97. *Comments on the Influence of the Solvent on the Relative Strengths of Monocarboxylic Acids.*

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Lately, our knowledge of the strengths of organic acids in solvents other than water has been extended, and it is now possible for the author to amplify his generalisations regarding the influence of the solvent on relative acid strengths (*Chem. Reviews*, 1939, **25**, 151). The results for substituted benzoic acids in certain aliphatic alcohols obtained by Elliott and Kilpatrick (*J. Physical Chem.*, 1941, **45**, 454) are particularly interesting, especially since it can be shown that, contrary to the belief of these investigators, the relative strengths of the acids in these solvents are in harmony with the dissociation constants in aqueous solution except when special factors are operative. Measurements made by the author on six monocarboxylic acids in 25% aqueous acetone and 20% aqueous sucrose support this finding.

THE ionisation constants of monocarboxylic acids have commonly been regarded as providing a measure of the relative polar effects of substituent groups. The constants employed have invariably related to aqueous solution, and it has been a matter of some speculation as to whether the same conclusions might have been reached if the ionisation constants of the same acids in solvents other than water had been available.

Measurements on organic acids in a variety of non-aqueous and partly aqueous solvents have been accumulating gradually, particularly in the last few years,* and although the data are still somewhat scanty it is now possible to state that, in general, the sequence of acid strengths remains the same in proceeding from solvent to solvent. It is upon the order of strengths of acids in water that the organic chemist has usually based his arguments, and it is now justifiable to say that if some solvent other than water had been the common one the same fundamental conclusions would have been reached (cf. Dippy, *loc. cit.*).

In addition to providing general qualitative agreement, the ionisation constants of the acids in two given solvents are sometimes quantitatively related in a simple fashion, and from a review of the data it appears that quantitative agreement is more common

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* Goldschmidt *et al.*, *Z. physikal. Chem.*, 1916, **91**, 46; 1924, **112**, 423; 1925, **117**, 312; 1927, **129**, 223; Briscoe *et al.*, *J. Physical Chem.*, 1929, **33**, 190, 1495; 1933, **37**, 787; Halford, *J. Amer. Chem. Soc.*, 1931, **53**, 2994; LaMer *et al.*, *ibid.*, 1933, **55**, 1840; 1938, **60**, 1252; Goodhue and Hixon, *ibid.*, 1934, **56**, 1329; 1935, **57**, 1688; Wooten and Hammett, *ibid.*, 1935, **57**, 2289; Kilpi and Warsila, *Z. physikal. Chem.*, 1936, *A*, **177**, 427; Verhoek, *J. Amer. Chem. Soc.*, 1936, **58**, 2577; Griffiths, J., 1938, 818; Kilpatrick *et al.*, *J. Amer. Chem. Soc.*, 1937, **59**, 572; *J. Physical Chem.*, 1939, **43**, 259; 1941, **45**, 454, 466, 472, 485; Harned, *ibid.*, 1939, **43**, 275; Adell, *Z. physikal. Chem.*, 1940, **186**, 27; Kleene, Westheimer, and Wheland, *J. Amer. Chem. Soc.*, 1941, **63**, 791.

than has hitherto been supposed (cf., *e.g.*, Hammett, " Physical Organic Chemistry," McGraw-Hill Book Co., 1940, p. 259).

It is also noteworthy that in order reasonably to satisfy the linear relationship, $\log K_r \propto 1/D$ (Wynne-Jones, *Proc. Roy. Soc.*, 1933, *A*, **140**, 440), it is desirable to select solvents of a similar chemical type. This is better understood when it is remembered that the dielectric constant of a medium is not solely responsible for the extent of dissociation of the electrolyte; there is at least the additional factor of the chemical rôle of the solvent in most cases (Hartley *et al.*, *Ann. Reports*, 1930, **27**, 326; Hovorka and Simms, *J. Amer. Chem. Soc.*, 1937, **59**, 92; Dippy, *loc. cit.*; Hammett, *op. cit.*, p. 256), for on occasion an acid in solvents of similar dielectric constants exhibits different strengths, *e.g.*, substituted benzoic acids in aliphatic alcohols and aqueous dioxan (Elliott and Kilpatrick, *J. Physical Chem.*, 1941, **45**, 485), and acetic acid in ethyl alcohol–water and dioxan–water (Kilpi and Warsila, *loc. cit.*; Lynch and LaMer, *J. Amer. Chem. Soc.*, 1938, **60**, 1252). It is found, however, that sequences of strengths are well preserved despite the varying character of the media used, which include aprotic solvents, *e.g.*, benzene.

The anomalous relative strengths exhibited by certain acids are particularly interesting; it is by excluding these acids that a given sequence of acid strengths is reproduced from solvent to solvent. In a survey of the strengths of organic acids the author (*Chem. Reviews, loc. cit.*) has stressed the fact that the relative strength is not likely to be reproduced with acids in which a specific interaction occurs between the substituent and the carboxyl group. Hammett (*op. cit.*, p. 207) advances the view that the chemical nature of the solvent may influence the extent of the abnormality. Included among these exceptional systems are the *o*-substituted benzoic acids (" ortho-effect "). It should be added that in any series of halogeno-aromatic acids a change in the sequence of strengths among the four acids might be brought about by a disturbance of the opposing electrical effects ($-I + M$) attending a change of solvent, although it is anticipated that the halogeno-acids will occupy the same position when taken as a series.

In the light of these qualifications it is interesting to examine the strengths of *o*-, *m*-, and *p*-substituted benzoic acids in methyl, ethyl, and *n*-butyl alcohols and ethylene glycol (in the presence of lithium chloride) recorded recently by Elliott and Kilpatrick (*J. Physical Chem.*, 1941, **45**, 454, 466, 472), using an e.m.f. method. These workers conclude that their data do not support the claim that organic acids, with certain exceptions, exhibit the same relative strengths in all solvents. In Table I is an analysis of the sequence of strengths (at 25°) obtained by them.

TABLE I.

Solvent.	
	para-*Substitution.*
Water *	NO_2 > Br > Cl > F > H > Me > OMe > OH
Methyl alcohol	NO_2 > Br > I† > Cl > F > H > Me > OMe > OH
Ethyl alcohol	NO_2 > Br > I > Cl > F > H > Me > OMe > OH
n-Butyl alcohol	NO_2 > Br > I ≈ Cl > F > H > Me > OMe > OH
Ethylene glycol	NO_2 > Br > I > Cl > F > H > Me > OMe > OH
	meta-*Substitution.*
Water *	NO_2 > Br > Cl > I > F > *OH* > H > Me
Methyl alcohol	NO_2 > Br > Cl > I > F > H > Me > *OH*
Ethyl alcohol	NO_2 > Br > Cl > I > F > H > Me > *OH*
n-Butyl alcohol	NO_2 > Cl > Br > I > F > H > Me > *OH*
Ethylene glycol	NO_2 > Br > Cl > I > F > H > *OH* > Me
	ortho-*Substitution.*
Water*	NO_2 > Br > I > Cl > *OH* > F > *Me* > OMe > H
Methyl alcohol	NO_2 > *OH* > Br > Cl > I > F > OMe > *Me* > H
Ethyl alcohol	NO_2 > *OH* > Br > Cl > I > F > OMe > *Me* > H
n-Butyl alcohol	NO_2 > *OH* > Br > Cl > I > F > OMe > *Me* > H
Ethylene glycol	NO_2 > *OH* > Br > Cl > I > F > OMe > *Me* > H

* Results for aqueous solution at 25° are due to Dippy *et al.* (see *Chem. Reviews, loc. cit.*).
† *p*-Iodobenzoic acid has not been examined in water.

TABLE II.

Substituent group.	Solvent.	Sequence of strengths.
NO_2	Water, *n*-butyl alcohol, and ethylene glycol	*o*- > *p*- > *m*- > H
	Methyl alcohol	*o*- > *m*- > *p*- > H
	Ethyl alcohol	*o*- > *p*- ∼ *m*- > H
Halogens	Water and all four alcohols	*o*- > *m*- > *p*- > H
Me	Water and all four alcohols	*o*- > H > *m*- > *p*-
OMe	Water and all four alcohols	*o*- > H > *p*-
OH	Water	*o*- > *m*- > H > *p*-
	Alcohols	*o*- > H > *m*- > *p*-

First, from Table I it will be seen that the results for *p*-substituted acids are in complete agreement in all five solvents. Among *o*-substituted acids agreement is reached (except with salicylic and *o*-toluic acids), *viz.*, NO_2 > Halogens > OMe > H. The enhancement of strength shown by salicylic and *o*-toluic acids in water has already been attributed to a specific interaction involving hydrogen-bond formation (Branch and Yabroff, *J. Amer. Chem. Soc.*, 1934, **56**, 2568; Dippy, Evans, Gordon, Lewis, and Watson, J., 1937, 1421), and it is quite reasonable to assume that this enhancement will not be proportionate in all solvents. As far as *o*-nitro- and *o*-halogeno-benzoic acids are concerned, evidence has been forthcoming to show that their strengths can be interpreted on the basis of classical electrostatic theory (Jenkins, J., 1939, 640). The hydroxy-acid is the only anomaly in the *m*-series, where the sequence NO_2 > Halogens > H > Me is followed throughout.

As already implied, a particular " partial inversion " of the strengths of halogeno-aromatic acids may not always be reproduced; even so, the only distinct case where the sequence in water has not been fulfilled elsewhere is to be found in the *o*-series. Moreover, such small differences in relative acid strengths in the alcohols are not indisputable, as indicated by the divergences in the results obtained with e.m.f. and colorimetric measurements, especially for ethyl-alcoholic solutions; actually, the two methods do not always place halogeno-acids in the same sequences.

In the light of this analysis, therefore, it can be concluded with some degree of confidence that the differences (exhibited by comparatively few instances) between the results obtained by Elliott and Kilpatrick and those recorded for aqueous solution can be attributed to the incursion of special factors. A still more striking demonstration of the harmony which obtains is given by the form of analysis adopted in Table II.

Further evidence in support of the foregoing contentions has been derived by the author in collaboration with Mr. I. Davey. Six monocarboxylic acids, examined in 25% aqueous acetone and 20% aqueous sucrose at 25° by the conductivity method, have been shown to possess dissociation constants falling in the order : diphenylacetic > benzoic > phenylacetic > cinnamic > β-phenylpropionic > propionic, which is that obtaining in aqueous solution.

It was also found that, although the dielectric constant (25°) of aqueous sucrose (73·6; Åkerlöf, *J. Amer. Chem. Soc.*, 1932, **54**, 4125) is less than that for water (78·5, *idem, ibid.*), the strengths of the series of acids throughout are slightly greater in the mixed solvent. This further supports the view that the chemical nature of the solvent, apart from the dielectric constant, has a bearing on the dissociation equilibrium. Details of this investigation will appear when conditions permit of its completion.

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