[Contribution from the Laboratory of General Chemistry of the University of Wisconsin]

THE DECOMPOSITION OF MALIC ACID BY SULFURIC ACID

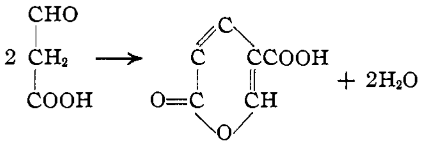
By Harry R. Dittmar

Received March 31, 1930 Published July 3, 1930

Although Döbereiner[1] showed that carbon monoxide resulted from the decomposition of malic acid by concentrated sulfuric acid, it remained for v. Pechmann[2] to demonstrate that the reaction was quantitative and that α-pyrone-β'-carboxylic acid was also formed in accordance with the equations

$$HOOCCH_2CHOHCOOH \longrightarrow CO + H_2O + HOOCCH_2CHO$$

then



Whitford[3] studied this reaction quantitatively, and found that it was an apparent first-order reaction, had a very high temperature coefficient and was inhibited by sodium, potassium and silver sulfates, acetic acid and dimethylpyrone. This investigator proposed an explanation for the mechanism of the reaction by postulating an unstable intermediate addition compound between malic and sulfuric acids, while the action of inhibitors was explained on the basis of a theory of negative catalysis formulated by Taylor.[4] It was suggested that an inhibitor such as dimethylpyrone, for instance, was effective because it combined with the sulfuric acid and so prevented the latter compound from taking part in the reaction.

The present investigation was undertaken with the object of making a study of the action of several more inhibitors at different temperatures and at more than one concentration in order to obtain the temperature coefficients of the inhibited reaction, which, in turn, might be used in gaining an insight into the mechanism of the inhibition.

Experimental

Preparation and Purification of Materials

Malic Acid.—Inactive malic acid obtained from Kahlbaum was used after being dried at 75° at a pressure of 2 mm. of mercury. The acid melted at 130.8° (corr.).

Sulfuric Acid.—One hundred per cent. sulfuric acid was prepared by adding c. p. 95% sulfuric acid to a given quantity of fuming sulfuric acid until the resulting solution melted at 10.42°, a value which was in good agreement with that obtained by other

---

[1] Döbereiner, *J. für Chem. Phys.*, **26**, 276 (1819).

[2] V. Pechmann, *Ber.*, **17**, 936 (1884).

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

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

investigators. A chemical analysis was also made by dissolving samples weighed by means of a weighing pipet in water and precipitating as barium sulfate. Two determinations gave 100.08 and 100.15% of sulfuric acid.

Phenol.—c. p. phenol (Mallinckrodt) was twice redistilled. The fraction which boiled at 182° (corr.) was used.

p-Cresol.—*p*-Cresol labeled "practical" (Eastman) was twice redistilled. The fraction which boiled at 201° (corr.) was employed.

Phosphoric Acid.—Pure crystalline orthophosphoric acid was used which melted at 42.3°. This acid was prepared by Mr. A. Weber in this Laboratory.

The other substances, which were the purest obtainable from reliable sources, were carefully dried before being used. The ethyl alcohol was dehydrated by calcium oxide in the usual manner. Acetophenone was redistilled. All of the solids with a melting point above 75° were dried at that temperature under a pressure of 2 mm. of mercury except benzophenone, which was dried at 35° at this pressure. All of the substances used were preserved in desiccators over phosphorus pentoxide.

Apparatus and Method of Procedure

The speed of the decomposition of malic acid by sulfuric acid was followed by measuring the volume of carbon monoxide which was evolved in various time intervals. The apparatus, including the mechanical agitator, reaction flasks and burets was identical with that used in a study of the decomposition of triphenylacetic acid by sulfuric acid and has been described in detail in another communication.[5] In each decomposition a 50-mg. sample of malic acid was decomposed in 10 cc. of sulfuric acid. This amount liberated about 9.51 cc. of carbon monoxide at 30° and 732.5 mm.

Solutions of various substances in 100% sulfuric acid were prepared by adding definite weights of the solutes to 50-cc. tightly stoppered Erlenmeyer flasks into which were weighed calculated quantities of 100% sulfuric acid. In cases where the solutes were hygroscopic, they were weighed into the flasks by means of either a weighing bottle or a weighing pipet.

Results

Decomposition by One Hundred Per Cent. Sulfuric Acid.—In accordance with Whitford's[3] results, the data obtained by measuring the volume of carbon monoxide evolved at various intervals of time when substituted in the equation for a monomolecular reaction, $K = (2.303/t) \log [a/(a - x)]$, gave constant values of K for any one decomposition. The first reading was usually taken after approximately 20% of the malic acid had been decomposed. This was necessary in order to allow the malic acid to first dissolve in the sulfuric acid. The carbon monoxide in cc. evolved between the first reading and the end of the reaction was substituted for a in the equation and the volume from the initial reading to that at time t as x.

The value of the velocity constant was constant until the reaction was 80–90% complete, after which k had the tendency to decrease. The values of $K \times 10^3$ obtained in a typical decomposition were: 30.6, 31.2, 31.1, 31.2, 30.8, 30.7, 30.5, 30.6, 30.6, 30.4, 30.2, 30.4. These constants were calculated from the data obtained between 27 and 83% of the

---

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

reaction. The value of the velocity constant for any particular decomposition was taken as the average value of $K \times 10^3$ between 25 and 70% of the reaction. In order to conserve space, only the mean value of the velocity constant is given in the subsequent tables rather than all of the data obtained from one decomposition. In studying the speed of decomposition under a given set of conditions, duplicate or more runs were always made, and the value of the velocity constant reported in the tables represents the average of the determinations. The check decompositions usually did not differ by more than 3%.

The absolute values of K were found to be somewhat higher than those obtained by Whitford.[3] For instance, $K \times 10^3$ was found to be 11.1, 47.1 and 182.0 for 20, 30 and 40°, respectively, whereas Whitford obtained values of 7.6, 28.7 and 106.0 for the same temperatures. This discrepancy may have been caused by a slight difference in the experimental procedure. In this investigation the solid malic acid, contained in a small glass capsule, was introduced directly into the sulfuric acid at the moment agitation of the reaction flask was begun; while in the other case the malic acid was first dissolved in the sulfuric acid, after which samples were pipetted into the reaction flasks and allowed to stand in the thermostat for about fifteen minutes before the experiment was begun. However, the temperature coefficient between 30 and 40° checks the latter's value quite well although the temperature coefficient between 20 and 30° is somewhat higher. These results are given in Table I.

TABLE I

EFFECT OF TEMPERATURE UPON THE RATE OF DECOMPOSITION OF MALIC ACID BY 100% SULFURIC ACID

Temp., °C.	$K \times 10^3$	Temp. coeff.	Crit. increment
20	11.1		
		4.24	25,510
30	47.1		
40 (calcd.)	182.0	3.86	25,480
25	23.8		
		3.92	25,000
35	93.2		

The speed of the decomposition at 40° was so great that reliable data could not be obtained. The value of $K \times 10^3$ at this temperature was obtained by extrapolation from the curve obtained by plotting temperature against the logarithm of $K \times 10^3$. This curve was a straight line from which the velocity constant at 40° was easily obtained.

The Effect of Various Substances upon the Reaction Rate.—The speed of the decomposition of malic acid was determined after various substances had first been dissolved in the sulfuric acid. All of the substances studied were found to inhibit the reaction. The effect of nine solutes was determined at two concentrations and at three different temperatures in order that the effect of the inhibitor upon the temperature coefficient could be observed. The results are summarized in Table II.

TABLE II

EFFECT OF SOLUTES ON THE RATE OF DECOMPOSITION OF MALIC ACID BY SULFURIC ACID

Molality, 0.25

Solute	$K \times 10^3$, 20°	$K \times 10^3$, 30°	$K \times 10^3$, 40°	$\frac{K\times 10^3, 30°}{K\times 10^3, 20°}$	Crit. increment	$\frac{K\times 10^3, 40°}{K\times 10^3, 30°}$	Crit. increment
Ammonium sulfate	3.04	13.9	60.4	4.58	26,870	4.33	27,640
Phenol	3.88	19.8	85.7	5.10	28,770	4.33	27,640
p-Cresol	3.71	18.3	78.3	4.95	28,240	4.27	27,380
Coumarin	5.68	23.5	103	4.14	25,090	4.39	27,900
Benzophenone	5.35	22.5	94.0	4.22	25,670	4.18	26,980
Benzoic anhydride	0.336	1.60	8.02	4.76	27,550	5.01	30,400
Ethyl alcohol	6.17	30.4	126	4.93	28,170	4.14	26,800
Benzoic acid	5.46	24.0	101	4.39	26,120	4.22	27,160
Phosphoric acid	5.60	25.7	107	4.58	26,870	4.16	26,890
Acetophenone	5.63	24.8	100	4.41	26,200	4.03	26,900
Triphenylcarbinol		16.6					
m-Nitrophenol		31.3					
o-Toluic acid		21.0					
Crotonic acid		24.9					

Molality, 0.50

Solute	$K \times 10^3$, 20°	$K \times 10^3$, 30°	$K \times 10^3$, 40°	$\frac{K\times 10^3, 30°}{K\times 10^3, 20°}$	Crit. increment	$\frac{K\times 10^3, 40°}{K\times 10^3, 30°}$	Crit. increment
Ammonium sulfate	1.33	6.18	27.6	4.64	27,100	4.47	28,240
Phenol	1.64	8.06	38.1	4.91	28,100	4.73	29,310
p-Cresol	1.59	8.10	35.8	5.08	28,670	4.42	28,030
Coumarin	3.20	13.9	61.8	4.34	25,920	4.44	28,120
Benzophenone	3.19	13.3	56.7	4.17	25,220	4.26	27,340
Benzoic anhydride		0.47	2.44			5.19	31,060
Ethyl alcohol	3.77	17.8	72.3	4.72	27,400	4.07	26,470
Benzoic acid	3.25	14.1	59.7	4.35	25,960	4.22	27,160
Phosphoric acid	3.56	16.3	69.9	4.58	26,870	4.29	27,470
Acetophenone	3.39	15.8	63.0	4.66	27,170	3.98	26,050
Triphenylcarbinol		6.30					
Crotonic acid		15.2					

Most inhibitors increase the critical increment slightly although coumarin, benzophenone and benzoic acid have practically no effect at the lower concentration. Benzoic anhydride, which has the greatest effect on the critical increment, is the most pronounced inhibitor. The temperature coefficient of the inhibited reaction decreases, within the limit of experimental error, with increase of temperature. The temperature coefficient of the reaction inhibited by benzoic anhydride at molality 0.25 increases from 4.76 to 5.01. This difference is slightly outside the limit of experimental error. Increase of concentration of the inhibitors from molality 0.25 to 0.50 either slightly increases or does not affect the critical increment. The critical increments were calculated from the Arrhenius equation $d \ln k/dT = E/RT^2$.

The concentrations of the inhibitors were plotted against the logarithms of the velocity constants at each of the temperatures at which the decomposition was studied. The curves so obtained deviated slightly from straight lines. Four typical curves are given in Fig. 1.

Compound Formation between Malic and Sulfuric Acids.—In discussing the possible mechanism of the decomposition of malic acid by sulfuric acid, Whitford postulated the formation of an unstable molecular compound between the two acids. This addition product was then assumed to decompose into water, carbon monoxide, α-pyrone-β′-carboxylic acid, and the original sulfuric acid.

In this investigation evidence for the existence of such a molecular complex was obtained. Knox and Richards[6] showed that it was possible to demonstrate the formation of molecular addition compounds between acids in solution by determining the solubility of one acid at a particular temperature in solutions of increasing concentration of the second acid. In cases of compound formation the solubility of the acid at first diminished with increasing concentration of the solvent acid in accordance with the effect of a common ion; but as the concentration of the solvent acid became greater, this influence was offset by the second influence, namely, compound formation between the acids, and the solubility of the solute acid then increased in proportion to the increase of concentration of the solvent acid. In cases where no compounds resulted, the solubility of the first acid continually decreased.

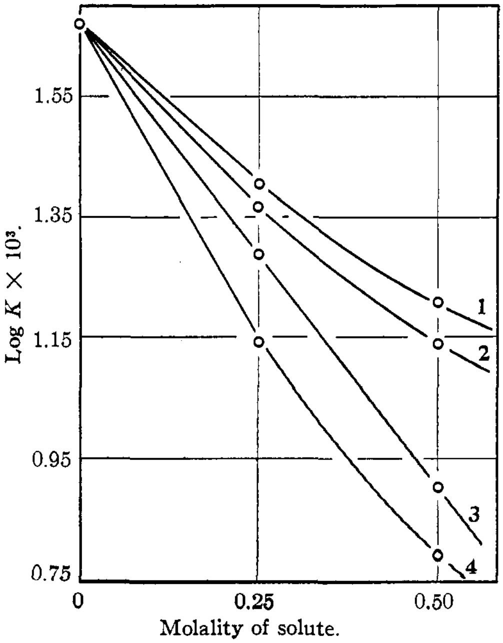


Fig. 1.—Effect of phosphoric acid, 1, coumarin, 2, phenol, 3, and ammonium sulfate, 4, on the reaction rate at 30°.

In accordance with this method the solubility of malic acid was determined in aqueous solutions of sulfuric acid of different concentrations. The concentrations of the sulfuric acid solutions were determined by titration with a standard solution of sodium hydroxide, after which they were saturated with malic acid at about 35° in tightly stoppered glass flasks

---

[6] Knox and Richards, *J. Chem. Soc.*, **115**, 508 (1919).

which were supported in a mechanical agitator. The temperature was decreased to 30° and after equilibrium had been established the solutions were filtered rapidly at 30° through a Gooch crucible. The total acidity of aliquots of the filtered solution was then determined by titration with the standard alkali, and the sulfuric acid present in the solution was determined gravimetrically as barium sulfate. The malic acid content was calculated by difference. In all the titrations phenolphthalein was used as an indicator.

The results are tabulated in Table III, in which the concentrations of both acids are expressed in terms of normality. These data are plotted in Fig. 2 and furnish evidence for the existence of a molecular addition compound between malic and sulfuric acids.

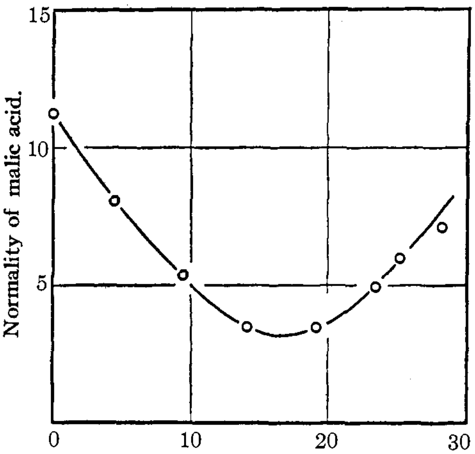


Fig. 2.—Solubility of malic acid in aqueous solutions of sulfuric acid.

TABLE III

SOLUBILITY OF MALIC ACID IN AQUEOUS SOLUTIONS OF SULFURIC ACID

Normality of sulfuric acid	Normality of malic acid	Normality of sulfuric acid	Normality of malic acid
0.000	11.21	19.08	3.568
4.212	8.045	23.54	5.005
9.416	5.451	25.26	6.071
14.00	3.568	28.44	7.090

Discussion of Results

Since data pointing to the actual existence of an intermediate compound between sulfuric and malic acids have been obtained, the assumption that the decomposition is affected through the decomposition of such a molecular complex does not appear unlikely. The reaction can be represented as taking place in the following way

$$C_4H_6O_5 + nH_2SO_4 \rightleftharpoons C_4H_6O_5 \cdot nH_2SO_4$$
$$C_4H_6O_5 \cdot nH_2SO_4 \longrightarrow nH_2SO_4 + CO + H_2O + C_3H_4O_3$$

The velocity of the decomposition of the malic acid will then be proportional to the concentration of the molecular complex, which in turn will be dependent upon the effective concentrations of malic and sulfuric acids.

Action of Inhibitors

Whitford postulates that sodium, potassium and silver sulfates, acetic acid and dimethylpyrone inhibit this decomposition because these compounds form molecular complexes with the sulfuric acid, thereby decreasing the active concentration of the latter and preventing it from reacting with the malic acid. In the present investigation all the inhibitors except phosphoric acid and ethyl alcohol have been shown to form molecular addition compounds with sulfuric acid.[7,8,9] McIntosh[10] has isolated an equimolecular addition compound between ethanol and nitric acid, but did not obtain a similar result with sulfuric acid, because at the low temperatures which were employed, the sulfuric acid became extremely viscous. It seems reasonable to suspect that sulfuric acid would show the same tendency toward compound formation with ethanol that nitric acid does.

These facts might be interpreted as substantiating the view that the inhibitors function by combining with the sulfuric acid, as postulated by Whitford, were it not that phosphoric acid inhibits the decomposition even though it has not been shown to form an addition complex with sulfuric acid.

The concentration of sulfuric acid was very much greater than that of the malic acid or the solute. When the molality of the inhibitor was 0.25, each reaction flask contained approximately 500 molecules of sulfuric acid and 12 molecules of inhibitor for every molecule of malic acid. In other words, there were forty molecules of sulfuric acid for every molecule of inhibitor. Granting that inhibition is affected by combination of sulfuric acid with the solute, it is difficult to conceive that such a small concentration would so profoundly affect the reaction velocity. On the other hand, sulfuric acid is a very highly associated liquid. Aston and Ramsay[11] have shown that sulfuric acid which corresponds to the formula $(H_2SO_4)_{12}\cdot H_2O$ has a formula of $(H_2SO_4)_{32}$ at room temperature. If such a large molecule is the active reagent, then the molecular concentration of inhibitor to associated sulfuric acid would be about equal and such an explanation of inhibition could be possible.

The retardation of the reaction rate by a solute can be more satisfactorily explained by assuming that the solute reacts with the malic acid to form a molecular complex, the formation of which decreases the active concentration of the malic acid and so diminishes the concentration of the unstable sulfuric–malic acid complex and hence the decomposition rate.

The reactions may be represented in the following way

---

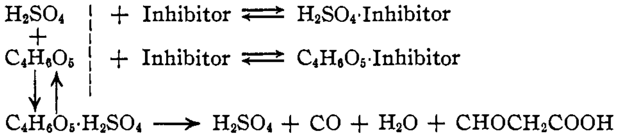
[7] Kendall and Carpenter, This Journal, **36**, 2498 (1914).

[8] Kendall and Landon, *ibid.*, **42**, 2131 (1920).

[9] Dittmar, *J. Phys. Chem.*, **33**, 547 (1929).

[10] McIntosh, This Journal, **27**, 1013 (1905).

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



$$\begin{array}{l} H_2SO_4 \;\; + \text{Inhibitor} \rightleftharpoons H_2SO_4\cdot\text{Inhibitor} \\ + \\ C_4H_6O_5 \;\; + \text{Inhibitor} \rightleftharpoons C_4H_6O_5\cdot\text{Inhibitor} \\ \downarrow\uparrow \\ C_4H_6O_5\cdot H_2SO_4 \longrightarrow H_2SO_4 + CO + H_2O + CHOCH_2COOH \end{array}$$

The last mechanism appears more plausible than the first, particularly since the molecular concentration of malic acid is one five-hundredth that of sulfuric acid, for then the effect of removing some of the malic acid by compound formation with the inhibitor would be very much more pronounced on the concentration of the unstable intermediate ($C_4H_6O_5\cdot H_2SO_4$) than would the removal of some of the sulfuric acid.

An attempt to show the existence of some molecular compounds of malic acid with phenol, *p*-cresol, and benzoic anhydride was undertaken by Miss Irene D. Anderson in this Laboratory by making temperature–concentration studies of the two-component systems. In the systems malic acid–phenol and malic acid–*p*-cresol no reliable data were obtained due to critical solution effects. In the system malic acid–benzoic anhydride decomposition took place, although the curve began to form a definite maximum indicating compound formation.

Since benzoic anhydride forms a molecular compound with malic acid, it should have a marked inhibitory effect upon the reaction rate. It can be seen from Table I that this substance is the most effective negative catalyst.

Kepfer[12] using the solubility method of Knox and Richards has shown that malic and phosphoric acids form an addition compound. This fact will explain the inhibitory power of phosphoric acid, which has not been shown to unite with sulfuric acid.

The lowering of the freezing point of 100% sulfuric acid produced by each inhibitor, at the two concentrations employed in the decomposition experiments, was determined in an attempt to correlate the freezing point depression of a solute with its power as an inhibitor. The results were so irregular that no relationship between these properties was found.

The effect of temperature upon the rate of the inhibited reaction is, as already stated, dependent upon the inhibitor used, although all the inhibitors increase the temperature coefficient. Granting that inhibition is affected through compound formation of the inhibitor with malic or even to some extent sulfuric acid, the effect of temperature upon the reaction rate will be determined by the change in the equilibrium constants in the two following reactions:

$$H_2SO_4 + \text{Inhibitor} \rightleftharpoons H_2SO_4\cdot\text{Inhibitor}$$
$$C_4H_6O_5 + \text{Inhibitor} \rightleftharpoons C_4H_6O_5\cdot\text{Inhibitor}$$

Other than the fact that the first reaction is accompanied, in the case of most inhibitors, with the liberation of heat, the equilibrium constants or

---

[12] Walton and Kepfer, *J. Phys. Chem.*, **34**, 543 (1930).

the heats of reaction of the above reactions are not known, and the effect of temperature cannot be accurately predicted. The temperature coefficients of the inhibited reaction at present do not seem to be as much help in the solution of the mechanism of the inhibition as had been anticipated.

Summary

1. The velocity of the decomposition of malic acid by sulfuric acid has been measured in the presence of nine different solutes, all of which retarded the reaction velocity, at two concentrations and three different temperatures.

2. Solubility measurements of malic acid in aqueous sulfuric acid solutions of different concentrations point to the existence of a molecular addition compound between the two, which strengthens the assumption previously expressed by Whitford that the first step in the decomposition of malic acid by sulfuric acid consisted of molecular compound formation.

3. The logarithm of the velocity constant of the inhibited reaction in most cases is not an exact linear function of the concentration of the inhibitor.

4. The critical increment of the reaction is in most cases only slightly increased by the inhibitor.

5. Although all of the inhibitors used, except two, form molecular compounds with one of the reactants of this decomposition—sulfuric acid—the mechanism of the inhibition can be satisfactorily explained, for some solutes, at least, by the formation of addition compounds between the inhibitor and malic acid.

Madison, Wisconsin

[Contribution from the Analytical Laboratory of Princeton University]

THE DETECTION AND ESTIMATION OF SMALL AMOUNTS OF LITHIUM

By Earle R. Caley

Received April 1, 1930 Published July 3, 1930

Due to the fact that lithium salts in general are freely soluble in a variety of solvents, few precipitation reactions for lithium are known. Of these none are suitable for the detection and quantitative estimation of very small quantities of this element. It has been found that a relatively sensitive reaction for lithium may be based upon the fact that lithium stearate, in contrast to the stearates of the other alkali metals, is relatively insoluble in certain organic solvents. Unfortunately this reaction cannot be applied in aqueous solutions due to hydrolytic effects, nor can it be used in dilute or concentrated solutions of ethyl alcohol by reason of the solubility of the lithium soap in this solvent. Amyl alcohol was found to be the most convenient medium to use. In the practical qualitative or quantitative appli-