germanium from this material, this new method is based upon the volatility of germanium tetrachloride, but it is superior to the earlier methods in that it eliminates the necessity for the use of hydrogen sulfide and concentrates germanium by successive distillations with the aid of a column still of new design.

Ninety-nine per cent. of the germanium in the crude material is recovered. Of this, 83% is obtained directly as germanium dioxide, and the remaining 16% is recovered indirectly by the return of the material to later runs.

The germanium dioxide produced by this method is of exceptional purity. Spectroscopic examination of the material indicated that it contained less than 0.001% of iron and less than 0.0005% of arsenic.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, DAIRY DIVISION, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE DETERMINATION OF MUCIC ACID[1]

BY E. O. WHITTIER

Received February 27, 1923

In the course of an investigation on the products of oxidation of certain sugars, it became necessary to determine mucic and oxalic acids in the same solution. The use of potassium permanganate was thought of immediately but, since both acids are oxidizable and are not quantitatively separable from each other, it was evident that a differential method was needed. Since considerable amounts of other substances, both oxidizing and reducing, were present, the problem was further complicated.

It is frequently stated that mucic acid is entirely insoluble in water.[2] Beilstein's Handbuch[3] states its solubility in water as 1 to 300 at 14°. In the preparation of mucic acid, it is separated and purified by making use of its slight solubility. It appears to be somewhat more soluble in the presence of certain other substances in solution. The calcium salt is stated to be insoluble in water, but soluble in acetic acid.[4]

The temperature at which potassium permanganate reacts with various substances in solution with acid is known to depend on the nature of the substances themselves. The temperature and speed of decolorization were determined roughly for a number of acids that are known to be

---

[1] Published with the permission of the Secretary of Agriculture.

Presented before the Division of Organic Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] Richter, "Organische Chemie," Friedrich Cohen, **1909**, vol. 1, p. 718.

[3] Beilstein, "Handbuch der organischen Chemie," Julius Springer, **1921**, vol. III, p. 582.

[4] Hagen, *Ann.*, **64**, 349 (1847).

formed from sugars or to accompany sugars. Formic and caproic acids showed a slow action at 30° and at higher temperatures. Acetic and propionic acids showed no action, even at 100°. Butyric and valeric acids both affected permanganate slightly at 100°. The action of oxalic acid is slow at 40°, fast at 50° and practically instantaneous at higher temperatures after the initial lag is past. Lactic and citric acids act slowly at 60° and rapidly at 80° and 100°. Racemic acid shows a very slow action at 60°; both racemic and tartaric acids show slow action at 80° and rapid action at 100°. Mucic acid has an extremely slow action at 70°, a slow action at 80° and a fairly rapid action at 90° and 100°.

Hetper[5] has tried the action of potassium permanganate in the presence of phosphoric acid on a large number of substances, heating at 92–93° on a water-bath for over an hour, and obtained quantitative oxidation to carbon dioxide and water in a large proportion of cases as measured by permanganate consumed. Formic, malonic, tartaric and citric acids and several sugars were among the compounds completely oxidized. He found that it was necessary to use the high temperature and a certain amount of time to make the reaction complete. In some cases he obtained quantitative oxidation to some acid that is oxidizable with difficulty; ethyl alcohol and lactic acid for example were each oxidized to acetic acid.

Two samples of mucic acid were used in this work—one obtained commercially, and the other prepared in this Laboratory by oxidation of lactose by means of nitric acid according to the directions of Kent and Tollens.[6] Both samples appeared on titration with standard alkali to be over 99.5% pure. The mucic acid solutions were prepared by dissolving a weighed quantity of mucic acid in a few drops more than the theoretically necessary amount of dil. sodium hydroxide solution. They were made up to a definite volume, and aliquot portions taken for titration. Each aliquot portion was diluted to 160 cc., and 40 cc. of 10% sulfuric acid was added.

Attempts to titrate mucic acid directly to an end-point with potassium permanganate at 90–100° were only partially successful. The reaction went slowly when near the end, the end-point was unsatisfactory, because of the formation of the brown intermediate reduction products of permanganate, and the results were inconsistent.

Finally, the following method was tried. About a 5 cc. excess of 0.05 N potassium permanganate solution was added to the mucic acid solution. This was then heated to boiling, a measured excess of 0.05 N oxalic acid solution added, the liquid shaken until the brown manganese compounds dissolved, and 0.05 N permanganate run in until the end-point was reached. Fairly consistent results were obtained; 0.0503 g. of mucic acid required 52.72, 53.09, 51.81, 52.38, 53.43 (av., 52.76) cc. of 0.05 N permanganate. The procedure was then varied by allowing the solution to stand for 5

---

[5] Hetper, *Z. anal. Chem.*, **50**, 343 (1911).

[6] Kent and Tollens, *Ann.*, **227**, 222 (1885).

minutes after heating to boiling, and before adding the excess of oxalic acid solution. This gave more consistent results; 0.0503 g. of mucic acid required 52.49, 53.04, 53.05, 53.09 (av. 52.92) cc. of 0.05 permanganate. In a determination carried out 2 months later on a different solution, to make sure that the earlier results could be duplicated, 0.0503 g. of mucic acid required 52.94 cc. of 0.05 *N* permanganate. Lengthening the time of standing to 30 minutes gave no greater titration value than that obtained after 5 minutes' standing. The effect of adding the excess of permanganate solution *after* the mucic acid solution had been heated to boiling was to cause less permanganate to be consumed; 0.0503 g. of mucic acid required 49.78, 49.70, 50.03, 48.81 (av. 49.58) cc. of 0.05 *N* permanganate. The second procedure of this paragraph was the one adopted for subsequent use.

A large number of titrations were then made on mixtures of mucic and oxalic acids. Ten cc. of 0.05 *N* oxalic acid solution was added to the usual aliquot of the mucic acid solution, the whole diluted to 160 cc., and 40 cc. of 10% sulfuric acid added. The solution was heated to the temperature for the oxalic acid titration, titrated with 0.05 *N* potassium permanganate solution to an end-point persistent for 10 seconds, excess 0.05 *N* permanganate run in, the solution heated to boiling, allowed to stand for 5 minutes, decolorized with an excess of 0.05 *N* oxalic acid solution and titrated with 0.05 *N* permanganate to the end-point. The oxalic acid was titrated at 40°, 50° and 60°, and the values obtained were equally good. Since at 40° decolorization was slow, and since 60° is rather close to the temperature at which mucic acid is perceptibly attacked, 50° was selected as the temperature to be employed subsequently. A few representative results are given in Table I.

TABLE I

TITRATION OF OXALIC AND MUCIC ACIDS IN THE SAME SOLUTION

Mucic acid taken: 0.0503 G.

No.	Amount taken 0.05 *N* oxalic acid Cc.	Time mixture was held at 100° before oxalic acid addition Minutes	0.05 *N* Permanganate consumed by oxalic acid Cc.	
			by oxalic acid Cc.	by mucic acid Cc.
1	10.00	0	11.58	48.31
2	10.00	0	11.62	49.39
3	10.00	5	11.49	51.60
4	20.00	5	21.66	51.53
5	20.00	5	21.81	51.31

In Titrations 1 and 2, no time was allowed to elapse between the time the solution reached the boiling point and the moment of addition of the excess oxalic acid solution. Five minutes was allowed in Titrations 3 to 5. The difference in titer of the mucic acid caused by this difference in time for reaction is very clearly shown. It will be noted, however, that all the values for the oxalic acid are higher, and those for the mucic acid lower, than was to be expected. The most reasonable explanation is that some mucic acid is attacked during the titration of the oxalic acid at 50°. With the purpose of finding out how variation in the ratio of the amounts of the oxalic and mucic acids present would affect these abnormal values, the amount of oxalic acid was doubled in Titrations 4 and 5. It appears that the error has a practically definite value and is not a proportional one, though there is a very slight tendency for both variations to be greater when the proportion of oxalic acid is increased. The average excess for the oxalic acid was 1.63 cc. of 0.05 *N* permanganate; the average deficiency for the mucic acid, not including No. 1 and No. 2, was 1.44 cc. of 0.05 *N* permanganate. A user of the method should determine for himself the corrections necessary to apply.

The procedure adopted and used for the determination of oxalic and mucic acids in the same solution is the following. Approximately 0.05 *N* potassium permanganate solution is prepared and, after 2 weeks' standing, is standardized against pure oxalic acid. Since the relationship between permanganate and mucic acid is not stoichiometric under the conditions of titration, it is also essential to standardize against pure mucic acid. After some experience with the method, it should be a safe procedure to calculate the ratio of equivalence between oxalic and mucic acids, and thereafter to calculate the mucic acid value of the permanganate solution from the oxalic acid value. 0.05 *N* oxalic acid solution is prepared and its titration value established against the 0.05 *N* permanganate solution. The solution of the sample is strongly acidified with 10% sulfuric acid and the volume made up to approximately 200 cc. with distilled water. It is then heated to 50° and the oxalic acid titrated to an end-point persistent for 10 seconds. The volume of 0.05 *N* permanganate consumed is designated by *A*. An excess of the permanganate solution is run in and the mixture heated to boiling. The liquid is allowed to stand for 5 minutes and is then decolorized with an excess of 0.05 *N* oxalic acid solution. The volume of 0.05 *N* permanganate solution equivalent to the oxalic acid solution used is designated by *B*. The solution is titrated with the permanganate solution to an end-point persistent for 10 seconds. The total volume of the permanganate solution used in the whole operation is designated as *C*. Then $A - 1.50$ cc. is equal to the volume of the permanganate solution equivalent to the oxalic acid originally present; $C + 1.50$ cc. $- A - B$ is equal to the volume of the permanganate solution equivalent to the mucic acid present.

If other substances of either oxidizing or reducing character are present, they should be removed before applying the above method. Precipitation of oxalic acid as the calcium salt is sometimes used as a means of obtaining it in a sufficiently pure condition for titration with permanganate. That method was tried for this mixture of acids; a few results obtained on solutions of known content are given in Table II. The mixed acids were precipitated at the boiling temperature by means of calcium acetate solution. After standing for the recorded lengths of time, the precipitates were filtered, washed with hot water, dissolved in warm dil. sulfuric acid, and titrated by the method of the preceding paragraph. If the solutions are to be divided into portions before titration, it is necessary to take these portions immediately, as crystallization takes place when the solutions are allowed to stand. Calcium mucate crystallizes very slowly, which accounts for Hagen's statements[4] regarding its solubility. Four days appears to be necessary for complete precipitation. The presence of oxalate seems to hinder the crystallization of the mucate, and the separation is somewhat slower from acid than from alkaline solution.

TABLE II

PRECIPITATION AND DETERMINATION OF OXALIC AND MUCIC ACIDS IN THE SAME SOLUTION

Acid taken: oxalic, 0.0225; mucic 0.0400

No.	Solution contained excess of	Time allowed for precipitation Hours	Found Oxalic acid G.	Found Mucic acid G.
1	NH_4OH	24	0.0230	0.0308
2	CH_3COOH	24	.0222	.0254
3		24	.0226	.0269
4		48	.0228	.0310
5		96	.0232	.0397

As tartaric and racemic acids are reported to be formed in small amounts in the oxidation of mucic acid and its isomers,[7] it was thought desirable to determine the effect of potassium permanganate in acid solution on these acids under the conditions employed in the titration of mucic acid; 0.03360 g. of racemic acid required 29.39, 29.05, 29.08, 29.36, 29.19 (av., 29.21) cc. of 0.05 *N* permanganate; 0.02047 g. of tartaric acid required 17.95, 18.05, 17.91, 17.80, 17.46, 17.96, 18.07, 17.89, 17.97, 17.98 (av., 17.97) cc. of 0.05 *N* permanganate. In the first 5 of the tartaric acid titrations, the usual 5 minutes for completion of the reaction was not allowed; in the fourth and fifth titrations, the permanganate was added after heating to boiling instead of before; these variations appear to have no effect on the results obtained in this case.

Evidently the tartaric acids are not end-products in any degree of the action of acid potassium permanganate on mucic acid at boiling temperatures. It should be noted that Fischer and Crossley obtained them in alkaline solution and at low temperatures.

Definite and reproducible relationships between the tartaric acids and permanganate were obtained, though these relationships are not stoichio-

---

[7] Hornemann, *J. prakt. Chem.*, [1] **89**, 283 (1863). Fischer and Crossley, *Ber.*, **27**, 394 (1894).

metrical. The ratios found were not exactly identical for the 2 acids, but this may be due to slight differences in purity of the samples used, or to the fact that one acid is more readily attacked than the other. Attempts at titration of oxalic and tartaric acids, and of oxalic and racemic acids, in the same solution gave too variable results to be of practical use. This is probably because permanganate in acid solution attacks racemic and tartaric acids somewhat more readily than it does mucic acid.

Discussion

Nine atoms of oxygen are necessary to convert a molecule of mucic acid completely into carbon dioxide and water: $C_6H_{10}O_8 + 9O = 6CO_2 + 5H_2O$. The method of titration herein described consumes potassium permanganate equivalent to 5.52 atoms of oxygen per molecule of mucic acid. Five atoms of oxygen are necessary to convert a molecule of tartaric or racemic acid completely into carbon dioxide and water. $C_4H_6O_6 + 5O = 4CO_2 + 3H_2O$. The titration described above consumes the equivalent of 3.29 and 3.26 atoms of oxygen per molecule of each of the 2 acids, respectively.

It has been known for some time that manganese dioxide and sulfuric acid convert mucic or tartaric acid into formic acid, carbon dioxide and water.[8]

Clarke[9] records the titration of tartaric acid by potassium permanganate in hot acid solution. Kling and Florentin[10] report a method of determining *d*-tartaric acid by precipitation with *l*-tartaric acid and a calcium salt as racemate and subsequent titration of the calcium racemate in boiling acid solution by potassium permanganate. They say nothing about the relationship between the permanganate and the racemic acid. Péan de Saint Gilles[11] found that, under varied conditions, tartaric acid consumed 3.08, 3.22, and 3.51 atoms of oxygen per molecule, when titrated with potassium permanganate in acid solution. By a further titration in alkaline solution he determined the formic acid formed in the first titration, and was thus able to account quantitatively for the low consumption of permanganate in acid solution. I have been able to confirm his statements regarding the double titration and to obtain similar results.

On the other hand, Hetper[5] reports having obtained quantitative permanganate consumption by tartaric acid in the presence of phosphoric acid by heating at 92–93° for 1.5 hours, indicating complete conversion to carbon dioxide and water. Hetper mentions using a reflux tube when he was oxidizing volatile substances. Presumably he did not protect his tartaric oxidation in this manner. To verify Hetper's results, two 0.0300g. samples of tartaric acid were oxidized by his method, 1 flask being open, the other protected by a water-cooled reflux condenser. Blanks were run simultaneously. The titration of the sample oxidized in the open flask indicated 0.0283 g. of tartaric acid, that in the protected flask 0.0309 g. Evidently, a small but measurable amount of volatile oxidizable substance was lost from the open flask. Steam distillations of mixtures

---

[8] Doebereiner, *Ann. chim.*, [2] **20**, 329 (1822). Peroz, *Compt. rend.*, **11**, 525 (1840).

[9] Clarke, *Am. Chem. J.*, **3**, 201 (1881).

[10] Kling and Florentin, *Bull. soc. chim.*, [4] **11**, 886 (1912). *Ann. chim.*, [9] **18**, 189 (1922).

[11] de Saint Gilles, *Ann. chim.*, [3] **55**, 391 (1849).

of acid permanganate with mucic acid and with tartaric acid have been carried out, and in both cases formic acid has been obtained, quantitatively determined, and identified by chemical tests and by Duclaux distillation. The sum of the permanganate consumed and that theoretically necessary to convert the formic acid formed into carbon dioxide and water was equal to that necessary to convert the mucic acid or tartaric acid taken directly and completely into carbon dioxide and water.

From all of the above facts it seems safe to conclude that, in the titration of mucic acid and of the tartaric acids by potassium permanganate in acid solution, formic acid is formed in considerable quantity, part of it being volatilized, part being further oxidized to carbon dioxide and water, and the balance remaining unchanged in the solution at the end of the titration.

The course of the reaction whereby formic acid is produced by oxidation of tartaric and mucic acids and other substances of similar structure, is being investigated further in this Laboratory along the lines of both its theoretical and practical significance.

Summary

Mucic acid may be determined in acid solution by oxidation with an excess of standard potassium permanganate solution at the boiling temperature, followed by a back-and-forth titration with standard oxalic acid solution and the standard permanganate solution. The same method may be applied to tartaric acid and to racemic acid. A mixture of oxalic and mucic acids may be precipitated quantitatively as calcium salts, the whole filtered, dissolved in sulfuric acid, and the acids determined in the presence of each other by first titrating the oxalic acid at 50° with standard permanganate and then applying the above method for the mucic acid. Tartaric and racemic acids cannot be titrated with any degree of accuracy in the same solution with oxalic acid. Other combinations of organic acids probably could be determined by this method.

The fact that the relationships between these dibasic oxy-acids and potassium permanganate are not stoichiometric under the conditions employed is shown to be due to the formation of formic acid, which is further oxidized only to a slight extent under the conditions of the titrations.

WASHINGTON, D. C.