[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

THE OXIDATION OF CALCIUM TELLURITE BY HEATING AND THE PREPARATION OF TELLURIC ACID FROM THE CALCIUM TELLURATE[1]

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Synopsis.—Tellurium dioxide mixed with five equivalents of calcium hydroxide was almost completely oxidized to calcium tellurate by heating for one hour at 975°. The percentage oxidation was less at lower temperatures and with smaller proportions of calcium hydroxide. The calcium tellurate thus formed was treated with an excess of concentrated nitric acid, whereby soluble calcium nitrate and insoluble telluric acid were formed. This telluric acid, after filtration or decantation, was dissolved in water and crystallized until pure.

Review.—Many methods are described in the literature for oxidizing tellurium or tellurium dioxide to telluric acid. Perhaps the method most generally used was suggested by Staudenmaier.[3] The tellurium dioxide, in nitric acid solution, is oxidized with chromic acid. The separation of the telluric acid from the chromium nitrate is rather slow and difficult. The slowness and the complexity of this method, commonly considered the best, is a proof of the difficulty of making telluric acid. All of the methods proposed can be criticized from the standpoint of expensive or difficultly obtainable reagents, of difficulties in manipulation, of the introduction of troublesome impurities or of low yields.

Aim of this Research and Outline of the Method.—The method developed in this research was based upon the observation of Lenher and Wolesensky[4] that many tellurites are oxidized to tellurates by heating in the air. However, they found that sodium or potassium tellurite required heating for fifty hours at 460° for complete oxidation.

The purposes of this research were, first, to improve the method of Lenher and Wolesensky for the oxidation of tellurites by heating; second, to find a suitable way of preparing telluric acid from these tellurates.

The extreme slowness of the oxidation in their experiments was thought to be due the fusion of the salts, whereby only the surface of the mass was exposed to oxygen. Calcium tellurite, or a mixture of it with hydrated lime, was heated in these experiments. Such a salt or mixture remained porous during the heating and therefore allowed more rapid oxidation.

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[1] From the thesis for the degree of Master of Arts by Mr. Gail M. Bradbury at Indiana University, 1928.

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[3] Staudenmaier, *Z. anorg. Chem.*, **10**, 189 (1896); Meloche and Woodstock, THIS JOURNAL, **51**, 172 (1929).

[4] Lenher and Wolesensky, *ibid.*, **35**, 729 (1913).

Method of Analysis.—The method of Brauner[5] using potassium permanganate was employed for the determination of the tellurite. The iodimetric method of Gooch and Howland[6] was used for the determination of the tellurate.

Materials Used.—The commercial tellurium dioxide[7] contained 49.59% of tellurium dioxide, 46.12% of sodium tellurite and 0.9% of selenium. This material was dissolved in concentrated hydrochloric acid and the solution thus formed was filtered through asbestos. The filtrate was evaporated to a small volume. The tellurium hydroxide or tellurous acid was precipitated by hydrolysis with a large volume of water. The precipitate was washed until free from chlorides and dried. This purified tellurium dioxide was a heavy, finely divided, slightly yellow powder.

The calcium hydroxide was a commercial high calcium "chemical" hydrated lime.

Experimental

All heating, unless otherwise noted was done in a Hoskins electric muffle furnace. The temperatures were measured with a platinum-rhodium thermocouple.

The tellurium dioxide and the lime were thoroughly mixed on a paper and then ground together in a mortar. The final mixtures, weighing from 10 to 30 g., were heated in small porcelain dishes. After heating, the entire mass of each mixture was ground to insure an accurate sample for analysis.

In all the early experiments, the heating was done at rather low temperatures because Lenher and Wolesensky had used 460°. It was soon found that the speed of oxidation increased as the temperature increased. A mixture of one formula weight of tellurium dioxide to two formula weights of calcium hydroxide was used in Table I.

TABLE I

EFFECT OF INCREASE OF TEMPERATURE

Temperature, ° C.	475	575	675	775
Heating, hours	25	25	20	5
Oxidation, %	21.4	44.7	64.7	39.3

The use of sodium carbonate with the calcium hydroxide and the tellurium dioxide greatly increased the speed of oxidation. However,

TABLE II

EFFECT OF SODIUM CARBONATE

Ratio of formula weights of	TeO_2	1	1	1	1	1
	$Ca(OH)_2$	1	1	1	0	0.5
	Na_2CO_3	0	0.1	0.5	1	1
Time of heating, hours		15	15	15	5	5
Oxidation percentage		12.6	46.4	84.7	36.9	99.1

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[5] Brauner, *J. Chem. Soc.* **59**, 238 (1891).

[6] Gooch and Howland, *Z. anorg. chem.*, **7**, 132 (1894); *Am. J. Sci.*, [3] **48**, 375 (1894).

[7] The authors wish to thank Mr. Skowronski of the Raritan Copper Company, Perth Amboy, New Jersey, for furnishing this material.

sodium carbonate without the lime was not satisfactory as is shown by Expt. 4 in Table II. The temperature of the experiments recorded in this table was 575°.

Although the rapidity and the completeness of oxidation of these mixtures containing sodium carbonate and hydrated lime were entirely satisfactory, the presence of the sodium salts made difficult the preparation of the pure telluric acid.

TABLE III

EFFECT OF HIGHER TEMPERATURES AND GREATER PROPORTIONS OF CALCIUM HYDROXIDE

Formula weights of calcium hydroxide to one of TeO_2	3	4	5	6	8	5	6
Temperature, °C.	975	975	975	975	975	1075	1075
Heating, hours	5	5	5	5	5	5	5
Oxidation, %	81.7	89.4	97.5	95.8	94.9	99.8	97.4

This table shows that the ratio of five formula weights of calcium hydroxide to one formula weight of tellurium dioxide is sufficient for maximum oxidation; also, that a temperature of 975° is sufficient, although 1075° does not lessen the yield through decomposition. The stability of the calcium tellurate at this high temperature was a great surprise.

Experiments were then made to determine the optimum time of heating required under these other optimum conditions of 975° and a mixture containing five formula weights of calcium hydroxide to one formula weight of tellurium dioxide.

TABLE IV

TIME OF HEATING REQUIRED

Heating, hours	0.25	0.5	1	2	4	5	6
Oxidation, %	93.6	95.7	98.7	98.8	99.3	98.7	98.1

Based upon experiments in which silver strips (melting point 960°) were embedded at different places in the mixtures being heated, it is thought that oxidation is practically complete as soon as the temperature has reached 975° throughout the mass.

Heating in a gas-fired pot furnace at a final temperature of 1100° gave about as good results as the careful heating in the electric furnace. A 25-g. mixture gave 98.1% oxidation in one hour. A 250-g. mixture gave 87.2% oxidation in two hours. These lower yields with the larger samples indicate that there was not enough air circulating through the mass. One important point that favors this method is that a carefully controlled heating temperature is unnecessary; it is important only to heat at 975 to 1100°. Higher temperatures could not be tried with the methods of heating that were available.

Barium hydroxide and barium carbonate mixtures with the tellurium dioxide gave almost no oxidation. Calcium carbonate gave as good results as calcium hydroxide under the same conditions.

Preparation of Telluric Acid from the Calcium Tellurate.—A description of one quantitative experiment will suffice to make clear the general conditions and method of operation for easily making telluric acid crystals. Seventy-five grams of the tellurium dioxide and 177 g. of calcium hydroxide (a 1:5 mixture) were placed in a clay crucible and heated in a gas furnace for a total of two hours with the final temperature reaching 1100°. The percentage oxidation was 88.5. Two hundred grams of this mixture was treated with 300 cc. of concentrated nitric acid, heated to boiling and cooled overnight. The supernatant liquid was decanted and 200 cc. more concentrated nitric acid was added to the residue of telluric acid. This was heated to boiling, cooled and again the supernatant liquid was decanted. The residue of telluric acid was dissolved in hot water and filtered to remove traces of insoluble matter. This filtrate, after evaporation to a small volume, smelled strongly of nitric acid. Again, after cooling overnight, the liquid was decanted. The residue of telluric acid was dissolved in water and crystallized. The weight of the pure crystals of telluric acid equaled 75.4% of the total telluric acid in the material used. The exact quantities of the acid used in this experiment need not be followed. Indeed, less nitric acid can be used in the washing. No research was made to determine the best quantities of reagents for the maximum yields.

Attempts to decompose the calcium tellurate with dilute sulfuric acid, whereby calcium sulfate was precipitated, were unsuccessful. So much calcium sulfate always remained in solution that its final separation from the telluric acid was difficult. Carbon dioxide or oxalic acid would not decompose the calcium tellurate.

It is possible to treat the calcium tellurate with an equivalent amount of nitric acid, evaporate to dryness and extract the calcium nitrate from the residue with alcohol, in which the telluric acid is insoluble.

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Summary

Maximum speed and completeness of oxidation were obtained by heating a mixture of one formula weight of tellurium dioxide with five formula weights of hydrated lime at 975 to 1075° for an hour.

Telluric acid was easily prepared from the calcium tellurate thus formed by the addition of an excess of concentrated nitric acid. The soluble calcium nitrate was decanted from the precipitate of crude telluric acid. Pure telluric acid was obtained from this residue by crystallization from water.

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