where $(m + m_1)$ was kept at 0.1 $M$ concentration, and both the acid and salt concentrations were varied.

4. From these measurements, the activity coefficients of the acid in these different solutions were computed.

PHILADELPHIA, PENNSYLVANIA

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[CONTRIBUTION FROM THE LABORATORIES OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

# THE DECOMPOSITION OF MALIC ACID BY SULFURIC ACID[1]

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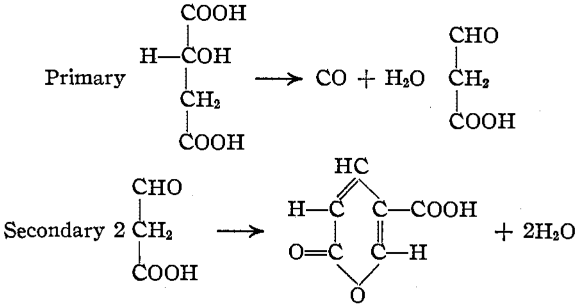
## Introduction

While dehydration reactions by sulfuric acid have been studied to a considerable extent, Bredig and Lichty[2] were the first to measure the velocity of such a reaction and study systematically the effect of varying the concentrations of the acid. Later, Schierz[3] made a similar study of the decomposition of formic acid. Both of these reactions may be looked upon as straight dehydration reactions according to the following equations: $(COOH)_2 \longrightarrow CO + CO_2 + H_2O$; $HCOOH \longrightarrow CO + H_2O$. Subsequent considerations, however, point to a more complex mechanism which will be discussed later.

Dobereiner[4] observed that malic acid is decomposed by concd. sulfuric acid with the evolution of carbon monoxide. This reaction was later studied by v. Pechmann[5] who showed that the reaction is quantitative in concd. sulfuric acid solutions and takes place in two steps. The two reactions may be represented by the following reactions.



$$\text{Primary}\quad \begin{array}{c}COOH\\|\\H\text{—}COH\\|\\CH_2\\|\\COOH\end{array} \longrightarrow CO + H_2O\quad \begin{array}{c}CHO\\|\\CH_2\\|\\COOH\end{array}$$

$$\text{Secondary}\quad 2\begin{array}{c}CHO\\|\\CH_2\\|\\COOH\end{array} \longrightarrow \begin{array}{c}HC\\ H\text{—}C \quad C\text{—}COOH\\ O{=}C \quad C\text{—}H\\ O\end{array} + 2H_2O$$

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[1] The work included in this paper is from the thesis presented by Earl L. Whitford in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin. This investigation was conducted under the supervision of Professor J. H. Walton.

[2] Bredig and Lichty, *Z. Elektrochem.* **12**, 459 (1906); *J. Phys. Chem.*, **11**, 255 (1907).

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

[4] Dobereiner, *Schweigger's J. Chem. Phys.*, **26**, 276 (1819).

[5] v. Pechmann, *Ber.*, **17**, 929, 936 (1884).

Apparently the primary decomposition of malic acid is quite similar to that of oxalic and formic acids. With this idea in mind, the present investigation was undertaken for the purpose of studying the kinetics of the reaction and the effect of various added substances on the rate of the reaction.

## Experimental Part

### Preparation and Purification of Materials

**Malic Acid.**—Kahlbaum's inactive preparation was used, as well as the levorotatory form secured from the Eastman Kodak Company. The absence of any marked crystalline habit precluded the possibility of purification by recrystallization. It was thought, however, that the chief impurity present was water, and therefore both varieties were dried in an oven at 90°, finely powdered and again dried. The inactive acid, after this treatment, melted at 130° and the *levo* form at 100°. Both values are in close agreement with the melting points given by Walden[6] which are 130–131° for the inactive and 100° for the active acid.

**Sulfuric Acid.**—One hundred per cent. sulfuric acid was prepared by adding to a weighed amount of fuming sulfuric acid, a calculated amount of 95% acid. Samples of the mixture were sealed in small glass bulbs and weighed. These bulbs were then broken under water and, after the glass had been filtered off, the samples were analyzed by precipitation of barium sulfate. Three determinations gave the following percentages of sulfuric acid: 99.97, 100.04, 100.02.

An even more accurate criterion of the purity of the sulfuric acid is furnished by its freezing point, since a change in concentration of 0.1% produces a change of 0.6° in the point of fusion. The acid used in this investigation froze at 10.42°. This value agrees closely with those obtained by Hantzsch[7] (10.46°), Lichty[8] (10.45°) and Kendall and Carpenter[9] (10.4°).

The dilute acid was prepared by adding known amounts of 79% acid to the 100% acid.

**Sulfates.**—In general, the sulfates used were C. P. varieties from a reliable source. Only the potassium and sodium sulfates were recrystallized, but in all cases water was removed by heating to constant weight and the samples were then stored in a desiccator over phosphorus pentoxide.

**Acetic Acid.**—Glacial acetic acid was recrystallized several times and then fractionally distilled. The fraction distilling between 116.9° and 117.2° (745 mm.) was used. The acid froze at 16.5°.

### Apparatus and Method of Procedure

The velocity of the decomposition of malic acid was determined by measuring the rate of evolution of carbon monoxide. The apparatus used was essentially the type designed by Walton.[10] Reaction flasks of a special design were supported by a shaking device in a thermostat. The gas evolved was conducted through a capillary tube to a water-jacketed buret where it was measured over water. The slight solubility of carbon mon-

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[6] Walden, *Ber.*, **29**, 1698 (1896).

[7] Hantzsch, *Z. physik. Chem.*, **61**, 258 (1907).

[8] Lichty, THIS JOURNAL, **30**, 1834 (1908).

[9] Kendall and Carpenter, *ibid.*, **36**, 2498 (1914).

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

oxide in water[11] made it possible to use this method without introducing any serious error.

The 100% sulfuric acid, previously described, was stored in a large bottle fitted with a siphon and a ground-glass stopcock. When samples of the acid were drawn out, air was admitted through a drying train consisting of two wash bottles filled with slightly fuming sulfuric acid. The first 10 or 15 cc. was discarded. That such a method was highly efficient was shown by the fact that the velocity of decomposition of malic acid determined at the end of three months checked with that measured with the freshly prepared acid. In preparing the solution, the malic acid and any added substances were dissolved in weighed amounts of 100% sulfuric acid in a glass-stoppered volumetric flask. Samples of 25 cc. each were then pipetted directly into the reaction flasks and the latter transferred to the thermostat. About 15 minutes was allowed for the contents to come to the temperature of the thermostat. The capillary tubes were then connected with the burets and the volume of the carbon monoxide was measured at given intervals. In general, the volume of carbon monoxide evolved from the time $t = 0$ to the end of the reaction was taken as "a" in calculating the velocity constants for a monomolecular reaction. For the determination of the completeness of the reaction, however, the malic acid was introduced by means of capsules which could be dropped into the sulfuric acid at any desired time. In all cases short pieces of glass rod were placed in the reaction mixture to insure more complete stirring and to prevent supersaturation.

## Completeness and Order of the Reaction

In order to check v. Pechmann's[5] statement concerning the completeness of the decomposition of malic acid in concd. sulfuric acid, samples of the acid were weighed in glass capsules carefully covered to prevent the absorption of moisture. These were then dropped into 25 cc. of 100% sulfuric acid after the contents of the flask had attained the temperature of the thermostat. At a temperature of 40° and atmospheric pressure of 740 mm. (vapor pressure of water, 55 mm.) 0.235 g. of malic acid should yield 50 cc. of carbon monoxide. Three such determinations gave the following results: 49.3 cc., 49.6 cc., 50.1 cc.

Undoubtedly the decomposition of malic acid involves more than one molecular species but, assuming sulfuric acid to be one of the primary reactants, in the presence of a large excess of that reactant the measured reaction should be monomolecular in character and can therefore be calculated from the well-known formula,

$$K = \frac{2.303}{t} \log \frac{a}{a - x} \tag{1}$$

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[11] Winkler, *Ber.*, 34, 1408 (1901).

in which $x$ represents the amount of malic acid decomposed in time $t$ (expressed as the volume of carbon monoxide evolved) and $a$ the concentration at time $t = 0$. That the above equation holds is shown in Table I which represents a typical run.

Table I

Order of the Reaction

$T = 40°$ $P = 740$ mm. $a = 15.8$ cc. Percentage of acid: 100

| $t$ | Vol. Cc. | $x$ | $a-x$ | $K \times 10^1$ |
|---|---|---|---|---|
| 0 | 8.5 | .. | .. | ... |
| 2 | 11.6 | 3.1 | 12.7 | 109 |
| 4 | 14.0 | 5.5 | 10.3 | 107 |
| 6 | 16.0 | 7.5 | 8.3 | 107 |
| 10 | 18.75 | 10.25 | 5.55 | 105 |
| 15 | 20.90 | 12.4 | 3.4 | 103 |
| 20 | 22.25 | 13.75 | 2.05 | 103 |
| | | | | Av. 106 |

It will be observed that the constants have a tendency to fall off toward the end of the reaction, probably due to the water formed during the course of the decomposition. In general, however, they do not differ from the mean value by more than 3–4%. In order to conserve space, only the mean value of the velocity constant is given in the succeeding tables. Each value represents the average of from four to seven determinations such as are shown in detail in Table I.

## The Effect of a Non-polar Lining

Since many reactions are influenced by the walls of the containing vessel, it was thought advisable to alter the nature of the walls of the reaction flasks. For this purpose the interiors of the flasks were covered with a thick coating of paraffin and the glass rods were treated in a similar manner. At the end of the run, neither the rods nor the reaction flasks showed any exposed glass. That the decomposition of malic acid by sulfuric acid is not influenced by the walls of the vessel is clearly shown by a comparison of the following constants at 40°: $K \times 10^3$ for glass walls and rods; 106, 105, 108; $K \times 10^3$ for paraffin-coated walls and rods, 107, 106, 107.

## The Effect of Space Arrangement in the Molecule of Malic Acid

Malic acid possesses one asymmetric carbon atom and may therefore exist in three forms; levorotatory, dextrorotatory, and as an equal mixture of the two, which is optically inactive. It was thought that one of these forms might be more susceptible to dehydration than the others. For that reason several determinations were made at 30° with the *levo* and the inactive forms and the velocity constants were found to check throughout, giving an average value of 28.7 for $K \times 10^3$. A similar agreement was observed in succeeding experiments where the two varieties were used since the values for $K \times 10^3$ in all cases checked within the limits of experimental error.

| | 30° | 40° |
|---|---|---|
| $K \times 10^3$ active malic acid | 28.7, 29.0 | 106, 108 |
| $K \times 10^3$ inactive malic acid | 28.5, 28.6 | 106, 107 |

## The Effect of Temperature on the Velocity of Decomposition

The velocity of decomposition of malic acid in 100% sulfuric acid was determined experimentally at the temperatures 20°, 30° and 40°. At 50° the decomposition was so rapid that the only measurements that could be made were at the period when the reaction was more than two-thirds completed and very probably complicated with side reactions. The velocity constant at this temperature was calculated from the value of the critical increment "$E$." The values for $K \times 10^3$ for the various temperatures as well as the temperature coefficients are given in Table II.

In order to express the effect of the temperature ($T$) on the reaction velocity constant ($k$), Arrhenius developed the following equation.

$$\frac{d\, ln\, k}{d\, T} = \frac{E}{RT^2} \tag{2}$$

The "critical increment," $E$, is defined by Tolman[12] as the difference between the average energy of the molecules and modes of electromagnetic vibration which actually take part in the reaction, and the average energy of those same elements whether or not they are in a reactive condition. On this basis, it would be expected that the quantity $E$ should vary but slightly with the temperature. Using the integrated form of Equation 2,

$$E = \frac{1.98\, T_2T_1 \times 2.303 \log k_2/k_1}{T_2 - T_1} \tag{3}$$

the values for $E$ were calculated in terms of calories and are listed in Table II. It will be noted that the "critical increment" varies but slightly over the temperature range studied.

TABLE II

EFFECT OF TEMPERATURE UPON THE REACTION RATE

| Temp., °C. | $K \times 10^3$ | Temp. coeff. | Crit. increment ($E$) |
|---|---|---|---|
| 20 | 7.6 | | |
| | | 3.78 | 23,600 |
| 30 | 28.7 | | |
| | | 3.72 | 24,300 |
| 40 | 106.0 | | |
| 50 | 385.0 (calcd.) | | |

In a recent paper on catalysis, Dhar[13] states that a negative catalyst always increases the temperature coefficient of a reaction, the increase being the greater, the higher the concentration of the inhibitor. The effect

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[12] Tolman, THIS JOURNAL, **42**, 2506 (1920).

[13] Dhar, *J. Phys. Chem.*, **28**, 951 (1924).

of water upon the decomposition of malic acid by sulfuric acid does not agree with this general statement. In 100% sulfuric acid the temperaure coefficient for the interval 20–30° is 3.78 and for the interval 30–40° is 3.72. By interpolation from Fig. 1, the temperature coefficient for the interval 30–40° at 1 *M* concentration of water is 3.66 and for the interval 40–50° is 3.63. It is thus evident that in this negatively catalyzed reaction the temperature coefficient changes but little with increased concentration of the inhibitor and, instead of increasing in value, falls off slightly.

## The Effect of Water on the Velocity of the Reaction

The equation for the decomposition of malic acid by sulfuric acid shows that water is one of the products of both the primary and secondary reactions. Its effect, therefore, upon the measured velocity is of tremendous importance. The reaction velocities in various concentrations of sulfuric acid were determined at the temperatures 30°, 40° and 50°. The mean values of the velocity constant ($K \times 10^3$) are given in Table III and shown graphically in Fig. 1 where the concentration of the added water is expressed in terms of molality.[14]

TABLE III

EFFECT OF WATER UPON THE REACTION RATE

| Molality | $K \times 10^3$ (20°) | $K \times 10^3$ (30°) | $K \times 10^3$ (40°) | $K \times 10^3$ (50°) |
|---|---|---|---|---|
| 0 | 7.6 | 28.7 | 106.0 | 385.0 (calcd.) |
| 0.335 | ... | 19.7 | 60.0 | .. |
| .448 | ... | .. | .. | 191.0 |
| .557 | ... | 14.5 | .. | .. |
| .600 | ... | .. | 41.0 | .. |
| .932 | ... | 7.1 | 23.0 | .. |
| 1.02 | ... | .. | .. | 76.0 |
| 1.25 | ... | .. | .. | 50.0 |
| 1.48 | ... | 4.6 | .. | .. |
| 1.59 | ... | .. | 10.5 | .. |
| 1.97 | ... | .. | .. | 29.0 |

NOTE: In studying the decomposition of malic acid, v. Pechmann was unable to accomplish any appreciable dehydration below the temperature of 70°. In this investigation, however, the reaction proceeded at a measurable rate at 20° when 100% sulfuric acid was employed. It frequently happens in the dehydration of organic compounds that the reaction is attended by charring and numerous side reactions. The acid invariably employed is approximately 95 to 96% and necessitates such a high temperature that the sulfuric acid is partially reduced. If the concentration of the acid is maintained at 100%, however, many of these dehydration processes may be carried out at much lower temperatures and kept free from complicated side reactions.

From the data given and a consideration of the graphical representation in Fig. 1, it will be observed that relatively small amounts of water exhibit a marked inhibitory effect upon the velocity of the decomposition. It has

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[14] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923, p. 259.

been noted previously in this paper that the velocity constants showed a tendency to decrease in value toward the end of the reaction, this being particularly noticeable when the reaction was carried out in very concentrated sulfuric acid. The primary decomposition of 0.23 g. of malic acid produces 0.0296 g. of water which would change its molality in 100% sulfuric acid from 0 to .035. The effect of such a small amount of water upon the earlier part of the reaction, however, was not particularly noticeable. It is very probable that the two additional molecules produced in the course of the secondary reaction would cause a much greater decrease in the reaction rate. Since the values for $K \times 10^3$ are constant within 4 or 5%, however, it is believed that the primary decomposition of malic acid is very much faster than the secondary reaction.

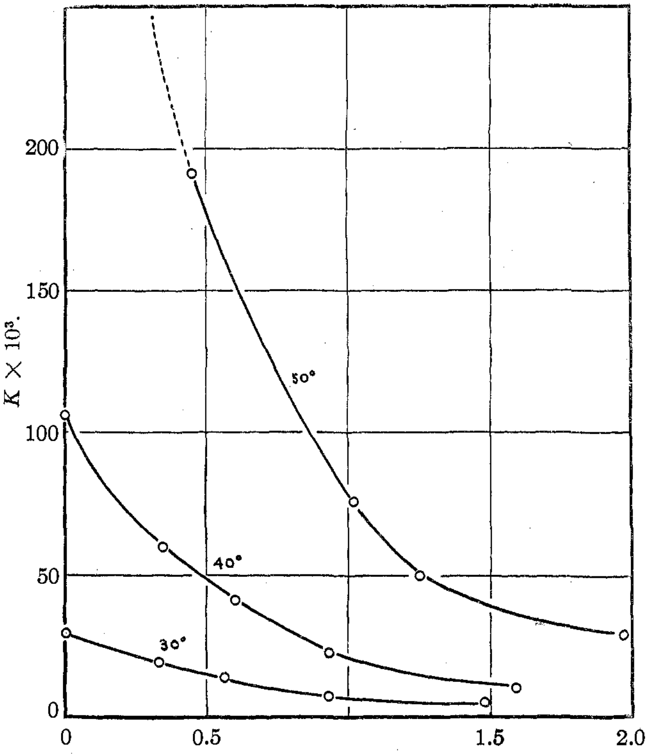

Fig. 1.—Effect of water upon the reaction rate.

Another point of interest to be observed is that the relative effect of water decreases with an increased amount of added water. This fact was also observed by Lichty in his study of the decomposition of oxalic acid by sulfuric acid and by Schierz in a similar study of formic acid. The graphical representation of the effect of water on the velocity of the reaction

TABLE IV
LOGARITHMIC FUNCTION OF WATER

TEMPERATURE, 30°

| Molality | 0 | 0.335 | 0.557 |
|---|---|---|---|
| $K \times 10^3$ | 28.7 | 19.7 | 14.5 |
| Log $K \times 10^3$ | 1.46 | 1.29 | 1.16 |

TEMPERATURE, 40°

| $M$ | 0 | 0.335 | 0.600 | 0.932 | 1.59 |
|---|---|---|---|---|---|
| $K \times 10^3$ | 106.0 | 60.0 | 41.0 | 23.0 | 10.5 |
| Log $K \times 10^3$ | 2.03 | 1.78 | 1.61 | 1.36 | 1.02 |

TEMPERATURE, 50°

| $M$ | 0 | 0.448 | 1.02 | 1.25 |
|---|---|---|---|---|
| $K \times 10^3$ | 397.0 (calcd.) | 191.0 | 76.0 | 51.0 |
| Log $K \times 10^3$ | 2.60[a] | 2.28 | 1.85 | 1.72 |

[a] By extrapolation.

(Fig. 1) yields a curve whose shape would indicate that the concentration of water is an exponential function of the velocity constant. It was found that when the logarithms of $K \times 10^3$ for the more concentrated solutions

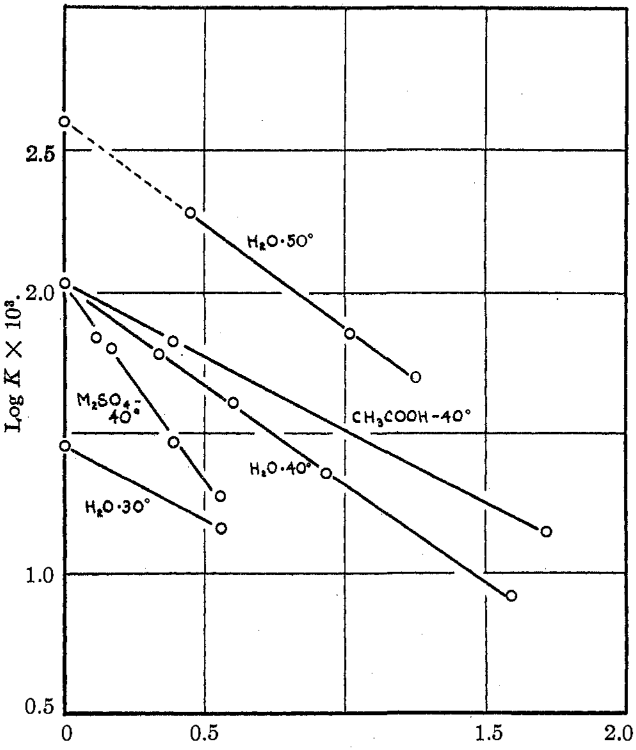

Fig. 2.—Logarithmic function of inhibitors.

of sulfuric acid were plotted as abscissas and the corresponding molalities as ordinates, a straight line was obtained. The values of log $K \times 10^3$ are given in Table IV and shown graphically in Fig. 2. The velocity constants for oxalic acid and formic acid were recalculated in a similar manner and are given in Tables V and VI and shown graphically in Fig. 3.

Table V

Oxalic Acid at 25° (Lichty)·

| Molality | 0 | 0.056 | 0.112 | 0.167 | 0.392 |
|---|---|---|---|---|---|
| $K \times 10^4$ | 213.6 | 139.3 | 94.3 | 57.2 | 23.0 |
| Log $K \times 10^4$ | 2.33 | 2.14 | 1.97 | 1.76 | 1.36 |

Table VI

Formic Acid at 25° (Schierz)

| Molality | 1.37 | 3.24 | 4.37 |
|---|---|---|---|
| $K \times 10^3$ | 244 | 72.5 | 24.2 |
| Log $K \times 10^3$ | 2.64 | 1.86 | 1.38– |

The establishment of the logarithm of $K \times 10^3$ as a straight-line function of the concentration of the water made the extrapolation to zero molality at 50° seem justifiable. The logarithm thus obtained corresponds to a value of $K \times 10^3$ equal to 397. The velocity constant calculated on the basis of the temperature coefficient for the same conditions is 385; a difference of about 3%, which is in closer agreement than most of the determinations made experimentally.

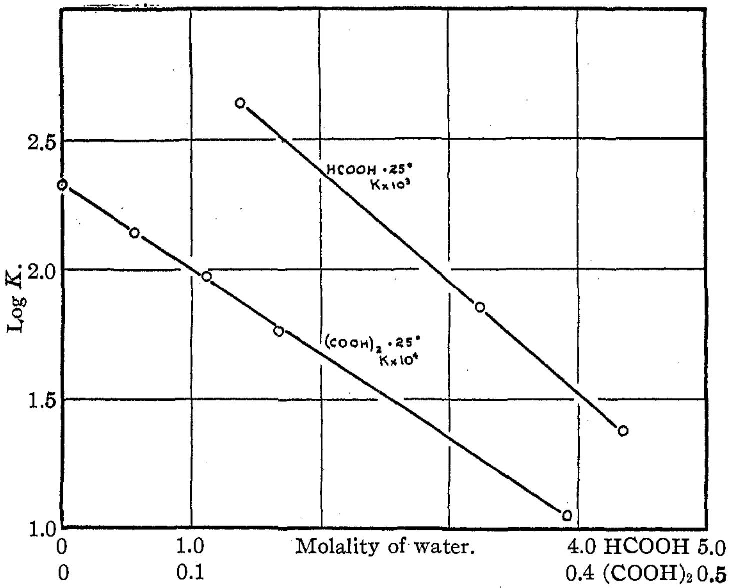

Fig. 3.—Logarithmic function of water in the decomposition of oxalic and formic acids.

The fact that the same relationship of concentration of the water to reaction velocity holds true for the decomposition of all three acids is also interesting. Apparently the inhibitory role of water, whatever it may be, is the same in all three cases. Furthermore, the mechanism of the decomposition of oxalic, formic and malic acids by sulfuric acid is probably very nearly the same.

## The Effect of Various Soluble Substances on the Rate of the Reaction

**Sulfates.**—Lichty found that the alkali sulfates as well as water cut down the rate of reaction between oxalic acid and sulfuric acid to a very marked extent. Schierz, in his studies with formic acid, tried the effect of saturated aqueous solutions of the sulfates and found the reaction rate to be about the same as when an equivalent amount of water was used.

Preliminary determinations of the effect of soluble sulfates on the rate of decomposition of malic acid were made by carrying out the reaction in saturated solutions of the following metallic sulfates; sodium, potassium, calcium, barium, ferrous iron, cadmium, copper, mercurous mercury and silver. In all cases, except that of copper, the rate of reaction was appreciably diminished, the diminution being most marked with the solutions of sodium, potassium and silver sulfates. These were selected for further study.

For this purpose, known amounts of the pure anhydrous salts were dissolved in weighed amounts of 100% sulfuric acid in glass-stoppered bottles. These were further protected from atmospheric moisture by storing them in a desiccator over phosphorus pentoxide. The malic acid was then added and the reaction carried out in the usual manner. The results obtained are shown in condensed form in Table VII and graphically in Fig. 4. The inhibitory action of the sulfates is more marked than the same molal concentration of water but the effect of the individual sulfates is about the same. Likewise, the shape of the curve is about the same as that of water and it was found that by plotting the logarithm of $K \times 10^3$ against the molality of the sulfates a straight line was obtained.

**Acetic Acid.**—Schierz also found that acetic acid showed a rather marked effect on the velocity of decomposition of formic acid, but he considered that it functioned merely as a diluent. A quantitative study of the effect of acetic acid upon the velocity of decomposition of malic acid was made at 40°. The results obtained, as shown in Table VII and Figs. 4 and 5, demonstrate the definite inhibitory power of acetic acid.

**Dimethyl-pyrone.**—Another substance that is soluble in concd. sulfuric acid is dimethyl-pyrone. The only available source of this material was a small quantity of its hydrochloride. In order to study the effect of this substance it was first necessary to determine the effect of hydrogen chloride. For this purpose, solutions of sulfuric acid were saturated with dry hydrogen chloride and the decomposition of malic acid was carried out in this medium. The velocity of the reaction did not vary appreciably from that measured in 100% sulfuric acid at the same temperature. A quantitative determination was then made with dimethyl-pyrone hydrochloride as the added substance, after all of the hydrogen chloride possible had been shaken out. The velocity constants for this run agreed within 3% and indicate the inhibitory power of dimethyl-pyrone to be a trifle greater than that of an equivalent concentration of water. At 40° and a concentration of 0.18 *M*, the velocity constant for water is 77. Those obtained for dimethyl-pyrone were 74, 75 and 74.

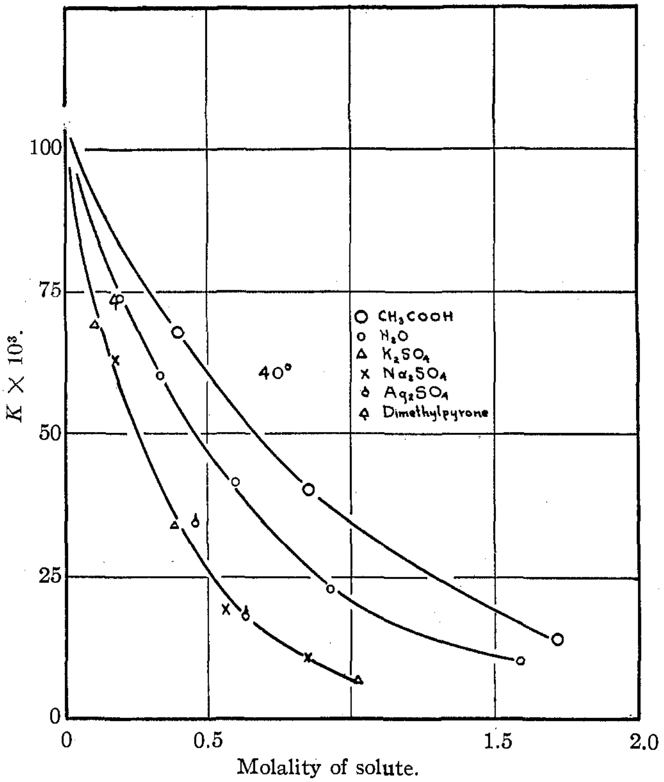

Fig. 4.—Relative effect of inhibitors.

**Sulfur Trioxide.**—The thermal dissociation of sulfuric acid into sulfur trioxide and water suggests the possibility of the following equilibrium in 100% acid: $H_2SO_4 \rightleftarrows H_2O + SO_3$. If such is the case, then the effect of an excess of sulfur trioxide is of obvious importance. Such a study is difficult to conduct at very high concentrations due to a loss caused by fuming. Fairly accurate determinations were made, however, at two concentrations. The addition of 1% of free oxide caused no variation in the reaction rate from that measured in 100% sulfuric acid. The average for several determinations at 40° gave a value for $K \times 10^3$ of 107. When a large excess of sulfur trioxide was added (approximately 12.5%), however, the average velocity constant for four such determinations was 63. The significance of this fact as well as the other experimental data will be discussed in another part of this paper.

TABLE VII

THE EFFECT OF SOLUBLE SUBSTANCES UPON THE RATE OF THE REACTION

Temperature, 40°

| Molality | $K \times 10^3$ ($K_2SO_4$) | $K \times 10^3$ ($Na_2SO_4$) | $K \times 10^3$ ($Ag_2SO_4$) | $K \times 10^3$ ($CH_3COOH$) |
|---|---|---|---|---|
| 0 | 106 | 106 | 106 | 106 |
| 0.111 | 69.0 | .. | .. | .. |
| .167 | .. | 63.1 | .. | .. |
| .392 | 29.2 | .. | .. | 68.2 |
| .448 | .. | .. | 29.0 | .. |
| .562 | .. | 19.1 | .. | .. |
| .620 | .. | .. | 18.2 | .. |
| .675 | 16.8 | .. | .. | .. |
| .845 | .. | 10.2 | .. | 40.0 |
| 1.02 | 7.2 | 7.1 | .. | .. |
| 1.72 | .. | .. | .. | 14.0 |

## Discussion of Results

**Mechanism of the Reaction.**—The primary decomposition of malic acid by sulfuric acid may be looked upon as one of simple dehydration according to the equation, $C_4H_6O_5 \longrightarrow CO + H_2O + C_3H_4O_3$. The velocity of the reaction in various concentrations of sulfuric acid would then be dependent simply upon the dehydrating power of the sulfuric acid. If this were the case, it is hardly probable that the addition of such small amounts of water could so profoundly inhibit the reaction. Such a conception is even more difficult to accept when the effect of the sulfates, acetic acid and dimethyl-pyrone is considered. The velocity constant, $K \times 10^3$, for 0.111 *M* potassium sulfate is 69 at 40° as compared with 106 for zero molality, a decrease of 35%. It is highly improbable that the introduction of such a small amount of anhydrous sulfate could so markedly reduce the mere capacity of sulfuric acid for water. It seems more likely that the addition of the soluble substances displaces some sort of an equilibrium.

Kendall and Carpenter[9] have shown that sulfuric acid forms molecular compounds with a number of organic acids and advanced the idea that sulfonation is preceded by molecular compound formation. Taylor,[15] in his discussion of negative catalysis, also considered the decomposition of oxalic acid to be preceded by the formation of a molecular compound,

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

$(COOH)_2.H_2SO_4$. Similarly, it is believed that malic acid in sulfuric acid solutions decomposes according to a reaction of the following type: $C_4H_6O_5 + H_2SO_4 \rightleftarrows C_4H_6O_5.H_2SO_4 \longrightarrow H_2SO_4 + CO + H_2O + C_3H_4O_3$. The velocity of the decomposition of malic acid will then be dependent upon the concentration of the molecular compound, $C_4H_6O_5.H_2SO_4$, which will be governed by the tendency of the reactants to form a molecular compound and the speed with which compound formation takes place.

Kendall and his students[16] have further demonstrated the fact that the tendency toward compound formation decreases as the individual chemical characteristics of the reactants become more similar in nature. In the case of compound formation with sulfuric acid, for example, the more acidic the character of the second component, the less will be the tendency toward compound formation. Undoubtedly, the factors governing the relative rates of decomposition of oxalic, malic and formic acids are more deeply seated than the mere tendency toward compound formation. If the electrolytic dissociation constant may be used as the index of acidity, however, it is interesting to note that the relative rates of decomposition are in the same order as would be predicted on the basis of the compound criterion. Table VIII shows this comparison for 0.562 *M* solution of water at 50°.

TABLE VIII

RELATION OF ACIDITY TO REACTION VELOCITY

| Acid | Dissociation constant | Velocity constant |
|---|---|---|
| Oxalic[17] | $3.8 \times 10^{-2}$ | 0.515 |
| Malic[18] | $4.0 \times 10^{-4}$ | 158.5 |
| Formic[19] | $2.1 \times 10^{-4}$ | Reaction immeasurably fast |

Christiansen,[20] in his discussion of negative catalysis, suggested that in 100% sulfuric acid there probably exists the equilibrium $H_2SO_4 \rightleftarrows H_2O + SO_3$. Since Lichty observed that the addition of 1% excess of sulfur trioxide caused the decomposition of oxalic acid to proceed with immeasurable rapidity, Christiansen further suggested that the sulfur trioxide, in preference to sulfuric acid, should be considered as one of the primary reactants. From the experimental results obtained for the effect of excess of sulfur trioxide on the rate of the reaction for malic acid, however, the possibility of any such unstable intermediate as $C_4H_6O_5.SO_3$ is practically excluded.

**Role of the Inhibitors.**—The tremendous effect of small amounts of added substances constitutes one of the most interesting phases of this re-

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[16] Kendall and others, THIS JOURNAL, **1914**, and elsewhere.

[17] Chandler, *ibid.*, **30**, 694 (1908). Ostwald, *Z. physik. Chem.*, **3**, 369 (1899).

[18] Walden, *Ber.*, **29**, 1699 (1896).

[19] Ostwald, *Z. physik. Chem.*, **3**, 170 (1899).

[20] Christiansen, *J. Phys. Chem.*, **38**, 145 (1924).

search. In a recent article on negative catalysis in homogeneous systems of this type, Taylor advanced the hypothesis of molecular compound formation between inhibitor and one or both of the reactants as an explanation for the marked decrease in the reaction rate. Since it is generally recognized that in the large mass of the reactants only a relatively small number of the molecules are in an "active" state at any one time, he points out the fact that the total concentration of the reactants is not the effective concentration, but rather only those molecules which are in a reactive state are to be considered. The inhibitor then functions as a competitor for the "active" molecules. It follows from this conception that the inhibitory power of the negative catalyst will depend upon two factors: (1) the tendency toward compound formation and (2) the speed with which the molecular compound is formed. Furthermore, it must be assumed that a large part of the added inhibitor is in a reactive state and that as soon as the "active" molecules of the reactant have been rendered inactive, by combination with the inhibitor, the inhibitor is regenerated so as to be free to combine with more molecules of the primary reactant which, in the meantime, have proceeded to the "active" state.

Applying this hypothesis to the decomposition of malic acid by sulfuric acid containing small amounts of water, there are essentially the following possibilities: (active) $H_2SO_4 + C_4H_6O_5 \rightleftharpoons H_2SO_4.C_4H_6O_5$; (active) $H_2SO_4 + H_2O \rightleftharpoons H_2SO_4.H_2O$. The same types of equilibria will also exist in the cases of the sulfates, acetic acid, dimethyl-pyrone and sulfur trioxide, all of which exhibit an inhibitory effect upon the velocity of the decomposition of malic acid.

A slightly different mechanism for these reactions has been suggested by Professor Homer Adkins of this Laboratory. Since sulfuric acid shows such a marked tendency toward compound formation with the substances mentioned above, it very probably forms complexes with itself. The researches of Aston and Ramsay[21] led them to believe that 95% sulfuric acid exists as $(H_2SO_4)_{32}$ rather than as simple molecules. One hundred per cent. acid is undoubtedly more highly associated. G. S. Johnson[22] arrived at similar conclusions from the study of vapor-pressure measurements.

Assuming that the sulfuric acid complex exists as a chain formation, only those molecules at the end of the chain are capable of reacting. The production of more "active" molecules must be attended by a breaking of the chain. This conception may explain in a sense the "active" molecules of Taylor and others.

As noted previously in this article, Kendall and his students have shown the marked tendency of sulfuric acid to form molecular compounds with the inhibitors studied. Of these, the sulfates are most marked, and on that

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[21] Aston and Ramsay, *J. Chem. Soc.*, **65**, 167 (1894).

[22] Johnson, *Chem. News*, **17**, 211 (1893).

basis we should expect them to show the greatest inhibition. Such is the case. Next in order, according to the molecular compound criterion, are dimethyl-pyrone and water. An examination of Figs. 2 and 3 shows that these inhibitors fall in the expected order. Acetic acid cuts down the reaction rate somewhat less than water but is more effective than perhaps might be anticipated from a consideration of its tendency toward compound formation with sulfuric acid. The second factor, however, namely, the speed of molecular compound formation, cannot be determined and it is highly probable that, in the case of acetic acid, the reaction rate is relatively greater than in the cases of the inhibitors discussed above. The inhibition caused by a rather large excess of sulfur trioxide may also be explained by means of the compound theory, pyrosulfuric acid being formed in this case. Since the trioxide is more acidic in character than any of the other inhibitors studied, its effect should be appreciably less, which is in agreement with the experimental observations.

Another important deduction from Taylor's theory of negative catalysis may be made regarding the relative effect of water on the rate of decomposition of oxalic, malic and formic acids. Using the tendency toward compound formation as a criterion, the effect of small amounts of water should be most marked upon the reaction rate of the strongest acid. Lichty observed that water to the extent of 0.01% occasioned a very considerable diminution in the velocity of the decomposition of oxalic acid and that the constants, calculated for a single run, fell off tremendously due to small amounts of water liberated during the course of the reaction. That the decomposition of malic acid is not so sensitive to water is shown by the fact that the constants calculated for the individual runs agree within the limits of experimental error. At dilutions below 94% sulfuric acid, however, the reaction rate was so slow as to be practically immeasurable. On the other hand, Schierz found that formic acid decomposed at a measurable rate in concentrations of sulfuric acid as low as 89%.

Christiansen[20] criticized Taylor's theory of negative catalysis on the basis that the inhibitors would have to display a certain amount of intelligence in picking out the "active" molecules of the reactant. While his criticism is undoubtedly justifiable, the fact remains that the experimental results obtained in this research fit in nicely with Taylor's theory and conform to his predictions.

The author desires to take this opportunity to express his appreciation to Professor J. H. Walton, under whose direction this research was carried out, for his kindly interest and guidance during its progress.

## Summary

1. The decomposition of malic acid by sulfuric acid is a reaction of the first order.

2. The rate of the reaction is independent of the nature of the walls of the vessel and the space arrangement in the molecule of malic acid.
3. The velocity of the reaction has been determined with various concentrations of water at the temperatures 30°, 40° and 50°. In all cases, small amounts of water produce a great retardation of the reaction.
4. Sodium, potassium and silver sulfates, acetic acid and dimethylpyrone retard the reaction to a great extent.
5. Dissolved hydrogen chloride does not alter the reaction rate and the effect of small amounts of sulfur trioxide cannot be detected, although a large excess causes appreciable diminution.
6. The inhibition increases logarithmically with the molality of the inhibitors, and the similarity of the decomposition of formic acid to that of oxalic acid in this respect is pointed out.
7. The temperature coefficient has been calculated for ten-degree intervals from 20° to 50°. The average value, 3.72, is abnormally large.
8. The value of the critical increment, calculated according to the equation of Arrhenius, changes but slightly with the temperature.
9. A mechanism for the decomposition of malic acid has been offered, postulating an unstable intermediate of the type $C_4H_6O_5.H_2SO_4$.
10. The role of the inhibitors has been discussed in the light of Taylor's theory of negative catalysis and found to conform to his predictions.

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

# SOLUTIONS OF SALTS IN 100% SULFURIC ACID. SOLVOLYSIS AND DOUBLE DECOMPOSITION REACTIONS

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## Introduction

Sulfuric acid has attracted the attention of a considerable number of investigators interested in the properties of non-aqueous solvents. Pure 100% $H_2SO_4$ is fairly easily prepared, is a liquid over a very wide temperature range (10.5° to 332°) and its physical properties, with the single exception of its very high viscosity,[1] are such as to present no serious experimental obstacles to its investigation.

The first systematic study of this solvent was undertaken by Walden.[2]

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[1] The viscosity of $H_2SO_4$ at 25° is approximately 21 times that of water at the same temperature. On this account, most substances dissolve in this liquid at a very slow rate, except at inconveniently high temperatures. On the other hand, crystallization from solutions in this solvent is also likely to be delayed, necessitating extreme supercooling, especially in concentrated solutions. The high viscosity also makes it difficult to free separated crystals from adhering liquid for the purpose of analysis.

[2] Walden, *Z. anorg. Chem.*, **29**, 371 (1902).