

ture, *o*-fluorobenzoyl chloride (8 g.) (b. p. 85° (14 mm.))<sup>2</sup> in chloroform (50 cc.) was added slowly. On standing, the condensation product (9 g.) crystallized; from the mother-liquid a second batch (2.5 g.) was obtained, when it was washed with water, dried and concentrated. It formed red leaflets, m. p. 154°, from ethyl alcohol; yield, 62%. *Anal.* Calcd. for C<sub>23</sub>H<sub>16</sub>ON<sub>2</sub>F: C, 74.8; H, 4.3; N, 11.6. Found: C, 71.9; H, 4.1; N, 11.4.

**N-(*p*-Fluorobenzoyl)-1-amino-4-(benzene-azo)-naphthalene.**—The above procedure, when carried out with *p*-fluorobenzoyl chloride (b. p. 104° (38 mm.)), gave in 65% yield brown-red needles from alcohol, m. p. 201°. *Anal.* Calcd. for C<sub>23</sub>H<sub>16</sub>ON<sub>2</sub>F: C, 74.8; H, 4.3; N, 11.6. Found: C, 73.6; H, 4.7; N, 11.4.

**N-(*o*-Fluorobenzoyl)-sulfanilamide.**—Sulfanilamide (8.6 g.) was dissolved in hot glacial acetic acid (45 cc.). The solution was quickly chilled with ice-water, and additioned with *o*-fluorobenzoyl chloride (8 g.), while stirring. The reaction product was collected after one hour and recrystallized from glacial acetic acid, m. p. 264°; yield, almost quantitative. *Anal.* Calcd. for C<sub>13</sub>H<sub>11</sub>O<sub>2</sub>N<sub>2</sub>FS: C, 53.1; H, 3.7; N, 9.5. Found: C, 51.9; H, 3.6; N, 9.4.

(3) Bergmann and Bondi, *Ber.*, **64**, 1474 (1931).

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## Identification of Organic Acids by Partition between Ethyl Ether and Water<sup>1</sup>

BY O. C. DERMER AND V. H. DERMER

Extraction of an acid from aqueous solution by an immiscible solvent is in some respects like steam distillation; in both processes the acid is distributed between phases in a characteristic ratio. The difference in volatility of various acids with steam is the basis of well-established procedures for their identification (the Duclaux method) and their estimation, but extraction with ether has been employed more for quantitative determination of organic acids<sup>2a-g</sup> than for their characterization. Werkman<sup>2c</sup> and Friedemann<sup>2g</sup> suggested using partition ratio as an aid in identifications, but both were interested primarily in mixtures of acids rather than single acids. Moreover, the usefulness of their data is somewhat limited because they measured equilibrium concentrations in the water layer only; the constants so obtained are not directly comparable to partition data in the literature because of the variation

(1) A preliminary study of this problem was made in this laboratory by Mr. Noble Smith and was reported in his M.S. thesis in 1940.

(2) (a) Behrens, *Z. anal. Chem.*, **69**, 97 (1926); (b) Werkman, *Ind. Eng. Chem., Anal. Ed.*, **2**, 302 (1930); (c) Werkman, *Iowa State Coll. J. Sci.*, **4**, 459 (1930); **5**, 1, 121 (1930); (d) Osburn and Werkman, *Ind. Eng. Chem., Anal. Ed.*, **3**, 264 (1931); (e) Werkman and Osburn, *ibid.*, **3**, 387 (1931); (f) Osburn, Wood and Werkman, *ibid.*, **5**, 247 (1933); **8**, 270 (1936); (g) Friedemann, *J. Biol. Chem.*, **123**, 161 (1938).

in mutual solubility of ether and water in the presence of different acids.

Physical constants obtained by distribution methods, such as the Duclaux constants or ratios of partition between solvents, differ from others commonly used in qualitative organic analysis in that they may be determined with samples containing water, or even in rather dilute solution. Steam-volatile acids in aqueous solution cannot readily be obtained anhydrous for melting point or boiling point determinations, and the same may be said of lactic, hydracrylic, cyanoacetic, polyhalogenated fatty acids, etc. Even if the pure unknown acid is at hand, a partition value is a useful constant—more trouble to measure than melting point or neutralization equivalent, but no more so than to prepare a solid derivative of the acid.

Advantages of the solvent-partition method over the Duclaux procedure have been discussed by Werkman<sup>2b</sup>; those most impressive are greater simplicity, wider applicability, and higher accuracy because values for different acids are more widely separated than the Duclaux constants. Both techniques fail if any impurity is present in appreciable amount. Clearly the present method does not safely distinguish acids with very large values of  $C_w/C_e$  ( $> 50$ ), but almost everywhere else the spread of values is gratifying. The use of ethyl acetate as extracting solvent would probably give lower and thus more useful values for hydroxy acids, but has not been tried. Another obvious but hardly very promising extension is the use of more dilute solutions initially, so as to include acids less soluble in water.

To use the extraction method in identifying an unknown acid, this procedure may be followed: Adjust the acid to  $0.100 \pm 0.005 N$  by preliminary titration and appropriate dilution. Measure 50 ml. of this solution and 50 ml. of water-saturated ether, made from c. p. reagent, into a glass-stoppered bottle and shake them together for five minutes<sup>2a</sup> or more at  $25.0 \pm 0.5^\circ$ . Allow several minutes for separation of layers, then pipet two 20-ml. portions from each layer and titrate them with standard 0.1 *N* alkali, with phenolphthalein as indicator. The mean value of  $C_w/C_e$  (in terms of normalities), used in conjunction with the series of values given, provides strong evidence of the nature of the acid.

(2a) Longer equilibration did not give us measurably different values; cf. McCoy, *This Journal*, **30**, 690 (1908); Friedemann, ref. 2g.

By this procedure the ratios of partition for a number of organic acids have now been determined at the arbitrary concentration specified. The acids were mostly Eastman Kodak Co. best grade, used without purification since that represents the purity in which they are most likely to be encountered. Acetylglycine, aconitic, benzoylformic, ethoxyacetic, hydracrylic, itaconic, methoxyacetic, oxamic, pimelic, and trimethylacetic acids were synthesized by standard procedures, usually from "Organic Syntheses."

Arranged in descending order to facilitate comparisons and supplemented by some values from an earlier paper, the ratios  $C_w/C_e$  are:

Benzenesulfonic, 300<sup>3</sup>; *d*-camphorsulfonic, 300; *d*-tartaric, 280<sup>3</sup>; acetylglycine, 150; citric, 150; glycine, 120<sup>3</sup>; mesotartaric, 120; *l*-malic, 75; *dl*-malic, 52; sulfosalicylic, 36; diglycolic, 35; glycolic, 35<sup>3</sup>; oxamic, 31; oxalic, 25; tricarballic, 20; lactic, 14; malonic, 12.0; maleic, 10.9; hydracrylic, 10.0; potassium acid phthalate, 8.1; succinic, 7.8<sup>3</sup>; methoxyacetic, 5.7; levulinic, 4.4;  $\alpha$ -hydroxyisobutyric, 4.4<sup>3</sup>; aconitic, 4.2; glutaric, 3.7; cyanoacetic, 3.3; itaconic, 3.0; formic, 2.8<sup>3</sup>; ethoxyacetic, 2.2; acetic, 2.1; adipic, 1.9<sup>3</sup>; fumaric, 0.80; phthalic, 0.79; pimelic, 0.73;  $\beta$ -bromopropionic, 0.70; propionic, 0.63; *dl*-mandelic, 0.50; acrylic, 0.49<sup>3</sup>; chloroacetic, 0.46<sup>3</sup>; bromoacetic, 0.31<sup>3</sup>; furoic, 0.26<sup>3</sup>; crotonic, 0.25<sup>3</sup>;  $\alpha,\beta$ -dibromopropionic, 0.24; trichloroacetic, 0.24<sup>3</sup>;  $\beta$ -chloropropionic, 0.24; butyric, 0.21; valeric, 0.20; isobutyric, 0.19; dichloroacetic, 0.18<sup>3</sup>; benzoylformic, 0.16;  $\alpha$ -chloropropionic, 0.14;  $\alpha$ -bromopropionic, 0.110; isovaleric, 0.108;  $\beta$ -iodopropionic, 0.103; *dl*-methylthylacetic, 0.092;  $\beta$ -chlorobutyric, 0.087; trimethylacetic, 0.077; isocaproic, 0.058;  $\alpha$ -bromobutyric, 0.056; phenylacetic, 0.047.

The precision of measurement of these ratios is about  $\pm 2\%$  of their own values in the region where  $C_w/C_e = 1$ , but decreases to  $\pm 4\%$  when  $C_w/C_e$  is as large as 35 or as small as 0.05. For still higher values of the ratio the precision is much poorer,  $\pm 10$ – $20\%$ . Comparisons with the literature values available<sup>4</sup> at or near the same equilibrium concentrations and temperature show excellent agreement except for lactic and oxalic acids. The ratio for lactic acid is not very reliable because of the considerable amount of in-

termolecular esters likely to be present in ordinary samples.

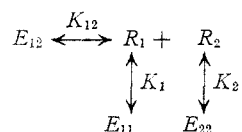
Acids that proved too slightly soluble to yield tenth-normal solutions are *n*-butoxyacetic, camphoric, *n*-caproic, gallic, nicotinic, phenoxyacetic, phenylsuccinic, salicylacetic, sorbic, and *dl*-tropic acids; obviously many others could be named, but these were tested as "borderline" cases.

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### The Dissociation of Hexaarylethanes. Equilibria Involving "Mixed Ethanes"

BY CHESTER M. HIMEL AND MAX B. MUELLER

The apparent dissociation of a number of "mixed ethanes" has been reported recently.<sup>1</sup> Since the "mixed ethane" exists in solution in equilibrium with the two symmetrical ethanes as well as with the two free radicals



the apparent dissociation is not a direct measure of the free energy of dissociation of the "mixed ethane." The equilibrium constant ( $K_{12}$ ) for the dissociation of a "mixed ethane" ( $E_{12}$ ) is, however, a direct measure of the free energy of dissociation and can be calculated from the following series of equations.

$$K_1 = (R_1)^2/(E_{11}) \quad (1)$$

$$K_2 = (R_2)^2/(E_{22}) \quad (2)$$

$$(R_1) + (R_2) = 2\alpha c \quad (3)$$

$$2(E_{11}) + (R_1) + (E_{12}) = c \quad (4)$$

$$2(E_{22}) + (R_2) + (E_{12}) = c \quad (5)$$

$$K_{12} = (R_1)(R_2)/(E_{12}) \quad (6)$$

where

( $R_N$ ) = concentration of radical N

( $E_M$ ) = concentration of ethane M

$c$  = nominal concentration of "mixed ethane"

$\alpha$  = apparent degree of dissociation of the "mixed ethane"<sup>1</sup>

For example, for the mixed ethane, 1-*o*-chlorophenyl-2-*o*-bromophenyltetraphenylethane, ref. 1, gives the following values

$$c = 0.1 M$$

$$\alpha_1 = 0.17 \text{ (di-}o\text{-bromophenyltetraphenylethane)}$$

$$\alpha_2 = 0.12 \text{ (di-}o\text{-chlorophenyltetraphenylethane)}$$

$$\alpha = 0.14$$

(3) Dermer, Markham and Trimble, *THIS JOURNAL*, **63**, 3524 (1941).

(4) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 422.

(1) Marvel and Himel, *THIS JOURNAL*, **64**, 2227 (1942).