ing constancy of yields also over this pressure range. Some features of the mechanism of the reaction are discussed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. XI. THE OXIDATION OF ORGANIC ACIDS

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Introduction

The permanganate oxidation method for a number of organic acids[1] such as tartaric, malic, malonic, etc., is not entirely satisfactory, due to the fact that formic acid, which is one of the oxidation products, is, in turn, slowly oxidized by permanganate in acid solution. If a direct titration of any of these acids with standard permanganate in hot solution is attempted, the end-point is unsatisfactory, and if even a slight excess of standard permanganate is added, followed by excess of standard oxalic acid and back titration with permanganate, some formic acid is oxidized, the amount depending on such factors as concentration of the formic acid, amount of permanganate in excess and time of its action, temperature and acidity of solution. Therefore, even fairly accurate results can be obtained only when experimental conditions are closely controlled. To avoid the error caused by oxidation of formic acid, the complete oxidation of a number of these acids to carbon dioxide and water has been proposed, first in acid, then in alkaline solution, using standard permanganate, followed by addition of sulfuric acid, excess of standard oxalate and back titration with permanganate.

Hatcher and West[2] found that formic acid was an intermediate oxidation product in the oxidation of complex organic acids and that the rate of its oxidation by permanganate was inversely proportional to the hydrogen-ion concentration of the solution.

Benrath and Ruland[3] studied the velocity of reaction of ceric sulfate with a number of organic compounds. They were interested in determining the course of the reactions, however, rather than in an analytical method for these acids. They stated that sulfuric acid retarded the velocity of oxidation by ceric sulfate, and that a solution containing ceric

[1] Representative references are given under the individual acids. It is obvious, however, that space is not available for complete lists of oxidation methods for determining these acids. The authors have made no attempt to prepare such a bibliography, which would be beyond the scope of the present paper.

[2] Hatcher and West, *Trans. Roy. Soc.*, **21**, 269 (1927).

[3] Benrath and Ruland, *Z. anorg. allgem. Chem.*, **114**, 267 (1920).

sulfate and a large excess of formic acid, if kept at 100° for a day, showed no change in the ceric ion content, as determined colorimetrically.

The present authors have studied the oxidation of oxalic acid with ceric sulfate[4] and have based an accurate method for the standardization of ceric sulfate solutions on this reaction.

It seemed probable that ceric sulfate, if its action on formic acid was negligible, could be used with much greater accuracy and under a much wider range of experimental conditions, than could permanganate or other oxidizing agents to determine such acids as tartaric, malic, malonic, etc. In the experimental work which follows such is shown to be the case. Obviously quantitative data can be given for only a few representative acids but the cases listed below will serve to illustrate the possibilities of ceric sulfate as a volumetric oxidizing agent in the determination of organic acids.

Experimental

The ceric sulfate solution was prepared by the method described by the authors[5] from high-grade ceric oxide and was 0.5 *M* in sulfuric acid. It was standardized against sodium oxalate.[4] The ferrous sulfate solution was standardized electrometrically against standard ceric sulfate.[4] A silver chloride–platinum electrode system was used and a thermionic voltmeter, Type DP-2, from the General Electric Company.

Formic Acid, HCOOH.—In five experiments 15–50 cc. of very pure formic acid 0.1 *N* as a reducing agent was taken, then 20–60 cc. of sulfuric acid, sp. gr. 1.5, and 25 cc. of 0.1 *N* ceric sulfate. After diluting to 200 cc. the solution was held just below the boiling point for thirty or sixty minutes. The volume of ceric sulfate used varied from 0.03 cc. at the shorter time and low acidity to 0.21 cc. at the longer time and highest acidity. The average error of 0.12 cc. would correspond to 0.28 mg. of formic acid. Thus formic acid is not appreciably oxidized in hot acid solution by ceric sulfate, a result scarcely to be expected when one considers the ease with which it is oxidized by many oxidizing agents. Its presence as an oxidation product from other organic acids should cause no interference in oxidations with ceric sulfate.

Corrections of 0.03–0.05 cc. have been applied to the above figures, for it was found that in blank experiments in which formic acid was omitted the oxidizing power of ceric sulfate decreased to this extent. In previous experiments[5] using a reflux condenser no change whatever was observed, but in this work a beaker was used.

Acetic Acid, CH_3COOH.—Acetic acid distilled from chromic acid was diluted to a 0.1 *N* acid solution. Two 50-cc. samples of this, after dilu-

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[4] Willard and Young, THIS JOURNAL, **50**, 1322 (1928); see also Furman, *ibid.*, **50**, 755 (1928).

[5] Willard and Young, *ibid.*, **51**, 149 (1929).

tion with 20 cc. of sulfuric acid, sp. gr. 1.5, 25 cc. of ceric sulfate, 0.1020 *N*, and water to 200 cc., were heated to boiling and held just below the boiling point over a free flame for thirty and sixty minutes, respectively. After cooling and determining the excess ceric salt in the usual way, it was found that 0.05 cc. and 0.10 cc. of the ceric sulfate had been used up in the two experiments. Therefore, acetic acid is not oxidized in hot solution by ceric sulfate.

Tartaric Acid, HOOCCH(OH)CH(OH)COOH.—Mestrezat[6] added a slight excess of permanganate to a hot sulfuric acid solution containing tartaric acid, then an excess of standard oxalic acid, and determined the excess of the latter by back titration with standard permanganate. He gave as the reaction

$$H_2C_4H_4O_6 + 3O = 2HCOOH + 2CO_2 + H_2O \qquad (1)$$

but obtained in this method an oxygen equivalent of 6.86 instead of 6, due to slow oxidation of formic acid. To avoid this error he attempted the complete oxidation of tartaric acid, first in acid, then in alkaline medium, to carbon dioxide and water.

$$H_2C_4H_4O_6 + 5O = 4CO_2 + 3H_2O \qquad (2)$$

and obtained an oxygen equivalent of 9.80 instead of 10. A number of other oxidation methods for tartaric acid have been described.[7]

Benrath and Ruland[3] stated that the velocity of the reaction of tartaric acid with excess ceric sulfate was retarded by the presence of sulfuric acid (their work was carried out at 0 and 20°). This was, therefore, the first matter to be investigated.

Very pure potassium acid tartrate was recrystallized from water, dried at 100° for a short time and used to prepare a standard solution. The tartrate, checked further by titrating three 1-g. samples of it with 0.1 *N* sodium hydroxide which had been standardized against Bureau of Standards potassium acid phthalate, was found to be 99.91% pure.

Twenty-five cc. portions of potassium acid tartrate solution containing 0.06916 g. of $KHC_4H_4O_6$ or 0.05439 g. of $H_2C_4H_4O_6$ were diluted with water, sulfuric acid, sp. gr. 1.5 and 40 cc. of 0.1020 *N* ceric sulfate to 200 cc., heated to 90–95° and kept at this temperature on a low temperature hot-plate for thirty minutes. The solutions were cooled to 30–35° and the excess ceric sulfate titrated electrometrically with standard ferrous sulfate.

With all factors but the acid concentration at time of oxidation held constant, the extent of oxidation of tartaric acid decreased at first and

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[6] Mestrezat, *Ann. chim. anal.*, **12**, 173 (1907); also Chapman and Whitteridge, *Analyst*, **32**, 163 (1907); Kling and Florentin, *Bull. soc. chim.*, **11**, 886 (1912); Meigen and Schnerb, *Z. angew. Chem.*, **37**, 208 (1924).

[7] For example—iodimetric, Strebinger and Wolfram, *Oesterr. Chem.-Ztg.*, **26**, 156 (1923); Cuny, *J. pharm. chim.*, [8] **3**, 112 (1926); Pirrone, *Riv. ital. essenze e profumi*, 101 (1928)—dichromate, Taufel and Wagner, *Z. anal. Chem.*, **67**, 16 (1925).

then increased to a constant value as the acid concentration was steadily increased. In the last four experiments in which the volume of sulfuric acid added varied from 30 to 60 cc., there was a deviation of 0.19 cc. of 0.1020 *N* ceric sulfate, which corresponds to 0.4 mg. of tartaric acid. In the following experiments, therefore, these conditions were used.

Measured volumes of a standard potassium acid tartrate solution (25 cc. = 0.06678 g. of $KHC_4H_4O_6$ or 0.05326 g. of $H_2C_4H_4O_6$) were taken, diluted with water, acid and 0.1020 *N* ceric sulfate to the volume indicated in Table I, and treated in the same way as the solutions for the experiments described above. The results obtained are shown in Table I.

TABLE I

THE OXIDATION OF TARTARIC ACID WITH CERIC SULFATE IN ACID SOLUTION

H_2SO_4 sp. gr. 1.5, before ox., cc.	Time of standing at 90–95°, min.	Vol. during ox., cc.	0.1020 *N* $Ce(SO_4)_2$ added, cc.	0.1 *N* $Ce(SO_4)_2$ used, cc.	$H_2C_4H_4O_6$ taken, g.	$H_2C_4H_4O_6$ found, g.
30	30	200	40	25.54	0.0533	0.0532
30	60	200	40	25.55	.0533	.0533
30	30	200	30	25.49	.0533	.0531
30	60	200	60	25.55	.0533	.0533
30	10	200	40	25.54	.0533	.0532
30	30	200	100	76.91	.1598	.1603
30	30	200	40	10.21	.0213	.0213
15	30	100	40	25.47	.0533	.0531
45	30	300	40	25.63	.0533	.0534

The amount of tartaric acid oxidized by 1 cc. of 0.1 *N* ceric sulfate is 0.002084 g. When this factor is used the values in the last column are obtained, the results agreeing very closely with those in the preceding column. Three other series of experiments similar to those in Table I were carried out, in which the sulfuric acid, sp. gr. 1.5, added before oxidation amounted in turn to 40, 50 and 60 cc. per 200 cc. of solution, and the results obtained were of the same degree of accuracy as those above. Thus it is seen that the amount of tartaric acid oxidized by 1 cc. of 0.1 *N* ceric sulfate remains constant over wide variations in acid concentration, excess of oxidizing agent and time of its action, volume of solution in which the oxidation is carried out and tartaric acid content. According to Table I, 1 mole of tartaric acid requires 7.2 equivalents of oxygen for oxidation; that is, the oxidation reaction, under the conditions used above, cannot be expressed by Equation 1.[8]

Succinic Acid, $HOOCCH_2CH_2COOH$.—Very pure succinic acid which had been recrystallized twice from nitric acid and once from water was used to prepare a 0.05 *M* solution. Twenty-five cc. portions of this so-

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[8] After this paper had been submitted for publication, Berry [*Analyst,* **54,** 46 (1929)] published some work in which he obtained an oxygen equivalent of 7.02 by the use of ceric sulfate, apparently by direct titration, a reaction too slow to be practicable.

lution were diluted with water, acid and 25 cc. of 0.1020 *N* ceric sulfate to 200 cc., and treated in the same way as the solutions for the experiments in Table I. The volume of ceric sulfate used varied from 0.06 cc. in half an hour to 0.17 cc. in two hours, indicating that succinic acid is not appreciably oxidized under these conditions.

Malonic Acid, $HOOCCH_2COOH$.—Malonic acid has been titrated directly in hot acid solution with permanganate,[9] the reaction being

$$H_2C_3H_2O_4 + 3O = H_2O + HCOOH + 2CO_2 \qquad (3)$$

Later investigators[10] found the method very irregular, due to appreciable oxidation of formic acid, and developed an accurate procedure for malonic acid, based on its complete oxidation, first in acid, then in alkaline medium

$$H_2C_3H_2O_4 + 4O = 2H_2O + 3CO_2 \qquad (4)$$

Pure malonic acid was recrystallized from ether and the first fraction of crystals used to prepare a standard solution. Titrations of three samples of this material with 0.1 *N* sodium hydroxide indicated a purity of 99.59%. Measured volumes of a standard solution (25 cc. = 0.04337 g. of $H_2C_3H_2O_4$) were diluted with water, 0.1020 *N* ceric sulfate and acid to the volume indicated in Table II, and treated in the same way as the solutions for the experiments with tartaric acid. With malonic acid it was important to add the ceric sulfate before the acid; otherwise, a slight error was introduced, due possibly to decomposition of the malonic acid by the sulfuric acid. The results obtained are shown in Table II.

TABLE II

THE OXIDATION OF MALONIC ACID WITH CERIC SULFATE IN ACID SOLUTION

Expt.	H_2SO_4, sp. gr. 1.5, before ox., cc.	Time of standing at 90–95°, min.	Vol. during ox., cc.	0.1020 *N* $Ce(SO_4)_2$ added, cc.	0.1 *N* $Ce(SO_4)_2$ used, cc.	$H_2C_3H_2O_4$ taken, g.	$H_2C_3H_2O_4$ found, g.
1	20	30	200	50	27.17	0.0434	0.0425
2	30	30	200	50	27.47	.0434	.0429
3	40	30	200	50	27.72	.0434	.0433
4	50	30	200	50	27.74	.0434	.0434
5	60	30	200	50	27.87	.0434	.0436
6	40	60	200	50	27.73	.0434	.0433
7	60	60	200	50	27.73	.0434	.0433
8	40	30	200	75	27.72	.0434	.0433
9	60	30	200	75	27.86	.0434	.0435
10	40	15	200	50	27.54	.0434	.0430
11	60	15	200	50	27.83	.0434	.0435
12	80	30	400	100	55.22	.0867	.0863
13	20	30	80	35	10.78	.0173	.0169
14	20	30	100	35	10.71	.0173	.0168
15	40	30	200	65	39.23	.0607	.0613
16	40	30	200	65	44.97	.0694	.0703
17	40	30	200	75	56.55	.0867	.0884

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[9] Durand, *Ann. chim. anal.*, **8**, 330 (1903).

[10] Cameron and McEwan, *Proc. Chem. Soc.*, **26**, 144 (1910).

Thus, an average of 0.001563 g. of malonic acid is oxidized by 1 cc. of 0.1 *N* ceric sulfate. By the use of this factor the values in the last column are obtained. Experiments 1 to 5 show that the extent of oxidation of a given amount of malonic acid is constant in a solution containing 40–60 cc. of sulfuric acid, sp. gr. 1.5, per 200 cc.; Expts. 3 to 13 show that the results are accurate for a given concentration of malonic acid over wide variations in acid concentration, excess of oxidizing agent and time of its action, and volume of solution in which the oxidation is carried out; Expts. 14 to 17 show that the results become less accurate as the concentration of malonic acid is changed. Because of this effect, the approximate strength of the solution, if unknown, should be determined by a preliminary experiment, that volume which will contain 40–50 mg. of malonic acid taken for the final analyses and the oxidation carried out in a volume of 200 cc. These experiments show that 1 mole of malonic acid requires 6.66 equivalents of oxygen for oxidation.

Glycolic Acid, $CH_2(OH)COOH$.—The acid was purified by recrystallizing from ether, and the first fraction of crystals used to prepare a standard solution. Titrations of three samples of acid with 0.1 *N* sodium hydroxide indicated a purity of 99.75%. Preliminary experiments showed that glycolic acid was not as easily oxidized by ceric sulfate as tartaric or malonic acid, a steady increase in oxidation being evident over a five-hour period with solutions kept at 90–95°. Therefore, measured portions of the standard solution (25 cc. = 0.05131 g. of $HC_2H_3O_3$) were diluted with water, 0.1020 *N* ceric sulfate and acid to the volume indicated in Table III, heated to boiling, held just below the boiling point over a small flame for the time indicated, then cooled to 30–35° and titrated electrometrically with standard ferrous sulfate. The results are shown in Table III.

TABLE III

THE OXIDATION OF GLYCOLIC ACID WITH CERIC SULFATE IN ACID SOLUTIONS

Expt.	H_2SO_4, sp. gr. 1.5, before ox., cc.	Time at b. p., min.	Vol. during ox., cc.	0.1020 *N* $Ce(SO_4)_2$ added, cc.	0.1 *N* $Ce(SO_4)_2$ used, cc.	$HC_2H_3O_3$ taken, g.	$HC_2H_3O_3$ found, g.
1	40	30	200	50	25.80	0.0513	0.0496
2	40	60	200	50	26.60	.0513	.0512
3	40	120	200	50	26.78	.0513	.0515
4	60	60	200	50	26.62	.0513	.0512
5	60	120	200	50	26.52	.0513	.0510
6	40	60	200	50	10.75	.0205	.0207
7	40	60	200	75	53.18	.1026	.1023
8	20	60	100	50	26.76	.0513	.0515
9	60	60	300	50	25.13	.0513	.0483
10	60	60	300	75	26.95	.0513	.0518
11	40	60	200	75	26.93	.0513	.0518
12	60	60	200	75	26.75	.0513	.0515

The amount of glycolic acid oxidized by 1 cc. of 0.1 *N* ceric sulfate, according to these experiments, is 0.001923 g. Experiment 1 shows that the extent of oxidation of glycolic acid is not constant after contact with excess ceric sulfate for thirty minutes in hot solution and Expt. 9 that the excess of ceric sulfate used there is not sufficient for the larger volume of solution. The other experiments indicate that an accurate determination of glycolic acid may be made within a wide range of conditions. According to Table VI 1 mole of glycolic acid requires 3.95 equivalents of oxygen for oxidation, that is, the reaction may be

$$HC_2H_3O_3 + 2O = HCOOH + CO_2 + H_2O \qquad (5)$$

Malic Acid, $HOOCCH_2CH(OH)COOH$.—Mestrezat[6] used procedures for malic acid similar to those developed for tartaric acid. By oxidation with permanganate in acid solution

$$H_2C_4H_4O_5 + 4O = 2HCOOH + 2CO_2 + H_2O \qquad (6)$$

he obtained an oxygen equivalent of 8.81 instead of 8, and by oxidation first in acid, and finally in alkaline solution

$$H_2C_4H_4O_5 + 6O = 4CO_2 + 3H_2O \qquad (7)$$

his oxygen equivalent was 11.40 instead of 12. Lange and Kline[11] did not obtain satisfactory results in titrating malic acid in hot solution with permanganate.

Malic acid was purified by dissolving in hot acetone, filtering and adding carbon tetrachloride to the hot solution and allowing the acid to crystallize on cooling. Three samples, dried at 100–110°, indicated a purity of 99.59% when titrated against 0.1 *N* sodium hydroxide. The treatment of measured portions of a standard solution of malic acid was similar to that described for the experiments in Table III. The volume at the time of oxidation was always 200 cc. Results obtained are given in Table IV.

Thus, 0.001449 g. of malic acid is oxidized by 1 cc. of 0.1 *N* ceric sulfate. Using this factor, the values in the last column are obtained. Experiments 1 to 5 show that the extent of oxidation of malic acid is constant in a solution containing 40–60 cc. of sulfuric acid, sp. gr. 1.5, per 200 cc.; Expts. 4 to 13 show that the results are accurate for a given concentration of malic acid over wide variations in acid concentration, excess of oxidizing agent and time of its action; Expts. 14 to 16 show that the results become less accurate as the concentration of malic acid is changed. With variations in the volume the results were not satisfactory. Therefore, it is necessary to determine the approximate concentration of the solution and to use a volume which will contain 40–60 mg. of malic acid, carrying out the oxidation in a volume of 200 cc. In these experiments 1 mole of malic acid requires 9.25 equivalents of oxygen for oxidation.

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[11] Lange and Kline, This Journal, **44**, 2709 (1922).

TABLE IV

THE OXIDATION OF MALIC ACID WITH CERIC SULFATE IN ACID SOLUTION

Expt.	H_2SO_4, sp. gr. 1.5, before ox., cc.	Time at b. p., min.	0.1020 *N* $Ce(SO_4)_2$ added, cc.	0.1 *N* $Ce(SO_4)_2$ used, cc.	$H_2C_4H_4O_5$ taken, g.	$H_2C_4H_4O_5$ found, g.
1	20	30	50	28.69	0.0423	0.0416
2	30	30	50	28.64	.0423	.0415
3	40	30	50	28.88	.0423	.0419
4	50	30	50	29.07	.0423	.0421
5	60	30	50	29.21	.0423	.0423
6	40	60	50	29.09	.0423	.0422
7	60	60	50	29.07	.0423	.0421
8	40	120	50	29.09	.0423	.0422
9	60	120	50	29.35	.0423	.0425
10	40	15	50	28.89	.0423	.0419
11	60	15	50	29.13	.0423	.0422
12	40	30	75	29.05	.0423	.0421
13	60	30	75	29.34	.0423	.0425
14	40	30	50	22.72	.0338	.0329
15	40	30	75	35.26	.0507	.0511
16	40	30	75	41.11	.0593	.0596

Citric Acid, $HOOCCH_2C(OH)COOHCH_2COOH$.—From a study of the oxidation of citric acid by permanganate, Wöhlk[12] found that these substances reacted with each other, with or without the addition of mineral acid. In a direct titration with permanganate in hot dilute sulfuric acid solution, he considered that acetone-dicarboxylic acid, a primary oxidation product, split up quickly into acetone and carbon dioxide, these being the chief products of the oxidation. In a secondary oxidation reaction, the acetone was further split up to some extent into acetic and formic acids.

$$H_3C_6H_5O_7 + O = C_3H_6O + 3CO_2 + H_2O \qquad (8)$$

$$C_3H_6O + 3O = HC_2H_3O_2 + HCOOH \qquad (9)$$

Pratt's method[13] for citric acid, depending upon its fractional oxidation by permanganate to acetone, removal of the acetone as fast as formed by distillation, formation of an insoluble mercury–acetone complex and the weighing of this precipitate, has been modified by Willaman[14] to give more satisfactory results. Cuny[7] has described an iodimetric method for citric acid, complete oxidation to carbon dioxide being effected.

$$5H_3C_6H_5O_7\cdot H_2O + 9I_2O_5 = 9I_2 + 30CO_2 + 25H_2O \qquad (10)$$

A solution of citric acid was prepared from pure material and standardized by titrating three 100-cc. samples with 0.1 *N* sodium hydroxide. The treatment of measured portions of this standard acid solution (25

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[12] Wöhlk, *Z. anal. Chem.*, **41**, 77 (1902); see also Mathieu and Ferre, *Ann. chim. anal.*, **18**, 352 (1913).

[13] Pratt, U. S. Dept. Agr., Bur. Chem., *Cir.* **88.**

[14] Willaman, THIS JOURNAL, **38**, 2193 (1916).

cc. = 0.04995 g. of $H_3C_6H_5O_7$) was similar to that described for the experiments in Table III. Results obtained are given in Table V.

TABLE V

THE OXIDATION OF CITRIC ACID WITH CERIC SULFATE IN ACID SOLUTION

Expt.	H_2SO_4, sp. gr. 1.5, before ox., cc.	Time at b. p., min.	Vol. during ox., cc.	0.1020 *N* $Ce(SO_4)_2$ added, cc.	0.1 *N* $Ce(SO_4)_2$ used, cc.	$H_3C_6H_5O_7$ taken, g.	$H_3C_6H_5O_7$ found, g.
1	20	30	200	75	40.75	0.0500	0.0494
2	30	30	200	75	41.29	.0500	.0500
3	40	30	200	75	41.14	.0500	.0498
4	50	30	200	75	41.22	.0500	.0499
5	60	30	200	75	41.29	.0500	.0500
6	30	30	200	100	41.25	.0500	.0500
7	50	30	200	100	41.71	.0500	.0505
8	30	30	200	60	40.92	.0500	.0496
9	50	30	200	60	41.04	.0500	.0497
10	30	60	200	60	41.11	.0500	.0498
11	50	60	200	60	41.30	.0500	.0500
12	50	30	200	60	32.72	.0400	.0396
13	50	30	200	75	50.18	.0600	.0608
14	50	30	200	75	58.31	.0700	.0706
15	25	30	110	60	42.38	.0500	.0513
16	75	30	300	75	40.59	.0500	.0492

Thus, 0.001211 g. of citric acid is oxidized by 1 cc. of 0.1 *N* ceric sulfate. Experiment 1 indicates that there was not enough sulfuric acid added. The results are somewhat less accurate in Expts. 12 to 14, as the citric acid content is changed and in Expts. 15–16 the volume is changed. The other experiments indicate that an accurate determination of citric acid may be made within a wide range of conditions. To use the conversion factor given above, the approximate strength of the solution if unknown should be determined by a preliminary experiment, that volume which will contain 40–60 mg. of citric acid taken for the final analyses, and the oxidation carried out in a volume of 200 cc. According to Table V, 1 mole of citric acid requires 15.85 equivalents of oxygen for oxidation, an indication that the oxidation of the acetone is very extensive.

Maleic and Fumaric Acids, HOOCCH=CHCOOH.—Lange and Kline[11] stated that maleic or fumaric acid could be titrated with permanganate in hot acid solution and assumed that the reaction was

$$H_2C_4H_2O_4 + 5O = 3CO_2 + HCOOH + H_2O \qquad (11)$$

Their results were not altogether satisfactory and they did not recommend the method. Sabalitschka and Tietz[15] reported that accurate results could be obtained if excess permanganate was added to the hot acid solution, followed by oxalate, and the excess of the latter determined by titration with permanganate. They gave as the reaction

$$H_2C_4H_2O_4 + 30O = 20CO_2 + 10H_2O \qquad (12)$$

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[15] Sabalitschka and Tietz, *Continental Met. and Chem. Eng.*, **2**, 232 (1927).

It was thought that both of these acids would be easily oxidized by ceric sulfate, but such did not prove to be the case. Several 31-mg. samples of each acid, in volumes of 200 cc. containing 20–60 cc. of sulfuric acid, sp. gr. 1.5, and 50 cc. of 0.1020 *N* ceric sulfate, reacted at 95° with 0.68–0.98 cc. (fumaric acid) or 0.35–0.61 cc. (maleic acid) of 0.1 *N* ceric sulfate in a half hour. In an hour with a 62-mg. sample of either acid, less than 2 cc. of 0.1 *N* ceric sulfate was used.

Benzoic Acid, C_6H_5COOH.—Benzoic acid, though resistant in general to oxidizing agents, was oxidized to a considerable extent by ceric sulfate. For example, a 0.0987-g. sample of the acid was dissolved, diluted with water, 60 cc. of sulfuric acid, sp. gr. 1.5, and 50 cc. of 0.1020 *N* ceric sulfate to 200 cc., heated to boiling and kept just below the boiling point for two hours. After cooling the solution and determining the excess ceric sulfate in the usual way, it was found that 29.10 cc. of 0.1 *N* ceric sulfate had been used for oxidation. Another sample of the same weight was dissolved, diluted with 40 cc. of sulfuric acid, sp. gr. 1.5, and 100 cc. of 0.1020 *N* ceric sulfate to 200 cc., and held just below the boiling point for three hours. In this case 39.63 cc. of 0.1 *N* ceric sulfate was used for oxidation. Other experiments covering a wide range of conditions indicated that the extent of oxidation of benzoic acid was not definite.

Phthalic Acid, *o*-$C_6H_4(COOH)_2$.—Several 43-mg. samples of phthalic acid, in volumes of 200 cc. containing 30–50 cc. of sulfuric acid, sp. gr. 1.5, and 25 cc. of 0.1020 *N* ceric sulfate, reacted at 95° with only 1.49–1.98 cc. of 0.1 *N* ceric sulfate in a period of one hour. The oxidation of phthalic acid by ceric sulfate was, therefore, very slight.

Salicylic Acid, $C_6H_4(OH)COOH$.—Several 19-mg. samples of salicylic acid, in volumes of 200 cc. containing 20–60 cc. of sulfuric acid, sp. gr. 1.5, and 50 cc. of 0.1020 *N* ceric sulfate, reacted at 95° with 28.50–32.18 cc. of 0.1 *N* ceric sulfate over periods of one-half to two hours. The oxidation of salicylic acid was very extensive but not constant.

Discussion

These results prove that the oxidizing action of ceric sulfate on organic materials may be very different from that of potassium permanganate or chromic acid. For this reason ceric sulfate may be of use in certain organic oxidations where permanganate or chromic acid either do not act or do not bring about the reaction desired—possibly, for example, in some oxidations to determine structure. The fact that formic acid, which is an aldehyde as well as an acid, is not oxidized by ceric salt but is slowly attacked by permanganate suggests the possibility of oxidizing alcohols quantitatively to aldehydes with ceric salt. The authors intend to investigate this matter as well as the action of ceric sulfate on other types of organic compounds. Preliminary experiments indicate that some organic substances can be oxidized by direct titration with ceric sulfate.

Though none of the acids listed above can compare in accuracy with oxalic acid (used as sodium oxalate) as primary standards in oxidimetry reactions, a number of them have been suggested as primary standards in acidimetry reactions, notably maleic, fumaric, malic and tartaric in the form of potassium acid tartrate. The authors found potassium acid tartrate to be by far the most satisfactory of these four. It is obtained in very pure form by one recrystallization, and compares favorably in accuracy with potassium acid phthalate, an accepted primary standard in acidimetry.

Summary

1. Formic, acetic, succinic, fumaric and maleic acids are not oxidized by ceric sulfate in hot sulfuric acid solution.

2. Tartaric, malonic, malic, glycolic and citric acids are oxidized under the same conditions, the products being, usually, formic acid and carbon dioxide. Because the formic acid is not oxidized by ceric sulfate, it has been possible to develop accurate analytical procedures for each of this last group of acids, based on their oxidation in hot sulfuric acid solution by excess standard ceric sulfate and titration of the excess with standard ferrous sulfate.

3. Benzoic, phthalic and salicylic acids are oxidized to a variable extent by ceric sulfate in hot sulfuric acid solution.

4. Attention is called to the possibility of using ceric sulfate in certain organic oxidations where the usual reagents, such as permanganate or dichromate, either do not act or do not produce the result desired.

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PYROPHORIC IRON. I. PREPARATION AND PROPERTIES[1]

BY T. G. FINZEL

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The pyrophoric property of properly prepared finely divided iron reacting with air at room temperatures is a well-known phenomenon.[2] It has been definitely established, moreover, that such material becomes non-pyrophoric when subjected to a high temperature.

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[1] The subject of this research was suggested by Professor James H. Walton and the investigation was conducted under his direction. (Manuscript first received August 30, 1928.)

[2] Magnus, *Pogg. Ann.*, **3**, 81 (1825); Moissan, *Ann. chim. phys.*, [5] **21**, 199–256 (1880); Birnie, *Rec. trav. chim.*, **2**, 273–294 (1883); Smits, Kettner and de Gee, *Verslag. Akad. Wetenschappen*, Amsterdam, [II] **16**, 999 (1913); Tammann and Nikitin, *Z. anorg. allgem. Chem.*, **135**, 201–204 (1924).