[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Association of Some Organic Acids in Benzene Solution

BY F. T. WALL AND F. W. BANES

It is well recognized that under suitable conditions carboxylic acids can undergo association into dimers, such association taking place through the formation of hydrogen bonds[1] and involving equilibria of the type

$$(RCOOH)_2 \rightleftarrows 2RCOOH \qquad (1)$$

It is naturally of interest to determine the equilibrium constants for reactions of type (1), and this has been done in numerous instances by various means.[2] In this paper there will be reported results obtained for the associations of benzoic acid, *o*-toluic acid and *m*-toluic acid in benzene solution. This work is an extension of an investigation reported earlier by Wall and Rouse.[3]

The apparatus used for the experiments is a modification of a system originally employed by Signer[4] and subsequently improved by Lassettre and Dickinson.[5] Further refinements were introduced by Wall and Rouse[3] and by the present authors, but the final methods employed were still quite similar to those of Lassettre and Dickinson.[5]

Described briefly, the apparatus consists of an isotensimeter made up of two solution bulbs joined by an inverted U-tube and provided with calibrated side arms for volume measurements. A benzene solution of the acid being investigated is placed in one tube and a benzene solution of a non-associating substance like phenanthrene is placed in the other, after which vapor is allowed to distill between them until equilibrium is reached. Assuming Raoult's law to hold, one can then calculate the equilibrium constant for the association from a knowledge of the equilibrium concentrations of acid and phenanthrene. Since the details of the experimental procedure and of the methods of calculation have been described earlier,[3] they will not be repeated here.

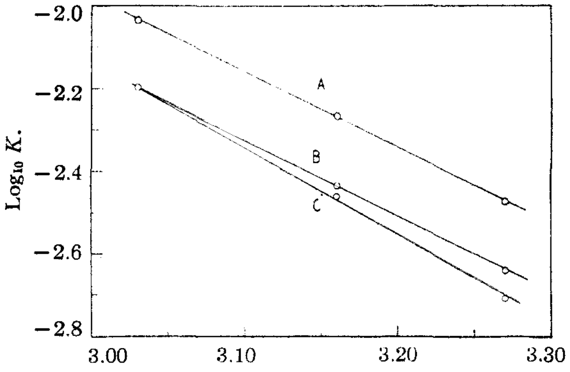

Fig. 1.—Logarithm of dissociation constant *versus* reciprocal of absolute temperature; A, *o*-toluic acid; B, benzoic acid; C, *m*-toluic acid.

The experiments were carried out in the neighborhood of each of three different temperatures, namely, 32, 43 and 57°. Although the temperature range was not large, it was sufficient to give an indication of the heats of dissociation. Phenanthrene was used as the standard non-associating substance and the concentrations of acid employed varied from about 10 to 25 g. per liter of benzene solution.

Experimental Results.—A summary of the experimental results appears in Table I. In this table are given the number of measurements carried out for each of the acids, the average temperature of the measurements, and the average values of the dissociation constants calculated for the following form

TABLE I

Acid	Number of measurements	Temp., °C.	$K \times 10^3$
Benzoic	5	32.5	2.30
		43.3	3.69
		56.5	6.33
o-Toluic	6	32.6	3.38
		43.4	5.43
		56.5	9.27
m-Toluic	7	32.0	1.97
		43.3	3.45
		56.5	6.31

$$K = [RCOOH]^2/[(RCOOH)_2] \qquad (2)$$

In Fig. 1 are plotted values of $\log_{10} K$ *versus* $1/T$ for each of the acids; it will be observed that all three give good linear relationships, especially benzoic acid and *o*-toluic acid. Using the methods of least squares, the complete sets of experimental data were used to determine the best linear functions of the forms

$$\log_{10} K = A - B/T \qquad (3)$$

Values for ΔH were then obtained from the values of B. A summary of the results follows

Benzoic acid:

$\log_{10} K = 3.383 - 1841/T \quad (\pm 0.4\%)$
$\Delta H = 8420 \pm 400$ calories

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[1] (a) See E. N. Lassettre, *Chem. Rev.*, **20**, 259 (1937), for a general discussion; (b) also L. Pauling, "Nature of the Chemical Bond," second edition, Cornell University Press, Ithaca, New York, 1940, p. 306.

[2] (a) A. S. Coolidge, THIS JOURNAL, **50**, 2166 (1928); (b) F. H. MacDougall, *ibid.*, **58**, 2858 (1936); **63**, 3420 (1941); (c) Creighton, *J. Franklin Inst.*, **180**, 63 (1915); (d) Nernst, *Z. physik. Chem.*, **8**, 110 (1891); (e) Hendrixson, *Z. anorg. Chem.*, **13**, 73 (1897).

[3] F. T. Wall and P. E. Rouse, THIS JOURNAL, **63**, 3002 (1941).

[4] Signer, *Ann.*, **478**, 246 (1930).

[5] Lassettre and Dickinson, THIS JOURNAL, **61**, 54 (1939).

o-Toluic acid:

$$\log_{10} K = 3.533 - 1836/T \quad (\pm 0.3\%)$$
$$\Delta H = 8400 \pm 200 \text{ calories}$$

m-Toluic acid:

$$\log_{10} K = 4.056 - 2063/T \quad (\pm 0.3\%)$$
$$\Delta H = 9440 \pm 200 \text{ calories}$$

Discussion.—It will be observed from Table I and Fig. 1 that at a given temperature, *o*-toluic acid has a substantially larger value for K than either of the other two acids. This is very likely due to steric effects since methyl substituents in the *ortho* position would be expected to make dimerization more difficult. *m*-Toluic acid and benzoic acid appear to associate approximately to the same extent.

The values of A and B which appear in equation (3) cannot be determined very accurately even though the values of $\log_{10} K$ are known much better. The reason for this is that the temperature range is so small that errors in A and B can easily compensate for each other. As a result the values for ΔH are much less certain than those for $\log_{10} K$. It is also possible to calculate entropies of dissociation from the values of A, but this has not been done since they would be even less accurate (on a percentage basis) than values for ΔH.

Although the probable errors in $\log_{10} K$ are not large, the corresponding errors in K are of course larger. The equation given above for benzoic acid differs somewhat from that of Wall and Rouse[8] although the actual dissociation constants which were found by the two separate investigations are not very different. The results given above are believed to be more accurate than the earlier ones.

Summary

The associations of benzoic, *o*-toluic and *m*-toluic acids in benzene solution have been studied by a method involving the indirect measurement of vapor pressure lowerings. Phenanthrene was used as a standard unassociated substance and Raoult's law was assumed to be valid. Benzoic and *m*-toluic acids are found to associate to approximately the same extent but *o*-toluic acid associates appreciably less than the other two at a given temperature. The heats of dissociation of the acid dimers have also been determined and found to be in the neighborhood of 9000 calories, with *o*-toluic acid showing the lowest value and *m*-toluic acid the highest.

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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

Condensation of Secondary Alcohols with Phenol in the Presence of Aluminum Chloride

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Previous contributions from this Laboratory have described the condensation of tertiary aliphatic alcohols with phenol[1] and benzene[2] using aluminum chloride as the condensing reagent.

Secondary alcohols have also been shown to condense with benzene[3] under the influence of the same catalyst to give in general mixtures of secondary alkylbenzenes, tertiary alkylbenzenes or mixtures of secondary and tertiary alkylbenzenes. Condensation without rearrangement took place only in the case of 2-propanol, 2-butanol, and 3,3-dimethyl-2-butanol.

As an extension of this work, the secondary alcohols, up to and including the secondary hexyl alcohols, have been condensed with phenol.

Separable mixtures of 2-*p*-hydroxyphenylpentane and 3-*p*-hydroxyphenylpentane were formed by the condensation of 2-pentanol and of 3-pentanol with phenol. The structures of these alkylphenols were established by conversion of corresponding alkylbenzenes[3] to their *p*-hydroxy derivatives by nitration, reduction, diazotization and hydrolysis. The melting point and mixed melting point determination of the α-naphthylurethans indicated that 3-pentanol yielded approximately equal quantities of the two isomers while 2-pentanol gave mostly 2-*p*-hydroxyphenylpentane.

2-Hexanol and 3-hexanol condensed with phenol to form mixtures of alkylphenols which could not be separated because of high viscosity, closeness of boiling points and like solubility. The α-naphthylurethans could not be crystallized to sharp melting points. These same alcohols, when condensed with benzene,[3] gave mixtures which could not be separated. Melting points of the α-naphthylurethans indicate that mixtures from both 2-hexanol and 3-hexanol contain, as the main product, 3-*p*-hydroxyphenylhexane with smaller amounts of 2-*p*-hydroxyphenylhexane.

The theory predicts the possible formation of three alkylphenols from 2-methyl-4-pentanol. Of these, 2-methyl-4-*p*-hydroxyphenylpentane and 2-methyl-2-*p*-hydroxyphenylpentane are known. Attempts to prepare 2-methyl-3-phenylpentane by the modified[3] Klages method[4] were not successful because of the failure to obtain complete reduction of the dehydration product of 2-methyl-3-phenyl-3-pentanol by means of sodium. Attempts to hydrogenate by means of zinc and hydro-

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(1) R. C. Huston and C. R. Meloy, THIS JOURNAL, **64**, 2655 (1942).

(2) R. C. Huston and J. Awuapara, *J. Org. Chem.*, **9**, 401 (1944).

(3) R. C. Huston and I. A. Kaye, THIS JOURNAL, **64**, 1576 (1942).

(4) A. Klages, *Ber.*, **36**, 622 (1903); **37**, 1447, 1721 (1904).