[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF PRINCETON UNIVERSITY]

A STUDY OF THE DEHYDRATION OF ORTHO-BENZOYLBENZOIC ACID

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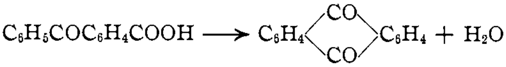
Introduction

It was first noted by Liebermann[1] that anthraquinone could be formed by the elimination of water from *o*-benzoylbenzoic acid.



$$C_6H_5COC_6H_4COOH \longrightarrow C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4 + H_2O$$

This process has come to have considerable technical importance because it is the principal step in the manufacture of synthetic anthraquinone. In addition, the reaction has certain unusual features which make it interesting from a purely theoretical point of view. For example, it is one of the few condensation reactions involving the use of strong dehydrating reagents such as sulfuric acid in which the yields are very high and side reactions negligible. In fact, under the proper conditions, *o*-benzoylbenzoic acid is converted apparently quantitatively into anthraquinone. This reaction should lend itself well to kinetic studies which might throw light on the mechanism of such processes in general.

In the synthetic method for producing *o*-benzoylbenzoic acid from phthalic anhydride and benzene in the presence of aluminum chloride, it is possible, by using substitution products of benzene and the anhydride, to prepare various substituted *o*-benzoylbenzoic acids which in turn can be condensed to the corresponding anthraquinones. This would seem to be a convenient way, therefore, of ascertaining the influence of different substituents in the benzene ring on this type of reaction. It has been our purpose, first to make a general study of the transformation using the unsubstituted acid, and then to attempt measurements showing the influence of substituents on the rate of reaction. The results of the first investigation are given in this paper.

The Dehydration of *o*-Benzoylbenzoic Acid under Various Conditions.—It has been found that the acid, when heated alone, yields small amounts of anthraquinone; the reaction temperature is quite high, 220°, and numerous by-products are formed, among them benzophenone.[2] Catalysts such as aluminum chloride, the sulfates of mercury, copper, tin, magnesium and silver and other anhydrous salts which might be expected to accelerate this type of reaction had little or no effect. Thallium chloride, however, had a marked influence on the reaction temperature and, in the

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[1] Liebermann, *Ber.*, 7, 805 (1874).

[2] Dougherty, THIS JOURNAL, 50, 571 (1928).

presence of traces of this salt, a strong positive test for anthraquinone was obtained at 180°.

It is known that phosphorus pentoxide will cause this condensation,[3] but the yields are not good. With meta- and pyrophosphoric acids the yield of anthraquinone is negligible even with prolonged heating at 100°. The *o*-benzoylbenzoic acid dissolves very slowly in these acids and hence would make accurate velocity measurements difficult even if the acids were good condensing agents.

Concentrated sulfuric acid proved to be a better condensing agent than the literature implied. That is, most preparation directions for forming anthraquinone from *o*-benzoylbenzoic acid call for fuming sulfuric acid. It was found that a solution containing ten parts of concentrated sulfuric acid to one of pure *o*-benzoylbenzoic acid gave a quantitative yield of anthraquinone when heated for two hours at 100°. Even at room temperature the reaction proceeds at a measurable rate with a yield of approximately 4% of the theoretical in one hundred hours. The addition of contact agents such as metallic sulfates to the sulfuric acid reaction mixture had no apparent effect on the rate of condensation. It would seem, from our experiments, that sulfuric acid is almost a specific in this condensation, and while *o*-benzoylbenzoic acid can be dehydrated by other means, side reactions occur and the yields are never good.

Reaction Velocity Measurements.—When solutions of one part of *o*-benzoylbenzoic acid and ten parts of 96% sulfuric acid were heated for varying lengths of time at a definite temperature, and the resulting amounts of anthraquinone determined (see Experimental Part), the rate of conversion, calculated as a monomolecular reaction, was found to give a good constant over the whole range.

t, hours	6	8	10	12	17	20	22	26	30	36
K at 65°	0.076	0.075	0.078	0.074	0.079	0.074	0.076	0.076	0.078	0.076
t, hours	2	3	4	5	6	7	8	10	12	15
K at 75°	0.242	0.257	0.272	0.255	0.256	0.263	0.256	0.272	0.256	0.272

The velocity constant at 85° was 0.838 and at higher temperatures the reaction was so rapid that accurate measurements could not be made by the method employed. It may be noted that the velocity constant is more than tripled for a 10° rise in temperature. These are rather remarkable results in view of the fact that water is eliminated during the reaction as the sulfuric acid is diluted. Frequently, reactions which proceed in the presence of sulfuric acid are markedly retarded when even small amounts of water are added, as the negative catalytic effect increases exponentially. This is true of the decomposition of oxalic acid by sulfuric acid, and has been explained[4] by the assumption that the

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[3] Behr and van Dorp, *Ber.*, **7**, 578 (1874).

[4] Bredig and Lichty, *J. Phys. Chem.*, **11**, 225 (1907).

reaction is dependent on the preliminary formation of an addition compound of sulfuric and oxalic acid; the addition of water results in a diminution in the amount of this complex formed.[5]

Since in the oxalic acid decomposition an addition of 0.05% of water, added at 25°, reduces the speed of reaction to one-sixth of that when no water is present, it would appear probable that the *o*-benzoylbenzoic acid condensation differs fundamentally from reactions of the oxalic acid type.

It might be thought that a monomolecular constant was obtained simply because an excess of the condensing agent was used, but experiments using much smaller ratios of reactant to condensing agent, down to 1:6, gave a good constant ($K = 0.238$, average deviation 1%, at 75°). When acids (sulfuric) of strength varying from 86–96% were used in the condensation, constants were also obtained. The results from runs with different acid concentrations were compared by plotting the amount of anthraquinone produced in a given time against acid concentration. It may be seen from Curve I, which is a straight line within the experimental error, that the condensing power of the acid solution is directly proportional to the sulfuric acid content. The conclusions to be drawn from these experiments are: the one molecule of water produced during the formation of anthraquinone from *o*-benzoylbenzoic acid has little or no retarding effect on the reaction velocity and does not cause deviation from the monomolecular order as the reaction proceeds; water added to the sulfuric acid does have a retarding action and in direct proportion to the amount added, but the effect is not as great as in reactions of the oxalic acid type.

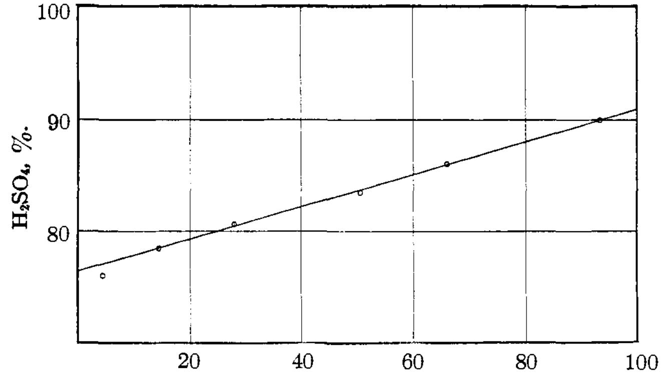

Fig. 1.—Theoretical yield when heated for 4 hours at 75°, %.

Formation of Anthraquinone from Esters and Acyl Derivatives.—It has been found that esters of *o*-benzoylbenzoic acid, which presumably have the formula $C_6H_5COC_6H_4COOR$, may be condensed by

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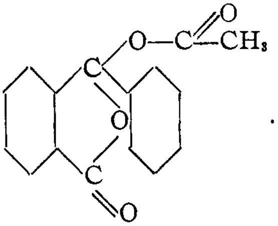
[5] Taylor, *J. Phys. Chem.*, **27**, 322 (1923).

sulfuric acid to anthraquinone, and in the case of the methyl, ethyl and *iso*propyl compounds the reaction is clean-cut and the yields are nearly as high as with the free *o*-benzoylbenzoic acid. Here, of course, the alcohols are eliminated instead of water. With esters containing alkyl groups of higher carbon content the reaction is complicated by the formation of unidentified by-products and the yields are not good. This is true of the normal butyl ester, which is a viscous liquid.

When equimolecular quantities of the methyl, ethyl and *iso*propyl esters are treated with concentrated sulfuric acid under the same conditions, the yields of anthraquinone are almost identical, but are smaller than with the free *o*-benzoylbenzoic acid: methyl ester 1.25 g., ethyl ester 1.23 g., *iso*propyl ester 1.28 g. of anthraquinone. Apparently the velocity of the ester reaction is independent of the particular alkyl group present and lower than that of the free acid due to a reaction between the alcohol and sulfuric acid which diminishes the concentration of the latter.

o-Benzoylbenzoic acid may be acylated, and it undoubtedly reacts with acetylating reagents in the enolic form, so that the structure of the acetyl derivative is . It was interesting to find out whether this compound could be condensed to anthraquinone and to compare the rate of the reaction with that of the free acid and the esters. The results indicated that the condensation took place with even greater ease than that of the esters and, in fact, is comparable with that of the free acid: acetyl derivative 1.40 g., *o*-benzoylbenzoic acid, 1.39 g. of anthraquinone. It was previously determined that glacial acetic acid and acetic anhydride did not effect the condensation of *o*-benzoylbenzoic acid.

Mechanism of the Reaction.—In order to account for the fact that this condensation, under our experimental conditions, gives a constant for a monomolecular reaction over the whole range, we must either assume an hypothesis in which two opposite effects just balance each other and the results are more or less due to chance, or that the reaction proceeds in such a way that all of the water is eliminated at the start and rapidly as compared to the subsequent reaction which we measure. As regards the first possibility, Francis,[6] from a study of certain ionic reactions, concludes that "the reactivity of a dissolved substance is increased by a change in environment in a direction which will tend to throw it out of solution." We have this condition in the *o*-benzoylbenzoic acid con-

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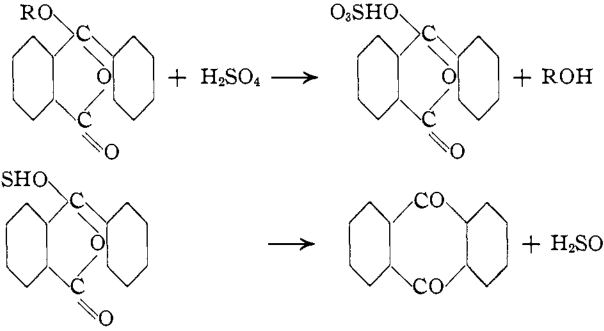
[6] Francis, This Journal, **48,** 662 (1926).

densation: water is eliminated and the solubility of the organic acid is appreciably lowered. On the other hand, the water dilutes the sulfuric acid and diminishes its efficiency as a condensing agent. In order that a monomolecular curve may be obtained, based on the concentration of the *o*-benzoylbenzoic acid, it is necessary that these two opposing effects be equal. It seems to us unlikely that such an explanation is the true one and we are inclined to believe that our experimental results point to a somewhat less complicated mechanism.

The similarity in the rates of condensation of the three esters indicates that the actual elimination of alcohol is not the reaction which is measured but that the *o*-benzoylbenzoic acid ester first reacts rapidly with the sulfuric acid and afterwards there is a slow decomposition of the resulting compound. It would seem probable that the free *o*-benzoylbenzoic acid behaves similarly. The equality of rates when the free acid and the acetyl derivative are condensed points to the same thing and suggests further that the two are in the same tautomeric condition during the reaction, that is, in the enolic form. The steps in the process are indicated by the following equations:

Fast reaction
R = H, Alkyl, Acyl

Slow reaction



The elimination of water during the fast reaction explains why it has no retarding effect in the process as measured, although when water is actually added to the sulfuric acid beforehand, the rate is lowered. However, the formation of sulfuric acid during the slow reaction would seem to reverse the difficulty since the increased acid concentration should accelerate the reaction. That it does not do so may be explained by the formation of an addition compound of one molecule of sulfuric acid and one of anthraquinone, which prevents the acid eliminated from being effective in the condensation. There is ample evidence for the formation of such addition complexes between concentrated sulfuric acid and organic compounds containing oxygen.[7]

An attempt was made to show directly by the freezing-point method the existence of the addition compound. This was not successful due to

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[7] Kendall and Carpenter, This Journal, **36**, 2498 (1914).

the fact that at the high melting points encountered, with even moderate concentrations of anthraquinone, there was decomposition and probably sulfonation. The formation of addition compounds is used frequently to explain reactivity, but in this case there is no appreciable reverse reaction and the only effect of the addition compound is to prevent the eliminated sulfuric acid from functioning as a condensing agent.

Experimental Part

For the qualitative determination of anthraquinone the anthraquinol test was used: heating with zinc dust and dilute sodium hydroxide solution produces a red color. In the preliminary experiments the depth of color was used as a rough estimation of the amount formed.

In determining the anthraquinone quantitatively use was made of the fact that it is insoluble in water and sodium hydroxide solution, while the *o*-benzoylbenzoic acid is soluble both in hot water and alkali solutions. The reaction mixtures, contained in large test-tubes fitted with rubber stoppers and calcium chloride tubes, were heated in a constant-temperature bath for definite lengths of time. The solutions were poured into cold water, stirred, heated to 80–90° and allowed to settle for five minutes. The more or less clear liquid was decanted off through a small Büchner funnel. To the precipitate in the beaker 2 *N* sodium hydroxide solution was added to definite alkalinity, the mixture was stirred and warmed and the precipitate collected on the funnel used above. After washing with hot water until the washings gave a neutral reaction with litmus, the anthraquinone was dried on the funnel for four hours at 110°. It was finally carefully removed to a clock glass, dried and weighed to constant weight. The average experimental error was less than 1%.

Summary

Attempts have been made to form anthraquinone by the elimination of water from *o*-benzoylbenzoic acid by various methods.

The reaction in which sulfuric acid is used as the condensing agent has been studied, and an explanation of the mechanism of this type of reaction has been offered.

It has been found that the esters and acyl derivatives of *o*-benzoylbenzoic acid form anthraquinone under the same conditions as the free acid.

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