Summary

The following physical properties for $C_2F_2Cl_4$ and $C_2F_3Cl_3$ have been determined over a wide temperature range: density, index of refraction, surface tension, vapor pressure and viscosity.

Critical temperatures, molal heat of vaporization, parachor and vapor pressure–temperature equation have been calculated for each liquid.

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The Decomposition of Formic Acid by Sulfuric Acid

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Introduction

A study of the decomposition of formic acid by sulfuric acid has been reported by Schierz,[1] who also cites early workers in this field. Schierz, and later Schierz and Ward,[2] determined the velocity of decomposition in sulfuric acid solutions as concentrated as 96.69%. The results obtained can be accounted for on the basis of Taylor's theory of negative catalysis.[3]

Since the decomposition of several organic acids by sulfuric acid, when small amounts are dropped into large amounts of sulfuric acid, follows the unimolecular law it was thought that some light might be cast on the mechanism of the reaction if the conditions were reversed. In this case the concentration of formic acid would not change; hence, the true order of the reaction might be determined.

The effect of water in smaller concentration and the effect of sulfur trioxide were also thought worthy of investigation.

Experimental Part

Preparation and Purification of Materials.—The 85% formic acid was concentrated by the method described by Schierz[1] and the last traces of water removed by the method described by Coolidge.[4] The formic acid thus obtained was run from a glass stoppered storage bottle through an all glass siphoning system to a micro-buret, air being admitted through a drying train.

Four sulfuric acid solutions corresponding to 94.74, 100.16, 100.08 and 106.5% were prepared. The first solution was the ordinary C. P. reagent, the second and third were prepared by mixing C. P. fuming sulfuric acid and the ordinary reagent, and the fourth solution consisted of C. P. 30% fuming sulfuric acid. The 94.74 and the 106.5% acids were analyzed by precipitation as barium sulfate, due precautions being taken to prevent absorption of water and loss of sulfur trioxide. The 100.16 and 100.08% solutions were found by preliminary experiment to be slightly fuming, they melted at 9.99 and 10.25°, respectively, so that their concentration could be determined from the data

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

[2] Schierz and Ward, *ibid.*, **50**, 3240 (1928).

[3] Wiig, *ibid.*, **52**, 4742 (1930).

[4] Coolidge, *ibid.*, **50**, 2166 (1928).

of Hantzsch.[5] Velocity coefficients of the decomposition of oxalic and citric acids in mixtures of these acids were in close agreement with those of Wiig,[6] a further proof of the analysis. The acids were run to burets in the same manner as the formic acid.

Apparatus and Method of Procedure.—The velocity of decomposition of the formic acid was observed by measuring the carbon monoxide evolved over certain periods of time. The reactions were carried out in 50-cc. round-bottomed flasks, of special design, supported in a thermostat by an agitator. Two types of agitators were used, one a pendulum type described by Bent[7] and the second of the type described by Walton.[8] The agitators were so arranged that the flasks were completely immersed in a thermostat regulated to ±0.01 °. Supersaturation of the solution by carbon monoxide was prevented by the addition of small pieces of Pyrex glass rods, and by indentations in the bottoms of the flasks. The carbon monoxide formed was conducted by capillary tubing to water-jacketed burets held at the same temperature as the thermostat.

In order to obtain sulfuric acid of the desired concentration, calculated amounts (total 25 cc.) of the stock solutions were run into the reaction flask, stoppered to the buret, the pressure being slightly diminished to permit flow of the acid. The sulfuric acid or formic acid was dropped into the reaction mixture when it had come to the temperature of the thermostat.

Experimental Results

I. Formic Acid as Solvent

In the investigations dealing with decomposition of formic acid by sulfuric acid, a small quantity of the acid was dropped into proportionately large quantities of sulfuric acid. The decompositions followed the unimolecular law. These data have not shown whether the reaction is truly unimolecular, *i. e.*, decomposition of an intermediate compound between the organic acid and sulfuric acid, or only apparently so, due to the negligible change in the sulfuric acid concentration. Since formic acid is the only organic acid studied which is liquid at room temperature, it lent itself as a medium into which small amounts of sulfuric acid might be dropped.

Samples of 0.5 to 1.0 cc. of 94.74 and 100.18% sulfuric acid were dropped into 10-cc. portions of formic acid. Temperatures from 25 to 50° were employed. In every case when the capsule dropped into the formic acid, 25 to 50 cc. of gas was suddenly evolved. This sudden evolution of gas slowed down abruptly, continuing at a steadily diminishing rate. Continuous experiments were carried out over a period of ten days, at the end of which time gas was still being evolved. The rate did not correspond to either the unimolecular or bimolecular law, but seemed to fall off as water was formed in the reaction. The volume of carbon monoxide evolved over long periods of time corresponded to an amount of water sufficient to hydrate each molecule of sulfuric acid with two to three molecules (of water).

If the decomposition is due to the disintegration of an intermediate compound between the sulfuric acid and the organic acid, the sulfuric acid must be regenerated after decomposition of the compound. The inhibitory

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(5) Hantzsch, *Z. physik. Chem.*, **61**, 257 (1908).

(6) Wiig, THIS JOURNAL, **52**, 4729, 4737 (1930).

(7) Bent, *Ind. Eng. Chem., Anal. Ed.*, **2**, 106 (1930).

(8) Walton, *Z. physik. Chem.*, **47**, 185 (1904).

effect of the water must be due to hydration of the sulfuric acid or intermediate compound, as the large quantity of formic acid present prevents any effect by hydration of it.

II. Sulfuric Acid as Solvent

A. The Effect of Water on the Reaction.—Schierz[1] and later Schierz and Ward[2] have shown the decomposition of formic acid by sulfuric acid to be a unimolecular reaction, and hence the equation $K = 2.303/t \log a/(a - x)$ applies. The velocity constants are independent of the speed of shaking, if rotary shaking of the type described by Walton[8] is employed. The velocity of the reaction may be dependent on the speed of shaking if a pendulum type shaker is used. Several shaking speeds were employed but concordant results with formic acid could not be obtained nor could the measurements of the decomposition of citric acid be repeated above a velocity constant of 200×10^3 with the latter shaking device.

A typical experiment is shown below. It is to be noted that at this concentration the velocity constants do not fall off rapidly. At higher concentrations of sulfuric acid these constants fall off considerably. At a concentration of 100% sulfuric acid the constants fall off as much as 35%, due to the strong inhibitory effect of water. This is in agreement with the results of Lichty[9] and of Wiig[6] on oxalic acid.

TYPICAL EXPERIMENT

Temp., 15°C. Molality of H_2O, 0.28 (99.5% H_2SO_4). $a = 33.5$

t	0.5	1	1.5	2	3
x	9.8	16.7	21.5	24.7	28.4
$a - x$	23.7	16.8	12.0	8.8	5.1
$k \times 10^3$	691	679	684	668	626

In Table I is given the velocity constant corresponding to various percentages of water present. Each value corresponds to the average velocity constant at 50% decomposition in from three to ten experiments.

TABLE I

THE EFFECT OF WATER ON THE REACTION RATE AT 15°

Water, %	3.98	2.99	1.97	1.49	0.83	0.50	0.23	0.10	0.00
Molality of water	2.30	1.71	1.12	0.84	.47	.28	.09	.06	.00
$K \times 10^3$	50.4	82.0	156.6	222.0	491	677	1686	2677	4126

Figure 1 shows the data graphically. These data show that the effect of water is to inhibit the decomposition, the relative effect decreasing with increasing amounts of water. Similar results have been obtained for the other organic acids studied, as cited by Wiig.[3]

B. The Effect of Sulfur Trioxide on the Reaction.—Due to the marked increase in the velocity of decomposition with decreased concentration of water, it was possible to make a quantitative determination of the

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(9) Lichty, *J. Phys. Chem.*, **11**, 225 (1907).

velocity at only one concentration above 100% H_2SO_4 at 15° and 100.08% H_2SO_4 (0.36% SO_3), $K = 4888 \times 10^{-3}$. This value shows how rapidly the velocity constants increase.

The temperature of the thermostat was then lowered to 5°. At this temperature it was impossible to determine velocity constants at concentrations of less than 100.2% H_2SO_4 because of freezing. Approximate velocity constants were determined for 0.89 to 3.31% SO_3 (100.2 to 100.7% H_2SO_4). Over this range the very rapid velocity constants increased only slightly, indicating that the effect of SO_3 was diminishing. Qualitative measurements at 4.44% SO_3 (101.0% H_2SO_4) and 28.88% SO_3 (106.5% H_2SO_4) gave immeasurably high velocity constants, but of the same order of magnitude.

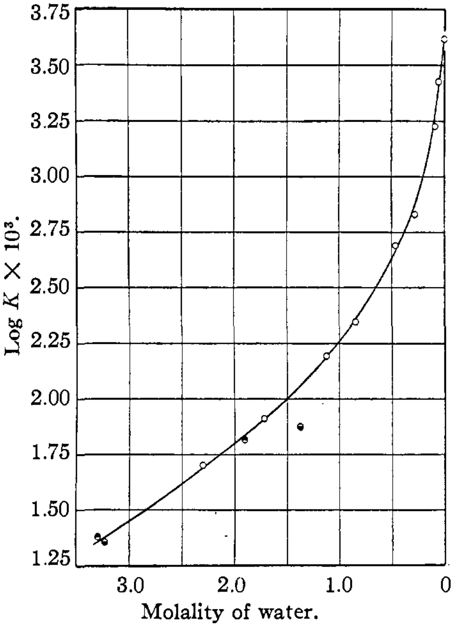

Fig. 1.—○, Author; ◒, Schierz; ◓, Schierz and Ward.

These qualitative relationships show the effect of sulfur trioxide on the decomposition of formic acid to be concordant with that obtained for oxalic, citric and malic acids. Discussion of these results will be postponed until further work, now in progress, is completed.

The author wishes to express his sincere appreciation to Dr. Edwin O. Wiig, under whose direction this work has been done and who has lent much material help in the completion of it.

Summary

1. The decomposition of formic acid by small quantities of sulfuric acid proceeds indefinitely, the rate of decomposition progressively diminishing as water is formed in the reaction.

2. Measurements of the decomposition of formic acid by sulfuric have been extended to a concentration of 100% sulfuric acid.

3. Qualitative determination of the effect of sulfur trioxide is concordant with that obtained in the case of oxalic, citric and malic acids.

4. A pendulum type of shaker does not give concordant results for rapid reactions.

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