bonyl compounds reacted with the reagent to form yellow or red solutions or, in some cases, a yellow precipitate. Dilution with water caused the deposition of the normal deep red or black D.N.P.

Table I lists twenty-five new 2,4-dinitrophenylhydrazones in order of the increasing depth of color. All melting points are corrected.

TABLE I

2,4-Dinitrophenylhydrazone of	Color	M.p., °C.	Analyses, % Nitrogen Calcd.	Analyses, % Nitrogen Found[a]
Methyl acetoacetate	Yellow	119.0–119.5	18.91	19.21
m-Nitroacetophenone	Orange	232.5–233.0	20.29	20.26
β-Benzoylacrylic acid	Orange	229.0–229.5	15.73	15.88
2-Hydroxy-5-methylbenzophenone	Orange	244.5–245.0	14.28	14.37
α-Bromoacetophenone	Orange	220.0–220.5	14.78	14.76
p,α-Dibromoacetophenone	Orange	218–219	12.23	12.14
p-Isopropylacetophenone[b]	Orange	182.0–182.5	16.37	16.48
2-Hydroxybenzophenone	Red-orange	250–251	14.81	14.83
m-Tolualdehyde	Red-orange	193.5–195.5	18.66	18.78
3,3′-Diisopropoxyanisil[b]	Red-orange	186.0–186.5	9.89	10.19
o-Hydroxyacetophenone	Red-orange	213–214	17.72	17.95
4-Phenyl-2-butanone[b]	Red-orange	128.5–129.0	17.07	17.19
α-Bromo-*p*-phenylacetophenone	Red-orange	228.5–229.0	12.31	12.57
p-Phenylacetophenone	Red-orange	241.5–242.0	14.89	15.04
2-Hydroxy-5-methylacetophenone	Red	273.0–273.5	16.96	17.26
Methyl 2-thienyl ketone	Red	243–244	18.29	18.29
3,4-Dihydro-1(2H)-naphthalenone	Red	262–263	17.17	17.14
2,3-Diphenyl-1-indanone[c]	Red	245.5–246.5	12.06	12.20
2,4-Dimethoxybenzaldehyde	Red	257–258	16.18	15.88
3-Benzyloxy-4-methoxybenzaldehyde[b]	Red	196–197	13.27	13.00
3,4-Diethoxybenzaldehyde	Red	219–220	14.97	14.82
1,7-Diphenyl-1,4,6-heptatrien-3-one[d]	Red	179–180	12.72	12.89
3,4-Dimethoxypropiophenone[b]	Violet-red	178.5–179.0	14.97	15.24
4,4-Bis-(dimethylamino)-benzophenone	Violet-red	273.0–273.5	18.74	18.81
p-Diethylaminobenzaldehyde	Purple-black	206.5–207.0	19.60	19.68

[a] The analyses were performed by Mrs. Alma Rosen. [b] The carbonyl compound was kindly furnished by Dr. E. E. Campaigne of this Laboratory. [c] The carbonyl compound was kindly furnished by Dr. J. H. Billman of this Laboratory. [d] This ketone was synthesized by the procedure of A. Rosenheim and W. Levy, *Ber.*, **37**, 3662 (1904).

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Hydrogen Bonding and Ionization of Carboxylic Acids in Aqueous Solutions

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The careful determinations of the ionization constant of acetic acid by MacInnes and Shedlovsky[1] and of a series of other carboxylic acids by Saxton and Darken[2] have proved that the limiting Debye–Hückel activity coefficient suffices only at extremely low concentrations of the acids. At slightly higher concentrations at which Debye's approximation should still hold the calculated thermodynamic ionization constants show pronounced deviations from the extrapolated value; these deviations are larger than would be deduced from the change in the dielectric constant and were attributed by Owen[3] to the "medium effect" of the non-ionized acetic acid molecules on the ionization of the acid. Saxton and Darken[2] found that the dependence of the apparent ionization constant of all the carboxylic acids investigated by them could be described to a very good approximation by the empirical equation

$$\log k - 1.013\sqrt{\alpha c} = \log K - B(1 - \alpha)c \qquad (1)$$

where k is the classical ionization constant, K the thermodynamic ionization constant, c the concentration of the acid in moles/liter, α its degree of ionization and $1.013\sqrt{\alpha c}$ the Debye–Hückel term, while B is the empirical constant correlating the classical ionization constant with the concentration of non-ionized acid $[(1 - \alpha)c]$.

As will be shown below, this apparently anomalous behavior of carboxylic acids may be ascribed to dimerization of the acids in aqueous solution and the values of the constant B may be derived from the known dimerization constants. Conversely, a knowledge of B presents a new and clear-cut method for the evaluation of the dimerization constant of carboxylic acids. The partial association of carboxylic acids to dimers in aqueous solutions has been established by a variety of experimental investigations, such as cryoscopic data,[4,5] Raman spectra[6] and vapor pressure measurements.[7] The latter method is the only quantitative, thermodynamically justified procedure recorded in the literature for the determination of the dimerization constant of acetic acid. MacDougall and Blumer found the constant to be (0.185 ± 0.011) at 25°; this value will be applied in our calculations.

Our major assumption is that the cyclic dimer[7] has a negligible degree of ionization compared to the unassociated monomer. The state of the solution is then governed by two equilibria

$$2\mathrm{HA} \rightleftarrows \mathrm{H_2A_2} \qquad [\mathrm{H_2A_2}]/[\mathrm{HA}]^2 = L \qquad (2)$$

where L is the dimerization constant

$$\mathrm{HA} \rightleftarrows \mathrm{H^+} + \mathrm{A^-} \qquad [\mathrm{H^+}][\mathrm{A^-}]/[\mathrm{HA}] = k' \qquad (3)$$

where k' is the apparent ionization constant, and the quantities in square brackets denote concentrations. The concentration c of the acid is given by

$$c = [\mathrm{A}\;\,] + [\mathrm{HA}] + 2[\mathrm{H_2A_2}] \qquad (4)$$

It is at once evident that the calculation of the ionization constants assuming $[\mathrm{HA}] = c - [\mathrm{A^-}]$ will lead to erroneous results whenever dimerization is appreciable. Denoting $[\mathrm{A^-}]/c = \alpha$ the degree of ionization, a simple calculation leads to the expression

$$k' = [\alpha^2 c/(1 - \alpha)]\cdot{}^1/_2\cdot[\sqrt{1 + 8L(1 - \alpha)c} + 1] \qquad (5)$$

At sufficiently small concentrations, Eq. (5) is approximated by

$$k' = [\alpha^2 c/(1 - \alpha)]\cdot[1 + 2L(1 - \alpha)c] \qquad (6)$$

The quantity $\alpha^2 c/(1 - \alpha)$ represents the classical ionization constant k which does not consider dimerization. Hence

$$k' = k[1 + 2L(1 - \alpha)c] \qquad (6a)$$

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(2) B. Saxton and L. S. Darken, *ibid.*, **62**, 846 (1940).

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Taking logarithms and again approximating ln $[1 + 2L(1 - \alpha)c] \sim 2L(1 - \alpha)c$ we obtain

$$\log k' = \log k + 2(0.4343)L(1 - \alpha)c \qquad (7)$$

Finally passing from apparent to thermodynamic constants by use of Debye's expression

$$\log k' = \log K + 1.013\sqrt{\alpha c} \qquad (8)$$

we get

$$\log k - 1.013\sqrt{\alpha c} = \log K - 2(0.4343)L(1 - \alpha)c \qquad (9)$$

in full accord with Saxton and Darken's empirical formula. The empirical factor B of Eq. (1) now becomes a direct measure of the dimerization constant L according to the equation

$$B = 2(0.4343)L \qquad (10)$$

Introducing for the dimerization constant L of acetic acid MacDougall and Blumer's value, we obtain $B = 0.16$, in good agreement with Saxton and Darken's empirical value $B = 0.14$. The degree of constancy obtained for the thermodynamic constant of acetic acid, from the experimental data of MacInnes and Shedlovsky[1] after introducing the dimerization hypothesis is shown in Fig. 1, where c is the concentration of acid in moles/liter. It was found that Eq. (6) was a satisfactory approximation up to $c = 0.1$; beyond this value the complete Eq. (5) was used. It will be noted that K is now a true constant; $K \times 10^5 = 1.753 \pm 0.004$.

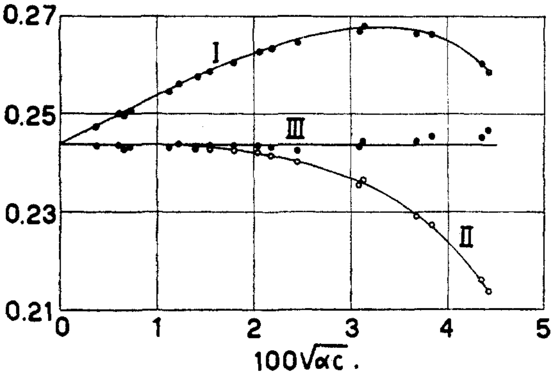

Fig. 1.—Ionization constants of acetic acid: I, log F = log k = log $[\alpha^2c/(1 - \alpha)$; classical dissociation constant. II, log F = log k − $1.013\alpha c$; ionization constant considering Debye–Hückel term. III, log F = log K = log k − $1.013\sqrt{\alpha c} + \log[\sqrt{1 + 8L(1 - \alpha)c} + 1]$; true ionization constant, considering both Debye–Hückel term and dimerization (from Eqs. 5, 8).

In Table I are given the dimerization constants deduced from the data of Saxton and Darken for the series of carboxylic acids. The dependence of L on the structure of the acid is plausible in view of the fact that with increasing van der Waals interaction between the monomers, dimerization is favored and L should therefore increase. The same behavior may be deduced qualitatively from cryoscopic data.[5]

TABLE I

DIMERIZATION CONSTANTS OF CARBOXYLIC ACIDS

Acid	B	L
Formic	0.035	0.04
Acetic	.14	.16
Propionic	.20	.23
Butyric	.31	.36
Chloroacetic	.35	.40
Cyanoacetic	.40	.46
Lactic	.40	.46
Benzoic	.65	.75

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α-Phenylethyl Alcohol

BY NATHAN KORNBLUM AND STEPHEN A. HERBERT, JR.

In the course of another investigation it became necessary to know the refractive index of α-phenylethyl alcohol. The literature contains an assortment of values for this constant (*cf.* Table I) and, consequently, a highly purified sample of the alcohol was desired. This report deals with the preparation of α-phenylethyl alcohol of 98.6 ± 0.2 mole per cent. purity and describes some of its characteristics.

TABLE I

α-Phenylethyl alcohol	n_D	Temp., °C.	Ref.
d	1.5211	20	1
dl	1.526	15	2
dl	1.5244	25	3
l	1.5270	20	4
dl	1.5275	20	5
dl	1.5275	20	6
dl	1.5281	20	4
d	1.5349	15	7

Experimental

Eastman Kodak White Label racemic phenylmethylcarbinol (n^{20}_D 1.5271) was converted to the acid phthalate ester according to Eliel.[8] Recrystallization from benzene to constant m.p. gave a product which melted at 107–108°; lit. values, 107–108°,[8] 108°[9]; yield 62–77%.

In a 2-liter Claisen flask set up for steam distillation was placed 270 g. (1 mole) of the acid phthalate ester and 480 ml. of 5 N aqueous sodium hydroxide. A stream of oxygen-free nitrogen[10] was bubbled through the solution for about an hour in order to purge the system of oxygen. Steam was then passed in and the distillate collected in a flask containing 200 ml. of saturated sodium chloride solution. The organic phase was separated mechanically, placed in a quartz flask and given a preliminary drying with anhydrous sodium sulfate. It was then kept in quartz over Drierite for about a week.[11,12] The α-phenyl alcohol so obtained has n^{20}_D 1.5265, is colorless, odorless and gives a negative ketone test with a sensitive 2,4-dinitrophenylhydrazine reagent.[13] When this sample of α-phenylethyl alcohol was kept in the dark in quartz over Drierite its properties were completely unchanged even after seven months.[14] By means of a time–temperature cooling curve this sample of α-phenylethyl alcohol which had stood for seven months

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(8) E. L. Eliel, THIS JOURNAL, **71**, 3970 (1949).

(9) A. J. Houssa and J. Kenyon, *J. Chem. Soc.*, 2260 (1930).

(10) The nitrogen was passed through Fieser's solution (L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, pp. 395–396).

(11) As a further precaution the alcohol was kept in the dark while it was drying.

(12) With comparatively small amounts of Drierite it may take weeks for the n^{20}_D to reach the terminal value. Apparently the alcohol rather tenaciously retains the last traces of water.

(13) This reagent is prepared by dissolving 10 g. of 2,4-dinitrophenylhydrazine in a mixture consisting of 17 ml. of 36% aqueous hydrochloric acid in *ca.* 100 ml. of methanol and then diluting the solution with methanol to a volume of 1 liter.

(14) α-Phenylethyl alcohol as ordinarily prepared from the phthalate half ester soon becomes light yellow and takes on the odor of acetophenone. Paralleling these changes is a rise in n^{20}_D and the appearance of a positive ketone test.