ART. XI.—*The Preparation of Selenic Acid and Sodium Selenate for Use as Reagents in the Determination of Bromine in Haloid Salts;* by PHILIP LEE BLUMENTHAL.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxxxix]

SELENIC acid and sodium selenate have been proposed in a previous paper from this laboratory* as reagents for the qualitative elimination of bromine, in determinable form, from haloid salts. These reagents when made by ordinary methods† may contain contaminating material likely to be objectionable. The following methods have therefore been devised for the preparation of these reagents in such condition that any foreign material remaining in them shall not interfere with the success of the analytical process.

Selenic Acid.

The method proposed for the preparation of selenic acid depends upon the action of nitric acid and potassium bromate upon selenious acid, the bromic acid formed reacting with the selenious acid according to the following equation:

$$3H_2SeO_3 + HBrO_3 = 3H_2SeO_4 + HBr.$$

Further action of the bromic acid breaks up the hydrobromic acid, according to the equation

$$HBrO_3 + 5HBr = 3Br_2 + 3H_2O.$$

Upon evaporating the solution to low volume, a second liberation of bromine accompanied by nitrogen oxides takes place, apparently according to a reaction like the following:

$$2HBrO_3 + 2HNO_3 = 2H_2O + Br_2 + 2NO_2.$$

The free bromine and the nitrogen oxides are, of course, easily volatilized. The preparation of selenic acid based upon these reactions was put to the test as follows:

Preliminary Test.—Selenious acid was prepared by dissolving elementary selenium in nitric acid and evaporating the solution to dryness. The crude selenious acid so obtained was sublimed from manganese dioxide according to the method used by Norton,‡ and the thin needle-like crystals were bottled as rapidly as possible. A solution convenient for use was made by dissolving 2 grm. of the purified selenium dioxide in 200^{cm^3} of water and a portion of 20^{cm^3}, containing 0·1 grm. of the dioxide, was used for each test. To each portion, contained in an Erlenmeyer flask, were added 10^{cm^3} of 1·1 nitric acid and a little potassium bromate, and this solution was evaporated to a low volume. When barium

* Gooch and Blumenthal, xxxv, 54.
† Gmelin-Kraut. Handbook, Anorg. Chem., i, 769, 1907.
‡ This Journal (4), vii, 290.

nitrate was added to the concentrated solution, and the free acid nearly neutralized with ammonium hydroxide, white barium selenate was precipitated. Though impure on account of its tendency to occlude foreign material, this precipitate proved to be practically free from selenious acid.

Preparation of the Reagent.—To 10 grm. of selenium dioxide dissolved in 75^{cm^3} to 100^{cm^3} of water were added 6 grm. of potassium bromate and 4^{cm^3} of strong nitric acid. This mixture was heated on the water bath until perfectly colorless. After the second evolution of bromine, which occurred when the volume was quite low, a little more bromate was added to decompose the excess of nitric acid and the heating was continued. When the addition of a crystal or two of bromate caused no further evolution of bromine, the colorless solution was made slightly ammoniacal, heated to the boiling point, and treated with a hot dilute solution of barium nitrate. The precipitated barium selenate, after settling, was filtered with suction, washed thoroughly with hot water, and finally transferred to a large crucible and dried at low redness. The weight of this product was about 25 grm., while the theoretical amount obtainable from the selenious acid taken was about 25·1 grams. After weighing, the selenate was treated in a porcelain crucible with 5^{cm^3} of strong sulphuric acid (sp. gr. 1·8) and some 20^{cm^3} of water. The pasty mass so obtained was heated about two and one-half hours on the water bath, and finally diluted, filtered, and washed. The filtrate and washings were made up to one liter, and an aliquot was taken for analysis by the method of Pierce.* This analysis showed about 94 per cent of the selenium taken to be present. From the determination of the selenious acid present by the method of Gooch and Clemons† it was found that 85 per cent of the selenium was present as selenic acid, the presence of selenious acid in the final product being due in this case to the fact that the barium precipitation was made in alkaline solution, under which conditions barium selenite is also precipitated. The total yield of selenic acid was 78 per cent of the theoretical. Later experiments have shown that the contamination by selenious acid may be to a large extent avoided by precipitating while the solution still contains free nitric acid.

Sodium Selenate.

The preparation of sodium selenate, to be used with sulphuric acid in place of free selenic acid, was also investigated.

Preliminary Test.—Elementary selenium (1 grm.) was fused in platinum with sodium peroxide (2 grm.) and sodium carbonate (6 grm.). The mass, after dissolving in water and filtering, barely bleached a few drops of dilute permanganate,

* This Journal (4), i, 416. † Ibid. (3), l, 51.

showing that the selenium had been oxidized almost completely to selenic acid, only a little selenious acid remaining.

Next, the finely powdered metal (1 grm.) was fused with sodium peroxide (5 grm.) in a nickel crucible, and after cooling, the melt was partially neutralized with sulphuric acid, to facilitate the analysis, and filtered. The filtrate and washings were made up to 100^{cm^3} and 10^{cm^3} of this solution were analyzed by the method of Gooch and Scoville.* Two analyses showed the yield to be fairly quantitative, and suitable for the analytical elimination of bromine.

Preparation of the Reagent.—In utilizing the method on a larger scale, about 105 grm. of powdered selenium and 500 grm. of sodium peroxide were thoroughly mixed and fused in charges containing 10 grms. to 15 grms. of selenium, nickel crucibles being employed. The reaction was rapid and a few minutes' heating over a Bunsen burner sufficed to bring the mass to liquid condition. After cooling, the crucible was placed in a beaker of cold water, and covered with a watch-glass to avoid loss by spattering. The melt dissolved with great evolution of heat, and cold water was added from time to time, to prevent boiling. Some finely divided material remained floating in the strongly alkaline liquid. A slight green color, probably due to the solution of small amounts of nickel, was also noticed. The solution could not be filtered through paper, and a platinum cone, lined with asbestos, was utilized, although the process was exceedingly laborious. The opaque filtrate consisted chiefly of sodium selenate and sodium hydroxide, with some sodium carbonate due to contact with the air.

In order to purify the selenate from sodium hydroxide, the attempt was first made to remove the latter by shaking the solution with alcohol. This procedure was found to have several disadvantages. The amount of time involved, the inconvenience of handling large quantities of strongly alkaline solution, and the not inconsiderable amount of carbonate formed, all militate against the process. But the greatest disadvantage lies in the fact that the dissolved carbonate and selenate of the lower aqueous layer are very difficultly crystallized. The successful method of purification ultimately developed consisted in evaporating the alkaline liquid to pasty condition over a free flame and removing as much caustic alkali as possible by continued extraction with alcohol which had been distilled from lime (97–99 per cent pure). The extraction was hastened by warming on the steam bath, but in this latter treatment, red, amorphous selenium was formed by reduction of the solution. Six or eight extractions sufficed to remove most of the hydroxide.

* Gooch and Scoville, this Journal (3), 1, 402.

The residue, consisting chiefly of sodium selenate and sodium carbonate, could not be crystallized from water. It was found necessary to convert the carbonate to sulphate in order to obtain crystallizable material, and after careful neutralization with sulphuric acid, the mixture of sulphate and selenate was crystallized by repeated evaporations. The sulphate tends to crystallize first, and a partial separation may be accomplished in this manner. The mixed crystals of sodium selenate and sulphate first obtained were quite efflorescent, but on warming and evaporating to greater concentration, crystals of a lower order of hydration were obtained. The selenate and sulphate can also be thrown out by alcohol, but this method was not satisfactory and was discarded.

The several crops of crystals were combined, filtered on a Buchner funnel with suction, well drained, and finally the mass was heated to 108° C. for some hours, whereby most of the water was driven out, and a mixture of nearly anhydrous sodium salts was obtained. Analysis of the mixed product showed it to average about 65 per cent of selenate and the total yield of sodium selenate was about 58 per cent of the theoretical amount. Considerable material was lost in the preliminary attempts at purification, in the tests made from time to time and in the mother liquor from the crystallizations.

This material thus prepared is serviceable for immediate use with sulphuric acid in the method proposed for the separation of bromine and chlorine, and no attempts were made to separate the sulphate and selenate completely. In view of experience obtained in this work, it seems probable that by rapidly evaporating the filtered solution of selenate and hydroxide over a free flame, and rapidly extracting the residue with absolute alcohol, the carbonate formation may be, to a large degree, inhibited. This, of course, reduces the amount of sulphate ultimately formed, since the greater part of the alkali, excepting the carbonate, is removed by the alcohol treatment. The resulting aqueous solution, containing a small amount of sulphate, but no selenite, can be purified fairly well by fractional crystallization, as the selenate is more soluble in water than the sulphate.

It is to be noted that sodium selenate may also be prepared by fusing with sodium carbonate the barium selenate obtained in the process previously described for making selenic acid, the amount of carbonate taken being less than that required to decompose the barium salt completely. Upon extracting the product with water the sodium selenate dissolves and may be crystallized from the filtered solution.

The processes described afford easy means for preparing selenic acid and sodium selenate in such condition that, though these products are not pure, they are suitable for use in the quantitative elimination of bromine from haloid salts according to the methods to which reference has been made.