

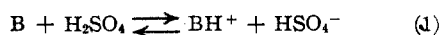
[CONTRIBUTION FROM THE CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

Normal and Complex Ionization of Organic Molecules in Solvent Sulfuric Acid. I. Methyl 2,4,6-Trimethylbenzoate; *o*-Benzoylbenzoic Acid and its Normal and Pseudo Methyl Esters^{1,2}

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Consideration of the facts known about the ionization of organic compounds in solvent sulfuric acid leads to a classification into two types,³ namely, normal and complex ionization. For convenience in future discussions these are defined below.

(a) **Normal ionization**, or ionization in which the organic compound combines with a proton to give the conjugate acid of the original compound and a bisulfate ion, as follows:



The maximum van't Hoff *i* factor (*i. e.*, for 100% ionization) for this type of ionization is 2.⁴

(b) **Complex ionization**, or ionization in which the originally formed conjugate acid is unstable and breaks down to give other products, which usually react further with sulfuric acid. These ionizations always have possible maximum *i* factors greater than two.

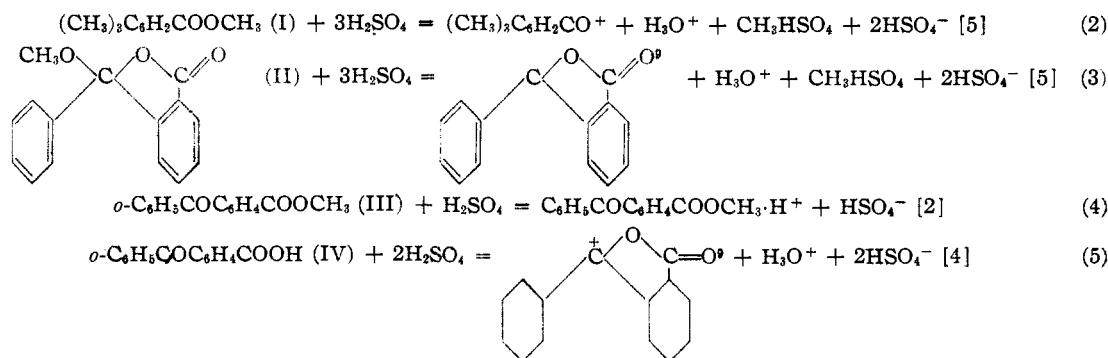
In this and later work, we hope to show that there is a distinct correlation between the type of ionization exhibited and the reactivity of the organic species in solution; in cases of normal ionization there is low reactivity and in cases of complex ionization there is high reactivity. The converse should also apply.

Specifically, the organic ions present in cases of normal ionization are of the type BH^+ , the

conjugate acids of the original organic compound, B. These conjugate acids are unreactive and, as such, undergo no other reaction than loss of a proton to a more basic medium. For example, on pouring a sulfuric acid solution of methyl benzoate into water the ester is recovered unchanged.⁵ One may generalize from this and other examples that if the original compound is recovered unchanged on pouring its sulfuric acid solution into water (or methanol) then this compound undergoes normal ionization.

In contrast, the ions formed in solutions involving complex ionization are quite reactive and may exhibit a variety of reactions, either in the sulfuric acid solution itself or on pouring into water (or methanol). For example, on pouring a sulfuric acid solution of methyl 2,4,6-trimethylbenzoate into water, 2,4,6-trimethylbenzoic acid is obtained.^{3,6} One may generalize from this and other examples that if some substance other than the original compound is obtained on pouring the solution into water (or methanol) then this compound undergoes complex ionization.

At the start of this investigation the following facts were known about the products formed when sulfuric acid solutions of the compounds in question were poured into water or methanol: methyl 2,4,6-trimethylbenzoate, I, gave (water) 2,4,6-trimethylbenzoic acid⁶; pseudo methyl *o*-benzoyl-



(1) Presented before the Organic Division of the American Chemical Society at the Cleveland meeting, April, 1944.

(2) This material is contained in the Thesis presented by Henry Kuivila to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the M.A. degree.

(3) For an excellent review of the behavior of organic compounds in sulfuric acid see Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 45-48, 53-56, and 277-283.

(4) It should be pointed out that it is conceivable for an organic compound to take up two or more protons and act like a di- (or poly), acid base, as follows: $B + nH_2SO_4 \rightleftharpoons (BH_n)^{n+} + nHSO_4^-$. No examples of this type of ionization are recognized. See ref. 3 top of page 48.

benzoate, II, gave (water) *o*-benzoylbenzoic acid; normal methyl *o*-benzoylbenzoate, III, was recovered (water) unchanged⁷; and *o*-benzoylbenzoic acid, IV, gave (methanol) a mixture of II and III.⁸ By applying the principles pre-

(5) Hammett and Treffers, *THIS JOURNAL*, **59**, 1708 (1937).

(6) For other examples see (a) Newman and McCleary, *ibid.*, **63**, 1539 (1941); and (b) Newman, *ibid.*, **63**, 2431 (1941).

(7) Newman and McCleary, *ibid.*, **63**, 1539 (1941).

(8) Newman, *ibid.*, **64**, 2324 (1942).

(9) The reasons for assigning the cyclic structure to this carbonium ion are discussed in ref. 8.

viously outlined and taking into account the known behavior of methanol the ionizations shown (maximum possible i factors are given in brackets) were predicted.

This paper presents the experimental cryoscopic data on sulfuric acid solutions of methyl 2,4,6-trimethylbenzoate and of *o*-benzoylbenzoic acid and its normal and pseudo methyl esters. The i factors were found to correspond closely to the predicted values as follows: (2) 5.0; (3) 4.9; (4) 2.1; (5) 3.8. Thus evidence in support of the hypotheses outlined above has been provided.¹⁰

Reagents

Sulfuric Acid.—Two thousand grams of C. P. concentrated sulfuric acid and 1300 g. of fuming sulfuric acid (20–30% SO₃) were mixed. That the acid contained an excess of sulfur trioxide was shown by the fact that upon addition of three successive increments of water, the freezing point of a portion of the acid changed from 7.80 to 8.96, 10.30 and 9.90°, respectively. This stock acid (f. p. 7.80°) was kept in a tightly stoppered bottle.

2,4,6-Trimethylbenzoic Acid.—Prepared by carbonation of the Grignard reagent from bromomesitylene,^{6b} recrystallized from benzene and dried at 100°; m. p. 153.2–154.0°.

Methyl 2,4,6-Trimethylbenzoate.—A sample of this ester^{6b} was redistilled and a middle cut used. It formed a colorless liquid, b. p. 130–131° at 23 mm., n_D^{20} 1.5076.

Methyl Esters of *o*-Benzoylbenzoic Acid.—The vacuum distilled esters⁹ were crystallized from dilute methanol: normal methyl ester, b. p. 165–166° at 2 mm., m. p. 51.0–51.6° cor.; pseudo methyl ester, b. p. 165–166° at 2 mm., m. p. 80.8–82.0° cor.

***o*-Benzoylbenzoic Acid.**—Recrystallized from benzene and dried to constant weight *in vacuo*; m. p. 128.8–129.6 cor.

Benzoic Acid.—Recrystallized from water and dried at 100°; m. p. 121.8–122.0° cor.

Ethyl Benzoate.—Dried over phosphorus pentoxide and vacuum distilled; b. p. 107°–107.5°, n_D^{20} 1.5051.

Apparatus

The apparatus is shown in Fig. 1. Temperatures were measured by the glass enclosed platinum resistance thermometer T (Leeds and Northrup No. 8163) which was calibrated at the National Bureau of Standards. It was protected by the shield S to which it was sealed at a and b with Picein wax. The agitator A was made of glass rod. It was motivated in a vertical piston-like motion by a windshield wiper motor. The mercury seal at M provided protection from the air. Solute was added through N. For introducing liquids, a medicine dropper was used and for solids the device shown in Fig. 1a. By raising the rod c the powdered sample contained in e was released through the opening created at d.

The air jacket J was made with a side arm C through which a piece of Dry Ice could be inserted to touch the side of the acid reservoir R to induce crystallization of the acid. B is the cooling bath.

Procedure and Data

In general the technique was the same as that described by Hammett and Deyrup.¹¹ The apparatus was always cleaned, dried in the oven and cooled in the air with protection from moisture before each series of determinations. It was then assembled as shown in Fig. 1 with the ex-

(10) The i factor of 4 as determined for *o*-benzoylbenzoic acid provides evidence in support of the mechanism for the formation of anthraquinone advanced by Newman, ref. 8 above.

(11) Hammett and Deyrup, *THIS JOURNAL*, **55**, 1900 (1933).

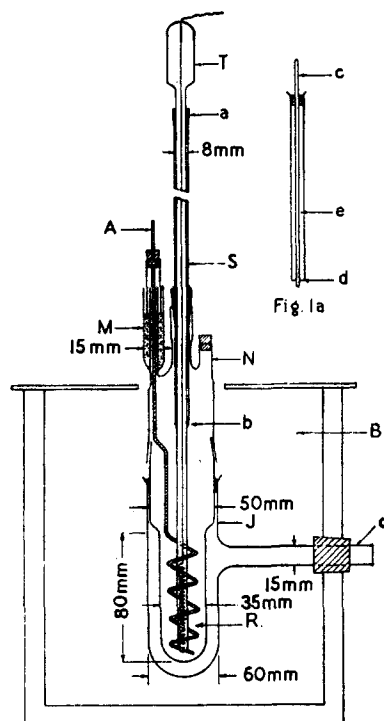


Fig. 1.

ception that the thermometer was omitted. A buret was filled with the stock sulfuric acid and fitted with a stopper into the thermometer opening. Then 40.0 ml. of the acid was drained into the apparatus allowing thirty minutes for drainage. In this way it was found that the weight of acid delivered (73.4 g.) was reproducible to within 0.1 g. The same buret was used in all experiments. The buret was replaced by the thermometer and a weighed amount (about 0.5 g.) of water was sufficient, as determined in a previous experiment, to make the concentration of the acid just less than 100%. In all runs the freezing point of the acid was in the range 9.80–10.25°.

After the acid had stood in the apparatus for at least twelve hours to ensure absorption of any moisture from the walls, the cooling bath B, was filled with chopped ice and the agitator started. Crystallization was induced after a slight supercooling by touching the side of the acid reservoir with Dry Ice. Temperature readings were taken at one-minute intervals for a period long enough to give sufficient data for calculating the freezing point according to the method described by Glasgow, Mair and Rossini.¹² Then the ice in the bath, B, was replaced by water at about 35° while the solute for a run was being weighed. Enough solute to lower the freezing point of the solution by 0.2 to 0.7° was then added and the mixture was well started. When the solute was all dissolved, ice was placed in the cooling bath and the new freezing point was determined. In this way

(12) Glasgow, Mair and Rossini, *J. Research National Bureau of Standards*, **26**, 59 (1941).

usually three to five portions of solute were added and the freezing point determined after each addition.

The van't Hoff factor i was calculated by the equation¹¹

$$i = \frac{\Delta\vartheta}{\Delta m \times 6.154(1 - 0.0047 \vartheta)}$$

where $\Delta\vartheta$ is the lowering in the freezing point of the solution due to the increment Δm in the molality of the solute; ϑ is the total freezing point depression and 6.154 is the molal freezing point constant for sulfuric acid.

TABLE I
FREEZING POINT DATA

| No. | Δm | F. p., °C. | $\Delta\vartheta$ |
|--|------------|------------|-------------------|
| Series A: Benzoic Acid | | | |
| 1 | | 9.899 | ... |
| 2 | 0.0154 | 9.738 | 0.161 |
| 3 | .0194 | 9.503 | .235 |
| 4 | .0108 | 9.370 | .133 |
| 5 | | 9.366 | ... |
| 6 | .1003 | 8.144 | 1.222 |
| Series B: Ethyl Benzoate | | | |
| 1 | | 10.040 | ... |
| 2 | .0265 | 9.731 | 0.309 |
| 3 | .0239 | 9.442 | .289 |
| Series C: Methyl 2,4,6-Trimethylbenzoate (I) | | | |
| 1 | | 9.601 | ... |
| 2 | .0206 | 8.963 | .638 |
| 3 | .0208 | 8.333 | .630 |
| Series D: Normal Methyl <i>o</i> -Benzoylbenzoate (II) | | | |
| 1 | | 10.099 | ... |
| 2 | .0193 | 9.844 | .255 |
| 3 ^a | | 9.849 | .250 |
| 4 | | 9.592 | ... |
| 5 | .0212 | 9.351 | .241 |
| 6 | .0116 | 9.197 | .154 |
| 7 | | 10.147 | ... |
| 8 | .0207 | 9.913 | .234 |
| 9 | .0292 | 9.532 | .381 |
| 10 ^b | .0260 | 9.159 | .373 |

Series E: Pseudo Methyl *o*-Benzoylbenzoate (III)

| | | | |
|---|-------|--------|------|
| 1 | | 10.222 | ... |
| 2 | .0231 | 9.537 | .685 |
| 3 | .0186 | 8.981 | .556 |
| 4 | .0131 | 8.588 | .393 |

Series F: *o*-Benzoylbenzoic Acid (IV)

| | | | |
|---|-------|-------|------|
| 1 | | 9.812 | ... |
| 2 | .0134 | 9.499 | .313 |
| 3 | .0206 | 9.018 | .481 |
| 4 | .0157 | 9.652 | .366 |

^a The temperature of run D-2 was raised to 33° for one and one-half hours and this value redetermined.

^b Series D-7 to 10 are duplicate data on this ester to verify the i value of *ca.* 2 and also to check on the increase in i values due to an increase in time. We have noted that for some compounds the i values increase with time and/or elevated temperature. This effect is being investigated and is to be the subject of another publication.

TABLE II

| Compound | i Found | i Predicted |
|---|-----------|---------------|
| Benzoic acid | 2.0 | 2.0 |
| Ethyl benzoate | 1.9 | 2.0 |
| 2,4,6-Trimethylbenzoic acid | 3.7 | 4.0 |
| Methyl 2,4,6-trimethylbenzoate | 5.0 | 5.0 |
| <i>o</i> -Benzoylbenzoic acid | 3.8 | 4.0 |
| Normal methyl <i>o</i> -benzoylbenzoate | 2.1 | 2.0 |
| Pseudo methyl <i>o</i> -benzoylbenzoate | 4.9 | 5.0 |

The data for each compound studied are tabulated in Table I and summarized in Table II. The general procedure and technique were checked by obtaining cryoscopic data on benzoic acid, ethyl benzoate and 2,4,6-trimethylbenzoic acid; these data are included for comparison.

Summary

The van't Hoff i factors of methyl 2,4,6-trimethylbenzoate, *o*-benzoylbenzoic acid, and its normal and pseudo esters in solvent sulfuric acid were determined cryoscopically and found to correspond very closely to the predicted values of 5, 4, 2, and 5, respectively.

The theoretical considerations leading to the predicted values are outlined.

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