not, or to any appreciable extent, the monomeric trimethylethylene nitrosate. The blue coloration is caused by a distillable, blue liquid, constituting only 20–25% of the total reaction product, which could not be polymerized, nor solidified at −80°. Oxidation as well as addition apparently enters into its formation. The remainder of the liquid reaction product is composed of the nitrous ester of 3-nitro-2-methylbutanol-2, constituting at least 35% of the total reaction product, and high boiling, complex oils, representing 10% of the total product, which could not be characterized.

CAMBRIDGE, MASS. RECEIVED JANUARY 26, 1937

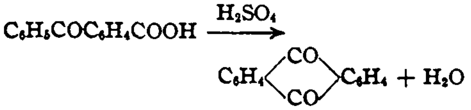
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ROCHESTER]

A Kinetic Study of the Sulfuric Acid Condensation of *o*-Benzoylbenzoic Acid[1]

BY CHARLES W. DEANE

Both for considerations of kinetic theory and for its practical interest as the principal step in the industrial synthesis of the dye intermediate, anthraquinone, an extension of the velocity measurements on the decomposition of *o*-benzoylbenzoic acid, particularly in fuming sulfuric acid concentrations, appears especially valuable.

The major historical points appeared in an earlier report[2] on this reaction



$$C_6H_5COC_6H_4COOH \xrightarrow{H_2SO_4} C_6H_4\langle{}^{CO}_{CO}\rangle C_6H_4 + H_2O$$

Since 1929 Wiig,[3] also Hammett and his co-workers,[4,5] have used the data upon *o*-benzoylbenzoic acid in dealing, respectively, with Taylor's theory of negative catalysis and with correlations of the kinetics to the acidity function, H_0.

With reference to Fig. 1, a graphical analysis using the data of Gleason and Dougherty shows that rather than as reported to the contrary,[2] *o*-benzoylbenzoic acid is not exceptional, but is like oxalic acid in having the velocity constant *k*, as a logarithmic or exponential function of the water present. The extra dotted line shows the result of using Gleason and Dougherty's kinetic value obtained at a decomposition of but 4% which resulted from employing an inflexible four-hour period to measure the reaction rate.

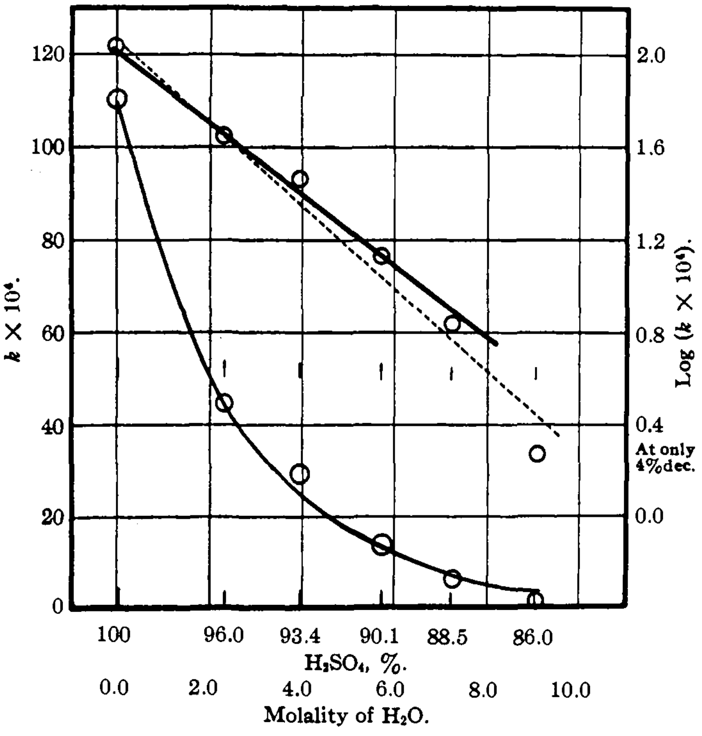


Fig. 1.—The velocity constant *k* for the condensation of *o*-benzoylbenzoic acid by sulfuric acid at 75°. Analysis of data obtained by Gleason and Dougherty.[2]

The main objectives in the present work have been to extend the data by certain basic improvements in the general method of Gleason and Dougherty,[2] and to obtain precise results at the far higher reaction speeds due to fuming sulfuric acid. This extension of data was undertaken to check general theoretical predictions of the kinetic effects[3] in the unexplored regions of fuming sulfuric acid.

Among the exceptional features and advantages afforded by this reaction for kinetic studies

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[1] The summary of a thesis presented to the Graduate School of The University of Rochester in partial fulfilment of the requirements for the degree of Master of Science.

[2] Gleason and Dougherty, THIS JOURNAL, **51**, 310 (1929).

[3] Wiig, *ibid.*, **52**, 4742 (1930).

[4] Hammett, *Chem. Rev.*, **16**, 67 (1935).

[5] Hammett and Deyrup, THIS JOURNAL, **54**, 2721 (1932).

are: a single reaction product, besides the equivalent of water, results; this is obtained instantaneously by a dilution of the reaction mixture, and accurate gravimetric measurements are possible; the reactants and products remain in the liquid phase; the substrate concentrations employed can be relatively very high; any slight side products of the reaction play in it a very negligible part.

Experimental Part

Preparation and Purification of Materials.—The following method of purifying *o*-benzoylbenzoic acid, similar to that used in the Eastman Synthetic Laboratories, is based on 500 g. of the original material. In a 1-liter wide-mouthed flask heat over a free flame to about 80° with mechanical stirring, 335 g. (5.55 moles) of glacial acetic acid (99.9%, m. p. 16.6°, sp. gr. 1.05). A current of air properly blown around the neck of the flask prevents any acetic acid vapors from flowing down around the flask to the heat source and igniting. With the temperature of the acetic acid at 80–85°, slowly add 500 g. (2.38 moles) of *o*-benzoylbenzoic acid, m. p. 127°. After continued stirring until this acid is dissolved, filter the mixture through flannel. While the filtrate is still hot pour it into a 2-liter flask and add cold water until the solution commences to become cloudy. Now add no more water until crystals of *o*-benzoylbenzoic acid begin to appear, which with mechanical stirring occurs within five minutes. At this point add slowly more cold water (if water is added too rapidly, undesirable large lumps of an *o*-benzoylbenzoic acid aggregate form) until the 2-liter flask is filled. With external cooling by a water jet, continue mechanical stirring until the mixture is cold. Filter the crystals by suction, and wash well to remove any remaining acetic acid. Accomplish the removal of the last water in a hot cabinet, drying the material at 105–110° on glass or porcelain.

The purified *o*-benzoylbenzoic acid when dry melted at 127.2–128.5° (corr.). Both Richter's "Lexikon" and the "International Critical Tables" give a m. p. of 127° for water-free material. Tests on the above purified material by twelve hours of drying at 110–115° showed a loss of weight of less than 0.2%. The water-absorbing power of this material on exposure to ordinary laboratory conditions of humidity was negligible (0.002%). Before purification, this material, upon heating for four hours in an oven at 110–115°, proved to be 3 to 5% volatile. Because the *o*-benzoylbenzoic acid furnished (Eastman product) became a deep brown on solution in sulfuric acid it was conjectured that, despite a sharp melting point, small aggregates of foreign materials might be causing coloration, or that possibly a breakdown and carbonization was occurring. Tests on the carefully purified materials, however, resulted in colored solutions both for anthraquinone and for *o*-benzoylbenzoic acid. This is in line with the basis of recent colorimetric determinations of acidity in the highly concentrated acids[4,5] in which slight concentrations of anthraquinone are used as indicators.

Three lots of sulfuric acid corresponding to 94.86, 100.42 (1.8% fuming), and 105.92% (26.2% fuming) were employed. Except for the first, these were prepared by mixing c. p. 95% sulfuric acid with Baker and Adamson reagent quality fuming sulfuric acid, 30%, in the calculated proportions for approximating the desired strengths. By precipitation as barium sulfate four samples of each were analyzed, due precautions being taken in weighing and manipulation to prevent either sulfur trioxide loss or moisture absorption. An independent and fuller check, as it included the calculating and mixing procedure universally employed in the experiments to obtain the sulfuric acid strengths used, was obtained by mixing in the calculated proportions 94.86 and 100.42% sulfuric acid for a 100% acid, and taking its melting point. By a triple determination this was 10.38°, or the acid thus proved to be within 0.1% of 100% by comparison with a plot of the data of Hantzsch[6] in which per cent. water concentration in the sulfuric acid was plotted against the melting point.

Apparatus and Procedure.—Solutions of *o*-benzoylbenzoic acid in sulfuric acid of the desired strength were prepared in 200-cc. round-bottomed flasks provided with propeller stirrers and adequately protected against the access of moisture from the air. In general 8.1021 g. of the ortho acid was added to 35 cc. of sulfuric acid solution at the reaction temperature and the stirring started. Independent tests showed that within six to nine minutes thereafter the temperature of the solutions came within one-tenth of a degree of that prevailing in the surrounding thermostat (constant within 0.1°), whereupon an initial sample was removed. Subsequent samples were removed by means of a 5-cc. pipet at 0.25, 0.40, 0.60, and 0.75 of the life period of the reaction, delivered into 100 cc. of water and analyzed according to the procedure of Gleason and Dougherty,[2] except that an asbestos mat in a Gooch crucible was employed for filtration.

The initial concentration, *a*, was ascertained in two ways; either by analysis after allowing the reaction to go to completion in triplicate samples, or by calculation from the original amounts of ortho acid added, correcting in each case for the expansions due to the temperature change and to the addition of the ortho acid. These corrections were at 75° 19.6 and 20.0%, and at 85° 20.1 and 20.4%, for 98.0 and 105.9% sulfuric acid, respectively.

Results

Completeness and Order of the Reaction.—Quantitative yields of anthraquinone from *o*-benzoylbenzoic acid have been reported.[2] In 8% fuming sulfuric acid, the author found the yields above 99%; however, at concentrations above 20% fuming acid, yields fell to 97–98%.

A set of typical kinetic measurements and the computed velocity constants, assuming a unimolecular reaction, appear in Table I.

As can be seen from the last column, the value of the constant decreases slightly as the reaction progresses, doubtless due to the water formed during the reaction. Further proof that the reaction is indeed unimolecular was obtained

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(6) Hantzsch, *Ber.*, **55**, 953 (1922); **63**, 1782 (1930).

TABLE I

A TYPICAL EXPERIMENT AT 75°

Sulfuric Acid = 100.4% (SO_3 = 1.8%)

Equiv. wt. anthraquinone at "zero" time in 5 cc. of solution = 0.7599 g. = a

t, min.	*a* − *x*	*k* × 10^4, min.$^{-1}$
20.0	0.5894	127.0
40.2	.4572	126.4
50.0	.4081	124.4
65.0	.3541	121.8
		Average, 124.9 or 125

by similar experiments at half the ortho acid concentration above, when values resulted whose average was 125.1.

The Effects of Water and of Sulfur Trioxide on the Reaction Rate.—Based on previous findings of sulfur trioxide and of water as negative inhibitors upon the oxalic, malic and the citric acid decompositions,[7–9] a maximum rate of decomposition would be expected with *o*-benzoylbenzoic acid. Tables II and III summarize the average velocity constants for each set of experiments at 75 and 85°. The mean deviation of the half-life average *k*'s is less than 0.4%, and at comparable points, the data agree well with the values of Gleason and Dougherty.[2] These determinations indicate that the ortho acid is really an exceptional case to the predicted maximum[8] based on Taylor's theory of negative catalysis.[10]

TABLE II

THE EFFECTS OF WATER AND OF SULFUR TRIOXIDE AT 75°

Molality of *o*-benzoylbenzoic acid = 0.55

% H_2SO_4	Molality H_2O	Molality SO_3	Average values of *k* × 10^4 for each experiment		Final av. *k* × 10^4
96.0	2.314		48.1		48.1
98.0	1.134		77.3	77.7	77.5
100.0	0.000	0.000	118.7	117.6	118
100.4		.233	124.9	124.9	125
101.8		1.086	128.3–129.0	129.1	129
103.16		2.033	135.8	136.3	136
104.5		3.122	145.5	144.7	145
105.9		4.434	170.4	171.0	171

TABLE III

THE EFFECTS OF WATER AND OF SULFUR TRIOXIDE AT 85°

Molality of *o*-benzoylbenzoic acid = 0.55

% H_2SO_4	Molality H_2O	Molality SO_3	Average values of *k* × 10^4 for each experiment		Final av. *k* × 10^4
98.0	1.134		227.1	229.3	228
100.0	0.000	0.000	344.1	342.8	343
100.4		.233	373.3	375.1	374
101.8		1.086	380.6	383.1	381
			380.8		
103.2		2.033	384.1	385.0	384
			386.8	381.8	
104.5		3.122	416.7	419.1	418
105.4		3.944	441.2	436.8	439
105.9		4.434	458.1	456.4	457
106.5		5.055	477.8	486.2	481

Figure 2 shows the relative effects of water and of sulfur trioxide upon the logarithm of the velocity constant, *k*. Up to the 100% point, the molality (moles per 1000 g. of solvent) of the inhibitor, water, plotted against the logarithm of *k* gives a straight line. Beyond the 100% point, the slope of the line lessens considerably, being nearly horizontal from 2% fuming acid to approximately the 14% point. Despite special experimental care, no peak was found at 14% sulfur trioxide, which point may possibly be the maximum for oxalic acid.[7] At 14% fuming acid and higher, the decomposition curve for *o*-benzoylbenzoic acid rises to assume a slope approximately one-fifth of the slope caused by a corresponding decrement in the molality of water below the 100% sulfuric acid point.

The Effect of Temperature on the Reaction Rate.—The development of a correlation of kinetic data with various postulated factors and mechanisms may be aided considerably by data on the temperature coefficient, and by a tabulation of *E*, the energy of activation. These values are given in Table IV for which the data of Tables II and III have been used to derive the values presented. The values of *E* were calculated from the following integrated form of the Arrhenius equation

$$E = \frac{1.98 \times T_2 \times T_1 \times \log k_2/k_1 \times 2.303}{T_2 - T_1}$$

The ratio of k_2/k_1 was evaluated by a large scale

TABLE IV

ENERGIES OF ACTIVATION AND TEMPERATURE COEFFICIENTS (FOR 75 TO 85°)

% H_2SO_4	Molality H_2O	Molality SO_3	k_2/k_1	*E*, cal.
98.0	1.134		2.94	26,700
100.0	0.000	0.000	2.92	26,400
100.4		.233	2.97	26,900
101.8		1.086	2.96	26,800
103.2		2.033	2.98	26,900
104.5		3.122	2.84	25,800
105.4		3.244	2.74	24,900
105.9		4.434	2.70	24,500
			Av. *E* =	26,100

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(7) Wiig, THIS JOURNAL, **52**, 4737 (1930).

(8) DeRight, *ibid.*, **56**, 618 (1934).

(9) Wiig, *ibid.*, **52**, 4729 (1930).

(10) Taylor, *J. Phys. Chem.*, **27**, 322 (1923).

plot of Fig. 2 on cross section paper. A computation of the data of Gleason and Dougherty yields temperature coefficients of 3.2 and 3.4, respectively, for the intervals 85–75° and 75–65° at 96% sulfuric acid. The results presented here indicate a temperature coefficient somewhat below three, as shown in Table IV, but the agreement is reasonably satisfactory. It is to be noted that the sulfur trioxide, *acting as a positive catalyst*, diminishes the temperature coefficient.

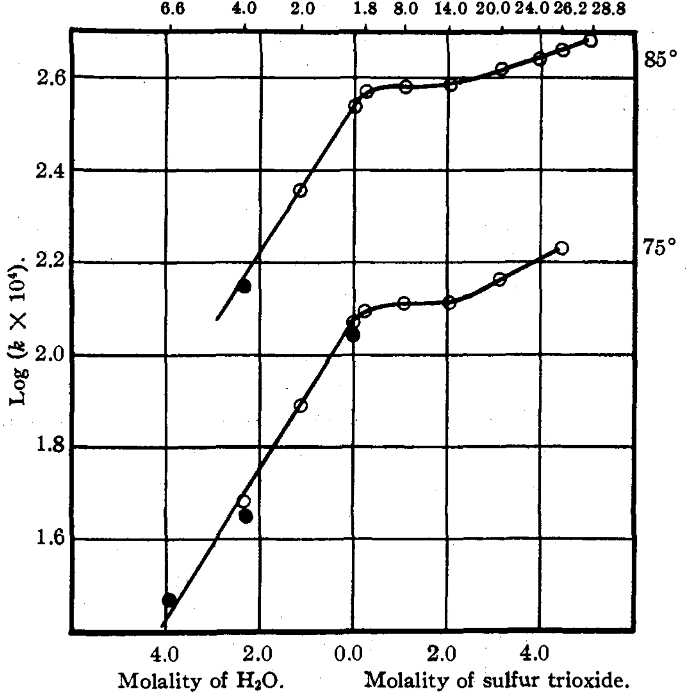

Fig. 2.—The velocity constant k for the condensation of *o*-benzoylbenzoic acid by sulfuric acid at 75 and 85°: ●, Gleason and Dougherty, ○, Deane.

Discussion

Figure 3 compares the effects of corresponding molalities of water and of sulfur trioxide upon the rates of decomposition of three organic acids with sulfuric acid. Table V lists these acids and states the widely variant effects of the catalysts upon the decomposition velocities. The unusual feature for *o*-benzoylbenzoic acid is the behavior of sulfur trioxide, particularly in fuming acid concentrations above 14%, as a positive catalyst.

TABLE V

COMPARISON OF THE INHIBITING POWER OF WATER AND OF SULFUR TRIOXIDE UPON THE DECOMPOSITION OF ORGANIC ACIDS

Organic acid	Relative inhibiting power For water	 For sulfur trioxide
Oxalic	++, very strong	o, weak, if at all
Malic	++, very strong	++, very strong
o-Benzoylbenzoic	o, +, quite weak	o, – not inhibition, but acceleration

Possible correlations on the basis of effective ionic and molecular concentrations to explain the sulfuric acid decompositions of the organic acids are now considered. Because organic oxygen compounds are highly ionized basically in strong sulfuric acid, it is possible that factors of acid–base catalysis are effective. Assuming that the hydrogen ion concentration is related to reaction velocity, then the kinetic data on *o*-benzoylbenzoic acid indicate an increasing acidity in fuming sulfuric acid. An interesting question is the validity of this correlation above 100% sulfuric acid. Thus, to test whether the hydrogen ion concentration in terms of the acidity function H_0,[5] is a prime variable, its measurement in fuming sulfuric acid is in order. Because of the variant kinetic features exhibited by the oxalic and malic acid decompositions (Fig. 3 and Table V) it definitely appears that other phenomena predominate, and that these reactions are *not* governed by simple ionic factors.

To consider the kinetics of *o*-benzoylbenzoic acid from the molecular standpoint up to 28.8% fuming sulfuric acid, also, the extent of the determinations is limited. Of the five organic acids[1,7,9,11,12] only the oxalic acid study[7] presents data over a sufficient range to permit general comparisons with the kinetics of the *o*-benzoylbenzoic acid.[13] In Fig. 3 it will be noted that the ortho acid rate remains nearly horizontal from approximately 2 to 14% fuming acid. This 14% point also appears the point of maximum decomposition velocity for oxalic acid. Above 14% sulfur trioxide, however, a marked difference is to be noted: the oxalic acid decomposition is probably very slightly inhibited, while that of *o*-benzoylbenzoic acid is definitely accelerated by additional sulfur trioxide.

To explain these phenomena molecularly, the oxalic acid behavior up to the 14% point is due

(11) (Formic), DeRight, THIS JOURNAL, **55**, 4761 (1933).

(12) (Triphenylacetic), Dittmar, *J. Phys. Chem.*, **33**, 533 (1929).

(13) However, it may be noted that in the cases for citric and malic acids, the reaction in fuming sulfuric acid at 14% sulfur trioxide approaches zero rate at room temperatures.

to the decreased water (a very strong inhibitor here) in the fuming sulfuric acid by the increase of sulfur trioxide. Above 14% sulfur trioxide the reaction is that of oxalic acid with sulfuric acid, slightly inhibited by the sulfur trioxide. This is in accord with Taylor's theory of negative catalysis.[10]

To rationalize the exceptional *o*-benzoylbenzoic acid, a new case may be postulated in that the predominant reaction above the 14% point is the decomposition caused by sulfur trioxide itself, or by pyrosulfuric acid. No inhibiting complex with sulfur trioxide is effective, so that Taylor's theory of negative catalysis does not here apply in fuming sulfuric acid above 14% sulfur trioxide.

Below 14% sulfur trioxide the same mechanism may apply for *o*-benzoylbenzoic acid as for oxalic acid. By Fig. 3 and Table V water is shown a relatively weak inhibitor for *o*-benzoylbenzoic acid. An explanation, then, as to why its curve (Fig. 3) remains flat to about 14% sulfur trioxide follows: the inhibiting water is furnished by the equilibrium $H_2SO_4 \rightleftarrows SO_3 + H_2O$. Owing to a displacement of this to the right by temperatures of 75 and 85°, the experiments for *o*-benzoylbenzoic acid require a strength of about 14% sulfur trioxide to overcome the water resulting from the dissociation at these higher temperatures.

A mechanism for the decomposition of *o*-benzoylbenzoic acid by sulfuric acid has been proposed by Gleason and Dougherty.[2] Their velocity measurements upon which this was partly based, however, were not such as would disclose the slowing down of the reaction during its course because the reaction speed is relatively quite insensitive to the slight amount of water formed. Inasmuch as the decrease of *k* as shown in Table I consistently occurred in all these experiments, the fast reaction they postulated because of no falling off of the rate receives no support here. The proposed intermediate reaction may take place but probably is not instantaneous.

From the industrial angle, the kinetic data above reported deal directly with a principal step in the production of anthraquinone. By the data presented, comparisons can be made of the relative condensing powers of concentrated and fuming sulfuric acids.

The author wishes to express his heartfelt appreciation to Dr. Edwin O. Wiig for his helpful suggestions and sincere interest in the progress of this work.

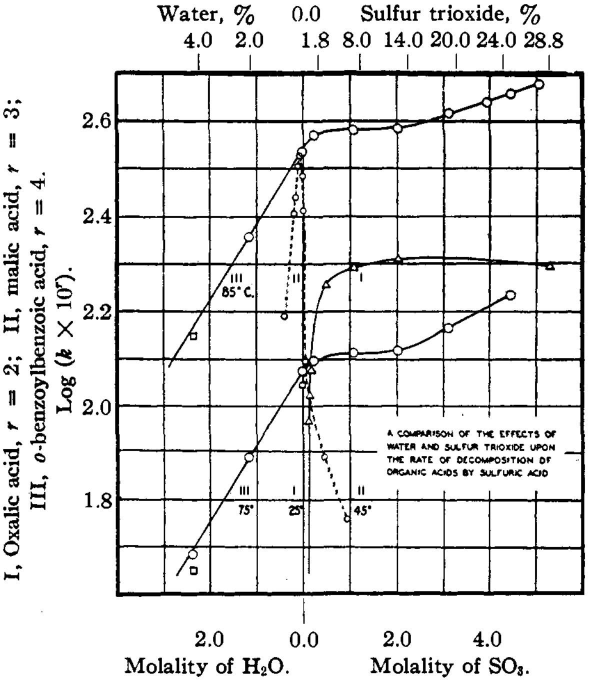

Fig. 3.—A comparison of the effects of water and of sulfur trioxide upon the rate of decomposition of organic acids by sulfuric acid.

Summary

This investigation of the decomposition velocity of *o*-benzoylbenzoic acid in concentrated and fuming sulfuric acid presents (1) an adequate method of determining the reaction rates in fuming sulfuric acid; (2) a suitable means of purifying *o*-benzoylbenzoic acid; (3) experimental evidence that the reaction follows the unimolecular law, and that yields are quantitative; (4) a check of earlier determined reaction rates and new reaction rate data, with energies of activation, for the decomposition of *o*-benzoylbenzoic acid in 98 to 106.5% sulfuric acid at 75° and 85°; (5) the discovery that, unlike other organic acids studied to date, *o*-benzoylbenzoic acid has no maximum decomposition velocity for a definite water or sulfuric trioxide concentration; and that sulfur trioxide at concentrations above 14% acts as a positive catalyst; (6) theories for the reaction mechanism briefly discussed and an explanation of the observed kinetics.

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