[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

THE DECOMPOSITION OF CITRIC ACID BY SULFURIC ACID

BY EDWIN O. WIIG[1]

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The effect of inhibitors on the decomposition of certain organic acids by sulfuric acid has been explained on the basis of the theory of negative catalysis proposed by Taylor,[2] who concluded from Lichty's study[3] of the retarding influence of water on the velocity of decomposition of oxalic acid that inhibitors functioned as negative catalysts by reducing, through molecular compound formation, the active mass of one or both of the reactants. Taylor's theory has been substantiated more or less by experimental investigations of the rate of decomposition of formic, malic, *o*-benzoylbenzoic and triphenylacetic acids in sulfuric acid by Schierz,[4] Whitford,[5] Gleason and Dougherty[6] and Dittmar,[7] respectively. However, the results obtained in these studies are not always in agreement with what might be expected on the basis of the theory. A study of the effect of inhibitors on the decomposition of citric acid by sulfuric acid was undertaken in the hope of clearing away some of the present inconsistencies and for the purpose of testing still further the theory of negative catalysis involved in these reactions.

The reaction between citric acid and sulfuric acid first was studied about 1839 by Robiquet,[8] who observed that on heating the two a gas was evolved which at first consisted of carbon monoxide and later of a mixture of that gas with carbon dioxide. Various workers investigated the reaction without throwing any light on it until, in 1884, it was finally explained by von Pechmann.[9] Sulfuric acid decomposes citric acid into carbon monoxide, water and acetone-dicarboxylic acid according to the equation

$$(CH_2COOH)_2C(OH)COOH \longrightarrow CO + H_2O + (CH_2COOH)_2CO$$

Acetone-dicarboxylic acid, which was isolated by von Pechmann, decomposes rather readily into acetone and carbon dioxide, so that its detection had escaped earlier investigators. Fortunately, the velocity of decomposition of acetone-dicarboxylic acid in sulfuric acid at the temperatures employed in the present research is extremely small compared to the rate at which citric acid decomposes. It was necessary to correct for the

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

[3] Bredig and Lichty, *Z. Elektrochem.*, **12**, 459 (1906); Lichty, *J. Phys. Chem.*, **11**, 225 (1907).

[4] Schierz, THIS JOURNAL, **45**, 447 (1923).

[5] Whitford, *ibid.*, **47**, 953 (1925).

[6] Gleason and Dougherty, *ibid.*, **51**, 310 (1929).

[7] Dittmar, *J. Phys. Chem.*, **33**, 533 (1929).

[8] Robiquet, *Ann.*, **30**, 229 (1839).

[9] Von Pechmann, *Ber.*, **17**, 2542 (1884).

carbon dioxide evolved from acetone-dicarboxylic acid in only three slow decompositions at 35°.

Experimental Part

Preparation and Purification of Materials.—U. S. P. citric acid was recrystallized from water three times and dried over calcium chloride in a desiccator. The resulting hydrated citric acid crystals melted at 153–154°, which agrees very well with the value of 153° given by Meyer.[10]

Four lots of sulfuric acid corresponding to 100.00, 100.44, 100.50 and 100.52% were used. These acids were prepared by mixing c. p. 95–96% sulfuric acid with Baker and Adamson's reagent 30% fuming sulfuric acid, and subsequently analyzed, using due precautions to prevent the loss of sulfur trioxide or the absorption of moisture, by titration with standard alkali and by precipitation as barium sulfate. Samples of the lot which analyzed 100.00% H_2SO_4 were found to have a melting point of 10.40°, which is in good agreement with the values obtained by previous investigators.[11] The acids containing excess sulfur trioxide were mixed with the calculated amount of 95.44% acid required to give exactly 100% sulfuric acid and the melting point of the resulting mixtures was found to be 10.42°. Moreover, when used for the determination of the velocity constant at a particular concentration of acid, the various lots of acid gave concordant results. Sulfuric acid of any desired concentration between 95.44 and 100.52% was prepared by mixing the calculated quantities of the dilute and fuming acids. These acids were run out of burets filled by an all-glass siphoning system from ground glass-stoppered storage bottles. To replace the acid withdrawn, air was admitted into the storage bottles by aspiration through two bubbling bottles containing 100% sulfuric acid.

Apparatus and Method of Procedure.—The velocity of decomposition of citric acid in sulfuric acid was determined by observing the volume of carbon monoxide evolved at various times during an experiment. The reaction was carried out in 50-cc. round-bottomed pyrex flasks supported in a shaking device similar to that designed by Walton.[12] The agitator was so arranged that the flasks were immersed completely in a thermostat whose temperature was regulated to within ±0.02°. The thermometer employed was calibrated against a Bureau of Standards and a P. T. R. thermometer. Supersaturation of the reaction mixture with carbon monoxide was prevented by adding short pieces of glass rod to the flasks. Capillary tubing conducted the gas evolved to water-jacketed burets which were maintained at the same temperature as the thermostat.

The dilute and concentrated acids (total volume, 20 cc.) were run from their respective burets into the reaction flasks while the flasks were stoppered onto the buret; the pressure in the flasks was first slightly reduced so as to permit flow of the acid. The citric acid, contained in a glass capsule supported in the neck of the flask, could be dropped into the sulfuric acid when the latter had come to the temperature of the thermostat. In the preliminary experiments solid citric acid was used but the velocity constants obtained were not concordant, varying with the size of the citric acid particles and the volume of solvent. This difficulty was finally overcome by using a concentrated solution of citric acid in water (58.43% acid and 41.57% water). From 0.25 to 0.50 cc. of this solution (molality of citric acid in sulfuric acid =0.027 to 0.052) was accurately measured out into the capsules from an arbitrarily calibrated microburet. Concordant results were then readily obtained. By varying the experimental procedure it was shown that the heat evolved on adding the aqueous solution of citric acid to the

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[10] Meyer, *Ber.*, **36**, 3599 (1903).

[11] Whitford, This Journal, **47**, 953 (1925).

[12] Walton, *Z. physik. Chem.*, **47**, 185 (1904).

sulfuric acid had no effect on the reaction velocity. Later a solution of citric acid in approximately 80% sulfuric acid was used in order to eliminate any possibility of citric acid crystallizing before dissolving in the reaction mixture. Obviously, the water thus added with the citric acid was always included in calculating the strength of the sulfuric acid.

Results

Completeness and Order of Reaction.—In the preparation of acetonedicarboxylic acid by the decomposition of citric acid in fuming sulfuric acid yields of 92–97% have been reported.[13] The decompositions effected in this research always gave the theoretical yield of carbon monoxide within the limits of experimental error, except that in solutions containing more than about 0.5% sulfur trioxide the reaction is only about 80% complete. For example, four experiments at 25° in 96.46% H_2SO_4 gave an average of 46.65 cc. of carbon monoxide compared with the theoretical yield of 46.60 cc., while from four samples at 15° in 97.34% H_2SO_4 was evolved an average of 41.63 cc. compared with 41.70 cc. for quantitative decomposition. At the end of the experiments the sulfuric acid was nearly always colorless, indicating the absence of side reactions due to oxidation.

The decomposition of citric acid, although undoubtedly involving reaction with sulfuric acid, follows the unimolecular law. This was indicated by the "constancy" of the velocity constants obtained at various times in any one experiment as illustrated by the data given in Table I. That the velocity constants were independent of the rate of shaking was demonstrated by the use of four shaking speeds.

Table I

A Typical Experiment

Temp., 35°; molality of H_2O, 1.67 (97.08% H_2SO_4); a = 42.4 cc.

t	x	$a - x$	$k \times 10^3$
2	7.8	34.6	102
4	14.2	28.2	102
6	19.2	23.2	100
8	23.4	19.0	100
10	26.8	15.6	100
12	29.4	13.0	99
14	31.7	10.7	98
16	33.4	9.0	97
22	37.3	5.1	96

At 50% decomposition $k \times 10^3 = 100$

The values of k in the above table were calculated by means of the equation for a unimolecular reaction

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

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[13] "Organic Syntheses," John Wiley and Sons, Inc., New York, **1925**, Vol. V, p. 5.

Volumes of carbon monoxide were substituted for concentrations of citric acid and the time *t* is in minutes. The concentration of water has been expressed in molality, *i. e.*, the number of moles of solute per 1000 g. of solvent.

It will be observed that the velocity constants in Table I fall off slightly. This is due to the water formed during the reaction, for at higher concentrations of sulfuric acid, where the reaction is much more sensitive to small amounts of water, the velocity constants decreased still more, while in more dilute solutions the values of *k* scarcely changed at all. The third product of the decomposition, acetone-dicarboxylic acid, may also contribute to the falling velocity constant. The addition of 0.047 molality acetone-dicarboxylic acid (equivalent to that formed during an experiment) to a reaction mixture containing 1.04 molality water changed $k \times 10^3$ from 78.2 to 65.3 at 25°, whereas an equal quantity of water would decrease $k \times 10^3$ to 67.7. Thus this acid appears to be fully as strong an inhibitor as water.

Independence of the velocity constant of the initial concentration of the reactant is another criterion of a unimolecular reaction. In 98.16% H_2SO_4 at 25° the average values of $k \times 10^3$ obtained with initial concentrations of citric acid of 0.051 and 0.027 molality were 77.2 and 80.5, respectively. The difference is small and almost within the limits of experimental error. The reaction is also apparently homogeneous since the addition of 5 g. of clean, dry sand to the reaction mixture had no effect.

The Effect of Water on the Reaction Rate.—In the hope of determining the mechanism of the inhibition by water and other substances, a

TABLE II

EFFECT OF WATER ON THE REACTION VELOCITY AT 15°

Water, %	Molality of water	$k \times 10^3$	Water, %	Molality of water	$k \times 10^3$
0	0	153	1.27	0.72	37.1
0.10	0.056	212	2.14	1.22	12.4
.19	.10	215	2.66	1.52	7.8
.26	.14	210	3.29	1.89	4.32
.39	.22	180	3.93	2.27	2.52
.68	.38	105	4.81	2.80	1.27
.81	.45	83.4			

TABLE III

EFFECT OF WATER ON THE REACTION VELOCITY AT 25°

Water, %	Molality of water	$k \times 10^3$	Water, %	Molality of water	$k \times 10^3$
0	0	440	1.27	0.72	156
0.052	0.029	630	1.84	1.04	78.2
.16	.09	740	2.41	1.37	41.5
.25	.14	795	2.97	1.70	25.0
.33	.18	760	3.54	2.03	15.4
.45	.25	650	4.44	2.58	7.2
.71	.40	387	5.23	3.07	4.16
1.00	.56	248			

TABLE IV

EFFECT OF WATER ON THE REACTION VELOCITY AT 35°

Water, %	Molality of water	$k \times 10^3$
0	0	1210
0.10	0.056	1700
.19	.10	1940
.28	.16	2090
.40	.22	2120
.50	.28	1920
.70	.38	1360
1.18	0.66	690
1.72	0.94	356
2.42	1.38	157
2.92	1.67	101
3.54	2.04	59.3
4.39	2.55	31.2
5.18	3.03	17.5

study was made of the influence of water on the velocity of decomposition. The data obtained are summarized in Tables II, III and IV, and are represented graphically in Fig. 1. Each value of the velocity constant is the average of those obtained at 50% decomposition in from three to twelve experiments.

From the data it can readily be seen that small amounts of water in excess of a certain minimum concentration have a very marked retarding effect on the reaction rate, the relative effect decreasing as the concentration of water increases. Similar results have been obtained by previous investigators, particularly Lichty, who found the decomposition of oxalic acid to be even more sensitive to water.

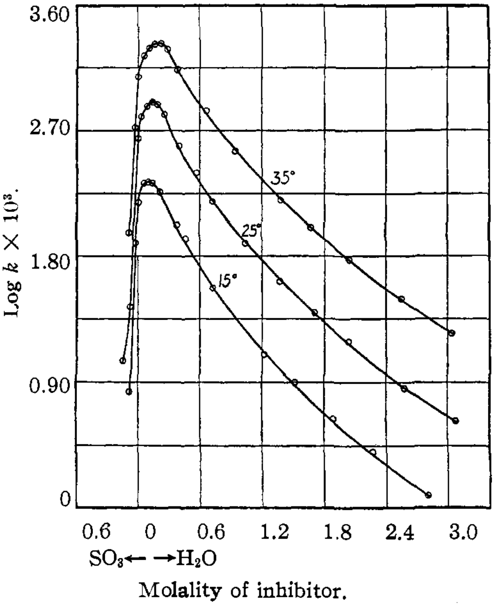

Fig. 1.—Effect of sulfur trioxide and of water on the reaction rate.

The curves for the reaction rate at various concentrations of water at 15, 25 and 35° (Fig. 1) exhibit a maximum at molalities of about 0.10, 0.14 and 0.20, respectively. This entirely unexpected result has not been observed with the other acids that have been studied and was at first rejected as being due to the measurement of the rate of solution of citric acid in sulfuric acid instead of the rate of reaction. The work was repeated using, instead of a water solution of citric acid, an 80% sulfuric acid solution in which the decomposition at ordinary temperature is negligible. On dropping the capsule containing 0.7 cc. of this solution into 20 cc. of approximately 100% sulfuric acid there can be no crystallization or precipitation of the citric acid since the solubility[14] of citric acid in aqueous solutions of sulfuric acid reaches a minimum at approximately 60% acid and then increases with increase in sulfuric acid content. It was thought that possibly the maximum really corresponded to 100% sulfuric acid and that the analysis of the acid was incorrect, but a careful rechecking of the analysis gave the same result as found originally. Furthermore, the melting point of a sulfuric acid mixture made up exactly as in carrying out a decomposition in 100% sulfuric acid, except for the replacement of the aqueous citric acid solution by a carefully weighed equivalent amount of water, was 10.42°, corresponding to the melting point of 100% acid. In addition the velocity of decomposition of oxalic acid at 25° was measured in a 100% sulfuric acid solution made by mixing the calculated amounts of 100.50% and 95.44% acids. Since oxalic acid yields equal volumes of carbon monoxide and carbon dioxide, the gases were collected over a saturated magnesium sulfate solution which had been saturated with carbon dioxide at 25°. The average of three experiments gave $k \times 10^3 = 18.0$ at 50% decomposition. By interpolation the data of Lichty[15] give 17.4 and 12.0 for $k \times 10^3$ at 50% decomposition in 100% and 99.99% sulfuric acids, respectively. Thus the acid mixtures used in these experiments were in error, on the basis of Lichty's acids, by less than 0.01% sulfuric acid, which is much less than the error involved in analysis.

It was observed that the inhibiting effect of water might be decreased by the addition of another substance. At 25° in the presence of 0.56 molality water $k \times 10^3$ is 248. When only 0.032 molality anhydrous oxalic acid was added to such a mixture, $k \times 10^3$ became 260. Possibly the oxalic acid removes some of the water through hydrate formation.

The Effect of Sulfur Trioxide on the Reaction Rate.—Since Lichty[15] observed that the decomposition of oxalic acid proceeded more rapidly in a solution containing 1% excess sulfur trioxide than in 100% sulfuric acid, while Whitford[11] found that 1% free sulfur trioxide had no effect on the velocity of decomposition of malic acid and 12.5% decreased the rate to about 60% of that observed in 100% sulfuric acid, it was important to determine the effect of the free oxide in the case of citric acid. The data obtained are given in Table V and shown graphically in Fig. 1

TABLE V

EFFECT OF SULFUR TRIOXIDE ON THE REACTION RATE

			$k \times 10^3$	
SO_3, %	Molality of SO_3	15°	25°	35°
0	0	153	440	1210
0.27	0.034	78	...	530
.67	.084	6.8	27.4	94
1.15	.15	...	11.3	..

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[14] Knox and Richards, *J. Chem. Soc.*, **115**, 520 (1919).

[15] Lichty, *J. Phys. Chem.*, **11**, 225 (1907).

as a continuation of the curves for the effect of water. The marked inhibiting effect of sulfur trioxide, even greater than water, was rather unexpected but it fits in very well with the finding of the maximum discussed in the preceding section.

The Effect of Temperature on the Reaction Rate.—Schierz and Dittmar indicate that the temperature coefficients for the decomposition of formic and triphenylacetic acids change very irregularly with the concentration of the sulfuric acid. To show that these apparent irregularities are probably due to experimental error the temperature coefficients for the decomposition of citric acid have been calculated. The curves in Fig. 1 were plotted on a much larger scale and the value of the temperature coefficient at various molalities of water was readily obtained from the distance between two curves. From the integrated form

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

of the Arrhenius equation expressing the relation between the absolute temperature and the reaction velocity constant, k, the "critical increment" or "energy of activation," E (in calories), was calculated. The results are shown in Table VI, where each value of the temperature coefficient is the average of those obtained from three separate sets of curves.

TABLE VI

TEMPERATURE COEFFICIENTS OF THE WATER INHIBITED REACTION

	Temperature coefficient		"E" in calories	
Molality of water	k_{25}/k_{15}	k_{35}/k_{25}	15–25°	25–35°
0.4	3.92	3.53	23200	22900
.6	4.09	3.70	23900	23800
.8	4.29	3.70	24800	23800
1.0	4.30	3.76	24800	24100
1.2	4.31	3.81	24800	24300
1.4	4.27	3.86	24700	24600
1.6	4.29	3.92	24800	24800
2.0	4.32	3.92	24900	24800
2.2	4.31	4.03	24800	25300
2.4	4.29	4.09	24800	25600
2.6	4.34	4.13	24900	25800
2.8	4.41	4.12	25200	25700

A study of the table reveals the fact that for the same temperature interval the temperature coefficient increases as the amount of water increases, although several values are slightly less than that at the preceding smaller molality of water. These differences, however, are comparatively small and well within the limits of experimental error. Furthermore, it is very difficult to draw a smooth curve that will average the errors in all the experimental points. The large irregularities observed by the other investigators do not manifest themselves in this investigation; in fact, when the temperature coefficients for the decomposition of triphenylacetic acid are calculated as above from Dittmar's data, the same rather regular increase in temperature coefficient with increase of water is obtained. The value of the critical increment, theoretically, is practically a constant quantity for a given reaction and it is interesting to note that there is fairly good agreement between the two values of the activation energy at a given concentration of water.

Discussion

The decomposition of citric acid, as with the other organic acids investigated, is probably best explained by the assumption of an unstable sulfuric acid–citric acid complex. From a study of the solubility of citric acid in various concentrations of aqueous sulfuric acid, Knox and Richards[14] concluded that the two acids form a molecular compound. That the compound is sufficiently stable so that indications of its presence may be obtained might seem to be an argument against its playing a role in the decomposition of citric acid. However, in the aqueous solutions employed, the unstable citric acid–sulfuric acid complex is stabilized by water, which is a powerful inhibitor of the decomposition, possibly through hydration, of which the solubility measurements give no indication.

Whitford and Dittmar have pointed out that the velocity of decomposition in sulfuric acid of the organic acids already investigated is apparently related to the strength of the acid as measured by its acid dissociation constant. On this basis the rate of reaction in the case of citric acid should be less than for malic acid, whereas experimentally a considerably higher value is found. This would indicate that there are other factors besides acid strength to be taken into consideration.

Since in 100% sulfuric acid there undoubtedly exists the equilibrium[16] represented by the equation $H_2SO_4 \rightleftharpoons H_2O + SO_3$, and since sulfur trioxide was found to be a more powerful inhibiting agent than water, an explanation readily suggests itself for the maximum in the curves showing the effect of water. As successively smaller amounts of water are used the reaction mixture approaches 100% sulfuric acid and the velocity of decomposition increases until a point is reached at which there is sufficient dissociation of the sulfuric acid into sulfur trioxide so that the accelerating effect produced by decreasing the water content is more than offset by the stronger inhibiting influence of the sulfur trioxide, and the reaction rate decreases. In agreement with this explanation, the maximum in the curves in Fig. 1 is shifted in the proper direction by an increase in temperature.

The action of the inhibitors may be explained on the basis of Taylor's theory[2] of negative catalysis in which it is postulated that the added substance decreases the concentration of the active mass of one or more of

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[16] Christiansen, *J. Phys. Chem.*, **28**, 145 (1924); *Trans. Faraday Soc.*, **24**, 596 (1928).

the reactants through compound formation. In the present case water and sulfur trioxide would be assumed to form molecular complexes with either sulfuric acid or citric acid, or with both. Such compounds are, of course, well known.

The mechanism of inhibition in the decomposition of organic acids by sulfuric acid will be discussed in detail in a later paper.

The author takes great pleasure in acknowledging his indebtedness to Professor Hugh S. Taylor for his kindly interest in the problem and to Princeton University for supplying adequate facilities for its prosecution.

Summary

The decomposition of citric acid by sulfuric acid has been found to be quantitative and to follow the unimolecular reaction law.

Small amounts of water and of sulfur trioxide both have a pronounced inhibiting influence on the velocity of decomposition.

As the concentration of sulfuric acid was increased, the reaction rate increased until a maximum, varying with temperature, was reached; further removal of water decreased the rate. No such maximum has previously been reported.

For a ten degree rise of temperature the temperature coefficient is approximately 4, and it increases fairly regularly as the water content of the sulfuric acid is increased.

The decomposition is assumed to proceed through the formation of an unstable citric acid–sulfuric acid molecular complex. Inhibition by water and sulfur trioxide may be accounted for on the basis of Taylor's theory of negative catalysis.

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THE EFFECT OF SULFUR TRIOXIDE ON THE DECOMPOSITION OF OXALIC ACID BY SULFURIC ACID

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The effect of water, and certain other substances, on the decomposition of oxalic, formic, malic, *o*-benzoylbenzoic, triphenylacetic and citric acids[2] by sulfuric acid is to inhibit to a marked degree the velocity of reaction. This would indicate that the reaction mechanisms are analogous. There is one notable exception, however, in the similarity of the inhibiting effects of added materials. Lichty[2b] observed, qualitatively,

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[1] National Research Fellow in Chemistry.

[2] (a) Bredig and Lichty, *Z. Elektrochem.*, **12**, 459 (1906); (b) Lichty, *J. Phys. Chem.*, 11, 225 (1907); (c) Schierz, THIS JOURNAL, **45**, 447 (1923); (d) Whitford, *ibid.*, **47**, 953 (1925); (e) Gleason and Dougherty, *ibid.*, **51**, 310 (1929); (f) Dittmar, *J. Phys. Chem.*, **33**, 533 (1929); (g) Wiig, THIS JOURNAL, **52**, 4729 (1930).