further, that, while the conductance curve for triisoamylammonium picrate is of simple form, the conductance increasing regularly with increasing concentration,[7,10] the association of this salt, as shown by freezing point measurements, is much less pronounced than is that of the other salts shown in Fig. 1.

While the building up of the ion dipoles to complex structures with increasing concentration follows fairly logically on the basis of existing concepts, the rapid dissociation of the complexes at concentrations above that of the maximum does not follow simply on a similar basis. There is reason for believing that this building down of the complexes is due to a modification of the forces acting between the dipoles and, indeed, between the ions themselves.

These cases are, perhaps, understood more readily from the point of view of Strong and Kraus[10] who look upon concentrated benzene solutions as solutions of benzene in the fused salt. The fused salt is completely dissociated into its ions and there is no interaction between individual ions; rather, the ions, so to speak, float in a field due to all the ions in a given small volume. If benzene molecules are introduced, these will serve to separate the ions, reducing and, perhaps, distorting the field in which the ions float. If sufficient benzene is introduced, the field will be weakened to such an extent that interaction will take place between individual ions with the resulting formation of ion pairs. The formation of ion pairs will tend to lower the conductance. On addition of larger quantities of benzene, the ion pairs will begin to interact with one another to form quadrupoles and more complex structures. This building up process will continue until a point is reached where the building down process sets in as a result of ordinary kinetic interactions. In other words, with increasing additions of benzene, association first increases, reaches a maximum and then decreases.

In solutions of salts in a non-polar solvent, such as benzene, we are dealing with interactions that have their seat in the charges on the ions. The solvent takes little or no part in these interactions, it serves merely as a medium in which the ions may exist without precipitation as a solid phase. The properties of these systems must ultimately be traceable to the ions of the electrolytes in solution. The correctness of this view is borne out by the sensitivity of the properties of these solutions to the constitutional and structural features of the ions that are involved.

PROVIDENCE, R. I. RECEIVED FEBRUARY 15, 1951

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

The Association Constants of Several Carboxylic Acids in Benzene as Determined Cryoscopically

BY BERNARD C. BARTON[1] AND CHARLES A. KRAUS

The apparent molecular weight of five carboxylic acids has been determined in benzene in the concentration range 0.01–0.1 molal. Constants have been derived for the monomer–dimer equilibrium. With the exception of hydrocinnamic acid, the order of these constants is the same as that of their ionization constants in water. The constant for benzoic acid at the freezing point of benzene is in agreement with that obtained by Wall, *et al.*, at higher temperatures by a vapor tension method.

I. Introduction

At the time that this investigation was initiated, there were no reliable data relating to the association of carboxylic acids in benzene. In the meantime, Gross and co-workers[2] have determined the association of acids at 25° by means of dielectric constant measurements. Wall and co-workers[3] have made similar determinations at several temperatures by means of a differential vapor tension method. More recently, Wolf and Metzger[4] have determined association constants of several acids at two temperatures.

While carboxylic acids are highly associated in benzene at concentrations where measurements can be most conveniently made (0.01 to 0.1 m), it appeared that fairly reliable constants could be obtained by the cryoscopic method in view of the precision with which freezing point depressions could be determined.

II. Experimental

1. **Apparatus and Materials.**—The apparatus and techniques employed were the same as those developed in this Laboratory for determining the molecular weight of electrolytes in benzene. The experimental details have been described in earlier papers.[5]

The following acids were employed after recrystallization from benzene: benzoic, m.p. 128.5–129.0°; *o*-bromobenzoic, m.p. 148.9°; hydrocinnamic, m.p. 48.0–48.5°; cinnamic (*trans*), m.p. 131.0–131.5°; phenylpropiolic, m.p. 135–136°. Benzene was purified as described in earlier papers.[5]

2. **Results.**—In Table I are recorded values of $r = \Delta T/\Delta T_0$, the ratio of the observed depression to that of an ideal substance at the same concentration. The concentration, m, is expressed as moles of solute per 1000 g. of benzene. The freezing point constant has been taken to be 5.085°/mole/1000 g. solvent.[6]

III. Discussion

The dissociation constants of the dimers are best evaluated by graphical methods. If K is the dissociation constant of the dimer, m is the stoichiometric concentration of the acid in moles per 1000

---

(1) University Fellow in Brown University, 1936–1939, inc.

(2) (a) A. A. Maryott, M. E. Hobbs and P. M. Gross, *J. Chem. Phys.*, **9**, 408 (1941); (b) H. A. Pohl, M. E. Hobbs and P. M. Gross, *Ann. N. Y. Acad. Sci.*, **40**, 389 (1940).

(3) (a) F. T. Wall and P. E. Rouse, Jr., THIS JOURNAL, **63**, 3002 (1941); (b) F. T. Wall and F. W. Baines, *ibid.*, **67**, 898 (1945).

(4) K. L. Wolf and G. Metzger, *Ann.*, **563**, 157 (1949).

(5) (a) C. A. Kraus and R. A. Vingee, THIS JOURNAL, **56**, 511 (1934); (b) F. M. Batson and C. A. Kraus, *ibid.*, **56**, 2017 (1934); (c) D. A. Rothrock, Jr., and C. A. Kraus, *ibid.*, **59**, 1699 (1937).

(6) B. C. Barton and C. A. Kraus, *ibid.*, **73**, unpublished (1951).

TABLE I

CRYOSCOPIC DATA FOR CARBOXYLIC ACIDS IN BENZENE

m	r	m	r
A. Benzoic		C. Hydrocinnamic	
0.00621	0.5989	0.01845	0.5827
.01703	.5833	.03484	.5584
.01418	.5736	.06087	.5456
.02616	.5535	.08886	.5356
.04372	.5418	D. Cinnamic (*trans*)	
.07072	.5315	0.01385	0.5437
.09462	.5280	.02545	.5327
		.06132	.5184
B. *o*-Brombenzoic		E. Phenylpropiolic	
0.00760	0.6252	0.02842	0.6126
.01763	.5835	.03527	.5930
		.07620	.5559

g. of benzene and γ is the fraction of the material existing as monomer, then

$$2m\gamma^2/(1 - \gamma) = K \qquad (1)$$

where

$$\gamma = 2r - 1 \qquad (2)$$

Rearranging (1), we have

$$2m\gamma = K/\gamma - K$$

If there is an equilibrium between the dimer and the monomer, then a plot of $m\gamma$ against $1/\gamma$ should yield a straight line having the slope K. Using the data of Table I, plots were constructed as shown in Fig. 1 and the dissociation constants were evaluated.

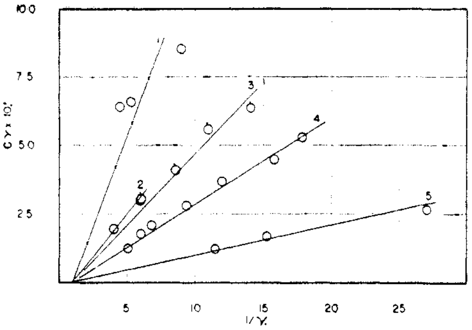

Fig. 1.—Mass law plots for acids in benzene: 1, phenylpropiolic; 2, *o*-bromobenzoic; 3, hydrocinnamic; 4, benzoic; 5, cinnamic (*trans*).

The constants so derived appear in column 2 of Table II. In column 3 are given values of the ionic dissociation constants of the acids in water at 25°.

With the exception of hydrocinnamic acid, the dimeric dissociation constants parallel the ionization constants in water. Why the latter acid should be exceptional is not apparent.

In the case of benzoic acid, we have the data of other investigators at higher temperatures[3] as well as at the freezing point of benzene.[4] A plot of $\log_{10}K_c$ (on a molar basis) against $1/T$ yields the line shown in Fig. 2. It will be noted that our value for the dissociation constant at the freezing point is in excellent agreement with the values of Wall, *et al.*, at higher temperatures. These values are not in agreement with the results of other workers.[3a,4]

TABLE II

DISSOCIATION CONSTANTS OF DIMERIC ACIDS IN BENZENE AND IONIZATION CONSTANTS IN WATER

Acid	$K_{(C_6H_6)}$ $\times 10^4$ at 5.4°	$K_{\text{Ion}\cdot(H_2O)}$[a] $\times 10^5$ at 25°
Phenylpropiolic	27	590
o-Bromobenzoic	12	140
Hydrocinnamic	10	2.19
Benzoic	6.4	6.27
Cinnamic (*trans*)	2.2	3.65

[a] J. F. J. Dippy, *Chem. Revs.*, **25**, 151 (1939).

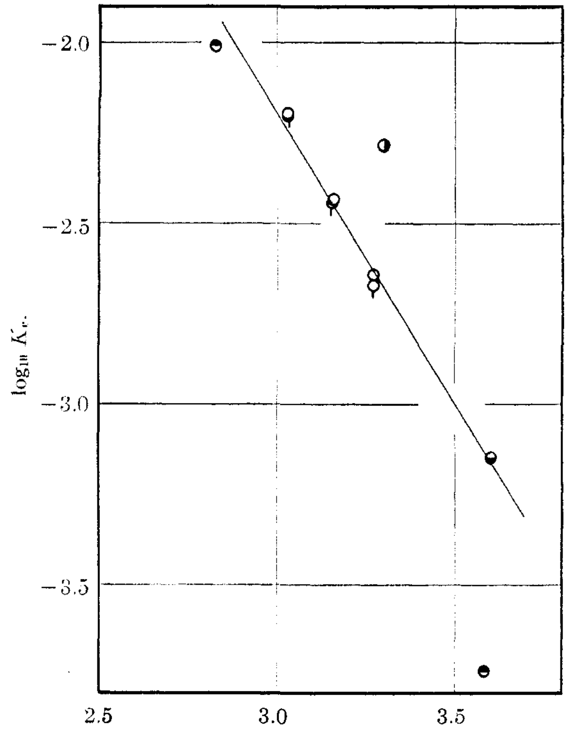

Fig. 2.—Plot of $\log_{10} K$ against $1/T$ for benzoic acid in benzene: ●, ref. 4; ◑, ref. 3a; ♀, ref. 2a; ○, ref. 2b; ◒, this investigation.

Wall and Baines[3b] represent their results by the equation

$$\log_{10}K = 3.383 - 1841/T$$

which leads to a value of 8420 ± 400 cal. for the enthalpy change associated with the dimer–monomer equilibrium.

PROVIDENCE, R. I.

RECEIVED JANUARY 27, 1951