CCCXVI.—*The Reduction of Selenious Acid.*

By Leslie Marshall Clark.

It has long been known that when selenious acid is reduced in the presence of copper or other heavy metals, the precipitate obtained does not consist of selenium alone but contains in addition some metallic compound of selenium (compare Keller, *J. Amer. Chem. Soc.*, 1897, **19**, 773). This point has been particularly exemplified by examination of the solutions obtained after estimation of nitrogen by the Kjeldahl method in certain organic selenium compounds, copper having been added in the sulphuric acid–potassium sulphate treatment as usual to aid the destruction of the organic material. It was found if the alkaline solutions remaining after the distillation of ammonia were made very slightly acid with hydrochloric acid and reduced with sulphurous acid, a black precipitate was obtained which had the composition of cuprous selenide. Moreover, it is of interest that in all cases a very considerable loss of selenium had occurred during the destruction of the organic matter.

The reaction has now been further examined by reducing selenious acid by sulphurous acid in solutions containing copper sulphate and hydrochloric acid. The precipitate obtained varies from pure selenium, in solutions containing much hydrochloric acid, to cuprous selenide in dilute acid solutions, a mixture of the element and salt being formed intermediately (see table, p. 2391). The hydrochloric acid concentration is evidently the factor determining the composition of the precipitate (Expt. A). As a possible explanation of this phenomenon the following has to be considered. Selenious acid may be reduced by sulphurous acid with intermediate formation of hydrogen selenide, which reacts with a further amount of unchanged selenious acid to give selenium :

$$2H_2Se + SeO_2 = 2H_2O + 3Se \quad . \quad . \quad . \quad . \quad (1)$$

In the presence of cuprous ions, the hydrogen selenide will form cuprous selenide, but the amount of this compound formed will depend on the hydrogen-ion concentration of the solution. This is largely determined by the hydrochloric acid concentration, which will also affect the rate of the reaction (1), increase of acid favouring the separation of selenium. The suggested intermediate reaction has been found to take place, for when hydrogen selenide is passed into an aqueous solution containing selenious acid, selenium is precipitated in the amount required by equation (1) (Expt. D). The mechanism which has been suggested above for the reduction of selenious acid may therefore be the correct one, but the experiment on the reaction between selenious acid and hydrogen selenide is not crucial, for the following reason. When finely ground metallic selenium is kept in contact with a hot solution of sulphurous acid containing copper sulphate, the selenium increases in weight owing to the formation of cuprous selenide (Expt. B). It has not been found possible to achieve complete conversion of the element into cuprous selenide, presumably owing to the arrest of further chemical action by the formation of a coating of selenide on the individual grains of selenium.

There is thus a secondary reaction between selenium, sulphurous acid, and copper sulphate in which cuprous selenide can be formed, and this makes it unnecessary to postulate the intermediate formation of hydrogen selenide when selenious acid is reduced. The fact that complete conversion of selenium into cuprous selenide cannot be brought about in Expt. B, whereas the theoretical amount of cuprous selenide can be obtained in the reduction of selenious acid when the proper hydrochloric acid concentration is present (see table), cannot be used as an argument against the hypothesis of this secondary reaction, for the red modification formed by the reduction of selenious acid possesses a higher degree of chemical reactivity than the metallic selenium powder used in Expt. B and is, moreover, in a much more finely divided condition.

Reinsch (Fresenius, "Qualitative Chemical Analysis," 10th Edtn., p. 118) observes that "metallic copper when placed in a warm solution of selenious acid containing hydrochloric acid becomes immediately coated black; if the solution remains long in contact with the copper it turns light red from the separation of selenium." These results are explicable on the theory that selenious acid is reduced to selenium by the cuprous ions formed at the copper–hydrochloric acid interface, and that this selenium is further reduced by cuprous ions to give cuprous selenide, the dark coating referred to by Reinsch. These reactions may be represented by the equations

$$SeO_2 + 2Cu_2Cl_2 + 4HCl = Se + 4CuCl_2 + 2H_2O \quad . \quad (2)$$

$$Se + 2Cu_2Cl_2 = Cu_2Se + 2CuCl_2 \quad . \quad . \quad . \quad . \quad (3)$$

The experiments on the formation of cuprous selenide already described suggested that the nature of the deposit produced on the copper would depend on the hydrochloric acid concentration. This was found to be the case (Expt. C), since when strips of copper are immersed in selenious acid solutions containing varying amounts of hydrochloric acid, the precipitate formed varies from pure selenium in high concentrations of acid to a black deposit of cuprous selenide adhering to the copper in low concentrations. The selenium formed in the most concentrated hydrochloric acid solution examined was slowly reduced to cuprous selenide, evidently by the cuprous chloride present.

The facts described in this communication may therefore be explained as follows : when selenious acid is reduced by sulphurous acid, reduction to the element probably occurs without intermediate formation of hydrogen selenide. The selenium so formed can be further reduced to cuprous selenide should cuprous ions be present in the solution, but the extent to which this can take place is determined by the hydrochloric acid concentration. It is probable that the hydrochloric acid affects the cuprous chloride concentration by formation of the known cuprous chloride–hydrochloric acid complex.

Evidently there is a close parallelism between these experiments and those described by Wardlaw and Pinkard (J., 1922, **121**, 216), who found that, in the reaction between sulphur dioxide and cuprous chloride dissolved in hydrochloric acid, there is some definite concentration of acid above which cuprous chloride and sulphur dioxide react with the separation of sulphur only, an intermediate concentration of acid in which both sulphur and cuprous sulphide are precipitated, and a stage in which sulphide only is produced. These authors also showed that if the concentration of hydrochloric acid fell below 35 c.c. of concentrated acid to 215 c.c. of water, no reduction of sulphur dioxide by cuprous chloride took place. In the present case, however, reduction of selenious acid was found even when less than 1 c.c. of concentrated acid was present in 75 c.c. of water [Expt. C (1)].

It had been intended to obtain further tests of the theory now put forward (*e.g.*, by studying the reduction of selenious acid by various concentrations of cuprous chloride), but the work has had to be abandoned.

EXPERIMENTAL.

Expt. A.—To a solution of sodium selenite (5·000 g.) in boiled, distilled water, 10 c.c. of concentrated hydrochloric acid were added, and the volume was made up to 500 c.c.; 25 c.c. of this solution gave 0·1053 g. of selenium when reduced with sulphurous acid in the presence of hydrochloric acid according to the usual method. Copper sulphate (1·25 g.) in water (75 c.c.) was added to each of a number of 25 c.c. portions of the selenite solution together with various amounts of hydrochloric acid; 30 c.c. of freshly prepared, saturated aqueous solution of sulphur dioxide were then slowly poured into the hot mixture, which was kept gently boiling for $\frac{1}{2}$ hour. Almost immediate precipitation occurred in each case, the colour of the precipitate with the higher concentrations of hydrochloric acid being reddish brown, changing to black. A further 30 c.c. of sulphurous acid solution was added, and the mixture kept on the steam-bath for $\frac{1}{2}$ hour longer. The precipitate was filtered on an asbestos mat in a Gooch crucible, well washed with sulphurous acid and water, dried in the steam oven, and weighed. (Moist cuprous selenide is quite stable to such a drying process, since when 0·2778 g. of the pure compound was moistened with water and dried as described, the residue was unchanged in weight.) The results are shown in the following table :

25 C.c. of the solution contain 0·1053 g. Se, equivalent to 0·2740 g. Cu_2Se.

HCl added, c.c.	Wt. of ppt., g.	Cu_2Se in ppt., %.	HCl added, c.c.	Wt. of ppt., g.	Cu_2Se in ppt., %.
1	0·2712	99	5	0.1680	61
2	0·2240	86	10	0·1266	27
3	0·2099	81	20	0·1076	3·5
4	0·1827	69	30	0·1050	0

Expt. B.—*Reaction between selenium, copper sulphate, and sulphurous acid.* Finely powdered selenium (0·1500 g.) was gently boiled for $\frac{1}{2}$ hour with copper sulphate (2·0 g.) in water (100 c.c.) to which hydrochloric acid (1 c.c.) and saturated sulphurous acid (30 c.c.) had been added, 3 c.c. of ethyl alcohol having been added before addition of the sulphurous acid, so that the solution could wet the selenium powder, which otherwise made a film on the surface. Another 30 c.c. of sulphurous acid were added, and the mixture was kept on the steam-bath for 1 hour. The residue after filtration and drying weighed 0·3054 g. (Calc. for complete conversion into Cu_2Se, 0·3900 g.). A qualitative test showed that the precipitate contained selenium and copper, but no sulphur.

No change in the weight of another sample of selenium was observed when the above experiment was repeated without addition of sulphurous acid.

Expt. C.—*Reduction of selenious acid by cuprous chloride.* 25 C.c. portions of a solution of 5·00 g. of sodium selenite in 250 c.c. of water containing 10 c.c. of hydrochloric acid were diluted with 50 c.c. of water, and varying amounts of hydrochloric acid were added. A piece of thin copper sheet (about 4 cm. square) was then introduced into each solution; reaction began almost immediately, but the delay was longest in the solution containing least hydrochloric acid :

(1) No extra hydrochloric acid added. The copper was rapidly completely coated with a black film.

(2) 1 C.c. of acid added. A black film was formed which flaked away after standing for some hours. After 24 hours some selenium was also being deposited.

(3) 5 C.c. of acid added. A reddish-brown deposit was formed, which clearly contained some red selenium, as well as cuprous selenide.

(4) 20 C.c. of acid added. Selenium was precipitated in a red cloud at the copper surface, but did not adhere thereto. After 24 hours the precipitate had darkened in colour, and then contained copper, but the filtered solution contained no selenium, complete reduction having been effected.

The formation of a mixture of red selenium and cuprous selenide described in Expts. C (2) and (3) would not be expected were the solution homogeneous. If the hydrochloric acid–cuprous chloride concentrations were such that selenium was partially reduced to cuprous selenide, then each particle of selenium would have a coating of the selenide and no red selenium would be distinguished. In the experiments in question, the results are ascribed to the presence of layers of solution which are not homogeneous in the vicinity of the copper plate. The hydrochloric acid and cuprous chloride contents of such layers will naturally vary with the distance of the layer from the metal and with time. The product of the reduction may then be non-homogeneous as described.

Expt. D.—*Reaction between selenium dioxide and hydrogen selenide.* A carefully dried, round-bottomed flask containing aluminium selenide was fitted with a funnel incorporating a three-way tap in order that water or hydrogen might be admitted at will. A tube from this flask dipped below a solution of selenium dioxide in cold, dilute, oxygen-free hydrochloric acid contained in a conical flask, from which a tube passed to a trap containing cadmium acetate solution for removal of uncombined hydrogen selenide. Dry hydrogen was passed through the apparatus for an hour to remove air, the gas was cut off, and cold, boiled, distilled water was admitted to the aluminium alloy. When sufficient water had been added, a slow stream of hydrogen was started to sweep the evolved gas through the reaction flask and thence into the cadmium acetate trap. Immediate reaction took place and selenium was deposited in the reaction flask. A rather colloidal precipitate of red selenium formed at first, but this slowly coagulated, leaving a clear aqueous liquid in which flocculent masses of the element were suspended. After 1¾ hours, the selenium formed was rapidly filtered through a Gooch crucible, washed with water, dried, and weighed.

The reaction flask initially contained 60 c.c. of water, 10 c.c. of concentrated hydrochloric acid, and selenium dioxide corresponding to 0·0696 g. of selenium, and at the conclusion of the experiment 0·2168 g. of selenium was obtained from it. According to equation (1), selenious oxide corresponding to 0·0696 g. of selenium should react with hydrogen selenide to produce 0·2088 g. of the element. The error in other similar experiments was never greater than 4% and the agreement between the calculated and observed figures is sufficiently close to be accepted as confirmation of the equation.

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