

dilute sulfuric acid. Evaporation of the solvent left a dark gum which when dissolved in benzene and treated with petroleum ether afforded crystalline material, m. p. 120–121° (0.15 g.). Recrystallized from benzene–ligroin, the substance formed colorless plates, m. p. 124° (toluhydroquinone, m. p. 124–125°). The sample was free from bromine.

Anal. Calcd. for $C_7H_8O_2$: C, 67.69; H, 6.49. Found: C, 67.91; H, 6.56.

Other Alkylations.—The principal results of the synthetic experiments are summarized in Table II. The procedure generally employed for the introduction of higher alkyl and alkenyl groups may be illustrated by the following account of the preparation of **2-methyl-3-pentadecyl-1,4-naphthoquinone**. A solution of 1 g. of dipalmitoyl peroxide in 10 cc. of purified ligroin (95–100°) in a boiling tube was treated with 0.25 g. of methyl-naphthoquinone, a chip of porous pot was added, and the mixture was warmed and stirred until the quinone had dissolved. The bath temperature was gradually raised until effervescence set in at 90°, and after one hour the temperature was raised to 100° during thirty minutes and then allowed to fall to 90°, when gas evolution had ceased.

The reaction products were isolated in one of the following ways.

A. Separation as a solid from the cooled solution was followed by recrystallization.

B. When no material crystallized on cooling, other than the fatty acid derived from the peroxide, the solution sometimes was evaporated to dryness and the residue fractionally crystallized (not recommended for quinones with long alkyl side chains).

C. As in B, but the residue was dissolved in alcohol and treated with aqueous sodium hydrosulfite solution accord-

ing to the procedure of Fieser¹⁷; the reduced mixture was shaken with ligroin (b. p. 30–60°), when the substituted hydroquinone usually appeared as a white solid at the interface and could be collected by suction filtration. The solid was dried and oxidized with silver oxide in ethereal solution in the presence of sodium sulfate.

D. As in C, except that after reduction the hydroquinone did not separate from the water–ligroin mixture as a solid but remained in the hydrocarbon layer. In this case the ligroin solution was washed with aqueous alkali-hydrosulfite and extracted with Claisen's alkali, etc., exactly as in a procedure described for the isolation of vitamin K_1 from alfalfa concentrates.¹⁷

Each of the analytical samples of fully substituted quinones gave a negative test with Craven's reagent.¹⁸

Summary

Both the methylation of quinones by lead tetraacetate in acetic acid solution and the decomposition of the tetraacetate to carbon dioxide and hydrocarbon gas in the absence of an acceptor are promoted by a number of hydroxylic and hydrocarbon solvents.

Diacyl peroxides are excellent agents for the alkylation of *p*-benzo- and 1,4-naphthoquinones having a free position in the quinonoid ring, and a number of new or difficultly accessible quinones have been prepared with ease by this method.

(17) Fieser, *THIS JOURNAL*, **61**, 3467 (1939).

(18) Craven, *J. Chem. Soc.*, 1605 (1931).

CONVERSE MEMORIAL LABORATORY

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

Relative Acid Strengths of Formic, Acetic, and Propionic Acids in Alcohols and Dioxane-Water Mixtures

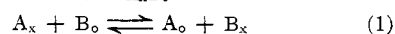
BY MARTIN KILPATRICK AND R. DEAN EANES

The determination, in various alcohols, of the acid strengths of substituted benzoic acids relative to benzoic acid, has shown that the logarithm of the acid strength varies linearly with the reciprocal of the dielectric constant of the medium over the range $D = 78.5$ to $D = 24.2$.¹ On the other hand, in dioxane–water mixtures, the logarithm of the acid strength does not vary linearly with the reciprocal of the dielectric constant. The present paper shows that these conclusions are also valid for certain aliphatic acids.

The acetic and propionic acids, free from homologs, were refluxed with the pure anhydrides and fractionally distilled. Formic acid was treated

with boric anhydride to remove water and distilled under reduced pressure. The purification of methyl and ethyl alcohol, ethylene glycol, and dioxane and the preparation of the solutions have been described in the earlier papers as has the e. m. f. method by which the experiments were carried out.²

Table I gives the ratio of the dissociation constant of formic acid to that of acetic acid in the various solvents containing lithium chloride. The ratio of the dissociation constants is the equilibrium constant, $K_{A_xB_0}$, for the reaction



where A_x is formic acid and B_0 acetate ion.

(2) Elliott and Kilpatrick, *J. Phys. Chem.*, **45**, 454, 466, 472, 485 (1941).

(1) For references see Kilpatrick, *Chem. Rev.*, **30**, 151 (1942).

TABLE I

RATIO OF THE DISSOCIATION CONSTANT OF FORMIC ACID TO THAT OF ACETIC

Solvent	Dielectric constant	Ionic strength	K_{AxBo}	Calculated K_{AxBo} by eq. (2)
Water	78.5	0.00	10.1 ^a	10.4
		.10	10.3 ^b	
Ethylene glycol	37.7	.05	14.0	14.0
Methyl alcohol	31.5	.05	17.3	16.4
Ethyl alcohol	24.2	.05	19.6	20.5
Dioxane-water	25	.05	19.4	19.8

^a From the thermodynamic dissociation constants of Harned and co-workers, ref. 4. ^b Solvent salt potassium chloride.

The logarithm of the ratio of the dissociation constants is plotted against the reciprocal of the dielectric constant in Fig. 1. The results for the pure solvents may be expressed by the equation

$$\log K_{AxBo} = 0.887 + \frac{10.3}{D}$$

Values thus calculated are given in column five of Table I. In agreement with our previous findings the relative acid strength in dioxane-water mixtures ($D = 25$) closely approximates that in ethyl alcohol.^{2,3} Figure 1 also includes the values

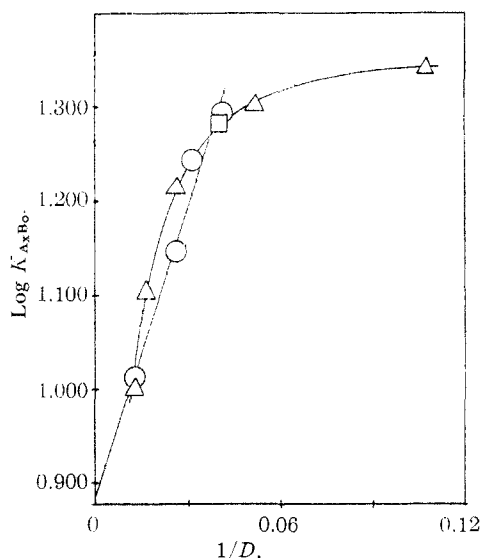


Fig. 1.—Formic acid vs. acetic acid: Δ , Harned and co-workers; \circ , pure solvents, this investigation; \square , dioxane-water, this investigation.

of the constant, K_{AxBo} , calculated from the thermodynamic dissociation constants at 25° of formic and acetic acids in water and dioxane-water mixtures of dielectric constant 60.8, 38.5, 17.7 and

(3) Minnick and Kilpatrick, *J. Phys. Chem.*, **43**, 259 (1938)

9.3.⁴ It is evident that $\log K_{AxBo}$ is not a linear function of the reciprocal of the dielectric constant, and that we are dealing with the same phenomenon observed in the case of the substituted benzoic acids.⁵

TABLE II

RATIO OF THE DISSOCIATION CONSTANT OF PROPIONIC ACID TO THAT OF ACETIC

Solvent	Dielectric constant	Ionic strength	K_{AxBo}	Calculated K_{AxBo} by eq. (3)
Water	78.5	0.00	0.762 ^a	0.773
Ethylene glycol	37.7	.05	.637	.617
Methyl alcohol	31.5	.05	.566	.566
Ethyl alcohol	24.2	.05	.477	.484
Dioxane-water	25	.05	.521	.495

^a From the results of Harned and co-workers, refs. 4 and 5.

Table II and Fig. 2 present the corresponding results for the ratio of the dissociation constant of propionic acid to that of acetic.

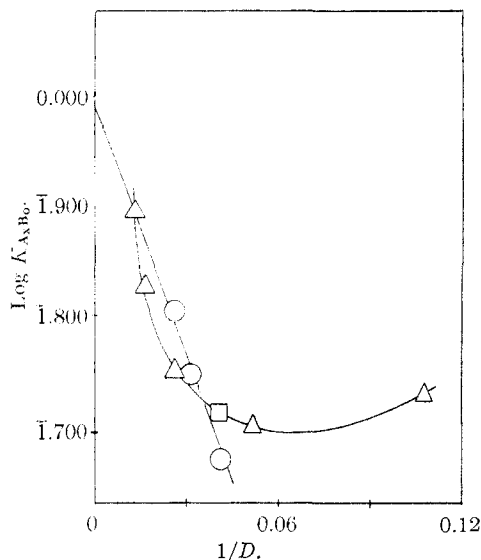


Fig. 2.—Propionic acid vs. acetic acid: Δ , Harned and co-workers; \circ , pure solvents, this investigation; \square , dioxane-water, this investigation.

The result for the dioxane-water mixture of dielectric constant 25 lies above the value for the solvent ethyl alcohol, but fits nicely on the smooth curve through the values for the other dioxane-water mixtures calculated from the recent data on the thermodynamic dissociation constant of propionic acid,⁶ and that of acetic acid.⁴ In the

(4) Harned and Ehlers, *THIS JOURNAL*, **54**, 1351 (1932); Harned and Kazanjian, *ibid.*, **58**, 1912 (1936); Harned and Fallon, *ibid.*, **61**, 2377 (1939); Harned and Embree, *ibid.*, **56**, 1042 (1934); Harned and Done, *ibid.*, **63**, 2579 (1941).

(5) Elliott and Kilpatrick, *J. Phys. Chem.*, **45**, 485 (1941).

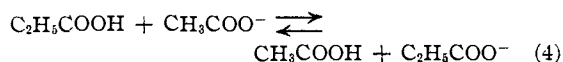
(6) Harned and Dofell, *ibid.*, **63**, 3308 (1941).

pure solvents, the results may be expressed by the equation

$$\log K_{A_xB_0} = -0.022 - \frac{7.1}{D}$$

and the values thus calculated are given in column five of Table II.

It should be emphasized that the values of $K_{A_xB_0}$ for the experiments reported in this paper are direct determinations of the equilibrium constant for the reaction



and the corresponding reaction for formic acid. The measurements were made in the presence of 0.045 mole per liter of lithium chloride with a 1.0 molar bridge solution of the same salt. For a reaction of the charge type of equation (4), the equilibrium constant would be expected to be independent of ionic strength, for the same solvent salt, and comparable to the thermodynamic equilibrium constant. This is borne out by the results at various ionic strengths given in the following table.

In addition, the value of $K_{A_xB_0}$ calculated from the thermodynamic constants in water given in

TABLE III

THE EFFECT OF IONIC STRENGTH ON THE EQUILIBRIUM CONSTANT OF THE REACTION

$$HCOOH + CH_3COO^- \rightleftharpoons CH_3COOH + HCOO^-$$

Solvent	$K_{A_xB_0}$					
	$\mu = 0.05$	0.10	0.20	0.50	1.00	2.00
Water	..	10.3	10.3	10.3	10.3	10.3
Methyl alcohol	17.3	17.8	17.6			
Ethyl alcohol	19.6	19.5	19.8			

Table I, agrees with the value in 0.095 molar potassium chloride.

The authors would like to take this opportunity to thank the Faculty Research Committee of the University for a grant.

Summary

In dioxane-water mixtures, the logarithm of the acid strength of formic acid relative to acetic, or of propionic relative to acetic, is not a linear function of the reciprocal of the dielectric constant of the medium. In the pure solvents studied—water, ethylene glycol, methyl alcohol and ethyl alcohol—a linear relationship holds. This same phenomenon has been observed in the case of the substituted benzoic acids.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO AND THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

Studies on High Molecular Weight Aliphatic Amines and their Salts. VIII. Soluble and Insoluble Films of the Amine Acetates. A. The Surface Tension of Aqueous Solutions of Dodecylamine Acetate

BY EVERETT J. HOFFMAN, G. E. BOYD AND A. W. RALSTON

Introduction

In the fifth paper of this series¹ we reported the results of an investigation of the surface properties of a simple, long chain cationic colloidal electrolyte, namely, dodecylamine hydrochloride. The present paper deals with a study of the surface properties of aqueous solutions of dodecylamine acetate. In this case the time effects of long duration which were observed for dilute solutions of dodecylamine hydrochloride were not found. In the case of $5 \times 10^{-3} N$ solutions at 25°, constant values of the surface tension were obtained within thirty minutes. No time effects were observed at other temperatures for this same solution. With a solution of concentration $7.5 \times 10^{-3} N$ (critical

micelle concentration = $1.2 \times 10^{-2} N$) no time effects were observed at any temperature. In contrast to this behavior, in the case of dodecylamine hydrochloride a steady decrease was observed even after five hours.

The absence of aging effects with unbuffered *n*-alkylamine acetate solutions may not, however, reflect the behavior in general of solutions containing this type of colloidal electrolyte. Preliminary experiments on a $5 \times 10^{-3} N$ solution of dodecylamine acetate in the presence of $10^{-2} N$ acetic acid-sodium acetate revealed an appreciable variation of surface tension with time. It is possible that the surface active species in our experiments consists of free amine in equilibrium with amine acetate in the interior of the solution.

(1) E. J. Hoffman, G. E. Boyd and A. W. Ralston, *THIS JOURNAL*, **64**, 498 (1942).