3. A few measurements were carried out with phenol–sodium phenolate buffer solutions to investigate the possibility of catalysis by the phenolate ion. If present, such catalysis must be quite small compared to the hydroxyl ion catalysis.

4. If this reaction has a spontaneous water reaction, its half time is greater than 800 days.

5. A value of 1.93×10^{-10} for the dissociation constant of phenol in 0.2 molal salt solutions was calculated.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF INDIANA UNIVERSITY]

OXIDATION OF SELENIUM DIOXIDE AND OF TELLURIUM DIOXIDE WITH LEAD DIOXIDE[1]

BY FRANK C. MATHERS AND FRANK V. GRAHAM[2]

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Introduction

DeCarli[3] tested the action of lead dioxide in the dry state upon several other oxides at temperatures varying from 250 to 300°. Barium, cuprous, stannous, ferrous, manganous, cobaltous and nickelous oxides reacted with the lead dioxide to form higher oxides. The lead dioxide was reduced to the monoxide. There was no evidence of reaction with calcium, cadmium, plumbous, zinc, magnesium, cupric, aluminum and titanium oxides. The less metallic oxides like arsenious, antimonous, chromium, molybdenum and tungsten reacted with the lead peroxide to form lead salts of the type of lead arsenate, lead antimonate, etc. He concluded that lead dioxide had a notable tendency to react with other oxides at relatively low temperatures.

This research was merely an extension of the above reaction to include selenium dioxide and tellurium dioxide, two oxides that had not been tried by DeCarli.

Lead selenate can be changed[4] easily to ammonium selenate. The ammonium selenate thus formed can be changed[5] into other selenates by crystallizing solutions of it with various metallic nitrates. The lead tellurate can be changed by sulfuric acid into telluric acid. There have been, heretofore, only indirect methods[6] of making lead selenate and lead

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[1] From the thesis for the degree of Master of Arts by Frank V. Graham at Indiana University, 1928.

[2] Professor of Chemistry, Ball State Teachers College, Muncie, Indiana.

[3] DeCarli, *Gazz. chim. ital.*, **56**, 55 (1926); *C. A.*, **20**, 1766 (1926).

[4] Mathers and Bonsib, THIS JOURNAL, **33**, 703 (1911).

[5] Unpublished work.

[6] (a) Becker, *Ann.*, **180**, 257 (1876); (b) Mathers, THIS JOURNAL, **30**, 1374 (1908); (c) Meyer and Moldenhauer, *Z. anorg. allgem. Chem.*, **116**, 193 (1921).

tellurate. Short direct methods for the rapid preparation of these salts are desirable as furnishing materials for making various selenates and tellurates.

Materials Used.—Two different samples of lead dioxide were used, one containing 90.09 and the other 94.94% of lead dioxide. The purity was always considered in calculating the weight to be used for a reaction.

Pure selenium dioxide was made by dissolving metallic selenium in nitric acid. This solution was filtered through asbestos and was then evaporated to dryness. The selenium dioxide thus formed was dissolved in water and filtered. This filtrate was evaporated to dryness and the solid selenium dioxide was sublimed. Its purity by analysis was 99.9%.

Tellurium dioxide was made by dissolving the commercial tellurium dioxide in hydrochloric acid. This strong acid solution was filtered through asbestos. The filtrate was hydrolyzed by the addition of a large volume of water. This precipitate of tellurous acid was washed and dried. Analysis showed its purity to be 98%.

The ammonium carbonate was the ordinary "ammonium carbonate" commonly bought for laboratory use.

Methods of Analysis.—The selenates and tellurates were determined by the iodometric method of Gooch and Howland.[7] The selenite and the tellurite were determined by the potassium permanganate method of Brauner.[8]

Reaction of Selenium Dioxide with Lead Dioxide.—Preliminary experiments at 90, 100, 110 and 120° showed that very satisfactory results could be obtained at 100°. The rest of the experiments were made at this temperature because of the ease with which the 100° could be maintained on a steam-bath.

Two ways were tried for obtaining intimate contact between the reacting substances. The "dry" way was to grind the dry materials thoroughly together in a dry mortar. The "wet" way was to grind the ingredients thoroughly in the mortar with just enough water to give a thick paste. The various samples were then placed in small beakers and set in the steam-bath.

TABLE I

VARIATION IN QUANTITY OF LEAD DIOXIDE AND IN TIME OF HEATING

Formula weights of PbO_2 to one of SeO_2	Selenium dioxide changed to selenate, % 0.5 hour Wet	0.5 hour Dry	3 hours Wet	3 hours Dry	12 hours Wet	12 hours Dry
1	91.8	88.5	94.6	92.5	98.9	93.1
1.05	97.9	93.5	98.3	94.5	97.9	95.3
1.1	97.7	94.6	99.5	95.8	99.9	96.1

The "wet" sample containing the 10% excess of lead dioxide was practically completely converted to selenate by heating for three hours or longer in the steam-bath. The "dry" mixed samples were not so com-

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

[8] Brauner, *J. Chem. Soc.*, **59**, 240 (1891).

pletely oxidized. It is thought that the better oxidation of the "wet" mixtures was due entirely to better contact. At the end of the experiments the water had been completely evaporated from all of the beakers and the residues were all dry. The results shown in this table are entirely satisfactory. This is the best method yet described for making lead selenate.

Making Ammonium Selenate from the above Lead Selenate.—A previous paper[4] showed that ammonium selenate can be made easily by the digestion of lead selenate with ammonium carbonate. The lead selenate in those experiments was prepared by precipitation and was pure. This lead selenate was made by a dry method and was not pure. This difference in the physical condition of the lead selenate made desirable new experiments on its action with ammonium carbonate. Five grams of lead selenate and 3 g. of "ammonium carbonate" were used. This was a ratio of one formula weight of lead selenate to about 2.6 "CO_3" radicals.

TABLE II

CONVERSION OF LEAD SELENATE INTO AMMONIUM SELENATE

Water, cc.	Temp., °C.	Time in hours	Selenate obtained as ammonium selenate, % Unstirred	Stirred
25	25	1	74.1	84.6
25	25	2	85.0	90.7
20	25	1	79.7	89.8
20	25	2	85.0	95.9
15	25	1	82.2	93.4
15	25	2	92.6	97.5
10	25	1	80.6	95.1
10	25	2	90.6	97.3
10	47	1	93.0	99.1
10	47	0.5	90.6	98.3
10	47	0.25	87.9	97.5
10	47	0.083	84.6	94.3

The yields were determined by filtering, washing the residues of lead carbonate and unchanged lead selenate with water and analyzing the filtrates for selenate. In the column marked "unstirred" the beakers were not agitated after the beginning of the experiment but the ammonium carbonate was dissolved before starting the experiment. In the column marked "stirred" a mechanical stirrer kept the mixtures in motion during the entire experiment. The table shows a yield of 99% using 10 cc. of water, 5 g. of lead selenate, 3 g. of ammonium carbonate, a temperature of 47° and stirring for one hour.

Crystals of ammonium selenate were easily obtained by evaporating the filtrate from this action of ammonium carbonate upon the lead selenate.

Reaction of Tellurium Dioxide with Lead Dioxide.—The amount of mixing of the tellurium dioxide and the lead dioxide affected the degree of oxidation. The materials in Table III were ground together in a dry mortar for one minute.

TABLE III

TELLURIUM DIOXIDE WITH LEAD DIOXIDE

Formula weights of PbO_2 to one of TeO_2	Temp., °C.	Tellurium dioxide converted into tellurate, % 1 hour	2 hours
1	300	62.9	71.2
1	205	58.6	79.2
1	170	85.1	89.8
1.05	170	93.5	93.7
1.1	170	98.1	99.8
1.1	155	89.7	92.7
1.1	185	94.1	97.5

This table clearly shows that 10% excess of lead dioxide is desirable and that 170° is the best temperature. Further experiments relative to the effect of the degree of mixing showed that the addition of enough water to form a paste after the tellurium dioxide and the 10% excess of lead dioxide had been ground together gave a yield of 99.5% at 170° for one hour. This result is compared to 97.3% when no water was used. However, grinding of the dry materials for two minutes gave the same yield of 99.9%.

Pure telluric acid was made from this lead tellurate by treatment with enough sulfuric acid to combine with all of the lead present in the mixture. This is a well-known old method.[6a] Three grams of sulfuric acid was used for each 10 g. of the lead tellurate mixture. All the telluric acid became soluble. The filtrate was evaporated nearly to dryness and the telluric acid was precipitated by an excess of nitric acid. The supernatant liquid was decanted and the residue was washed with a little concd. nitric acid to remove all the sulfuric acid. The residue was warmed on a water-bath until the nitric acid volatilized. This residue was dissolved in water and pure crystals of telluric acid, $H_2TeO_4 \cdot 2H_2O$, were prepared by slow evaporation.

Summary

1. The oxidation of selenium dioxide to selenate by heating with lead dioxide has been investigated under various conditions. The reaction proceeds very satisfactorily at 100°, the degree of completion varying with the time of heating and the mixing of the sample. The lead selenate produced may be converted to ammonium selenate by digestion with ammonium carbonate, followed by crystallization.

2. The process has been applied to the oxidation of tellurium dioxide, the optimum temperature being 170°. The yield varies with the amount of lead dioxide used and the intimacy of mixing of the sample taken. Telluric acid may be prepared from the lead tellurate produced by treatment with sulfuric acid and subsequent crystallization.

BLOOMINGTON, INDIANA