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THE DECOMPOSITION OF OXALIC ACID BY ACETIC ANHYDRIDE[1]

BY EARL L. WHITFORD

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Introduction

In a recent investigation, Schierz[2] made a systematic study of the decomposition of formic acid in acetic anhydride, which he believed to be preceded by the formation of a mixed anhydride. Behal[3] was the first to describe such a compound. While Schierz was unable to isolate the anhydride as such, it seems reasonable to believe that the decomposition of formic acid is due to the unstable character of an intermediate molecular compound. That such compounds are easily formed has been demonstrated by Kendall and Carpenter.[4] Schierz also found that the reaction investigated was catalyzed by various tertiary nitrogen bases. Preliminary experiments showed a somewhat similar behavior of acetic anhydride toward oxalic acid although, due to the solubility of carbon dioxide in acetic anhydride, no quantitative measurements were made at that time.

The present investigation was undertaken for the purpose of studying the mechanism of the decomposition of oxalic acid by acetic anhydride and the effect of added substances upon the rate of the reaction.

Experimental Part

Preparation and Purification of Materials. Acetic Anhydride.—A commercial preparation labeled 92% was purified by the method of Walton and Withrow.[5] The acetic anhydride prepared in this manner boiled at 139.4° (740 mm.) and showed no test for acetone and practically none for aldehyde.

Anhydrous Oxalic Acid.—This was prepared from the hydrated crystalline product by the method of Hultman, Davis and Clarke.[6]

Pyridine.—The pyridine for the earlier investigation was prepared by the method of Wilcox.[7] The fraction that distilled at 115–115.3° (corr.) was used.

Apparatus and Method of Procedure.—The apparatus used was the same as that

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[1] The work included in this paper is taken 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] Schierz, THIS JOURNAL, **45**, 455 (1923).

[3] Behal, *Compt. rend.*, **128**, 1460 (1899).

[4] Kendall and Carpenter, THIS JOURNAL, **36**, 2498 (1914).

[5] Walton and Withrow, *ibid.*, **45**, 2689 (1923).

[6] Hultman, Davis and Clarke, *ibid.*, **43**, 366 (1921).

[7] Wilcox, *J. Phys. Chem.*, **14**, 584 (1910).

employed in the study of malic acid decomposition by sulfuric acid.[8] The gases, carbon monoxide and carbon dioxide, were measured over mercury and later over water saturated with these gases. The acetic anhydride was also saturated with dried carbon monoxide and carbon dioxide which were generated by heating oxalic acid with concd. sulfuric acid. The reaction mixture was then prepared as follows. A weighed amount of anhydrous oxalic acid was dissolved in 100 cc. of acetic anhydride, and samples of 25 cc. each were pipetted directly into the reaction flasks. Since oxalic acid is decomposed by acetic anhydride at ordinary room temperature, the volume of the gas from the time $t = 0$ to the end of the reaction was takan as "a" in calculating the velocity constants for a first-order reaction.

Preliminary Experiments

Completeness and Order of the Reaction.—On account of the solubility of carbon dioxide the acetic anhydride was saturated with the two gases as described above and, after a preliminary shaking, weighed amounts of oxalic acid were added by means of glass capsules. The results of numerous determinations showed that in this reaction 99% of the calculated amount of gas is evolved.

Eight different runs were made to determine the order of the reaction, and the constants thus obtained showed it to be of the first order. The average value of the constant multiplied by 10^3 was 12.8 and the individual values varied between 12.5 and 13.2.

Effect of Temperature upon Reaction Rate

To determine the effect of temperature upon the rate of the reaction, similar measurements were made at 35° and 45°. Table I shows the average values for the velocity constants at the different temperatures as well as the temperature coefficients and the critical increment calculated from the equation of Arrhenius. The value of the critical increment does not vary to any great extent with temperature. This is in accordance with the theory of Arrhenius, Tolman and others.

TABLE I

THE EFFECT OF TEMPERATURE UPON THE REACTION RATE

Temp., ° C.	$K \times 10^3$	Temp. coeff.	Crit. increment, calcd.
25	12.8	..	...
35	37.5	2.93	19,450
45	110.5	2.95	20,150

Effect of Added Substances.—To find the influence of various substances upon the speed of the decomposition of oxalic acid, small amounts of the substances listed below were added to 15cc. portions of acetic anhydride saturated with oxalic acid and any increase or decrease in the evolution of gas was carefully noted.

1. Quinoline, cocaine, morphine, alanine, strychnine and brucine, all formed insoluble addition compounds and the evolution of gas practically ceased.

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[8] Whitford, THIS JOURNAL, **47**, 953 (1925).

2. Urea, pyrrole, aniline, phenylhydrazine and methyl, ethyl and propyl cyanides showed no appreciable effect upon the rate of decomposition.

3. Impure samples of picoline, lutidine and collidine showed a tremendous positive catalytic effect, the systems remaining homogeneous. The fact that it is practically impossible to obtain these compounds in a pure state made it inadvisable to conduct a quantitative study.

4. Pyridine, prepared according to the method of Wilcox, showed a marked, positive, catalytic effect but the reaction was attended by the formation of a white precipitate which disappeared as the reaction proceeded.

Possible Mechanism of the Reaction and the Effect of Acetic Acid upon the Reaction Velocity

It seems highly probable that the decomposition of oxalic acid by acetic anhydride is preceded by the formation of a molecular compound similar to that with sulfuric acid as suggested by Taylor.[9] That such compounds are easily formed has been demonstrated by Kendall and Carpenter.[4] The decomposition of oxalic acid will then proceed according to Equation 1.

$$(COOH)_2 + (CH_3CO)_2O \rightleftarrows (COOH)_2.(CH_3CO)_2O \rightarrow CO + CO_2 + 2CH_3COOH \quad (1)$$

Further evidence pointing toward this mechanism as the true one is given by the fact that the amount of oxalic acid decomposed by acetic anhydride is in accordance with the ratio expressed by the above equation. This will be discussed more fully in another part of this paper.

If the reaction as written is the true one, then the effect of acetic acid upon the reaction rate is of obvious importance. The fact that the velocity constants for a single run agree within 3 or 4% and show no diminution as the reaction proceeds, indicates that its effect in small quantities is negligible. In order to test this point more rigidly, several determinations were made at 25° in reaction mixtures containing as high as 5% of acetic acid. In no case, however, did the average value of the velocity constant differ appreciably from 12.8, the value for pure acetic anhydride. Kendall and his students[10] have shown that in the case of molecular compounds formed from two acidic substances, the tendency toward compound formation is governed largely by the relative acidity of the reactants. In this case, the acid characters of acetic acid and acetic anhydride are very likely about equal; consequently, there would be practically no tendency for reaction to take place between them. On the other hand, they would exhibit about equal tendencies toward compound formation with oxalic acid, but concentrations as low as 5% acetic acid would produce no noticeable effect upon the extent of the formation

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[9] Taylor, *J. Phys. Chem.*, **27**, 330 (1923).

[10] Kendall and others, THIS JOURNAL, **1914** and later.

of the compound $(COOH)_2.(CH_3CO)_2O$ which governs the rate of decomposition.

Catalytic Effect of Pyridine

The positive catalytic effect of pyridine, with the attendant white precipitate formed, pointed toward a definite compound between oxalic acid and pyridine which is more rapidly decomposed by acetic anhydride than oxalic acid alone. It was found that a similar crystalline precipitate could be prepared by adding pyridine to an acetone solution of oxalic acid. The precipitate, when filtered and dried, was readily decomposed by the addition of acetic anhydride with the evolution of carbon monoxide and carbon dioxide. It was insoluble or only slightly soluble in all varieties of solvents except water, ethyl and methyl alcohols and pyridine. In the first three solvents the solubility of the pyridine oxalic acid compound was very high. Pfeiffer[11] prepared an acid oxalate of pyridine by dissolving oxalic acid in hot pyridine and then allowing the solution to cool. The crystals which he obtained by this method were of the composition $C_5H_5N.(COOH)_2$. Analysis of the crystalline product prepared by precipitation from acetone showed it to be identical with that of Pfeiffer.

The Decomposition of Oxalic Acid by Acetic Anhydride in Pyridine Solutions

It has been stated in a previous part of this paper that pyridine acid oxalate is moderately soluble in an excess of pyridine. When acetic anhydride is added, even in small amounts, the oxalic acid-pyridine compound is decomposed with the concomitant evolution of carbon monoxide and carbon dioxide. A semiquantitative study of this system was made by adding small quantities of a 10% solution of acetic anhydride in pyridine, to 25 cc. of pyridine saturated with oxalic acid. The course of the resulting reaction was followed as before. It was found that the volume of gas evolved is approximately proportional to the amount of acetic anhydride added, as shown in Table II.

Table II

The Ratio of Gas Evolved to Acetic Anhydride Used

Ratio of acetic anhydride in reaction mixtures	Volumes of gas, cc. (1)	(2)	Ratio of volumes (1)	(2)
1	4.8	4.2	1.08	1.06
3	14.0	12.2	3.17	3.07
5	22.4	20.3	5.07	5.11
10	44.2	39.7	10.0	10.0

Furthermore, the reaction-velocity constants are identical regardless of the amount of acetic anhydride added. Table III shows the calculations for two concentrations of acetic anhydride.

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[11] Pfeiffer, *Ber.*, **47**, 1582 (1914).

Table III

Reaction Velocity in Pyridine Solutions

0.5 Cc. of 10% soln. of acetic anhydride in pyridine

t	Vol.	x	$a - x$	$k \times 10^3$
0	6.3	..	..	...
2	11.5	5.2	10.9	189
3.5	14.33	8.0	8.1	184
6.5	17.7	11.4	4.7	181
10.5	20.1	13.8	2.3	184
			Av.	184

1.0 Cc. of 10% soln. of acetic anhydride in pyridine

t	Vol.	x	$a - x$	$K \times 10^3$
0	9.5	..	..	...
1	15.4	5.9	28.8	186
2	20.1	10.6	24.1	184
3.5	25.9	16.4	18.3	189
5	30.1	20.6	13.7	186
8	35.7	26.2	8.1	182
10	38.1	28.6	5.7	181
14	41.0	31.5	2.8	180
			Av.	184

Purification of Pyridine through the Formation of Pyridine Acid Oxalate

The preliminary experiments, which indicated that the oxalates of the picolines, lutidine and collidine are soluble in acetone, suggested the following method of separating pyridine from its troublesome derivatives.

To a solution of oxalic acid in acetone a quantity of commercial pyridine was added during rapid stirring. The insoluble oxalate was then filtered off, washed several times with acetone and dried at about 70°. The dry salt was then mixed thoroughly with finely powdered lime and the pyridine distilled. The product thus obtained still contained some water which was removed by refluxing in the usual manner with barium oxide. Very nearly the entire volume of pyridine (approximately 100 cc.) then distilled at 115.2–115.3° (760 mm.). The pyridine acid oxalate is a rather bulky precipitate and this method would not be practical for the purification of large quantities of pyridine. For small amounts, however, it serves very well and yields a product whose boiling point is in close agreement with the best values given in the literature.

Summary

1. The decomposition of oxalic acid in acetic anhydride solution is a reaction of the first order.
2. The reaction velocities have been determined at 25°, 35° and 45°.
3. The picolines, lutidine and collidine catalyze the reaction markedly.
4. Pyridine also shows a positive catalytic effect but the reaction is complicated by the formation of a solid phase.
5. Pyridine acid oxalate has been prepared by precipitation from acetone solutions. This was used as a basis for purifying pyridine.
6. The extent of the decomposition of oxalic acid in pyridine solutions by acetic anhydride is proportional to the amount of anhydride added. The value of reaction-velocity constant in this system is independent of the amount of anhydride added.
7. A possible mechanism of the decomposition of oxalic acid by acetic anhydride has been suggested.

Madison, Wisconsin