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PRECIPITATED SELENIUM DIOXIDE[1]

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Many unsuccessful attempts have been made to prepare the hypothetical trioxide of selenium analogous to the trioxides of sulfur and tellurium. Worsley and Baker[2] were the first investigators to report the preparation and properties of this compound. In brief, their method of preparation consisted of the oxidation of selenium dissolved in vacuum distilled selenium oxychloride by ozone. Following the publication of their researches, two former students of V. Lenher attempted the preparation of selenium trioxide but failed to obtain products which corresponded in selenium content to the trioxide and which responded to available oxygen tests for hexavalent selenium. Recently Julius Meyer and Anton Pawletta[3] reported their failure to obtain the trioxide by the above method and concluded that the oxidation product was selenium dioxide containing selenium monochloride as an impurity.

The following investigation was begun in 1925 and completed in January 1927, previous to the publication of Meyer and Pawletta. The data given not only establish the identity of oxidation products obtained, but prove the non-existence of selenium trioxide in products prepared according to Worsley and Baker's method.

Materials

Selenium.—Pure, resublimed selenium dioxide was dissolved in 10% hydrochloric acid and selenium subsequently precipitated by the addition of sulfur dioxide. Precipitated selenium was washed by decantation until free from acid, then boiled in distilled water, filtered and finally fused and cast in the form of sticks.

Selenium Oxychloride.—Lenher's[4] method of preparation was used. The oxychloride was fractionally distilled several times at 17 mm. pressure in a moisture-free

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[1] Extract from a dissertation submitted by G. F. Hoffmann in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

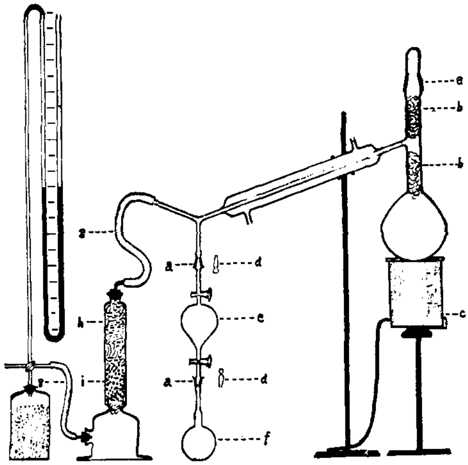
[2] Worsley and Baker, *J. Chem. Soc.*, 2870 (1923).

[3] Meyer and Pawletta, *Ber.*, **60**, 985 (1927).

[4] Lenher and Kao, THIS JOURNAL, **42**, 2498 (1920).

system (Fig. 1). Extremely dry selenium oxychloride was obtained by fractional distillation at reduced pressure from resublimed phosphorus pentoxide. The purity of the distillate was confirmed by freezing point determinations and the molybdate test for phosphate. Absorption of moisture by selenium oxychloride during transference from the still receiver was avoided by draining the distillate directly into reaction flasks through ground-glass joints.

Ozone.—Oxygen produced by the fractional distillation of liquid air was employed. Precautions to insure the absence of impurities such as hydrogen, carbon dioxide and water were taken, as shown in Fig. 2. Concentrations of ozone varying between 2 and 6% were produced in a triple cell ozonizer.



a,a,a, Ground glass joints; b,b, glass wool; c, electric heater; d,d, ground glass stopper; e, receiver bulb; f, fractionating bulb; g,g, suction tubing; h, phosphorus pentoxide; i, calcium chloride.

Fig. 1.—Selenium oxychloride distilling apparatus.

Carbon Tetrachloride.—Dry carbon tetrachloride was prepared by double distillation from phosphorus pentoxide immediately before use.

Analytical Methods

Selenium.—Selenium was determined gravimetrically according to the method of Lenher and Kao.[5] It was precipitated in the presence of 15% hydrochloric acid by sulfur dioxide and hydroxylamine hydrochloride. Precipitation was allowed to take place slowly at room temperature. The supernatant liquid was decanted through a tared Gooch crucible and the precipitate remaining in the beaker was converted to gray crystalline selenium in boiling water. It was then brought on the same crucible, washed with water and alcohol, dried at 105° and weighed.

Available Oxygen.—Selenic acid and all selenates liberate free chlorine from hydrochloric acid solutions.[6] According to Worsley and Baker the product of ozone oxidation of selenium in selenium oxychloride reacts with water to give selenic acid; hence a water solution of the product should liberate chlorine from a hydrochloric acid solution.

Available oxygen was accurately determined by gently boiling a 10% hydrochloric acid solution containing a hexavalent selenium compound and conducting the liberated chlorine into a solution of potassium iodide slightly acidic with sulfuric acid. Iodine was titrated with $N/10$ sodium thiosulfate solution. The distillation of chlorine into iodide solution was aided by a slow current of carbon dioxide. This method is in common use for the determination of hexavalent selenium.

Chlorine.—Chlorine was determined in the presence of selenium by precipitation as silver chloride from solutions containing approximately 10% nitric acid and an excess of silver nitrate. The accuracy of such analyses was established by numerous trial analyses of solutions which were prepared to contain known amounts of selenious or selenic acid, nitric acid and chloride.

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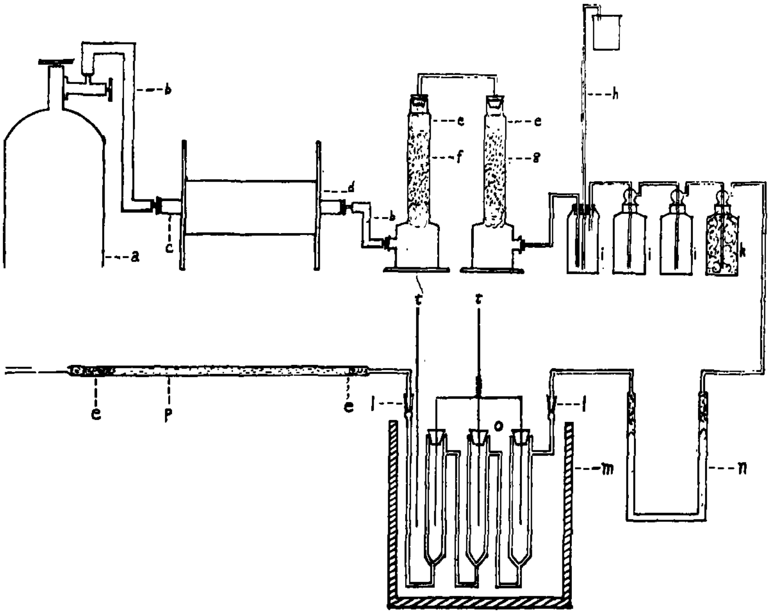
[5] Lenher and Kao, This Journal, **47**, 769 (1925).

[6] Petterson, *Fres. Zeit.*, **12**, 287 (1873).

Water.—The water content of precipitated selenium dioxide was determined according to the method developed by A. Julien[7] for sublimed selenium dioxide. Samples were manipulated in a box desiccator as a precaution against absorption of moisture from the air in the laboratory.



a, Oxygen tank; b,b, suction tubing; c, porcelain tube, filled with copper oxide; d, electric furnace; e,e,e, glass wool; f, soda lime; g, calcium chloride; h, safety tube; i,i,i, concentrated sulfuric acid; k, glass wool and phosphorus pentoxide; l,l, ground glass joints; m, cooling bath; n, phosphorus pentoxide; o, triple cell ozonizer; p, pure phosphorus pentoxide; t,t, high tension leads.

Fig. 2.—Preparation of pure ozone.

Experimental Details

A reaction flask similar to that described by Worsley and Baker was used in the preparation of the first products. One modification of their apparatus was adopted. It consisted of an additional tube filled with resublimed phosphorus pentoxide inserted between the ozonizer and the reaction flask. This additional drying precaution was taken following the observation that water was formed in the ozonizer when hydrogen was not completely removed from the oxygen by reaction with hot copper oxide. The low selenium results of Worsley and Baker might be traced to this point since their ozonizer was connected directly with the reaction flask, allowing any water formed to be absorbed by the product.

The time required for a precipitate to appear on passing ozone through the selenium oxychloride solution of selenium varied between twenty and seventy hours. A white sublimate was formed on the walls of the reaction flask and gas outlet tube. Precipitates were brought on dry asbestos filters and thoroughly washed with dry carbon tetrachloride in the absence of moist air. Dry air was drawn through the washed precipi-

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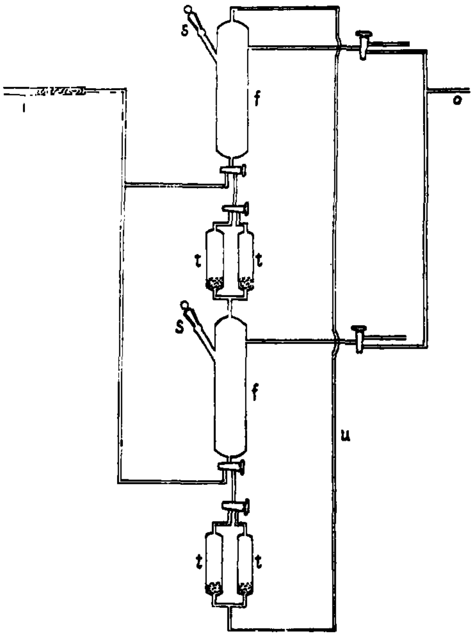
[7] Julien, This Journal, **47**, 1799 (1925).

tates to remove the carbon tetrachloride. The use of absolute ether for washing purposes was abandoned following the observation that the color of the product was changed from white to yellow or pink when in contact with pure ether. Upon mixing the oxychloride filtrate of a product with dry carbon tetrachloride a white precipitate was formed. This precipitate resembled the original product in appearance and composition.

Analytical results of the products of ozone oxidation of selenium oxychloride solutions are summarized in Table I. For preparations I–VII, inclusive, vacuum distilled selenium oxychloride was used as the solvent medium. Due to the variable selenium content of the first products, analyses for water and chlorine were included for all subsequent products. After the presence of water in Products V, VI and VII was definitely established, it was concluded that vacuum distilled selenium oxychloride was not dry in spite of numerous fractional distillations. In an attempt to prepare dry products, an apparatus consisting of two reaction flasks connected in tandem but separated by filtering tubes was constructed. A series of products was obtained in this apparatus by reusing the same solvent. In Table I the third and fourth precipitates of Preparation VIII and the second and third of Preparation IX represent products prepared in such an apparatus. Although a few drops of water were added to the solution of selenium in selenium oxychloride before starting Preparation IX, Precipitate 2 was found to contain only 0.23% of water. The major portion of the water presumably was removed from the solution by the first precipitate.



f,f, Reaction flasks; i, ozone–oxygen inlet tube; o, gas outlet; s,s, ground glass stoppers; t,t, filters; u, tube used for returning filtrate to upper reaction flask by means of gas pressure in f and suction applied at the upper three-way cock on the gas outlet tube.

Fig. 3.

It was found practically impossible to wash products entirely free from $SeOCl_2$. Several products were found to contain chloride after having been washed continuously with dry carbon tetrachloride for one week. It appeared perfectly logical to consider the chlorine in the product to be present as selenium oxychloride. It is not likely that chlorine should be present as the monochloride, as supposed by Meyer and Pawletta, because selenium monochloride is readily oxidized by ozone, as is evident from the change in color of its solutions during contact with ozone. The presence of appreciable amounts of monochloride in the solution or in the product would impart a distinct reddish color to them.

Products X, XI and XII were prepared from oxychloride fractionally distilled from phosphorus pentoxide. Product XII was prepared in a different type of reaction flask shown in Fig. 4. Manipulation was greatly simplified in that the product was precipitated, washed, dried and weighed in the same container without coming in contact with moist air.

TABLE I

ANALYTICAL RESULTS

Preparation	Selenium, %	Available O_2, %	Chlorine, %	Water, %	SeO_2, %	$SeOCl_2$, %	Total, %
I	66.30	0.0	..	..	...	...	...
	66.66	.0	..	..	...	...	...
II	70.42	.0	..	..	...	...	...
III	64.15	.0	..	..	...	...	...
	63.86	.0	..	..	...	...	...
IV	63.64	.0	..	..	...	...	...
V	...	..	..	0.66	...	...	...
	...	..	..	.95	...	...	...
VI	68.34	..	4.52	.96	88.80	10.59	100.35
	68.28	..	4.57	.97	88.78	10.71	100.45
VII	70.07	.0	1.56	.46	95.80	3.65	99.91
	70.19	..	1.59	..	96.04	3.72	100.22
VIII	70.88	..	0.20	.00	99.33	0.67	100.00
(3d Precip.)	71.06	..	.30	.00	99.50	.45	99.95
VIII	71.07	..	.09	.00	99.72	.16	99.98
(4th Precip.)	71.07	..	.08	.00	99.70	.18	99.98
IX	...	..	..	..	...	...	...
(2d Precip.)	70.80	..	Trace	.23	99.41	Trace	99.67
	70.97	..	Trace	.26	99.69	Trace	99.92
IX	...	..	..	..	...	...	...
(3d Precip.)	...	..	..	.00	...	...	...
X	66.47	.0	8.46	.00	80.05	17.49	97.54
	66.26	.0	8.41	.03	79.87	17.39	97.29
XI	70.52	..	0.94	.00	97.52	2.24	99.76
	70.51	..	.00	..	...	...	...
XII	69.04	.0	4.46	.00	...	...	...
	69.05	..	4.45	..	...	...	...
	68.97	..	..	..	...	...	...
	69.00	..	..	..	...	...	...

Analytical results of precipitates formed by mixing filtrates of the products with dry carbon tetrachloride are given in Table II.

The original filtrates of several products also were analyzed. Samples were weighed in tightly stoppered weighing bottles and then slowly hy-

TABLE II

ANALYTICAL RESULTS

Precip. from filtrate of product no.	Selenium, %	Chlorine, %	Water, %	SeO_2, %	$SeOCl_2$, %	Total, %
IV	70.81	..	0.31	99.63	..	99.93
	70.99	..	.37	99.67	..	100.04
VI	70.11	1.45	.00	96.20	3.40	99.60
	69.95	1.45	.00	96.00	3.40	99.40

drolyzed under water. Aliquots of the resulting solutions were analyzed for selenium and chlorine content. Results given in Table III indicate the composition of the selenium–selenium oxychloride solutions after reaction with dry ozone.

TABLE III

COMPOSITION OF FILTRATE

Sample no.	Selenium, %	Chlorine, %	SeO_2, %	$SeOCl_2$, %	Total, %
1	47.91	42.09	1.13	98.59	99.72
2	48.18	42.02	1.76	98.41	100.17
3	47.79	42.43	0.52	99.39	99.91
4	47.94	42.42	0.75	99.38	100.13
5	47.86	42.38	0.65	99.39	100.04
6	48.05	42.42	1.01	99.27	100.28

The above results and the general properties of the filtrates indicate the solvent, $SeOCl_2$, to be unchanged apparently by ozone during the oxidation of the dissolved selenium. Pure dry selenium oxychloride, however, was found to react with dry ozone when the latter was passed through a porous glass plate serving as a support for the liquid (see Fig. 4). The ozone–oxygen mixture passed through the solvent as thousands of tiny bubbles, thereby exposing an enormous surface of the liquid to the powerful oxidant. The oxidation product of $SeOCl_2$ was similar in every respect to the products obtained from Se–$SeOCl_2$ solutions.

Some Properties of Precipitated Selenium Dioxide.—Exposed to the air of the laboratory this substance rapidly absorbs water until its water content approaches 14% of the total weight of the sample; then the absorption of water practically stops. Although only approximate, this result corresponds to the water content of selenious acid.

The vapor pressure of the precipitated dioxide when moistened with water was observed to be lower than that of water alone at the same temperature; therefore, it is unlikely that oxygen was evolved when the products were dissolved in water.

Molecular Weight in Selenium Oxychloride.—A freezing point constant for selenium oxychloride was determined experimentally with solutions of ignited potassium chloride and barium chloride. An average of six determinations gave a value of 26. The molecular weights of the precipitated dioxide and the sublimed dioxide were then determined and found to be approximately three times 111.2, the calculated molecular weight of selenium dioxide. Absorption of moisture by selenium oxychloride solutions during determination of freezing points was avoided.

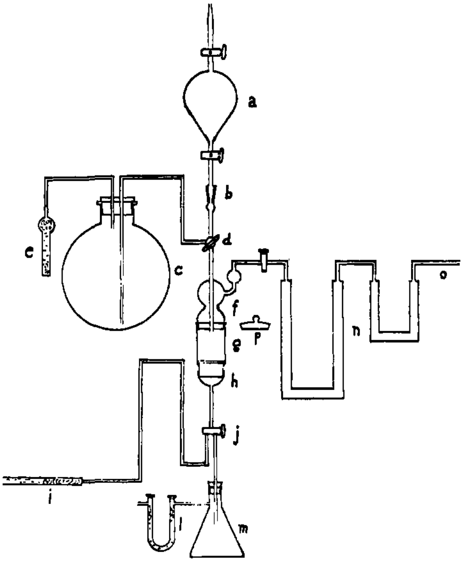
Table IV

Results of Molecular Weight Determinations

Drop in f. p., °C.	Grams of pptd. SeO_2/ 1000 g. $SeOCl_2$	Mol. wt., calcd.	Drop in f. p., °C.	Grams of sublimed SeO_2/ 1000 g. $SeOCl_2$	Mol. wt., calcd.
0.264	3.4285	338	0.252	3.221	334
.259	3.2717	328	.239	3.078	333
.236	3.000	332	.236	2.947	325
.233	3.000	336	.227	2.886	331
.205	2.571	327	.209	2.613	325
.195	2.400	326	.184	2.347	330
.186	2.361	332	.180	2.289	331

Density of Precipitated Selenium Dioxide.—The density of precipitated selenium dioxide was determined in benzene at 20°. Two separate determinations gave 3.590 and 3.595 as the density of the product. Worsley and Baker reported 3.6 as the density of their product; therefore there can be little doubt concerning the similarity of their product and that of the authors.

A sample of precipitated selenium dioxide was exposed to moist air until a calculated amount of water was absorbed, corresponding to the water content of selenious acid. A subsequent water analysis gave 13.87% of water as compared to 13.92% of water in selenious acid. A density determination of the same hydrated oxide gave a value of 2.982 at 20°. The true density of selenious acid is d_4^{15} 3.004. Hence, within the limits of experimental error, the density of hydrated, precipitated dioxide of selenium is identical with that of ordinary selenious acid.



a, Receiver of oxychloride still; b, ground-glass joint; c, 4-liter flask for washing liquid; d, 3-way stopcock; e, drying tube; f, top of Drechsel bottle; g, Jena glass crucible with sealed-in sintered glass plate; h, Gooch funnel; i, oxygen-ozone delivery tube; j, 3-way stopcock; l, drying tube; m, filter flask; n, sulfuric acid traps; o, gas outlet; p, stopper for Jena glass Gooch crucible.

Fig. 4.

That the different densities of

precipitated and sublimed selenium dioxide indicate merely a difference in physical state and not in composition, is shown definitely by analyses.

"Chloroselenic Acid."—Worsley and Baker reported their selenium oxide product to absorb hydrochloric acid gas, forming chloroselenic acid, a fuming straw-colored liquid. The density of this liquid was found by them to be 2.26. The density of selenium hydroxychloride (a fuming straw-colored liquid) is 2.24 at 25°.[8]

Several samples of this substance were prepared by the authors from the precipitated selenium oxide. The resulting straw-colored liquids varied in composition and density, depending on the temperature and the time allowed for absorption. This is a characteristic property of selenium hydroxychloride. Upon plotting chlorine percentages against densities of respective samples, it was found that a straight line drawn through the plotted points passed through a point representing the density and calculated chlorine content of $SeO_2 2HCl$.

Summary

1. Attempts to prepare selenium trioxide by the method of Worsley and Baker failed.

2. The product of ozone oxidation of $Se-SeOCl_2$ solution was identified by analyses as precipitated selenium dioxide.

3. The density of precipitated selenium dioxide was found to be appreciably lower than that of the sublimed dioxide.

4. Precipitated selenium dioxide absorbs moisture rapidly to form selenious acid.

5. The molecular weights of precipitated and sublimed SeO_2 dissolved in $SeOCl_2$ were found to be identical.

6. The product of ozone oxidation of $Se-SeOCl_2$ solutions absorbs dry hydrogen chloride gas to form a fuming, straw-colored liquid similar in composition and density to selenium hydroxychloride and not chloroselenic acid.

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[8] Muehlberger and Lenher, THIS JOURNAL, **47**, 1842 (1925).