Analysis.—The compound was analyzed by weighing a sample into an erlenmeyer flask and then adding acidified potassium iodide solution, the liberated iodine being determined with standard sodium thiosulfate solution.[3]

$$I^+ + I^- \longrightarrow I_2$$

The results of this investigation are shown in Table I.

Acknowledgment.—The author is indebted to Dr. Jacob Kleinberg for guidance in this investigation.

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The Effect of Water and of Glycerol on the Decarboxylation of Oxalic Acid

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It has long been known that oxalic acid is readily decomposed by heat, yielding formic acid and carbon dioxide.[1] Well known also is the fact that decarboxylation of oxalic acid takes place in glycerol.[2] Up to the present time, however, quantitative data on the reaction have not been available. The results of kinetic studies on this reaction which have been made in this Laboratory are reported herein.

Experimental

Reagents.—Oxalic Acid Anhydrous, Analytical Reagent Grade, Oxalic Acid Dihydrate, Analytical Reagent Grade, and Glycerol, Analytical Reagent Grade, 95% by volume, were used in these experiments.

Apparatus.—The experiments described in this paper were carried out in an apparatus similar to that used by the author in studying the decomposition of trichloroacetic acid alone and in glycerol.[3]

Effect of Glycerol on the Decomposition of Oxalic Acid.—In studying the effect of glycerol on the decomposition of oxalic acid, 0.1607 g. of anhydrous oxalic acid (sufficient to yield 40.0 ml. of carbon dioxide at STP on complete reaction) was weighed into a paper thin glass capsule. The sample was introduced in the usual manner into the reaction flask containing 100 ml. of glycerol, and the evolved gas was collected and measured. The volumes of gas evolved with time at five different temperatures are shown in Fig. 1.

Effect of Water on the Decomposition of Oxalic Acid.—Oxalic acid dihydrate decomposes at a measurable rate when heated to its melting point (101.5°) and above when a sufficient quantity of the acid (at least one mole) is used. If additional water is added to the molten dihydrate the reaction slows down. However, the rate can still be measured even when six moles of water per mole of acid is present. A straight line is obtained when the logarithm of the rate is plotted against moles of water.

In studying the effect of water on the decomposition of oxalic acid, one mole (126.06 g.) of the dihydrate was weighed into the reaction flask which was placed in the constant temperature oil-bath. The acid quickly melted, the mercury sealed stirrer was started, and the evolved carbon dioxide was collected and measured in the usual manner. This, of course, gave the effect of two moles of water on the decomposition of the acid at the particular temperature concerned. To obtain the effect of three, four, five and six moles of water per mole of oxalic acid the procedure was exactly the same, except that in addition to the mole of dihydrate, one, two, three and four moles, respectively, of distilled water was introduced into the reaction flask before inserting it in the oil-bath. When all the data at one temperature had been collected and checked for reproducibility the oil-bath temperature was raised and the procedure repeated at a higher temperature. The data thus obtained at four different temperatures are shown graphically in Fig. 2.

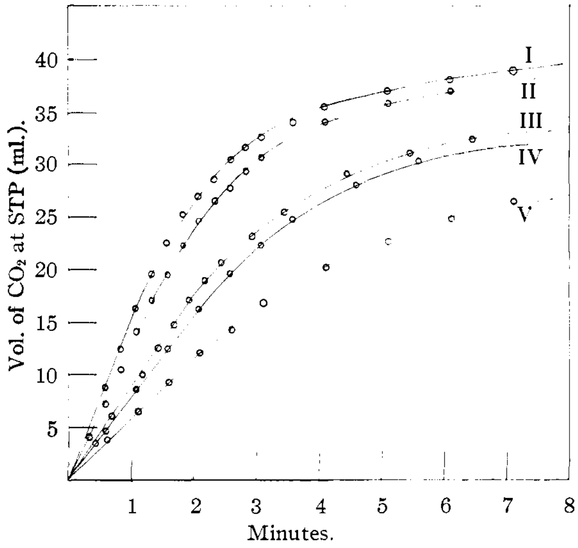

Fig. 1.—Volume of CO_2 (at STP) evolved with time at different temperatures, using 0.1607-g. samples of anhydrous oxalic acid in 100 ml. of glycerol: I, 158.2°; II, 154.2°; III, 148.2°; IV, 145.9°; V, 139.5°.

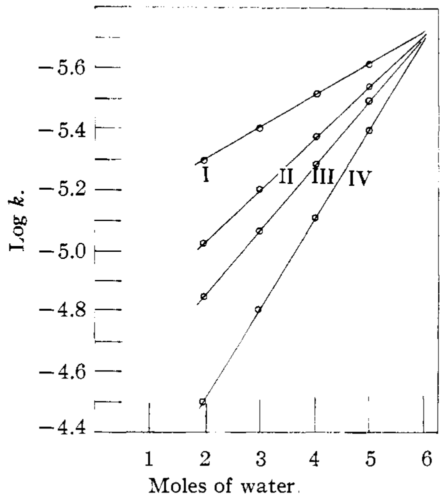

Fig. 2.—Effect of water on the decarboxylation of oxalic acid at different temperatures: I, 117.1°; II, 121.8°; III, 124.8°; IV, 130.8°.

Results and Discussion

The Reaction in Glycerol.—In glycerol it was found that the stoichiometric amount of carbon dioxide was not obtained in every experiment. For example, at 123.6°, the final observed volume of carbon dioxide collected (corrected to STP) was 24.6 ml.; at 132.4°, 32.6 ml.; at 139.5°, 33.3 ml.; at 145.9°, 35.4 ml.; at 150.1°, 37.8 ml.; at 151.8°, 38.6 ml.; at 154.2°, 38.7 ml.; at 156.2°, 40.0 ml.; at 158.2°, 39.4 ml.

It is seen from these data that the decomposition of oxalic acid in glycerol is not stoichiometric at temperatures below 150°. Above 150°, however, the reaction appears to be practically quantitative, considering the limit of error of the experiment and the limitations of the ideal gas law.

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(1) H. J. Lucas, "Organic Chemistry," American Book Co., New York, N. Y., 2nd Ed., 1953, p. 190.

(2) Reference 1, p. 250.

(3) L. W. Clark, This Journal, **77**, 3130 (1955).

Apparently, when oxalic acid is heated in glycerol, two simultaneous reactions take place—(1) decarboxylation, a very fast reaction, and (2) a much slower reaction, probably esterification. Above 150° the decarboxylation appears to be completed before the esterification can become appreciable. Below this temperature a portion of the oxalic acid apparently combines with the glycerol to form a stable compound, since no matter how long the solution is heated at temperatures below 150° no further increase in gas volume can be detected. This observation is at variance with the proposed mechanism for the decomposition of oxalic acid in glycerol.[2]

When points on the isotherms in Fig. 1 are inserted in the equation for a first-order reaction the values obtained for the specific reaction velocity are constant for each temperature as shown by the typical example given in Table I. These results indicate that the decomposition of oxalic acid in glycerol is a first order reaction.

TABLE I

DECOMPOSITION OF OXALIC ACID IN GLYCEROL, SPECIFIC REACTION VELOCITY CONSTANT

(Temperature 154.2 ± 0.01°.)

Time, sec.	Vol. CO_2 at STP, ml.	Completion of reaction, %	Specific reaction vel.
90	18.7	46.75	0.00700
120	23.7	59.25	.00747
150	27.4	68.50	.00768
180	30.2	75.50	.00780
210	32.1	80.25	.00770
240	33.7	84.25	.00768
270	35.0	97.50	.00770
300	35.8	89.50	.00750

Kinetic Data.—Figure 3 shows a plot of log *k* *versus* $1/T$ for the decomposition of oxalic acid dihydrate and the decomposition of oxalic acid in glycerol.

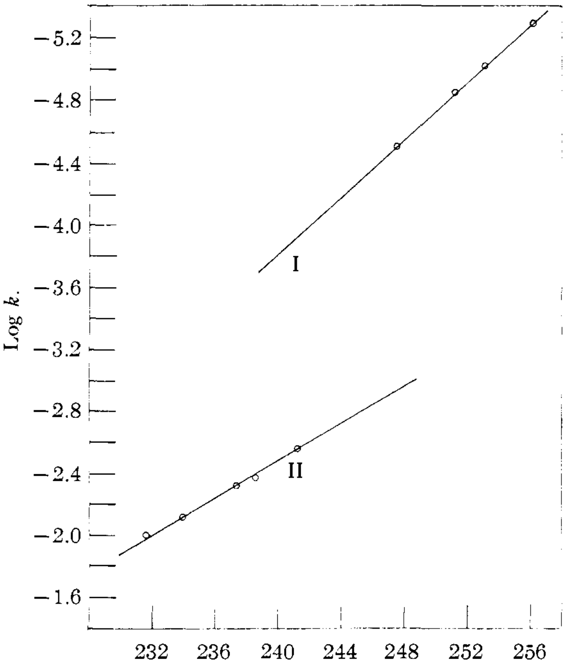

Fig. 3.—Arrhenius plot, log *k* *vs.* $1/T$: I, decomposition of oxalic acid dihydrate; II, decomposition of oxalic acid in glycerol.

For the decomposition of oxalic acid dihydrate the energy of activation is found to be 40,400 cal., and for the decomposition of oxalic acid in glycerol it is 27,400 cal. The enthalpy of activation, the entropy of activation and the free energy of activation at 125°, for the decomposition of the molten dihydrate, is 39,400 cal., +26.8 e.u., and 28,800 cal., respectively; for the decomposition of oxalic acid in glycerol the corresponding values are 26,400 cal., +42.5 e.u., and 9,500 cal., respectively.

The temperature coefficient (the increase in rate per each 10° rise in temperature) is 3.62 for the molten dihydrate, and 1.90 for the reaction in glycerol.

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Note on the Complexes of Ferric Chloride with Phosphorus Oxychloride

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Walden and Oddo[1] reported that sublimed ferric chloride formed a yellowish brown solution with phosphorus oxychloride and subsequently Ruff and Einbeck[2] described a yellow compound having the composition $2FeCl_3 \cdot POCl_3$. During the course of our investigations on the chlorination of ferruginous phosphatic minerals, we observed a reddish brown crystalline deposit in the colder regions of the reaction tube which did not correspond to the composition given above. On account of this discrepancy a detailed study was undertaken.

Experimental Procedure

A. Preparation of the Complexes. (i) **Materials Used.**—Phosphorus oxychloride (B.D.H.) was subjected to fractional distillation in an all-glass apparatus, the fraction distilling between 103 and 104° (690 mm. pressure) was employed. *Anal.* Calcd.: P, 20.19; Cl, 69.39. Found: P, 20.08; Cl, 68.64.

(ii) **General Procedure.**—The reaction of ferric chloride with excess phosphorus oxychloride was carried out at 95° in an all-glass apparatus. The unreacted $POCl_3$ was driven off by evacuation (20 mm. pressure). The deep red solution left behind was warmed (35°) under reduced pressure when red crystals separated. The crystals were freed from the mother liquor and dried in a current of dry air. During the entire procedure, care was taken to avoid contamination with atmospheric moisture. A weighed amount of the crystals was dissolved in water and the total P and Cl present in the solution estimated by the ammonium phosphomolybdate and Volhard's methods, respectively. The iron was estimated volumetrically. The analytical data (mean of six determinations) showed that the crystals had the composition $2FeCl_3 \cdot 3POCl_3$. *Anal.* Calcd.: Fe, 14.25; Cl, 67.79; P, 11.84. Found: Fe, 14.35; Cl, 66.94; P, 11.64.

Preparation of the Complex $FeCl_3 \cdot POCl_3$.—The red crystals of $2FeCl_3 \cdot 3POCl_3$ were subjected to further evacuation in a flask (2–3 mm.) at 50° with periodic weighing. In the initial stages there was a rapid loss in weight due to loss of $POCl_3$. After about an hour, loss of $POCl_3$ was not noticed and the pressure of the system remained constant at about 4 mm. The color of the crystals had in the meanwhile changed from red to brown. The average results of analysis of the crystals from six independent experiments were: Fe, 17.63 (theor. 17.72); Cl, 66.73 (theor. 67.41);

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(1) P. Walden and G. Oddo, *Z. anorg. Chem.*, **25**, 212 (1900).

(2) O. Ruff and H. Einbeck, *Ber.*, [IV] **37**, 4518 (1904).