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; $K \times 10^5 = 1.753 \pm 0.004$.

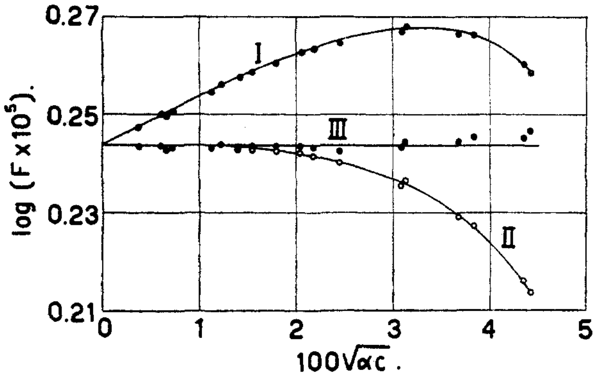

Fig. 1.—Ionization constants of acetic acid: I, $\log F = \log k = \log [\alpha^2c/(1 - \alpha)$; classical dissociation constant. II, $\log F = \log k - 1.013\alpha c$; ionization constant considering Debye–Hückel term. III, $\log F = \log K = \log k - 1.013\sqrt{\alpha c} + \log[\sqrt{1 + 8L(1 - \alpha)c}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

THE WEIZMANN INSTITUTE OF SCIENCE
REHOVOT, ISRAEL

RECEIVED MAY 28, 1951

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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[1] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99**, 45 (1911).

[2] G. Vavon, *Compt. rend.*, **155**, 287 (1912).

[3] J. F. Norris and F. Cortese, THIS JOURNAL, **49**, 2645 (1927).

[4] H. E. De La Mare, Ph.D. Thesis, Purdue Univ., 1951.

[5] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **70**, 3759 (1948).

[6] R. Descamps, *Bull. soc. chim. Belg.*, **33**, 270 (1924).

[7] G. Vavon, C. Riviere and B. Angelo, *Compt. rend.*, **222**, 959 (1946).

[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.

was found to have a purity of 98.6 ± 0.2 mole per cent.[15]; its freezing point is 19.15 ± 0.06° and the f.p. calculated for zero impurity is 20.2 ± 0.3°.[16] Descamps[6] reported m.p. 20.1°.

Storage of the alcohol of 98.6 ± 0.2 mole per cent. purity in quartz without a drying agent (in a desiccator kept in the dark) for two months did not result in any change in the properties of this alcohol. In contrast, when a solution consisting of 4 ml. of the 98.6 ± 0.2 mole per cent. alcohol and 4 drops of distilled water ($n^{20}D$ 1.5169) was placed in a brand new glass-stoppered Pyrex flask and the flask was stored in a desiccator kept on the desk-top out of direct sunlight, the solution soon underwent change. Thus after 15 days the $n^{20}D$ had risen to 1.5193, the solution had become pale yellow, it had taken on a strong odor of acetophenone, and on treatment with 2,4-dinitrophenylhydrazine[13] it gave the 2,4-dinitrophenylhydrazone of acetophenone; m.p. and mixed m.p. 248–249° (uncor.). After 19 weeks $n^{20}D$ had gone up to 1.5258 and the yellow color was much more pronounced.

Acknowledgment.—The authors are grateful to the Research Corporation for generous financial assistance.

[15] The method of F. D. Rossini, *et al.*, as modified by K. L. Nelson of this Department was employed. This will be published shortly. We are indebted to Mr. Nelson for his assistance in the determination and interpretation of the cooling curve data.

[16] The relevant data are to be found in the doctoral dissertation of S. A. Herbert, Jr., Purdue University, 1952.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA
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Ultrasonic Velocity in a Series of Alkyl Acetates

BY R. T. LAGEMANN,[1] E. G. MCLEROY AND O. MILNER

Measurements of ultrasonic velocity are being made on various homologous series of organic compounds. These measurements generally show an increase of ultrasonic velocity with increase in molecular weight from the first member of the series onward. Certain series, however, show a definite minimum in the velocity, as has been shown recently for some ketones,[2] and some series would seem to show a decrease of velocity with increase in molecular weight. It has been thought in the past that the alkyl acetates belong to the last-named class. In a review article, Parthasarathy[3] says "the esters show a diminution in velocity with increasing length of the alcohol radical," and in support of his contention he presents a table taken from an earlier paper[4] giving data on five alkyl acetates.

Upon repeating the measurements on these five compounds and extending the series further at three temperatures, it is found that actually there is only a decrease as one goes from the first to the second member of the series, and that for the ethyl through heptyl members of the *n*-alkyl acetates there is a steady increase in the velocity. This may be seen in Table I. It may also be noted, in agreement with what has been found elsewhere[5] for certain other compounds, that the iso-isomer has a lower velocity than the corresponding normal one. Indeed, it was the inclusion by Parthasarathy of his results on the *i*-amyl acetate with those for four normal ones, which no doubt was in part responsible for the enunciation of the erroneous rule. For all the compounds investigated the temperature coefficient of velocity is nearly the same, as is commonly found.

TABLE I

ULTRASONIC VELOCITY IN A SERIES OF ALKYL ACETATES

Acetate	Velocity of sound, m./sec. 10°	20°	30°	Density, g./cc. at 30°	Adiabatic compressibility, dyne^{-1} cm.^{2} at 30° (× 10^{12})
Methyl	1228	1181	1136	0.9207	84.16
Ethyl	1209	1164	1119	.8886	89.87
n-Propyl	1232	1189	1146	.8777	86.75
n-Butyl	1256	1214	1170	.8707	83.90
n-Amyl	1280	1238	1197	.8685	80.36
n-Hexyl	1300	1258	1220	.8642	77.74
n-Heptyl	1319	1280	1241	.8618	75.34
Isopropyl	1178	1144	1100	.8616	95.92
Isobutyl	1219	1175	1134	.8600	90.42
Isoamyl	1258	1218	1179	.8645	83.21

Experimental

The compounds were Eastman Kodak Co. chemicals freshly fractionated in a Todd column of 30–50 theoretical plates before the ultrasonic velocity was measured. The velocity measurements were made on a variable-path ultrasonic interferometer[6] operated at 500 kc. per second and with the liquid under study kept at the stated temperature to within ± 0.03° with a constant temperature water-bath. The densities were measured with a 3-ml. double-arm pycnometer of the kind described by Lipkin and his co-workers.[7]

The three iso-alkyl acetates were obtained from Dr. W. Joe Frierson, to whom we are grateful. The work was also assisted by a Grant-in-Aid from the Research Corporation.

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[1] Department of Physics, Vanderbilt University, Nashville, Tennessee.

[2] R. T. Lagemann, R. Gwin, C. T. Lester, J. R. Proffit and E. C. Suratt, THIS JOURNAL, **73**, 3213 (1951).

[3] S. Parthasarathy, *Current Sci.*, **6**, 322 (1938).

[4] S. Parthasarathy, *Proc. Ind. Acad. Sci.*, **3A**, 482 (1936).

[5] A. Weissler, THIS JOURNAL, **70**, 1634 (1948); S. Parthasarathy, *Proc. Ind. Acad. Sci.*, **4A**, 59 (1936); W. Schaaffs, *Z. physik. Chem.*, **196**, 413 (1951).

[6] D. R. McMillan, Jr., and R. T. Lagemann, *J. Acoust. Soc. Am.*, **19**, 956 (1947).

[7] M. R. Lipkin, J. A. Davison, W. T. Harvey and S. S. Kurtz, Jr., *Ind. Eng. Chem., Anal. Ed.*, **16**, 55 (1944).

DEPARTMENT OF PHYSICS
EMORY UNIVERSITY
EMORY UNIVERSITY, GEORGIA
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N-Monosubstituted 2-Aminopyridines, 2-Aminopyrimidines and 2-Aminolepidines

BY IRVING ALLAN KAYE AND IRVING C. KOGON

In this investigation a number of N-monosubstituted 2-aminopyridines, 2-aminopyrimidines and 2-aminolepidines were prepared by two general methods as intermediates for the subsequent synthesis of compounds having possible chemotherapeutic application. Most of the pyridyl- and lepidylamines were obtained by heating a mixture of either 2-bromopyridine or 2-chlorolepidine and two or more equivalents of a primary amine at 170–180° for about 18 hours.[1] Yields were increased when a considerable excess of primary amine was employed. The remaining products were synthesized by alkylation of a heterocyclic amine with an alkyl halide in the presence of lithium amide.[1] Some reactions were conducted in the conventional two-step manner, *i.e.*, a lithium derivative of a heterocyclic amine was formed from

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[1] I. A. Kaye, THIS JOURNAL, **71**, 2322 (1949).