[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE ADDITION PRODUCTS OF SELENIUM DIOXIDE WITH THE HALOGEN ACIDS

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RECEIVED JANUARY 19, 1925 PUBLISHED JULY 3, 1925

Little has been done with the compounds of selenium dioxide *with the halogen acids* since Ditte[1] showed that selenium dioxide unites with these gases to form $SeO_2.2HCl$, $SeO_2.4HCl$, $SeO_2.4HBr$, $SeO_2.5HBr$.

The question of the true chemical composition of these compounds is raised by the observation[2] that certain dehydrating agents remove water from $SeO_2.2HCl$, leaving selenium oxychloride. To this end the compounds $SeOCl_2.H_2O$ and $SeO_2.2HCl$ have been compared and as far as physical properties are concerned they appear to be identical.

Both are of a pale straw color, have a specific gravity of 2.246 at 25°, a surface tension of 55 dynes per sq. cm. when measured by the DuNouy method at 25°, an electrical conductivity of 2.7×10^{-2} mhos. at 25°, a melting point below —100°, and a refractive index of 1.642 observed at 20°.

When these substances are boiled, dissociation begins at 94°, the boiling point rising gradually to 179° without indication of any constant-boiling mixture. The dissociation taking place may be expressed as follows: $SeO_2.2HCl \longrightarrow SeO_2 + 2HCl$; $SeO_2.2HCl \longrightarrow SeOCl_2 + H_2O$. The chemical deportment of $SeO_2.2HCl$ and $SeOCl_2.H_2O$ toward various substances is similar to that of selenium oxychloride diluted with water.

Action on Metals.—Most of the metals react forming chlorides and selenites. There is also a simultaneous reduction to selenium monochloride and later to elementary selenium. Sodium and potassium react with explosive violence. Mercury, magnesium and antimony react vigorously, while zinc, tin, cadmium and tungsten are slowly attacked. Chromium and platinum are not appreciably attacked in the cold.

Behavior toward Non-Metals.—Sulfur reacts to form sulfur dioxide, sulfuric acid and selenium monochloride. Red phosphorus reacts violently, while with yellow phosphorus the reaction is explosive. Arsenic reacts readily with it. Selenium and tellurium dissolve with formation of selenium monochloride. Iodine, bromine and chlorine dissolve in the reagent, while graphite, silicon and boron are not attacked. The oxides of the metals in general are attacked, giving selenites and chlorides.

The carbonates are all attacked, giving chlorides and selenites, evolving carbon dioxide at the same time.

In all of the above-mentioned reactions, $SeO_2.2HCl$ and $SeOCl_2.H_2O$ have been proved to be identical.

Molecular-weight determinations by the cryoscopic method of Beckmann show the molecule to be $SeO_2.2HCl$ while with $SeOCl_2.H_2O$ the same

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[1] Ditte, *Ann. chim. phys.*, [5] **10,** 82 (1877).

[2] Lenher, THIS JOURNAL, **42,** 2499 (1920).

molecular weight is obtained. The same method when applied to selenium oxychloride gives the formula $SeOCl_2$.

The Dehydration of $SeO_2.2HCl$ by Means of Sulfuric Acid.—It has been shown by Lenher[2] that $SeO_2.2HCl$ loses a molecule of water to such dehydrating agents as phosphorus pentoxide, zinc chloride and calcium chloride. Later studies have shown that under proper conditions sulfuric acid also can be used quite efficiently. When the concentrated acid is added to pure $SeO_2.2HCl$ considerable heat is evolved and a white precipitate forms which on further addition of the acid dissolves to give a clear solution.

When a small amount of water is added to this solution the two liquids separate into selenium oxychloride and dil. sulfuric acid. It is necessary to adjust the proportions of $SeO_2.2HCl$ and the concentration of the sulfuric acid so that the separation will take place at a maximum efficiency. Above 90% concentration of sulfuric acid, $SeO_2.2HCl$ and the acid are completely miscible; below a concentration of 60% of acid, the dehydration power of the acid is insufficient to prevent hydrolysis of the oxychloride; 70% acid gives the best separation. With four parts of $SeO_2.2HCl$ and one of sulfuric acid (d., 1.84) the separation is most efficient and the acid after the separation will be approximately 70%. When more dilute selenium oxychloride is to be hydrated it is advisable to use fuming sulfuric acid, and in such amount that concentration of the acid after the dehydration will be approximately 70%. The use of excessive amounts of acid causes a considerable proportion of the oxychloride to pass into solution. Ordinarily, the yields by this procedure are very high when the ratio of four parts of oxychloride to one of 70% sulfuric acid is used. The oxychloride produced in this way boils at 176° and melts at 10.9°; d_{22}, 2.424.

The use of such solvents for the oxychloride as benzene, carbon tetrachloride or chloroform is not successful for the removal of selenium oxychloride from $SeO_2.2HCl$ solution.

The reaction of selenium dioxide with hydrogen bromide according to Ditte gives $SeO_2.4HBr$ and $SeO_2.5HBr$. We have been able to produce $SeO_2.2HBr$ at the ordinary temperature by passing hydrogen bromide over selenium dioxide, when a red-brown liquid is produced which analysis showed to correspond exactly to the formula $SeO_2.2HBr$, d_{22}, 3.077. This compound Ditte did not believe to exist. When heated at atmospheric pressure it begins to decompose at 115° with the production of bromine, selenium monobromide, selenium tetrabromide, hydrogen bromide, selenium oxybromide, selenium dioxide and water. The compound is less stable than its analog, $SeO_2.2HCl$, in the same degree that selenium oxybromide[3] is less stable than selenium oxychloride. When it is cooled to

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[3] Lenher, THIS JOURNAL, **44**, 1668 (1922).

—10° fine, red crystals of selenium tetrabromide separate from the solution but the liquid has no definite melting point. It is significant that $SeO_2.2HBr$ can be dehydrated by selenium dioxide. An excess of dry selenium dioxide introduced into the liquid gives a crop of yellow, needle-shaped crystals that melt at approximately 40°, dissolve in chloroform and on analysis conform to the formula $SeOBr_2$. The action of concd. sulfuric acid or of phosphoric acid is to precipitate selenium tetrabromide from $SeO_2.2HBr$, but owing to the unstability of the selenium oxybromide, they cannot be used for its preparation from $SeO_2.2HBr$.

The existence of the compound $SeO_2.4HBr$ reported by Ditte has been verified, but no evidence could be obtained of the existence of the compound $SeO_2.5HBr$.

Summary

The compounds $SeO_2.2HCl$ and $SeO_2.2HBr$ have been shown to be identical with the hydrates $SeOCl_2.H_2O$ and $SeOBr_2.H_2O$.

A new method is given by which selenium oxychloride can be produced from $SeO_2.2HCl$ and as well from hydrated selenium oxychloride.

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A LABORATORY OZONIZER YIELDING HIGH CONCENTRATIONS OF OZONE

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RECEIVED FEBRUARY 12, 1925 PUBLISHED JULY 3, 1925

The researches of Harries and his pupils[1] upon the properties of ozone have shown that this substance is an excellent reagent for purposes of oxidation and structure determination of unsaturated organic compounds. Indeed, Harries has characterized it as a reagent "par excellence," and if this statement be true, ozone has not become nearly as common a reagent as it should be. This is, no doubt, because rather high concentrations of ozone are usually required for the formation of ozonides, and it is not possible to purchase in this country apparatus capable of producing ozone of high concentrations, while such apparatus purchased abroad is rather expensive. The construction of a satisfactory ozonizer also offers difficulties, for although many directions are available for making ozonizers capable of giving low concentrations of ozone, Harries,[2] and recently Briner, Patry and deLuserna,[3] are the only ones who have published anything concerning high-concentration ozonizers. Moreover, in his paper describing his ozonizer,[2] Harries did not give dimensions and anyone

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[1] Harries, "Untersuchungen uber das Ozon," Springer, Berlin, **1916**.

[2] Harries, *Ann.*, **343**, 311 (1905).

[3] Briner, Patry and deLuserna, *Helvetica Chim. Acta*, **7**, 62 (1924).