio of 0.77 (assuming $m = 0.0105$ for methanol in linear enthalpy-versus-frequency shift relationship); ethanol was estimated to be between that of methanol and ROH values; ROH estimated to be similar to TBA; water value calculated from frequency shift and measured enthalpy of 3.4 kcal/mole (assuming $m = 0.105$ for water in linear relationship).

^c These values are calculated from the enthalpy-versus-frequency shift relationship assuming a slope of 0.105 and using measured frequency shift and b value (water value is the same as that measured since the measured value was used to determine b).

^d The following measured values are from Pimeatel and McClellan¹⁷: phenol, TBA, methanol, ethanol, ROH, 3.4 value for water. The lower value for DTBC is from Rider,¹³ and the upper value is from Patterson.²² The 5.1 value for water is from Dill et al.²³

the literature. Several values for each compound are reported, and the predicted values are on the low side of the ranges indicated. Lower values tend to be measured in experiments in which the alcohols are present in dilute solutions of inert solvents, a situation that tends to favor the formation of smaller complexes, perhaps involving single hydrogen bonds. The predicted value for water is the same as the lower literature value because this value was used to derive the b parameter for water.

It is possible to calculate C parameters for alcohols and water from these results, and these are given in Table VII. It is interesting to note that the C values for aliphatic alcohols are similar to those of diethyl ether and tetrahydrofuran, which involve oxygen atoms with the same kind of orbital hybridization.

Owing to the range of enthalpies that have been experimentally measured for the self-association of alcohols and the continuing uncertainty about the actual character of the self-association complexes present, the result of using eq. (3) to predict enthalpies, or using eq. (2) and b and C values for the alcohols, can be considered approximate. In some unpublished results of the author on the self-association of some sterically hindered 3-pentanol, measured enthalpies are in the range of from 2 to 3 kcal/mole. It is probable that only one hydrogen bond is involved in the self-association of these compounds, which suggests that the parameters predict the energy for a single bond.

DONATING PARAMETERS (b) FOR NONHYDROXYL COMPOUNDS

A pure liquid is held together by fairly weak forces. The enthalpy of vaporization reflects the magnitude of these forces for a given liquid. Hildebrand and Scott²⁴ developed the concept of the "cohesive energy density" of a pure liquid based upon this notion. Further, the cohesive energy density is the fundamental idea behind their "solubility parameter" theory in which the solubility behavior of liquids in one another can be related to their solubility parameters, a number derived from their cohesive energy densities. A discussion of these concepts can be found elsewhere, the one by Hansen²⁵ being fairly comprehensive.

It has become customary to separate the cohesive energy density into three components. These are related to dispersion forces, dipolar forces, and hydrogen bonding. Different methods have been employed to estimate each of these contributions for a large number of compounds. Hansen and Skaarup²⁶ report values for solubility parameters for compounds related to each of these three contributions. The hydrogen-bonding contribution, in their approach, is assigned to what remains of the cohesive energy density (based upon heats of vaporization) after account has been made of dispersion and polar contributions. The hydrogen-bonding contribution is present in many compounds that are not normally regarded as capable of self-associating through hydrogen bonding. The contributions usually amount to energies of 1 kcal/mole or less to the cohesive energy density. Fritz²⁸ reports values for autoprotolysis equilibrium constants of several compounds that are not usually regarded as being self-associated through hydrogen bonding. Since these compounds can undergo proton transfer from one molecule to another like molecule to a limited extent, it is not unreasonable to assume that some hydrogen bonding might also be present which accounts for the hydrogen-bonding contribution to the cohesive energy density

reported by Hansen and Skaarup.²⁶ This concept is somewhat controversial and should be viewed with caution.

In Table VIII, the residual hydrogen-bonding parameters of Hansen and Skaarup, in units of $(\text{cal/ml})^{1/2}$, are listed for several compounds along with their molar volumes at room temperature. Squaring the parameters and then multiplying by the molar volume yields a hydrogen-bonding energy that can be considered that for self-association of the compound. There is also a listing of C parameters for these compounds. These were derived from measured frequency shifts of the OH stretching frequency of methanol bonded to these compounds reported by Nelson et al.²⁷ The C values were calculated using the frequency shifts, assuming an m value of 0.0105 for methanol and a b value of 1.8 kcal/mole.

The donating parameters b for these compounds also appear in Table VIII. These values were calculated from the self-association hydrogen-bonding energies and the C values derived from methanol. In order to examine these b values along with those of alcohols and water in terms of their appropriateness as a measure of the tendency of a compound to donate a proton, it is interesting to correlate them with the equilibrium constants for the autoprotolysis reaction below:

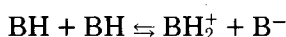


TABLE VIII
Hydrogen Bond-Donating Parameters for Bases Determined from Using Methanol OH Frequency Shifts when Bonded to the Base and Residual Cohesive Energy Density of Bases after Accounting for Dispersion and Polar Interactions

Base	Molar volume, ml/mole	Residual H bonding, ^a $(\text{cal/ml})^{1/2}$	C^b	Residual H bonding, ^c (kcal/mole)	b , kcal/mole
Acetone	74.0	3.4	1.77	0.855	0.492
Methyl ethyl ketone	90.1	2.5	1.61	0.563	0.350
Methyl isobutyl ketone	125.8	2.0	1.61	0.503	0.313
Methyl isoamyl ketone	142.8	2.0	1.64	0.571	0.348
Cyclohexanone	124.0	2.5	1.80	0.775	0.430
Diisobutyl ketone	177.1	2.0	1.57	0.708	0.451
Isophorone	150.5	3.6	1.85	1.950	1.054
Ethyl acetate	98.5	3.5	1.63	1.207	0.754
Isobutyl acetate	133.5	3.1	1.51	1.283	0.850
<i>n</i> -Butyl acetate	136.2	3.1	1.47	1.309	0.890
Amyl acetate	148.8	3.4	1.48	1.720	1.162
Isobutyl isobutyrate	163.0	2.9	1.47	1.371	0.933
Tetrahydrofuran	81.7	3.9	1.99	1.243	0.624
1,4-Dioxane	85.7	3.6	1.85	1.111	0.600
Toluene	106.8	1.0	1.25	0.107	0.085
Xylene	121.2	1.5	1.26	0.272	0.216
Ethylbenzene	123.1	0.7	1.25	0.060	0.048
Chlorobenzene	107.1	1.0	1.16	0.107	0.092
2-Nitropropane	86.9	2.0	1.23	0.348	0.283
Dimethylformamide	77.0	5.5	2.10	2.329	1.109

^a The residual hydrogen-bonding energy parameters are taken from Hansen and Skaarup.²⁶

^b The C values are based upon measured methanol OH frequency shifts when bonded to the base from Nelson et al.,²⁷ using a b value of 1.8 kcal/mole for methanol and assuming a slope of 0.0105 for methanol (in linear enthalpy–frequency shift relationship).

^c The residual hydrogen-bonding energies (in kcal/mole) were calculated by squaring values in column 2 and multiplying by molar volume values in column 1.

TABLE IX
Donating Parameters and Autoprotolysis Constants for Several Compounds

Compound	b , kcal/mole	K_s^a	$\log K_s$
Phenol	3.080	10^{-10}	-10
Water	2.000	10^{-14}	-14
Methanol	1.800	$10^{-16.7}$	-16.7
Ethanol	1.700	$10^{-19.5}$	-19.5
Isopropyl alcohol	1.600	$10^{-20.8}$	-20.8
Dimethylformamide	1.110	10^{-18}	-18
Dimethylsulfoxide	0.770	$10^{-17.3}, 10^{-33}$	-17.3, -33
Methyl isobutyl ketone	0.313	$10^{-28.6}$	-28.6
Acetonitrile	0.301	$10^{-28.6}$	-28.6
Acetone	0.491	10^{-30}	-30

^a Values are taken from Fritz.²⁸ They are all autoprotolysis constants, except for phenol, which is the equilibrium constant for the protonation of phenol in water.

Values for the constants along with $\log K_s$ have been reported by Fritz²⁸ and are listed in Table IX for several compounds along with corresponding b values. It can be noted that there is a direct correlation between b and $\log K_s$, which gives some validity to b as a measure of the tendency for a compound to donate a proton. The K_s value for phenol is not the autoprotolysis constant but instead is the value for the protonation constant of phenol in water. However, it appears to fit the correlation fairly well.

CONCLUSIONS

The two-parameter model developed in this article involving a proton-donating parameter (b) for one compound and a proton-accepting parameter (C) for another compound to predict the enthalpy of hydrogen bond formation between the two compounds appears to work reasonably well. Further, it is possible to assign both a donating and an accepting parameter to compounds regarded as both strongly donating and accepting (alcohols, water) as well as to weakly donating and strongly accepting compounds (typical organic bases). Even for weak donating and accepting compounds (aromatic hydrocarbons), parameters may be assigned.

The model as well as the ability to assign both donating and accepting parameters have important practical consequences as will be described in a second publication related to this work.

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References

1. R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, **87**, 3571 (1965).
2. R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Am. Chem. Soc.*, **93**, 6014 (1971).
3. A. P. Marks and R. S. Drago, *J. Am. Chem. Soc.*, **97**, 3324 (1975).
4. G. Klopman, *J. Am. Chem. Soc.*, **90**, 223 (1968).
5. P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).

6. A. D. Sherry and K. F. Purcell, *J. Phys. Chem.*, **74**, 3535 (1970).
7. P. Kollman, J. McKelvey, A. Johansson, and S. Rothenberg, *J. Am. Chem. Soc.*, **97**, 955 (1975).
8. P. Kollman, *Acc. Chem. Res.*, **10**, 365 (1977).
9. R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).
10. P. M. Badger and S. H. Bauer, *J. Phys. Chem.*, **5**, 839 (1937).
11. E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, T. Gorrie, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **92**, 2365 (1970).
12. E. M. Arnett, E. Mitchell, and T. S. S. R. Murty, *J. Am. Chem. Soc.*, **96**, 3875 (1974).
13. P. E. Rider, Ph.D. Thesis, Kansas State University, 1969.
14. R. S. Drago, N. O'Bryan, and G. C. Vogel, *J. Am. Chem. Soc.*, **92**, 3924 (1970).
15. K. F. Purcell, J. A. Stikeleather, and S. D. Brunk, *J. Am. Chem. Soc.*, **91**, 4019 (1969).
16. M. S. Nozari and R. S. Drago, *J. Am. Chem. Soc.*, **92**, 7086 (1970).
17. G. Pimentel and A. McClellan, *The Hydrogen Bond*, Freeman, San Francisco, 1960, Appendix A.
18. R. M. Hammaker, R. M. Clegg, L. K. Patterson, P. E. Rider, and S. L. Rock, *J. Phys. Chem.*, **72**, 1837 (1968).
19. E. Tucker, S. Farnum, and S. D. Christian, *J. Phys. Chem.*, **73**, 3820 (1969).
20. E. Tucker and S. D. Christian, *J. Phys. Chem.*, **81**, 1295 (1977).
21. S. N. Vinogradov and R. H. Linnell, *Hydrogen Bonding*, Van Nostrand Reinhold, New York, 1971, p. 57.
22. L. K. Patterson, Ph.D. Thesis, Kansas State University, 1967.
23. J. D. Dill, L. C. Allen, W. C. Tropp, and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 7220 (1975).
24. J. H. Hildebrand and R. L. Scott, *The Solubility of Non-Electrolytes*, 3rd ed., Dover, New York, 1964.
25. C. Hansen, Solubility parameters, in *Encyclopedia of Chemical Technology, Supplemental Vol. 2*, 2nd ed., Wiley, New York, 1971, p. 809.
26. C. M. Hansen and K. Skaarup, *J. Paint Technol.*, **39**, 511 (1967).
27. R. C. Nelson, R. W. Hemwall, and G. D. Edwards, *J. Paint Technol.*, **42**, 636 (1970).
28. J. S. Fritz, *Acid-Base Titrations in Non-Aqueous Solvents*, Allyn and Bacon, Boston, 1973.

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