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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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

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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[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).

that 1% of sulfur trioxide greatly increased the velocity of decomposition of oxalic acid whereas Whitford[2d] found 1% of sulfur trioxide to have no effect, while 12.5% decreased the reaction rate in the case of malic acid to about 60% of that observed in 100% sulfuric acid. In the decomposition of citric acid[2g] sulfur trioxide has a very marked inhibiting influence, much greater than water. It was pertinent, therefore, for the theories of negative catalysis involved in these reactions to determine quantitatively the effect of sulfur trioxide on the rate of decomposition of oxalic acid.

Apparatus and Materials

The velocity of decomposition of oxalic acid was followed by observing the volume of gas (carbon monoxide and dioxide) evolved at various times during an experiment. The apparatus and procedure employed were the same as in the previous investigation.[2g] The sulfuric acid mixtures were made up as before, except that those marked "approximate" in the data were prepared by mixing the calculated weights of 30% fuming and c. p. 96% acids. These mixtures may be in error by as much as 2% sulfur trioxide but are sufficiently accurate to indicate the trend of the velocity constants with change in acid concentration. The oxalic acid (Kahlbaum's "zur Analyse") was dissolved in 95% sulfuric acid, in which the decomposition is negligible, and 0.7 cc. of this solution used in an experiment. Where necessary the water thus added was taken into consideration in calculating the final sulfuric acid concentration.

Results

As Lichty has shown that the decomposition of oxalic acid follows the unimolecular law, the velocity constants were calculated by the usual equation. The data obtained at 15 and 25° are given in Table I, where

TABLE I

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

Temp., °C.	SO_3, %	Molality of SO_3	$k \times 10^5$
25	0	0	18.0
	1.11	0.140	930
	1.47	.186	1050
	1.60	.203	1190
	4[a]	.5	1800
	8[a]	1.1	1960
	14[a]	2.0	2040
	30[a]	5.3	1960
15	4[a]	0.5	1130
	8[a]	1.1	1260
	14[a]	2.0	1430
	30[a]	5.3	1290

[a] Approximate composition.

each value is the average of $k \times 10^3$ at 50% decomposition obtained in three or four experiments. In 100% sulfuric acid $k \times 10^3$ is 18.0, which agrees very well with the value of 17.4 obtained by interpolation from Lichty's data. The results given in the table, together with the data of Lichty, are represented graphically in Fig. 1. For comparison part of the analogous curve for citric acid has been reproduced in the figure.

It will be observed that the rate of decomposition of oxalic acid in sulfuric acid increases with increase in sulfur trioxide until a maximum is reached in about 14% fuming acid, after which the rate falls off slightly. As the velocity of decomposition is extremely rapid at 25° ($t_{1/2}$ is of the order of one-third minute at 14% SO_3), a series of experiments was performed at 15° to confirm the maximum observed at 25°.

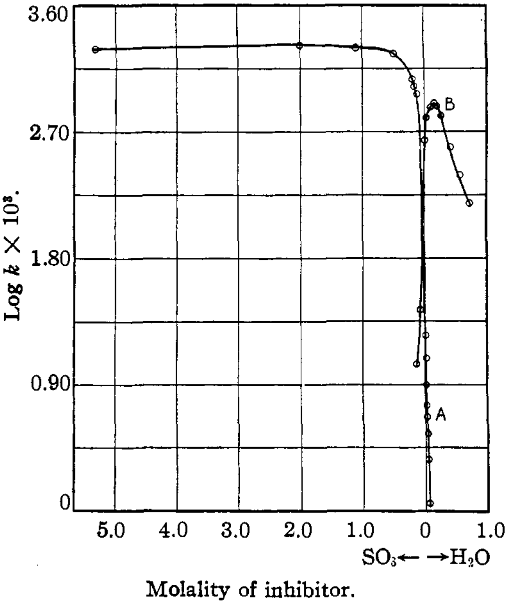

Fig. 1.—Effect of sulfur trioxide and of water on the reaction rates of oxalic and citric acids. A—oxalic; B—citric.

Discussion

The results obtained for the effect of sulfur trioxide on the decomposition of oxalic acid by sulfuric acid appear to conform with the analogous effects in the case of citric and malic acids. From the figure it may be seen that water has an extremely large inhibiting influence on the decomposition of oxalic acid while sulfur trioxide is a very weak inhibitor, as shown by the slight falling off in the velocity at a molality of 5.3. The increase in the reaction rate on increasing the sulfur trioxide molality from 0 to 2.0 may be attributed to a decrease in concentration of minute amounts of water formed by the thermal dissociation of sulfuric acid ($H_2SO_4 \rightleftharpoons H_2O + SO_3$) rather than to an accelerating effect of sulfur trioxide. The slope of the curve for the effect of water on the oxalic acid decomposition would indicate the plausibility of such an assumption. An analogous explanation was given to account for the maximum in the citric acid curve. Christiansen[3] has previously pointed out that displacement of the equilibrium $H_2SO_4 \rightleftharpoons SO_3 + H_2O$ may determine the rate at which oxalic acid decomposes, but he also sug-

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

gests that the reaction actually measured may be between oxalic acid and SO_3 or some other "sulfuric acid" which is less hydrated than H_2SO_4.

If the equilibrium constant at 25° for the reaction $H_2SO_4 \rightleftharpoons H_2O + SO_3$ were known, the concentration of water and of sulfur trioxide inhibiting, respectively, the oxalic and citric acid reactions in 100% sulfuric acid could be calculated. Fortunately there are sufficient data available in the literature so that such a calculation may be made.

Bodenstein and Katajama[4] have studied the thermal dissociation of sulfuric acid in the gas phase. From the empirical equation which they give for the variation of the equilibrium constant with temperature, K_c (in moles/liter) may be calculated for the constant boiling acid (317°).[5] Since the vapor and liquid of a constant boiling mixture have the same composition and since the liquid analyzes 98.54% H_2SO_4, the concentration of sulfur trioxide, water and sulfuric acid in the gas phase may be obtained. The same ratio must hold for the liquid, from which the composition of the mixture, expressed in molalities, is calculated to be $H_2O = 3.976$, $SO_3 = 2.815$, $H_2SO_4 = 10.20$. These data readily give K, expressed in molalities, for the liquid at 317°.

The equilibrium constant at 25° may now be calculated by means of the equation of the reaction isochore[6] $d \ln K/dT = \Delta H/RT^2$. To make use of the integrated form of this equation, it is necessary to know the heat of reaction and the specific heats of the substances involved over the temperature range 25–317°. From heats of formation,[7] the heat absorbed by the reaction $H_2SO_4(l) \longrightarrow H_2O(l) + SO_3(l)$ is found to be 20,290 calories at 18°. The known specific heats[8] (in joules/gram) are $H_2O(l) = 4.18–4.35$ from 20 to 300° and $H_2SO_4(l) = 1.42 + 0.0016t$ from 10 to 45°. The specific heat of $SO_3(l)$ was estimated to be about 1.40 from analogy with SO_2 (= 1.37–1.43 from 20 to 40°) and from the similarity in specific heats of $H_2SO_4(l)$ and $H_2S_2O_7(l)$ (= 1.4 at 35°). The values for the specific heats used in the calculations are $H_2O(l) = 4.18$, $H_2SO_4(l) = 1.45$, $SO_3(l) = 1.4$; these values are probably sufficiently accurate. At 25° the value 1.09×10^{-8} was found for K. This gives for the water and sulfur trioxide concentrations[9]

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[4] Bodenstein and Katajama, *Z. Elektrochem.*, **15**, 224 (1909).

[5] Tammann, *Z. anorg. Chem.*, **161**, 363 (1927); Knietsch, *Ber.*, **34**, 4069 (1901).

[6] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, **1923**, p. 613.

[7] "International Critical Tables," Vol. V, pp. 176–178.

[8] "International Critical Tables," Vol. V, pp. 106, 113, 114.

[9] The calculation is, of course, only approximate since it has been tacitly assumed that the molecular species in the gas and liquid phases of the constant-boiling mixture are the same and that 100% sulfuric acid at 25° is not polymerized. If these factors could be taken into consideration, smaller values for the concentrations of sulfur trioxide and of water in 100% sulfuric acid would be obtained. The indicated concentrations are therefore maxima but they show very well the tremendous influence of minute amounts of inhibitors.

in 100% sulfuric acid a molality of 3.3×10^{-4}, which corresponds to 0.0026% SO_3 and 0.0006% H_2O. The concentrations of the stronger of the two inhibitors at the maxima of the two curves must be still smaller. By extrapolating the curve for the effect of water on the citric acid reaction rate to zero water, $k \times 10^3$ is found to be about 1800. Thus 0.0026% SO_3 decreases $k \times 10^3$ from 1800 to 440 in the case of citric acid. On the assumption that sulfur trioxide is not an accelerator for the oxalic acid reaction but that water is the inhibitor, a concentration of 0.0006% water reduces $k \times 10^3$ from about 2000 to 18.

It is interesting to note that the maxima in the two curves correspond to a minimum and a maximum in electrical conductance. The maximum in the citric acid curve is at about 0.25% water while Knietsch[10] and Kohlrausch[11] found a maximum in electrical resistance for aqueous resistance for aqueous sulfuric acid solutions at 0.05–0.10 and 0.25–0.26% water, respectively. Similarly in fuming acids Knietsch found a minimum in electrical resistance at 14–16.7% sulfur trioxide whereas oxalic acid decomposes most rapidly at about 14% sulfur trioxide.

Inhibition in the decomposition of organic acids by sulfuric acid is best explained by Taylor's theory[12] of negative catalysis. The experimental results for the effect of sulfur trioxide on the oxalic, malic and citric acid reactions are shown by the present work to be in accord with that theory. A discussion of the application of Taylor's theory of negative catalysis to these reactions will be given in another paper.

The writer wishes to express his gratitude to Professor Hugh S. Taylor for his interest in the progress of the work.

Summary

The rate of decomposition of oxalic acid has been studied in sulfuric acid mixtures containing from 0 to 30% free sulfur trioxide. The maximum velocity is obtained at about 14% sulfur trioxide (2.0 molality).

The data have been interpreted to indicate that sulfur trioxide is not a positive catalyst for the reaction but merely decreases the concentration of water, which is a very powerful inhibitor, the sulfur trioxide in this case being a relatively weak inhibitor.

PRINCETON, NEW JERSEY

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[10] Knietsch, *Ber.*, **34**, 4069 (1901).

[11] Kohlrausch, *Wied. Ann.*, **17**, 69 (1882).

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