7. None of the preservative methods here tested is recommended for use when the determination of soluble protein is required.

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THE DECOMPOSITION OF FORMIC ACID BY SULFURIC ACID[1]

BY ERNEST R. SCHIERZ

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Introduction

That formic acid decomposes in the presence of sulfuric acid with the liberation of carbon monoxide was first reported by Doebereiner.[2] This reaction has been studied by Meyer,[3] Veley,[4] Morgan,[5] and Okaya.[6] The last mentioned author observed that it proceeded with the rythmic evolution of carbon monoxide if no precautions were taken to prevent supersaturation. Sabatier and Maihle[7] showed that in presence of sulfur trioxide below 100° and anhydrous oxalic above 105° the decomposition products are the same as with sulfuric acid. That the reaction is a quantitative one has been established by Wegner.[8]

The present investigation was undertaken in order to study the kinetics of the decomposition of formic acid by sulfuric acid and the effects of various soluble substances on the rate of the reaction.

Experimental Part

Preparation and Purification of Materials.—Formic acid was prepared by dehydrating an 85% acid by warming to about 50° and then adding an amount of anhydrous oxalic acid[9] sufficient to combine with the water present. The liquid when cooled was decanted from the crystals of hydrated oxalic acid and distilled. This very concentrated distillate was completely dehydrated by the method proposed by Schlesinger and Martin.[10] The resulting acid distilled at 31.0–31.5° at 37–39 mm.; d^{25} 1.217.

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[1] The work included in this paper is from the thesis presented by Ernest R. Schierz 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] Doebereiner, *Schweiger-Meinecke's J. Chem. Phys.*, **32**, 345 (1821); *Gilbert's Ann.*, **71**, 107 (1822).

[3] Meyer, *Z. Elektrochem.*, **14**, 506 (1909).

[4] Veley, *Phil. Mag.*, [6] **6**, 271 (1903).

[5] Morgan, *J. Chem. Soc.*, **109**, 274 (1916).

[6] Okaya, *Proc. Phys. Math. Soc. Japan*, [3] **1**, 43 (1919).

[7] Sabatier and Maihle, *Compt. rend.*, **152**, 1212 (1911).

[8] Wegner, *Z. anal. Chem.*, **42**, 427 (1903).

[9] Beilstein, *Handbuch der organischen Chemie*, **1893**, 3rd ed., I, p. 393.

[10] Schlesinger and Martin, THIS JOURNAL, **36**, 1589 (1914).

According to Kahlbaum pure formic acid has a specific gravity of 1.219 under the same conditions.

The acetic acid was obtained by redistilling glacial acetic acid. The portion boiling between 118.5° and 119.2° (corr.) was used for these experiments.

The other materials were the purest obtainable and were not further purified, for the experiments in which they were used were semiquantitative only.

Apparatus.—The velocity of decomposition of formic acid by sulfuric acid was determined by measuring the rate of evolution of the carbon monoxide. The apparatus was of the type designed by Walton.[11] Reaction flasks of a special design were supported by a shaking device in a thermostat. The gas evolved was conducted through a capillary tube into a water-jacketed buret where it was collected over water. The slight solubility of oxygen[12] in water (0.02831 volumes of gas for 1 volume of water at 25°) made it unnecessary for Walton to correct for solubility when he collected the gas over water in the burets. The solubility of carbon monoxide in water is less than that of oxygen[13] so no error was introduced in collecting the gas over water. A capsule was supported in the neck of the reaction flask in such a way that it could be dropped into the reaction mixture at any desired instant. In the experiments to be described, the sulfuric acid was placed in the flask and the formic acid in the capsule. In order to obtain efficient stirring and thereby prevent supersaturation, short pieces of a glass rod were put into the flask with the reaction mixture.

Order of the Reaction

Okaya[6] showed that the decomposition of formic acid by sulfuric acid is a monomolecular reaction. The velocity constant can, therefore, be calculated from the formula

$$0.4343\ K = \frac{1}{t} \cdot \log \frac{a}{a - x} \qquad (1)$$

in which x represents the amount of substance decomposed (expressed as the amount of carbon monoxide evolved) in time t, and a represents the concentration of formic acid present at $t = 0$; a may therefore be represented by the total amount of carbon monoxide evolved *after* $t = 0$. In the determinations made at 25° and 45°, the value of x was expressed in milligrams of dry carbon monoxide. In the other determinations the observed volumes were multiplied by a factor to convert a of the formula to 50 cc. This made it possible to read constants from a nomograph, devised by Mr. J. D. Jenkins of this Laboratory.[14]

These constants were compared with those calculated in the usual way and were found to agree within the error of the experiment. The variation from the average did not exceed 5%.

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

[12] Bohn and Bock, *Wied. Ann.*, **44**, 318 (1891).

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

[14] This nomograph was based on the following considerations. Since $K = \frac{1}{t} \cdot \log \frac{a}{a-x}$, $Kt = \log a - \log a - x$. a was taken as a constant, that is the values of x were multiplied by a factor to convert a to 50. Then a series of lines was drawn on semi-logarithmic paper for known values of K, plotting t in minutes on axis of abscissa and log $(a-x)$ on axis of ordinates. The values of log $(a-x)$ on axis of ordinates were indicated by the corresponding values of x.

In cases where the barometric pressure changed during a determination, the necessary corrections were made.

The Effect of Water on the Decomposition of Formic Acid by Sulfuric Acid

From the equation showing the decomposition of formic acid by sulfuric acid the reaction appears to be one of dehydration. The study of the effect of water on the reaction is obviously of importance for several reasons, such as (1) water is one of the products of the reaction, (2) it was necessary to use diluted acid because the reaction in pure sulfuric acid proceeded too rapidly to be measured.

Lichty[15] made a similar study of the decomposition of oxalic acid by sulfuric acid and concluded that the reaction was one of dehydration. He found that water even in small amounts produced a marked lowering of the reaction velocity and, therefore, suggested that the measurement of reaction velocity could be used to determine the concentration of sulfuric acid.

To study the effect of water on the decomposition of formic acid by sulfuric acid a measured amount (25 cc.) of reaction mixture, composed of sulfuric acid containing various but known amounts of water, was pipetted into the reaction flask. Approximately 0.07 cc. of formic acid, measured with a pipet graduated to 0.01 cc., was placed in the glass capsule which was supported in the neck of the flask. The flask was then stoppered with a rubber stopper through which passed a short piece of capillary tubing, and fastened in the shaking apparatus which was then lowered into the thermostat. When the contents of the flask reached the temperature of the thermostat the outlet tube was connected to the gas burets, the capsule was dropped into the reaction mixture and the shaker started. After approximately 4 cc. of gas had been evolved, readings were taken at measured intervals of time. The reading obtained after no change in volume had occurred during a long interval of time was taken as the final reading.

In some cases, the velocity constant decreased as the reaction proceeded but in no case did the individual values vary more than 5% from the average.

The results of the experiments with various concentrations of sulfuric acid are summarized in Table I. In order to conserve space, the data are given in a condensed form in which K_s represents $0.4343\ K \times 10^3$. Fig. 1 is a graphic representation of the effect of water on the velocity of the reaction at 25°.

It will be noted that the addition of water causes a progressive decrease in the velocity of decomposition of formic acid. The effect is most marked at the higher concentrations of sulfuric acid. These results are analogous

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[15] Lichty, *J. Phys. Chem.*, 11, 225 (1914).

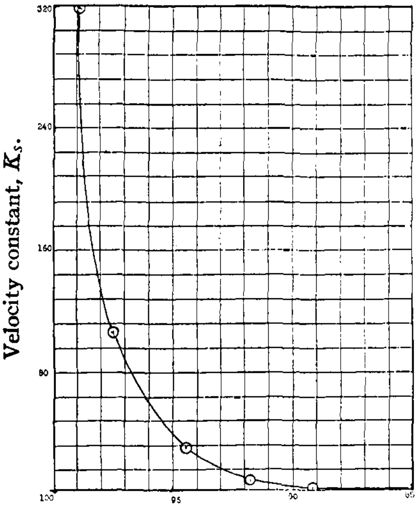
to those obtained by Lichty who found that the decomposition of oxalic acid was sensitive to very small amounts of water. The constant obtained by Lichty changed from 0.02365 for 3% of water to 0.00073 for 15% of water. For the addition of the same amount of water to the sulfuric acid in the decomposition of formic acid, the constant changes from 80 (obtained by interpolation on Fig. 1) to 0.751. This shows that for this range the rate of decomposition of formic acid is more sensitive to water. In the range 1.5% – 3.0% of water, the constant obtained by Lichty changed from 0.00315 to 0.00094. Over the same range the constant for the decomposition of formic acid changed from 170 to 80 (interpolation values from Fig. 1). To very small amounts of water the reaction of oxalic acid is more sensitive than that of formic acid.

TABLE I

DECOMPOSITION OF FORMIC ACID BY SULFURIC ACID WITH VARIOUS CONCENTRATIONS OF SULFURIC ACID AT SEVERAL TEMPERATURES

H_2SO_4	K_S			
%	15°	25°	35°	45°
98.9	..	320	..	..
97.6	32.6	106.0	..	..
94.5	9.9	31.5	..	..
91.78	3.29	10.5	28.0	97.9
89.2	..	2.38	..	..
88.9	..	...	10.8	31.0
85	..	0.751	..	..

The amount of water liberated by the decomposition of 0.07 cc. of formic acid is so slight (0.0319 g.) that it has practically no effect on the concentration of the sulfuric acid. This is evident from the following facts: (1) the values for K_s are constant; (2) the addition of 0.0319 g. of water to 25 cc. of 94.6% sulfuric acid reduces the concentration of the acid about 0.07%; from Fig. 1, it will be seen that the effect on the constant at these concentrations is within the limit of experimental error.



Per cent. H_2SO_4.

Fig. 1.

The Effect of Temperature on the Reaction

In order to determine the effect of temperature on the reaction, a series of experiments with various concentrations of sulfuric acid was conducted at 15°, 35° and 45°. The result of these determinations are summarized in Table I.

Skrabal[16] arrived at a very general conclusion that the relations between reaction velocity, temperature effects, influence of solvent, added catalyst and photochemical action are all essentially the same. Accordingly, change in the reaction effected by any one of these factors diminishes as the magnitude of the velocity constant increases. For the interval 45 – 35° the temperature coefficients for 91.8% and 88.9% sulfuric acid are 3.49 and 2.89 respectively; for the interval 35 – 25° the coefficient for 91.8% acid is 2.67; and for the interval 25 – 15°, the coefficients for acids of concentrations 97.6%, 94.5% and 91.8% are 2.92, 3.18, and 3.19, respectively.

It will be noted that the temperature coefficients for concentration of 91.8% sulfuric acid show some irregularities Instead of decreasing regularly with increase in temperature, the value for the interval 45 – 35° is larger than that for the lower interval,[17] 35 – 25°.

The value of E (critical increment) calculated for the temperature interval 25–15° for the following concentrations of sulfuric acid, 97.6%, 94.5% and 91.8%, was found to be 18,520, 19,670 and 19,720 calories, respectively.

Lewis[18] gives an example of a reaction in which a change of 1% in the concentration of sulfuric acid has a marked effect on the value of E.

In a mixture of sulfuric acid and water, containing 94.6% acid, the value of E for the transformation of acetophenone oxime into acetanilide[19] is 21,270 calories per gram molecule; while for a mixture containing 93.6%, E is 24,670 calories.

In his study of the contact process for sulfuric acid, Knietsch[20] found that the specific conductance, melting point and viscosity do not increase continuously on progressive dilution of the acid. The abnormal values for these properties are at concentrations 92.01%, 92.0% and 93.5%, respectively. This peculiar behavior in the reaction investigated, occurs at the concentration 92–93.5%. This is not offered as an explanation for the failure of the temperature coefficient to be in accord with the theory, but is merely cited as another instance of peculiar behavior of sulfuric acid of that concentration.

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[16] Skrabal, *Monatsh.*, **37**, 495 (1916).

[17] The value of E (critical increment) as calculated from the equation $\frac{dk}{dt} = \frac{E}{RT^2}$ varies with the temperature. This is not in accord with the empirical equation of Arrhenius or the equation of Lewis and Perrin based on the radiation hypothesis, a fact which indicates some kind of complicating mechanism.

[18] Lewis, *Trans. Faraday Soc.*, **17**, 575 (1922).

[19] Lobry de Bruyn and Sluiter, *Verslag. Akad. Wetenschappen, Amsterdam*, **6**, 773 (1904).

[20] Knietsch, *Ber.*, **34**, 4089 (1901).

Lichty states that in his experiments the velocity of reaction was a direct function of the concentration of the sulfuric acid.

The Effect of Dissolved Substances on the Reaction

Sulfates, Hydrochloric Acid, Acetic Acid.—1. In order to test the effect of sulfates on the reaction, the following experiments were carried out. One reaction mixture was prepared by using a saturated aqueous solution of silver sulfate as the diluent for sulfuric acid instead of water. The formic acid was introduced by means of the capsule in the usual way. The reaction velocity constant calculated for the first order reaction was not appreciably different from that obtained when an equal amount of water was used. The results with saturated solutions of mercurous, copper, potassium and sodium sulfates were similar.

2. Branch[21] studied the effect of hydrogen chloride on the thermal decomposition of formic acid in aqueous solution at 156.1° and 217.9° and found that the equilibrium was attained much more rapidly in the presence of this strong acid. In order to determine whether its effect on the decomposition of formic acid in sulfuric acid solution was similar, a reaction mixture was prepared by saturating 89.2% sulfuric acid with hydrogen chloride. The formic acid was introduced in the usual way. It was found that the decomposition proceeded more rapidly in the presence of the acid.

It was observed that the values for K_s fell off rapidly due to the displacement of hydrogen chloride from solution by the carbon monoxide evolved. Some idea of the effect of the hydrochloric acid present, however, can be obtained from the value of the first constant ($K_s = 7.35$). The constant value obtained finally, agrees within the error of the experiment with those obtained for 89.2% sulfuric in absence of hydrochloric acid. The amount of hydrochloric acid present was not determined. Cappadoro[22] found that at 17°, a solution containing 89 g. of sulfuric acid and 0.068 g. of hydrogen chloride per 100 g. of solution was saturated with hydrogen chloride.

The results of these experiments show that the hydrochloric acid is a very active catalyst toward this reaction.

3. In order to determine the effect of diluents other than water, some experiments were performed using glacial acetic acid and acetone. It was found that when 10 cc. of glacial acetic acid or acetone was used as a diluent in place of an equal volume of water, the reaction proceeded so rapidly that reliable readings could not be obtained. The velocity was of the order of magnitude of that of pure sulfuric acid. In order to study the effect of acetic acid, it was found necessary to use it as a diluent *with* water.

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[21] Branch, This Journal, **37**, 2316 (1915).

[22] Cappadoro, *Gazz. chim. ital.*, **39**, 625 (1909).

The reaction mixtures were made by pipetting definite volumes of water and acetic acid into a 100cc. volumetric flask and then filling to the mark with 100% sulfuric acid at 25°. The sum of the volumes of water and acetic acid added was always 15 cc. When the solution containing 10 cc. of acetic acid and 5 cc. of water was analyzed by precipitating the sulfate as barium sulfate, it was found that the concentration of sulfuric acid was 91.5%. This figure agrees very well with that obtained when 15 cc. of water was used.

These experiments were conducted in the usual way, by dropping the formic acid into the reaction mixture.

Table II

Comparison of Velocity Constants

H_2O Cc./100 cc.	Acetic Acid Cc./100 cc.	K_s	H_2O[a] Cc./100 cc.	K_s
15	0	9.9	15	9.9
14	1	11.2	..	..
13	2	12.7	..	..
10	5	16.8	10	33.3
8	7	23.6	..	..
5	10	42.8	5	106.0

[a] Cc./100 cc. of reaction mixture.

Upon comparing the velocity constants, calculated for the first order of reaction in the acetic acid solutions, with those obtained with the same concentration of sulfuric acid in which water was the only diluent, it will be observed that the former are greater. The values are brought together for comparison in Table II.

This again points to the role of water in the reaction. On the basis of the volume of water present per 100 cc. of reaction mixture, it will be observed that the constant is decreased by the presence of the acetic acid. In the light of these comparisons, it appears that acetic acid acts merely as a diluent of the sulfuric but does not react with it and diminish its dehydrating action as water does. A mixture consisting of 1 volume of sulfuric acid diluted with 10 volumes of acetic acid does not decompose formic acid with the liberation of carbon monoxide.

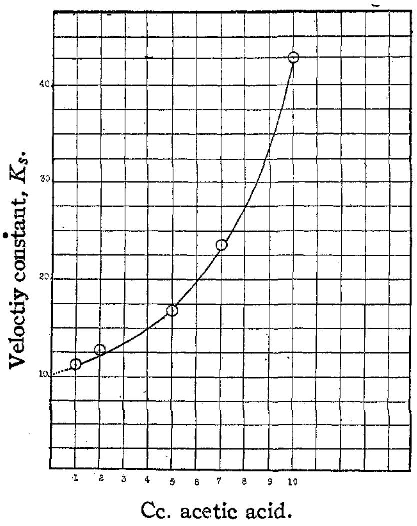

Fig. 2.

An extrapolation of the curve, Fig. 2, to zero cc. of acetic acid gives a value for the velocity constant practically identical with that obtained experimentally.

Conclusions

The addition of small amounts of water to the reaction mixture decreases the dehydrating power of the sulfuric acid, thereby decreasing the velocity of the reaction. Busnikoff[23] studied the rate of hydration of various concentrations of sulfuric acid and found that the more hydrated the original acid, the slower the rate of hydration. The results of the present investigation are in accord with these results. If sulfuric acid acted merely as a catalyst, the addition of such small amounts of water would not affect the rate of reaction appreciably. The role of the sulfuric acid is primarily that of a dehydrating agent.

The possible mechanism of the reaction may be expressed in three ways: (1) an incomplete reaction which goes to completion because one of the products of reaction is removed as rapidly as formed; (2) the formation of an intermediate compound with sulfuric acid as suggested by Mueller and Peytral;[24] (3) the direct dehydration of formic acid. A brief discussion of these possibilities follows.

1. Löb[25] showed that carbon monoxide reacts with water, under the influence of the silent electric discharge, to form formic acid, thereby establishing the fact that the reaction is a reversible one and may be expressed by the following equation, $H.COOH \rightleftharpoons H_2O + CO$. If this equilibrium be disturbed by the removal of water by sulfuric acid, the reaction would go to completion.

2. The suggestion of Mueller and Peytral has been formulated by them as follows,

$$HCOOH + HOSO_2OH \rightleftharpoons HCO.OSO_2OH + H_2O \qquad (2)$$

$$HCO.OSO_2OH \longrightarrow CO + HOSO_2OH \qquad (3)$$

These authors have not prepared this compound. They assume that its existence explains the course of the reaction. The marked effect of small amounts of water on the velocity of the reaction cannot be accounted for by assuming a reaction illustrated by Equation 2. In view of the large amount of sulfuric acid present, the inhibitory effect of the small amounts of water would be negligible.

3. The simplest explanation is contained in the suggestion of the direct dehydration of formic acid according to the equation,

$$nH\text{—}C(O)\text{—}OH + mH_2SO_4 \longrightarrow nCO + mH_2SO_4.nH_2O \qquad (4)$$

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[23] Busnikoff, *J. Russ. Phys. Chem. Soc.*, **29**, 482 (1897); **30**, 418 (1898); **32**, 551 (1900); **33**, 412 (1901).

[24] Mueller and Peytral, *Bull. soc. chim.*, **29**, 34–39 (1921).

[25] Löb, *Z. Elektrochem.*, **12**, 282 (1907).

Due to the large amount of sulfuric acid present compared with the amount of water liberated, the concentration of sulfuric acid is not altered appreciably during the reaction; hence, the reaction would appear to be one of the first order.

The author desires to take this opportunity of expressing his appreciation to Professor J. H. Walton, at whose suggestion this research was undertaken and under whose direction it was carried out, for his kind interest and guidance during its progress.

Summary

1. The velocity of decomposition of formic acid by sulfuric acid has been measured for the following concentrations of sulfuric acid: 98.9%, 97.6%, 94.5%, 91.8%, 89.2%, 88.9%, 85%, at temperature intervals of 10° from 15° to 45°.

2. The reaction was found to be one of the first order.

3. The reaction is probably one of dehydration.

4. Copper, silver, potassium, sodium and mercurous sulfates added separately to the sulfuric acid retard the reaction but slightly.

5. Acetone and acetic acid act as inert diluents, not decreasing the dehydrating power of sulfuric acid.

6. Hydrochloric acid increases the velocity of the reaction markedly, probably acting as a catalytic agent.

7. The temperature coefficients of the reaction have been given and an irregularity in them pointed out for 91.8% sulfuric acid.

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

THE CATALYTIC DECOMPOSITION OF FORMIC ACID IN ACETIC ANHYDRIDE[1]

BY ERNEST R. SCHIERZ

Received August 21, 1922

Introduction

The dehydration of formic acid by sulfuric acid with the concomitant formation of carbon monoxide[2] suggested the use of another dehydrating agent. Formic acid is soluble in acetic anhydride and under certain conditions decomposes, yielding carbon monoxide copiously. It is possible

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[1] The work included in this paper is from the thesis presented by Ernest R. Schierz 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] THIS JOURNAL, **45**, 447 (1923).