[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN]

The Oxidation of Selenium in the Glow Discharge

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After many unsuccessful attempts by previous investigators[1] to obtain selenium trioxide, Rheinboldt, Hessel and Schwenzer[2] obtained a white product by the action of oxygen on selenium in a high frequency field at a pressure of 15–20 mm. of mercury at room temperature which, dissolved in water, yielded a mixture of selenious and selenic acids.

Recently, emphasis has been placed on the study of chemical action in the glow discharge by Brewer and his associates.[3] The unusual conditions produced in such a system, where there are not only atoms and molecules, but excited molecules and ions of both positive and negative charge, suggested that here the oxidation of selenium might be studied profitably.

Materials

Oxygen.—Tank oxygen was purified by passing the gas over hot copper oxide and removing the water by means of sulfuric acid and phosphorus pentoxide.[1]

Selenium.—Fused selenium was prepared according to the method of Lenher and Hoffmann.[1]

Analytical Methods

A sample of the reaction product (presumably a mixture of selenium dioxide and selenium trioxide) was transferred in a dry atmosphere to a weighing bottle, dissolved in water and the solution analyzed for selenate by the method of Gooch and Evans.[4] Total selenium was determined in the residual liquid by the method of Lenher and Hoffmann.[1]

Apparatus

The arrangement of the apparatus is shown in Fig. 1. The glass system was made of Pyrex. A liquid air trap (B) separated the discharge tube (A) from the mercury vapor pump and the McLeod gage and thus kept the mercury vapor out of the discharge tube. The McLeod gage at (D) was constructed to accommodate pressure changes between 5 and 1×10^{-5} mm. of mercury. A mercury valve at (E) made possible the separation of the mercury vapor and the Hy-Vac pumps from the remainder of the system. In order to obtain the desired electrical energy, a 20,000-volt, one-kilowatt transformer (J) was connected to a 110-volt alternating current line. The current used was measured by an a. c. milliammeter (K) and was controlled by a choke coil placed in the primary circuit of the transformer. The aluminum electrodes of the discharge tube were clamped on tungsten leads which in turn were coated with glass in order to prevent sputtering. In the usual Geissler tube, the electrodes are at such a distance apart that the positive column, negative glow, Faraday and Crookes' dark spaces can all be distinguished; in the tubes used in this research, the electrodes were not more than 32 mm. apart and the discharge appeared to be chiefly negative glow.

Procedure

Dry precipitated selenium was melted on a glass rod which was placed in a vertical position between the electrodes of the previously cleaned and dried discharge tube. The tube was then sealed to the apparatus and the system evacuated by means of the Hy-Vac and mercury vapor pumps. When the pressure was reduced to a value less than 10^{-6} mm. of mercury, the valve at (E) was closed. If the vacuum held, this was considered evidence that there were no leaks in the apparatus and that the walls were relatively free of moisture.

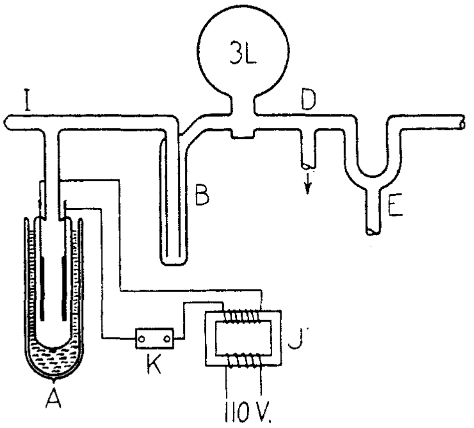

Fig. 1.

Oxygen was admitted to 4 mm. pressure by means of a gas pipet. The discharge tube was then immersed in liquid air, the valve at E closed and the discharge started. As the reaction progressed the pressure diminished, whereupon the reaction was stopped and a further addition of oxygen made. The initial supply of oxygen was not sufficient to react with all of the selenium.

After a quantity of product had been prepared in this manner, the discharge was stopped and dry air was admitted until atmospheric pressure was reached. When the liquid air bath was removed from the discharge tube, moisture condensed and froze on the outside of the tube. This excess moisture was allowed to dissipate before the reaction tube (A) was cut from the system. The tube was cut at the narrow section above the electrodes, stoppered and transferred to the desiccating box. Working in the dry atmosphere of the desiccator box, the rod containing the unreacted selenium was removed from the discharge tube and the white product scraped from the

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(1) Worsley and Baker, *J. Chem. Soc.*, **123**, 2870 (1923); Meyer and Pauletta, *Ber.*, **60**, 985 (1927); Lenher and Hoffmann, THIS JOURNAL, **51**, 3177 (1929).

(2) Rheinboldt, Hessel and Schwenzer, *Ber.*, **63**, 84, 1865 (1930).

(3) Brewer *et. al.*, *J. Phys. Chem.*, **36**, 2133 (1932); and earlier papers.

(4) Gooch and Evans, *Z. anorg. Chem.*, **10**, 253 (1895).

walls of the tube and transferred to a dry weighing bottle. The product was then analyzed for available oxygen and total selenium, care being taken to prevent contamination by moisture during the weighing process.

The following table shows results obtained by the analysis of three typical products.

TABLE I

	% SeO_3	% SeO_2	Total %
1	11.0	89.3	100.3
2	11.6	88.0	99.6
3	11.4	88.9	100.3

The value for selenium trioxide was calculated from results obtained by the determination of available oxygen. The selenium equivalent to this selenium trioxide was subtracted from the total selenium and the remaining selenium calculated to selenium dioxide. Although the above results do not constitute sufficient evidence to prove that the product is a mixture of selenium dioxide and selenium trioxide, it is improbable that a more complex combination is present.

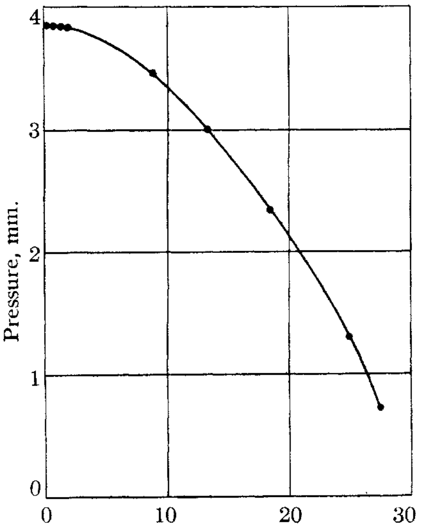

Fig. 2.

Since we were interested primarily in the preparation of selenium trioxide, an attempt was made to determine the effect of pressure on the composition of the product obtained. In the closed system just described there was a continual decrease of oxygen pressure due to the reaction between the oxygen and selenium. In order to study the effect of pressure it was necessary to develop some technique whereby oxygen could be admitted during the reaction and the pressure maintained at a constant level. A Hoke microvalve was attached to the apparatus at (I), Fig. 1, through which pure oxygen was admitted at a rate just balancing its removal by the Hy-Vac pump. With this constant stream of gas into the system the slow consumption of oxygen by the reaction did not change the pressure.

The results recorded in Table II represent analyses of products prepared at various pressures.

TABLE II

Pressure, mm.	% SeO_3 behind electrodes	% SeO_3 other parts of tube	% SeO_3 total throughout
0.65	29.8	18.5	28.4
1.2	46.3	28.2	41.3
1.5	57.0	18.25	35.0
2.5	22.6	14.3	18.9
4.3	17.0	7.5	11.2

A current of 42 m. a. was used in all of these experiments. Early results seemed to indicate that the yield of selenium trioxide increased as the pressure decreased. However, present indications are that for each type of discharge tube there is an optimum pressure and current at which the greatest yield of selenium trioxide is obtained.

Perhaps the most interesting information which appears in the above table is that the product which formed behind the electrodes was richer in selenium trioxide. It is believed that due to the close proximity of the vessel walls behind the electrodes the selenium trioxide formed is so rapidly cooled and deposited that decomposition is less likely to take place. In other portions of the tube the product is not cooled so rapidly because the walls are farther away from the active region. For this reason some of the selenium trioxide may be decomposed before deposition takes place and the resulting product is less rich in selenium trioxide. In this connection it is well to note that the walls are cooled by liquid air. In experiments where carbon dioxide–acetone mixtures were used the undercooling of the product was not so rapid and the character of the product was changed, its probable composition being red elemental selenium–selenium dioxide–selenium trioxide.

Practically all of the reactions heretofore studied in the glow discharge have involved homogeneous systems. It is therefore interesting to note a peculiarity in the behavior of the heterogeneous system studied in this investigation. In the curve, Fig. 2, showing pressure plotted against time, the slope of the curve indicates the rate of oxygen consumption by reaction with selenium.

The slow rate of consumption at the beginning of the reaction is probably due to the fact that in this heterogeneous system there is no appreciable selenium vapor concentration until the selenium on the rod has been warmed by electronic bombardment. If the selenium is independently vaporized by a separate electrical heating unit, there is no lag in the initial consumption of oxygen. It is observed that the pressure change indicated by the curve is not solely dependent upon the rate of oxidation of selenium, but is also dependent upon the rate of vaporization. It would seem desirable therefore to introduce the selenium vapor into the field of reaction by use of a separate heating unit; however, experiment has shown that if the rate of vaporization is faster than the rate of oxidation of the selenium, the excess unreacted selenium contaminates the reaction product by depositing on the walls of the vessel as red selenium. Since it was extremely difficult to control the rate of vaporization by a separate heat source, all of our oxidation products were prepared by supporting the selenium on a glass rod between the electrodes, in which case the selenium was slowly vaporized by electronic bombardment.

In handling the product prepared in the above experiments, there was no indication of decomposition at room temperature. When the product was prepared in the prescribed manner and the pressure in the system was reduced to 2.75 mm. of mercury with the reaction tube at room temperature, the pressure remained constant for a period of eighteen hours.

Using alternating current as a source of energy, it seems apparent that any attempt to explain the mechanism of the reaction on the basis of present information would be largely speculation. Experiments are now being conducted using direct current.

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Summary

Using the procedure described for the oxidation of selenium in the region of negative glow of the discharge tube, a white product was deposited on the walls of the tube which upon analysis seemed to be a mixture of selenium dioxide and selenium trioxide. The product which deposited on the walls behind the electrodes (where the walls were closest to the field of reaction and the product was most rapidly undercooled and deposited) contained a higher equivalent of selenium trioxide than the product which deposited elsewhere in the tube, the highest concentration of selenium trioxide being 57%.

An optimum pressure and current probably exist at which the greatest yield of selenium trioxide is obtained for any one tube.

The initial lag in oxygen consumption shown in the time-pressure curve may be attributed to the time required for the electronic bombardment to heat the selenium sufficiently so that a perceptible selenium vapor concentration is produced.

The mixture of $SeO_2 + SeO_3$ is stable at room temperature and dissolves readily in water to give a solution containing selenious and selenic acids.

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