RELATIVE ACID STRENGTHS IN ACETONITRILE

MARTIN KILPATRICK, JR., AND MARY L. KILPATRICK
Department of Chemistry, University of Pennsylvania, Philadelphia,
and
Marine Experimental Station of the Lankenau Hospital Research Institute, North Truro, Massachusetts

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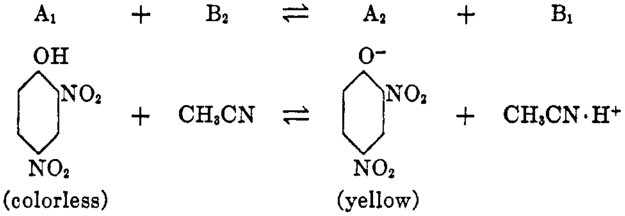
Acetonitrile, as Hantzsch (1) has shown, is a weakly basic solvent. When an acid is dissolved in acetonitrile there is established a double acid–base equilibrium; for hydrochloric acid, for example,

$$\begin{array}{ccccccc} A_1 & + & B_2 & \rightleftharpoons & A_2 & + & B_1 \\ HCl & + & CH_3CN & \rightleftharpoons & CH_3CN \cdot H^+ & + & Cl^- \end{array}$$

If the acid A_1 is an indicator, the equilibrium constant can be determined directly by the colorimetric method. We determined colorimetrically the equilibrium constants of a number of indicator acids, preparing the complete acid and basic forms of the indicator in acetonitrile by the addition of small amounts of suitable acid or base. In the case of α-dinitrophenol, for instance,

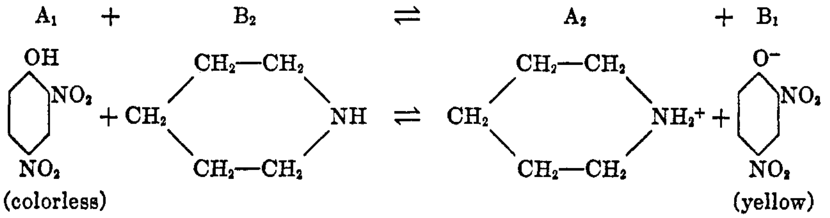


and

$$K = [CH_3CN \cdot H^+]\,[\alpha\text{-dinitrophenolate}]/[\alpha\text{-dinitrophenol}]$$

where the brackets indicate concentrations. With brom phenol blue two color changes were observed,—colorless-yellow and yellow-blue. Only the second is found in aqueous solution.

Knowing the constant for the equilibrium between the solvent and the indicator acid, it is possible to obtain the constant for the equilibrium between the indicator acid and a suitable base. Thus the constant for the equilibrium between α-dinitrophenol and piperidine



was obtained from the stoichiometric relationships, the colorimeter reading, and the constant

$$K = [\mathrm{CH_3CN \cdot H^+}][\alpha\text{-dinitrophenolate}]/[\alpha\text{-dinitrophenol}]$$

due correction being made for the basicity of the solvent.

Knowing the constant for the equilibrium between the base and the indicator acid, it is possible to obtain the constant for the equilibrium between the base and a second acid, not an indicator, present in the solution. For example, the constant for the equilibrium between mandelic acid and piperidine

$$\begin{array}{ccccccc} A_1 & + & B_2 & \rightleftharpoons & A_2 & + & B_1 \\ \mathrm{C_6H_5CHOHCOOH} & + & \mathrm{C_5H_{10}NH} & \rightleftharpoons & \mathrm{C_5H_{10}NH_2^+} & + & \mathrm{C_6H_5CHOHCOO^-} \end{array}$$

was obtained from the stoichiometric relationships, the colorimeter reading giving the ratio [α-dinitrophenolate]/[α-dinitrophenol], and the constant

$$K = \frac{[\alpha\text{-dinitrophenolate}][\text{piperidinium ion}]}{[\alpha\text{-dinitrophenol}][\text{piperidine}]}$$

The determination of the constants for the equilibria between acids and basic indicators was carried out in a similar way. In the case of dimethyl yellow it was not possible to get quantitative results because of the fading of the red color of the indicator. Similar chemical difficulties were encountered with other indicators in the presence of trichloroacetic acid.

In all, some forty equilibrium constants were determined. The electrolyte concentration in the experiments ranges from $\mu = 1 \times 10^{-6}$ to 1×10^{-3}. No correction was made for salt effect, and furthermore it was assumed that at these concentrations association was negligible.

The important question of a general scale of acidity has been discussed by Brönsted (2) and by others (3, 4, 5, 6) and the fundamental difficulties have been pointed out in connection with the impossibility of obtaining ionic free energies (7). For this reason the logical definition of acid strength

$$K_{\mathrm{A}} = a_{\mathrm{H}^+} c_{\mathrm{B}}/c_{\mathrm{A}}$$

cannot be used from solvent to solvent without arbitrary assumptions. It has been shown, however, that in constant medium relative acid strengths can be found in reference to some suitable acid–base system (2). Although an acid is defined by the equation

$$\mathrm{A} \rightleftharpoons \mathrm{B} + \mathrm{H}^+$$

$$K'_{\mathrm{A}} = [\mathrm{B}][\mathrm{H}^+]/[\mathrm{A}]$$

the acid strength of A cannot be expressed by the equilibrium constant of the process above. This constant can, however, be related to the equilibrium constant K_0 which defines the acid property of the system having the solvent as the conjugate base

$$K_0 = [\mathrm{CH_3CN}][\mathrm{H}^+]/[\mathrm{CH_3CN \cdot H^+}]$$

Dividing K_{A}' by K_0 one obtains

$$K_{\mathrm{A}}'/K_0 = [\mathrm{B}][\mathrm{CH_3CN \cdot H^+}]/[\mathrm{A}][\mathrm{CH_3CN}]$$

the ratio being equal to the equilibrium constant for the double acid–base equilibrium. Considering the concentration of solvent as constant and transposing it to the other side, one has

$$K = K_{\mathrm{A}}'[\mathrm{CH_3CN}]/K_0 = [\mathrm{B}][\mathrm{CH_3CN \cdot H^+}]/[\mathrm{A}]$$

where K is the customary dissociation constant of the acid A. The dissociation constant may therefore be taken as a measure of the acid strength in any given solvent. For solvents which are aprotic, like benzene, it is not possible to refer to the acid of which the solvent is the conjugate base. Brönsted has pointed out that in such cases one may arbitrarily choose as standard some suitable acid–base system.

Even when work is confined to one solvent the medium is changed upon the addition of solutes, so that it is impossible to work in truly constant medium. For this reason the experiments described in this paper were carried out in as dilute solution as was practicable. An alternative method would have been to maintain a medium of high and constant electrolyte concentration, employing the principle of "swamping salt" effect so successful in kinetic studies. As a general method, the latter is not so useful in non-aqueous solution, owing to the fact that many salts are insufficiently soluble, and to the fact that it is difficult to find a salt the anion or cation of which is not an acid or a base.

TABLE 1

Order of decreasing acid strength of various acids

IN ACETONITRILE	IN WATER
o-Toluidinium ion	β-Naphthalenesulfonic acid
Brom phenol blue, colorless-yellow	Picric acid
β-Naphthalenesulfonic acid	Dichloroacetic acid
Picric acid	Monochloroacetic acid
Neutral red	Salicylic acid
Dichloroacetic acid	*o*-Chlorobenzoic acid
Salicylic acid	Mandelic acid
β-Dinitrophenol	*o*-Toluic acid
Brom phenol blue, yellow-blue	β-Dinitrophenol
Diphenylguanidinium ion	Glycolic acid
α-Dinitrophenol	α-Dinitrophenol
Mandelic acid	Brom phenol blue, yellow-blue
Glycolic acid	Benzoic acid
Monochloroacetic acid	*o*-Toluidinium ion
Piperidinium ion	Acetic acid
o-Chlorobenzoic acid	Neutral red
Isoamylammonium ion	Diphenylguanidinium ion
o-Toluic acid	Isoamylammonium ion
Benzoic acid	Piperidinium ion
Acetic acid	

Table 1 presents a list of acids arranged in order of decreasing acid strength in acetonitrile. The acid dissociation constants from which the list was made up were obtained either directly from the colorimetric measurements or by combination of equilibrium constants. For purposes of comparison, the second column of the table gives the order of decreasing acid strength for water as solvent. An examination of the table shows that the order of acid strength is not the same throughout in the two solvents. The three hydroxy-substituted carboxylic acids—salicylic, mandelic, and glycolic acids— are stronger than monochloroacetic acid in acetonitrile, whereas in water they are weaker. The influence of electric charge is shown by the greater strength

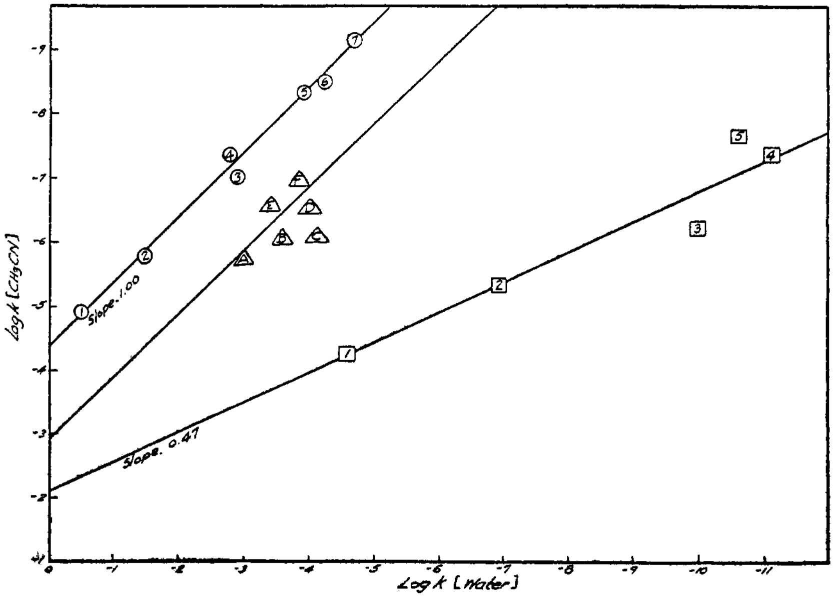


FIG. 1

○
1. Picric acid
2. Dichloroacetic acid
3. Monochloroacetic acid
4. *o*-Chlorobenzoic acid
5. *o*-Toluic acid
6. Benzoic acid
7. Acetic acid

△
A. Salicylic acid
B. β-Dinitrophenol
C. Brom phenol blue yellow-blue
D. α-Dinitrophenol
E. Mandelic acid
F. Glycolic acid

□
1. *o*-Toluidinium
2. Neutral Red
3. Diphenylguanidinium
4. Piperidinium
5. Isoamylammonium

of the charged acids, relative to the uncharged, in acetonitrile than in water.

In figure 1 the logarithm to the base 10 of the dissociation constant in acetonitrile is plotted against the logarithm of the dissociation constant in water. For the carboxylic acids, excluding the hydroxy-substituted acids,

$$\log K_{CH_3CN} - \log K_{H_2O} = -4.4$$

For salicylic, mandelic, and glycolic acids

$$\log K_{CH_3CN} - \log K_{H_2O} = -3$$

For the cation acids of the amine type the slope is no longer unity, the relationship being

$$\log K_{CH_3CN} = 0.47 \log K_{H_2O} - 2.2$$

Similar comparisons of dissociation constants have been made by Larsson (8) between alcohol and water, and by Hall (9) between acetic acid and water, and by La Mer and Downes (6) for benzene.

In connection with the quantitative estimation of acids in acetonitrile solution, acids such as perchloric acid were titrated quantitatively with diphenylguanidine using dimethyl yellow, benzoyl auramine, or thymol blue as indicator. In the case of weak acids like acetic acid, bases of sufficient strength were not available. However, Lavine and Toennies (9) have demonstrated that for mixtures of perchloric acid and acetic acid in acetonitrile it is possible to titrate quantitatively in mixed solvents using the ethylate ion as the base and thymol blue as the indicator. The first change (pink-yellow) gives the perchloric acid end-point and the second (yellow-blue) gives both.

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