

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE RELATION BETWEEN THE RELATIVE STRENGTHS OF ACIDS IN TWO SOLVENTS

BY J. O. HALFORD¹

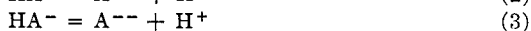
RECEIVED MAY 26, 1931

PUBLISHED AUGUST 5, 1931

The expression, the strength of an acid, is frequently used in referring to either of two quantities between which a distinction should be made. In the general sense, the strength of an acid is a measure of its intrinsic tendency to lose protons, independent of the interference of a solvent. This property eludes specific evaluation. More frequently, the expression refers to a measured value in some solvent, expressed quantitatively on an arbitrary scale of proton potential, such as the P_H scale of aqueous solutions. We are concerned here not with acid strength in the general sense, but rather with a procedure by which to express the position of an acid on an arbitrary scale of strengths in one solvent in terms of its position on a similar scale in another.

Several years ago, Brönsted² made the statement that "Absolute comparison of the strengths of two acids or two bases is impossible because it requires the absence of any solvent medium." In other words, the three molecular species involved in the characteristic equilibrium of dissociation are affected differently and specifically by transfer from one medium to another, and the measured relative strength of two acids is, in general, dependent upon the solvent as well as the characteristics of the acids. For convenience, we may say that two effects require consideration when we compare the acidities of a series of substances in two solvents. The one, which involves the relation of the P_H scales, or their equivalent, we avoid by selecting these scales arbitrarily; the other is an irregular variation of relative strengths.

The dissociation of the three types of acids most frequently encountered may be represented by the equations



The first includes the substances usually classed as weak acids, the second applies to acids of the type of ammonium ion and the third to the second dissociation of a polybasic acid. We may refer to these classes as different valence types. It is evident that in going from one solvent to another of different dielectric constant, the relative strength of two acids of different valence types will be considerably changed. For example, Reaction 1, in

¹ Alfred H. Lloyd Fellow in the Graduate School, University of Michigan.

² Brönsted, *J. Phys. Chem.*, **30**, 777 (1926).

which the ions appear only on one side of the equation, should be much more sensitive to the dielectric properties of the medium than Reaction 2, in which a singly charged positive ion appears on each side.

In the comparison of reactions of any one type, we find relative strengths fairly concordant, as in the summary by Hall³ of reactions of type 2 in glacial acetic acid. However, minor variations occur, even within one valence type, and Hall's results indicate that they are usually within one pK unit.

Considering valence type 1, we find, in the measurements of Michaelis and Mizutani⁴ in ethyl alcohol, water and their mixtures, that similar variations of relative strength occur, again of the order of one pK unit. The fact that these variations are small is ascribed by Hammett⁵ to the circumstance that a solvent which is better for the free acid is also better for its salts. This is equivalent to a statement that the reaction of the ion A^- to forces other than those concerned with the ionic charge and its distribution is not greatly different from that of the free acid HA .

The relation between the ionization equilibria of an acid in two solvents and the distribution coefficients of the acid and its ions has been considered in detail by Bjerrum and Larsson.⁶ They have employed solubility measurements in the evaluation of the distribution ratios of the ions. In this way, they have expressed the relation between the dissociation constants in two solvents in terms of the solubilities of the acid and its salts.

If we accept the importance of placing a large number of acid strengths on the same scale, such a relation becomes necessary, for it is improbable that we shall be able to make the required number of measurements in any one solvent. For example, acids which are classed as strong in water show differences in glacial acetic acid, while water is the better solvent for bringing out the differences between the stronger bases. In the selection of a solvent for the study of a given series of acids or bases, two main factors must be considered. The first is that the substances shall be sufficiently soluble to permit accurate measurement, and, if a potentiometric method is to be used, the solubility requirement also applies to the salts of the substances under investigation. The second requirement is that the solvent shall be sufficiently sensitive to variations of strength of the magnitude to be measured. The amphiprotic type of solvent is best suited to measurement, and it is this type which, because of its ability to reduce markedly the apparent strength of strong acids and bases, per-

³ Hall, *THIS JOURNAL*, **52**, 5115 (1930).

⁴ Michaelis and Mizutani, *Z. physik. Chem.*, **116**, 135 (1925); Mizutani, *ibid.*, **116**, 350 (1925).

⁵ Hammett, *THIS JOURNAL*, **50**, 2666 (1928).

⁶ Bjerrum and Larsson, *Z. physik. Chem.*, **127**, 358 (1927).

mits the narrowest range of application. In order to place the desired number of measurements on a comparative scale, more than one solvent, probably at least three, will be necessary, if the requirements of solvent power and range of application are to be met. Further, since at present we have no good reason for preferring one scale to another, it becomes desirable to compare results on several scales.

We present here a derivation of the relation between acid strengths in two solvents, in a form which, in our opinion, is more convenient than that of Bjerrum and Larsson. The concept of ion distribution coefficients is not directly involved. The following equations apply to valence type 1. Consider the dissociation constants, K_1 and K_2 , of an acid in two solvents, distinguished by the subscripts 1 and 2.

Equation	ΔF	
HA (standard) = HA ₍₁₎	$-RT \ln a_1$	(a)
HA ₍₁₎ = H ⁺ ₍₁₎ + A ⁻ ₍₁₎	$-RT \ln K_1$	(b)
HA ₍₂₎ = HA (standard)	$RT \ln a_2$	(c)
H ⁺ ₍₂₎ + A ⁻ ₍₂₎ = HA ₍₂₎	$RT \ln K_2$	(d)
H ⁺ ₍₁₎ = H ⁺ ₍₂₎	B	(e)
MA(s) = M ⁺ ₍₂₎ + A ⁻ ₍₂₎	$-RT \ln \sigma_2^2$	(f)
M ⁺ ₍₁₎ + A ⁻ ₍₁₎ = MA(s)	$RT \ln \sigma_1^2$	(g)
M ⁺ ₍₂₎ = M ⁺ ₍₁₎	C	(h)

Since the sum of these equations is zero

$$RT \ln (a_2/a_1 \times K_2/K_1 \times \sigma_1^2/\sigma_2^2) = -(B + C) \quad (4)$$

or

$$\frac{a_2 K_2 \sigma_1^2}{a_1 K_1 \sigma_2^2} = \text{constant} \quad (5)$$

Here a_1 designates the activity, in solvent 1, referred to the usual standard state at infinite dilution, of the acid HA, when at equilibrium with HA (standard). For moderately soluble solid acids, this is approximately equal to the solubility. MA is the salt of the acid with the positive group M, and Equations f and g imply that the activity methods commonly employed with strong electrolytes are applicable. The quantity σ is the mean activity of the ions, M⁺ and A⁻, in the saturated solution of the salt MA, the activity again so defined as to approach the concentration at infinite dilution. For slightly soluble salts, σ^2 is approximately equal to the solubility product. The quantity $B + C$, by which the constant of Equation 5 may be evaluated, should be the same for all acids of type 1. This is probably best determined by measurement, for at least one acid, of the other quantities in the equation. Also, it is directly related to the difference between the distribution coefficients, expressed logarithmically, of the ions H⁺ and M⁺.

Similar equations may be developed for each of the other types of dis-

sociation equilibrium. We give here the result for type 2, representing the dissociation of such acids as ammonium ion

$$RT \ln (a_1/a_2 \times K_2/K_1 \times \sigma_2^2/\sigma_1^2) = -(B + D) \quad (6)$$

or

$$\frac{a_1 K_2 \sigma_2^2}{a_2 K_1 \sigma_1^2} = \text{constant} \quad (7)$$

Here a refers to the free base A, and σ to the salt AHX, so that D applies to the work of transfer of the ion X^- . C and D have opposite signs, and the constants of Equations 5 and 7 are different. However, the corresponding equation for type 3 contains the same constant term as that for type 1. In order, then, to correlate the scales of two solvents for a number of acids involving all three valence types, it will be necessary to evaluate independently the constant terms of Equations 5 and 7.

These equations impose no restriction on the method of setting up the scale of acidities or P_H values in any one solvent. Equations 6 and 7 imply that the scales are to be developed in the manner in which the P_H scale of aqueous solutions has been established, so that the pK of an acid is equal to the negative logarithm of the dissociation constant. However, the appearance of the constant term in Equation 5 removes this apparent restriction. This is clearer if we examine the logarithmic form of the equation, employing the symbol pK , as defined above.

$$\log \frac{a_2 \sigma_1^2}{a_1 \sigma_2^2} + pK_1 = pK_2 + \text{constant} \quad (5')$$

It is evident that either pK_1 or pK_2 , or both, may be altered by the addition of an arbitrary constant, without interference with the validity of the equation. Such an alteration is equivalent to the use of an arbitrary P_H scale. However, it will probably be most convenient, when circumstances are favorable, to employ the scale similar to that of aqueous solutions, in which the simple relation between pK and the dissociation constant is retained.

The shift of relative strength of two acids, in going from one solvent to another, is entirely a function of the quantities a and σ . From Equation 5', for two acids, it follows that

$$\Delta pK_2 - \Delta pK_1 = \log \frac{a_2 \sigma_1^2}{a_1 \sigma_2^2} (A) - \log \frac{a_2 \sigma_1^2}{a_1 \sigma_2^2} (B) \quad (8)$$

where A and B refer to the two acids compared, and $\Delta pK = pK(A) - pK(B)$ in either solvent. In the first approximation, the calculation of the variation of relative strength is independent of the actual values of acid strength in either medium. However, the accurate evaluation of the activity of the undissociated part of the acid may require knowledge of its dissociation constant.

The above equations are exact if a and σ are interpreted as activities. However, a useful approximation may be introduced by assuming that solubilities, when sufficiently low, may be employed to replace the activities. We have carried out this approximate calculation for several acids and their silver salts, in water and in 50% alcohol by volume, at $24 \pm 1^\circ$. The solubility data have been taken from various sources. Where data on the free acids were lacking, we have obtained them by weighing the residue from evaporation of samples of the saturated solutions. The solubility of silver salicylate was determined as residue from evaporation, that of the other silver salts by titration of the saturated solutions with ammonium thiocyanate to a ferric thiocyanate end-point.

The results are summarized in Table I. The first column shows the acid, the second its solubility in water corrected for dissociation, the third its solubility in 50% alcohol, used without correction, the fourth and fifth the solubility of the silver salt in water and in 50% alcohol. Concentrations are expressed as moles per liter. The sixth column shows the quantity on the right side of Equation 8, the shift of acid strength relative to salicylic acid. The last column gives the corresponding measured value, taken from the following paper.⁷

TABLE I
DIFFERENCE OF STRENGTHS, RELATIVE TO SALICYLIC ACID, IN WATER AND IN 50%
ALCOHOL BY VOLUME, AT $24 \pm 1^\circ$

Acid	a_1	a_2	σ_1	σ_2	Diff. of rel. strength Calcd. Measd.	
Acetic	0.0670	0.0180	-0.20	0
Benzoic	0.0264	0.918	.0115	.00763	+ .56	0.5
Salicylic	.0142	.552	.0069	.0092	0	0
<i>o</i> -Nitrobenzoic	.0278	.898	.0291	.0204	.46	.5
α -Naphthoic	.00040	.0388	.00405	.00440	.60	.6

In the calculation for acetic acid, a_2/a_1 was taken arbitrarily as unity. The values in the last column, which were obtained by combining known relative strengths in water with measurements in 50% alcohol with the antimony electrode, may be in error by as much as 0.2 unit.

The writer is grateful to Professor James B. Conant, who suggested this problem and contributed valuable advice.

Summary

Equations which connect the relative strengths of acids in one solvent with those in another by means of solubility data, or their equivalent, have been discussed. Some applications to acids in water and in 50% alcohol are presented.

CAMBRIDGE, MASSACHUSETTS

⁷ Halford, THIS JOURNAL, 53, 2944 (1931).