added 17.6 g. (0.10 mole) of benzenesulfonyl chloride. The solution was refluxed six hours and poured into ice-water. The precipitated white solid was filtered, washed with water and recrystallized from ethanol–water to give 17.2 g. (64%) of N-(γ-diethylaminopropyl)-benzenesulfonamide, melting at 75–77°. Additional recrystallizations from ethanol–water gave fine white crystals melting at 77–78°.

Anal. Calcd. for $C_{13}H_{32}N_2O_2S$: C, 57.74; H, 8.20; N, 10.36. Found: C, 57.43; H, 7.72; N, 10.49.

DEPARTMENT OF CHEMISTRY
DUKE UNIVERSITY
DURHAM, NORTH CAROLINA
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Dissociation Constants of Higher Alkyl Phosphate Esters, Phosphonic Acids, Phosphonous Acids, Phosphinic Acids and Carboxylic Acids

BY J. R. WHITE

The dissociation constants in 50% by weight ethanol in water at 25° have been determined for the acids: benzoic, palmitic, oleic; mono-*n*-dodecyl ester of cyclohexene-3-1,6-dicarboxylic, 2-ethylhexanoic, di-*n*-decylphosphoric, di-*n*-dodecylphosphoric, mono-*n*-decylphosphoric, dodecanephosphonic, dodecanephosphonous and di-2-ethylhexylphosphinic. Measurements were made with a non-thermodynamic cell of the type

Glass electrode Beckman 1190E	KA HA ethanol (50% by wt.), H_2O (50% by wt.)	Satd., KCl	Hg, Hg_2Cl_2

and employing a Beckman model G potentiometer. An e. m. f.-p_aH function in water solutions was established experimentally for each of several electrode systems by measuring the buffer solutions to which the p_aH values recommended by Bates, Hamer, Manov and Acree were assigned.[1]

$HKC_8H_4O_4$ (acid potassium phthalate) (0.05 molal) $p_aH = 4.008$
KH_2PO_4 (0.02877*m*), Na_2HPO_4 (0.01834 *m*), NaCl (0.02877*m*) $p_aH = 6.640$
$Na_2B_4O_7$ (0.006045*m*), NaCl (0.01210*m*) $p_aH = 9.165$

The electrode systems were then regarded as establishing a similar e. m. f.-p_aH function in the aqueous ethanol solutions. Hydrogen ion activities in the aqueous ethanol solvent have thus been referred experimentally to a standard activity scale in water. Other ion and undissociated acid activities have been referred to a standard state of unit molarity with unit molar activity coefficients in the aqueous ethanol solvent. The resulting dissociation constants are essentially the "reduced" constants of Michaelis and Mizutani,[2] differing in the electrode system chosen to secure experimental reference with the hydrogen ion activity scale in water. pK' values computed on the molar scale have been converted to the molal scale by adding log $d(= -0.04)$, where d is the density of the aqueous ethanol solvent.

Uncertainties in the use of glass electrode liquid junction cells particularly when one electrode is responding to activity changes in the solvent[3] have been frequently discussed[4] and need not here be repeated. Justification for such a cell may derive from ready convenience and comparison of pK' values obtained with those from other cells. The pK' values for the series of acids here reported showed no systematic variance with particular electrode pairs; the pK' value obtained for benzoic acid is in excellent accord with the value Speakman[5] reported with a similar glass electrode cell and in good accord with the pK' value Michaelis and Mizutani obtained with a hydrogen electrode; Speakman found a pK value only 0.2 unit lower with a thermodynamic cell.

For the monobasic acids, pK' values were computed from the relation

$$pK' = p_aH + \log \frac{C_{HA}}{C_{A-}} + \log \frac{y_{HA}}{y_{A-}} \qquad (1)$$

where the C's refer to molar concentrations and the y's to molar activity coefficients. y_{HA} has been taken as unity and y_{A-} has been evaluated from the limiting law expression

$$-\log y_{\pm} = S\,\Gamma^{1/2} \qquad (2)$$

where Γ is the ional concentration and S has the value of 0.71 for uni-univalent electrolytes in a solvent of dielectric constant 50. While (2) cannot with full justification be applied to a single ionic species, its application results in correction terms, $\log y_{HA}/y_{A-}$, not greater than 0.05.

TABLE I

DISSOCIATION CONSTANTS IN 50% (BY WT.) AQUEOUS ETHANOL 25° (MOLAL SCALE)

Acid	No.[a]	pK'_1[b]	Concn., mM.
Benzoic	8	5.87 ± 0.02[c]	0.7–2
Palmitic	8	6.46 ± 0.06	0.8–1.5
Oleic	5	6.42 ± 0.05	1–2
Monododecyl ester of cyclohexene-3-1,6-dicarboxylic	6	6.53 ± 0.08	0.7–1.5
2-Ethylhexanoic	5	6.74 ± 0.01	1–2
Di-*n*-decyl ester of orthophosphoric	7	3.28 ± 0.08	0.4–3
Di-*n*-dodecyl ester of orthophosphoric	7	3.40 ± 0.07	0.5–1
Mono-*n*-decyl ester of orthophosphoric	5	3.59 ± 0.13[d]	1.5–6
Dodecanephosphonic	6	4.22 ± 0.04[e]	1.7–4
Dodecanephosphonous	3	3.58 ± 0.06	1–4
Di-2-ethylhexylphosphinic	6	5.51 ± 0.03	0.9–4

[a] No. of determinations. [b] Average deviation. [c] Ref. 5, 5.87, glass electrode cell, 20°; 5.65, silver, silver chloride quinhydrone cell, 20°. Ref. 2, 5.78, H_2-electrode (interpolated value), 19°. [d] $pK'_2 = 8.75 \pm 0.16$. [e] $pK'_2 = 9.81 \pm 0.12$.

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[1] Bates, Hamer, Manov and Acree, *J. Research Natl. Bur. Standards*, **29**, 183 (1942).

[2] Michaelis and Mizutani, *Z. physik. Chem.*, **116**, 135 (1925).

[3] Dole, "The Glass Electrode," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 141.

[4] Dole, *ibid.*, p. 105; Manov, De Lollis and Acree, *J. Research Natl. Bur. Standards*, **34**, 115 (1945); Bates, *Chem. Revs.*, **42**, 1 (1948).

[5] Speakman, *J. Chem. Soc.*, 270 (1943).

The dibasic acids have been computed by the method of Speakman,[6] working out the activity coefficient terms as above and employing an analytical rather than graphical method of extrapolating the resulting functions.

These measurements and those of Speakman and Michaelis and Mizutani assign a ΔpK ($= pK' - pK$) from 50 weight per cent. aqueous ethanol to water of about 1.6 units for benzoic acid. Of eight monobasic acids studied by Michaelis and Mizutani and Mizutani,[7] ΔpK's varied from 1.1 to 1.6 with a mean of 1.4. Employing Michaelis and Mizutani's value of $pK' = 5.62$ for benzoic acid in 50 volume per cent. aqueous ethanol, it is possible to compute ΔpK's from this latter solvent to water from Halford's[8] tabulation. Within a group of twenty-one acids ΔpK's range from 0.2 for *p*-nitrophenol to 1.5 for α-naphthoic with a mean of 1.1. Comparison of the strengths of two acids, the one in water, the other in these aqueous ethanol mixtures, appears on the basis of incomplete data experimentally justified only if an uncertainty of the order of one pK unit is accepted. Fundamental difficulties introduced by specific solvent effects in acid strength comparison have been discussed elsewhere by Brönsted,[9] Hall,[10] Halford,[11] Speakman,[5] Wynne-Jones,[12] and others. Comparison is of particular interest, however, in relating the strengths of alcohol soluble higher members of homologous series, not in general sufficiently soluble in water for measurement, to the known strengths in water of lower water-soluble homologs. A convenient device for making such comparison is to arbitrarily adopt an average ΔpK ($= 1.4$) from 50 weight per cent. aqueous ethanol to water and, from this, to compute what may be termed "water equivalent" values of pK for acids whose pK's are determined in the aqueous ethanol solvent, recognizing that these water equivalent values embrace the very considerable solvent effect uncertainties.

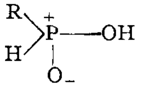
Kumler and Eiler[13] report pK_1 values in water for diesters of orthophosphoric acid increasing from 1.29 for dimethyl to 1.72 for dibutyl; the water equivalent values for di-*n*-decyl and di-*n*-dodecyl esters are 1.9 and 2.0, respectively. The same investigators find pK_1 and pK_2 values for mono esters of orthophosphoric acid increasing from $pK_1 = 1.54$, $pK_2 = 6.31$, for monomethyl to $pK_1 = 1.89$, $pK_2 = 6.84$, for monobutyl; the water equivalent values for the mono-*n*-decyl ester are $pK_1 = 2.2$, $pK_2 = 7.4$.

Rumpf and Chavane[14] present pK values in water for phosphonic acids increasing from $pK_1 = 2.35$, $pK_2 = 7.1$ for methane, to $pK_1 = 2.6$, $pK_2 = 7.9$ for hexane; the water equivalent values for dodecanephosphonic acid are $pK_1 = 2.8$, $pK_2 = 8.4$.

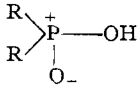
From the measurements here reported the water equivalent values of pK for palmitic and oleic acids are 5.06 and 5.02, respectively. These are to be compared with pK values in water from 4.75 for acetic acid to 4.85 for caprylic acids. From measurements in assorted alcohol-water mixtures Jukes and Schmidt[15] infer that the pK's in water of capric, lauric, myristic, palmitic, stearic and oleic acids are approximately 4.9 to 5.0.

In all three homologous series, fatty acids, partial esters of orthophosphoric acid and phosphonic acids, the higher alkyl members differ in acidic dissociation constants from the lower alkyl members by no more than the errors in comparison inherent from solvent effects. This is in full accord with the principles of inductive transmission through an alkyl chain summarized by Branch and Calvin.[16]

It is convenient to regard dodecanephosphonous acid and di-2-ethylhexylphosphinic acid, respectively, as the mono- and dialkyl analogs of hypophosphorous acid. The formal structures



and



appear not to offer a ready explanation for the differences in dissociation constants observed.

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[6] Speakman, *ibid.*, 855 (1940).

[7] Mizutani, *Z. physik. Chem.*, **116**, 350 (1925).

[8] Halford, THIS JOURNAL, **53**, 2948 (1931).

[9] Brönsted, *Chem. Revs.*, **5**, 291 (1928).

[10] Hall, *ibid.*, **8**, 191 (1931).

[11] Halford, THIS JOURNAL, **53**, 2944 (1931).

[12] Wynne-Jones, *Proc. Roy. Soc.* (*London*), **A140**, 440 (1933).

[13] Kumler and Eiler, THIS JOURNAL, **65**, 2355 (1943).

[14] Rumpf and Chavane, *Compt. rend.*, **224**, 919 (1947).

[15] Jukes and Schmidt, *J. Biol. Chem.*, **110**, 9 (1935).

[16] Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 217.

SOCONY-VACUUM LABORATORIES
RESEARCH AND DEVELOPMENT DEPT.
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A New Method of Preparation of Esters of Difluoroacetic Acid[1]

BY JOHN A. YOUNG AND PAUL TARRANT

Difluoroacetic acid has been prepared recently by the oxidation of 1,2-dichloro-3,3-difluoropropene[2,3] while methyl difluoroacetate has been formed by the reaction of methyl dichloroacetate and potassium fluoride.[4] The latter method, although requiring only one step, gives a yield of about 18% when the reaction is carried out at 220–30° for twenty-five hours. The preparation of the acid by the oxidation of the olefin necessi-

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[1] The material in this paper is abstracted from a portion of a thesis to be submitted by John A. Young to the Graduate Council of the University of Florida in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

[2] Henne, Alderson and Newman, THIS JOURNAL, **67**, 919 (1945).

[3] Whaley and Davis, *ibid.*, **70**, 1026 (1948).

[4] Gryszkiewicz-Trochimovsky, Sporzynski and Wnuk, *Rec trav. chim.*, **66**, 427 (1947).