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

The precision of measurement of these ratios is about ±2% of their own values in the region where $C_w/C_e = 1$, but decreases to ±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, ±10–20%. Comparisons with the literature values available[4] 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 intermolecular 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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[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.

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.[1] Since the "mixed ethane" exists in solution in equilibrium with the two symmetrical ethanes as well as with the two free radicals

$$\begin{tikzcd}
E_{12} \arrow[r, leftrightarrow, "K_{12}"] & R_1 + \arrow[d, leftrightarrow, "K_1"] & R_2 \arrow[d, leftrightarrow, "K_2"] \\
 & E_{11} & E_{22}
\end{tikzcd}$$

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"
α = apparent degree of dissociation of the "mixed ethane"[1]

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

$c = 0.1\ M$
$\alpha_1 = 0.17$ (di-*o*-bromophenyltetraphenylethane)
$\alpha_2 = 0.12$ (di-*o*-chlorophenyltetraphenylethane)
$\alpha = 0.14$

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

hence

$$K_1 = 4\alpha_1^2c/(1 - \alpha_1) = 1.39 \times 10^{-2}$$
$$K_2 = 4\alpha_2^2c/(1 - \alpha_2) = 0.655 \times 10^{-2}$$

and solving equations 1, 2, 3, 4 and 5 above for (R_1)

$$(R_1) = \frac{K_1(K_2 + 4\alpha c) - \sqrt{K_1K_2(K_1 + 4\alpha c)(K_2 + 4\alpha c)}}{2(K_1 - K_2)}$$

$$(R_1) = 1.63 \times 10^{-2}M$$

from equation 4

$$(R_2) = 2\alpha c - (R_1)$$
$$(R_2) = 1.17 \times 10^{-2}M$$

then (equation 1)

$$(E_{11}) = (R_1)^2/K_1 = 1.91 \times 10^{-2}M$$

and from equation 5

$$(E_{12}) = c - 2(E_{11}) - (R_1)$$
$$(E_{12}) = 4.60 \times 10^{-2}M$$

therefore (equation 6)

$$K_{12} = 0.415 \times 10^{-2}$$

Equilibrium constants calculated in a similar manner for the "mixed ethanes" for which the apparent dissociation has been measured (1) are listed in Table I.

TABLE I

EQUILIBRIUM CONSTANTS FOR "MIXED ETHANES"

Chlorides used	$K_1 \times 10^2$	$K_2 \times 10^2$	$K_{12} \times 10^2$
o-Chlorophenyldiphenylmethyl		0.655	0.415
o-Bromophenyldiphenylmethyl	1.39		
o-Tolyldiphenylmethyl		3.33	1.82
α-Naphthyldiphenylmethyl	3.99		
o-Tolyldiphenylmethyl		3.33	1.03
Di-*o*-tolylphenylmethyl	149.0		
Tri-*p*-biphenylmethyl		3.33	1.67
Tri-β-naphthylmethyl	3.33		
p-*t*-Amylphenyldiphenylmethyl		0.278	0.0138
Phenyldi-*p*-*t*-amylphenylmethyl	0.356		
Tri-*p*-*t*-butylphenylmethyl	2.00		.0118
p-*t*-Butylphenyldiphenylmethyl		.243	

Since K_{12} is, in all cases, smaller than either K_1 or K_2, it is evident that the "mixed ethanes" have a greater free energy of dissociation than either of the parent ethanes.

There appears to be no simple mathematical relation between K_1, K_2 and K_{12}. It is probable that the value of K_{12} depends not only upon K_1 and K_2, but also upon such factors as polarization of the ethane bond, steric hindrance and the effect of symmetry upon the entropy of dissociation.[2]

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[2] Symmetry effects on the entropy of dissociation have been outlined in a private communication from Professor P. D. Bartlett.

2'-Hydroxydiphenylphthalide

BY MAX H. HUBACHER

We have discovered that interaction of 2-benzoylbenzoyl chloride with phenol yields not only 4'-hydroxydiphenylphthalide, isolated previously from this reaction by Blicke and Swisher,[1] but also the hitherto unknown, isomeric 2'-hydroxydiphenylphthalide (I).

In conformity with its structure, we find that Compound I can be converted into a monoacetyl derivative, and a monomethyl ether; the melting point of the latter corresponds to that of 2'-methoxydiphenylphthalide which has been obtained by other investigators[2] by an entirely different procedure.

Compound I does not react with hydroxylamine; when fused with potassium hydroxide, it is converted into 9-phenylxanthene.

Experimental Part[3]

2'-Hydroxydiphenylphthalide (I).—The acid chloride, made from 45.2 g. (0.20 mole) of 2-benzoylbenzoic acid and 26 g. (0.22 mole) of thionyl chloride, was warmed for two hours at 40° with a solution of 18.8 g. (0.20 mole) of phenol in 300 ml. of benzene.[1] The crude 4'-hydroxydiphenylphthalide produced was recrystallized from acetic acid: 46 g. melting at 151–155° was obtained. All of this material, in 2-g. portions, was placed in a sublimation apparatus fitted with a water-cooled condenser,[4] and kept at 150° under 10 microns pressure. The total sublimate (m. p. 160–210°), after several recrystallizations from acetic acid, weighed 2.1 g., and melted at 240.5–241.3°. This compound, 2'-hydroxydiphenylphthalide (I), dissolved completely in 2.5 *N* sodium hydroxide to form a colorless solution. Its solution in concentrated sulfuric acid was orange.

Anal. Calcd. for $C_{20}H_{14}O_3$: C, 79.45; H, 5.00; mol. wt., 302. Found: C, 79.20, 79.35; H, 5.30, 4.43; mol. wt., 282 ± 12 (Rast, in camphor).

The portion of the 4'-hydroxydiphenylphthalide (m. p. 151–155°) which had not been sublimed, was recrystallized several times from acetic acid, whereupon pure 4'-hydroxydiphenylphthalide (m. p. 170.1–170.4°) (1) was obtained.

The acetyl derivative of 2'-hydroxydiphenylphthalide was formed when 0.608 g. of it, 3 ml. of acetic acid, 1 ml. of acetic anhydride and a drop of concentrated sulfuric acid were refluxed for one hour. It melted at 136.6–137.7° after recrystallization from ethanol (1 g. in 10 ml.).

Anal. Calcd. for $C_{22}H_{16}O_4$: C, 76.73; H, 4.70. Found: C, 76.44; H, 4.52.

2'-Methoxydiphenylphthalide was obtained when I was

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[1] F. F. Blicke and R. D. Swisher, THIS JOURNAL, **56**, 924 (1934), report a m. p. of 168–170° for the 4'-hydroxydiphenylphthalide.

[2] F. F. Blicke and O. J. Weinkauff, *ibid.*, **54**, 1452 (1932), reported this compound as melting at 127–128°.

[3] All melting points are corrected.

[4] This apparatus is described in *J. Ind. Eng. Chem., Anal. Ed.*, **15**, 448 (1943).