

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

SELENIUM OXYBROMIDE

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The oxybromide of selenium, SeOBr_2 , was originally prepared by Schneider.¹ It was later made by Glauser² who noted a few of its properties.

The various methods used for its preparation and its properties in general are closely related to those of selenium oxychloride.³

Preparation.—One of the simplest and most direct procedures to assure a satisfactory product is to unite pure dioxide and pure tetrabromide of selenium. To this end, we have used freshly sublimed selenium dioxide, special care being taken to obtain it as dry as possible.⁴ To this is added the calculated amount of powdered fused pure selenium. The operation can be conveniently conducted in a glass flask closed by a rubber stopper carrying a dropping funnel and a tube containing freshly ignited pure calcium bromide to protect the products from atmospheric moisture. The requisite amount of pure bromine is added through the dropping funnel in small portions at a time. The heat evolved in the bromination of elementary selenium to monobromide and subsequently to tetrabromide is so great that it is advisable to chill the flask nearly to 0° in order to prevent loss of bromine. The heat evolved in bromination of the monobromide to the tetrabromide is so much less than in the production of the monobromide that the last portions of bromine can be added very rapidly. After the calculated amount of bromine has been added the mixture of tetrabromide and dioxide is gently warmed until all of the dioxide has dissolved to form oxybromide. When the selenium dioxide is finely powdered this takes place quickly, but when large crystals are used a number of hours may be required to effect complete solution.

Physical Properties.—Selenium oxybromide is a reddish-yellow solid that melts at $41.5\text{--}41.7^\circ$ and boils at 217° under 740 mm. pressure with considerable decomposition. Its decomposition at even slightly elevated temperatures is so great that it has not been found practical to attempt to purify it by distillation under diminished pressure. Its density at 50° is 3.38. Its electrical conductivity as observed by A. P. Julien in this laboratory in a modified Washburn cell using platinum electrodes and working just above the melting point, $45\text{--}50^\circ$, is approximately 6×10^{-8} .

Selenium oxybromide is hydrolyzed by water into selenious and hydrobromic acids. It dissolves readily without apparent chemical action in

¹ Schneider, *Pogg. Ann.*, **129**, 459 (1866).

² Glauser, *Z. anorg. Chem.*, **80**, 277 (1913).

³ Lenher, *THIS JOURNAL*, **42**, 2498 (1920); **43**, 29 (1921); **44**, 1664 (1922).

⁴ *Ibid.*, p. 1664.

carbon disulfide, chloroform, benzene, toluene and xylene, and the fused material is miscible in all proportions with these solvents, as is selenium oxychloride.

Carbon tetrachloride dissolves selenium oxybromide but the fused substance is soluble to the extent of only about 6%. Carbon tetrachloride and selenium oxybromide do not immediately react chemically when brought into contact, but when heated together for several days phosgene is produced in large quantities.

With the saturated aliphatic hydrocarbons there is apparently little if any chemical action. The pure hydrocarbons hexane, heptane, octane and decane are immiscible with the reagent. The lighter hydrocarbons float on melted selenium oxybromide. Similarly, melted paraffin or vaseline floats on liquid selenium oxybromide.

Chemical Properties

Selenium oxybromide is a very active chemical reagent. Its deportment and activity in general much resemble those of the oxychloride. When selenium oxybromide is distilled it dissociates somewhat into selenium dioxide and tetrabromide. Heating the tetrabromide causes further decomposition into monobromide of selenium and free bromine. It is possible to distil the substance, but there is considerable loss in the operation. Even when distilled under greatly diminished pressure there is considerable decomposition. In order, therefore to avoid confusion of the behavior of selenium oxybromide with the various materials studied, comparative experiments have been made with the particular substances and bromine.

Action on Non-Metals.—The members of the sulfur group, sulfur, selenium and tellurium, react immediately with selenium oxybromide. Sulfur even in the cold with solid selenium oxybromide liquefies in a few minutes and evolves sulfur dioxide with effervescence. Selenium dissolves in large quantities in melted selenium oxybromide forming the monobromide. Tellurium reacts in the cold but not so energetically.

White phosphorus with solid selenium oxybromide explodes violently, while red phosphorus with solid selenium oxybromide takes fire and burns with a flame.

Iodine dissolves in large quantities in selenium oxybromide, while chlorine displaces the bromine and converts it to pure selenium oxychloride. Crystalline silicon is unattacked by the reagent even at 217°. Carbon in all forms, graphite, charcoal, activated carbon and diamond are not attacked even at its boiling point by selenium oxybromide.

Action on Metals.—Selenium oxybromide reacts with most of the metals forming the bromide and selenium monobromide. Sodium reacts in the cold with selenium oxybromide with slight explosion evolving

light and heat. Potassium in the cold with solid selenium oxybromide explodes violently.

Metallic mercury, arsenic, antimony, tin, bismuth, iron, calcium, copper, lead, silver, molybdenum, thallium, gold, platinum and zinc are attacked by selenium oxybromide. Zinc dust burns beautifully in selenium oxybromide, making a striking experiment. Aluminum and magnesium are only very slightly corroded by heating in a sealed tube with selenium oxybromide for a week at 100°. Chromium, cadmium, nickel, cobalt, tungsten and tantalum are not attacked when heated with selenium oxybromide in a sealed tube for 10 days to 100°.

Action on Oxides.—Selenium oxybromide reacts with certain of the oxides, such as mercuric oxide, silver oxide, lime and sodium peroxide with great energy, while arsenic trioxide, tin dioxide, tellurium dioxide, tellurium trioxide react more slowly and less energetically.

Such oxides as those of columbium, tantalum, vanadium, thorium, titanium, zirconium, uranium and antimony are apparently unaffected even on heating in a sealed tube for a number of days to 100°. Ignited cerium oxide is only very slightly attacked.

Carbonates.—Selenium oxybromide reacts slowly and sluggishly with the carbonates of calcium, strontium, barium, magnesium, lead, copper, sodium, potassium and the alkaline bicarbonates, even when warmed. When water is present the action is, of course, vigorous. Dry cobalt carbonate is not appreciably acted upon.

Sulfides.—Arsenious, arsenic, antimonous, stannous, cadmium, zinc, bismuth, mercuric, lead, strontium, and ferrous sulfides react with selenium oxybromide, evolving heat. The metallic bromides and selenium monobromide are formed. Pyrite, marcasite, arsenopyrite, and tetrahedrite react with selenium oxybromide with production of selenium monobromide.

Calcium Hydride, Carbide and Phosphide are only very slowly and sluggishly attacked by selenium oxybromide even on boiling.

Barium Sulfate is not acted on by selenium oxybromide nor is it rendered colloidal as is the case when brought in contact with selenium oxychloride.⁵

Oxidizing Agents.—Potassium chlorate reacts with selenium oxybromide and bromine is evolved. When the two are gently warmed together the bromine is completely expelled in a few minutes. Potassium perchlorate does not react with selenium oxybromide.

Potassium permanganate, potassium dichromate and chromium trioxide do not react with selenium oxybromide, even on boiling.

Action of Various Gases.—When dry air is bubbled through pure selenium oxybromide heated to 60°, bromine is gradually driven off. This is

⁵ THIS JOURNAL, 43, 32 (1921).

due to a primary dissociation of the oxybromide into dioxide and tetrabromide of selenium and to a secondary slow decomposition of the tetrabromide into monobromide and free bromine which is volatile. After dry air is bubbled through heated pure selenium oxybromide for several days and the resulting product treated with water, a very large amount of monobromide appears as the characteristic heavy red-brown liquid which hydrolyzes very slowly. Indeed, the slow hydrolysis of selenium monobromide is one of its striking features. Selenium monobromide is only slowly decomposed by boiling water into elementary selenium, selenious and hydrobromic acids, while when allowed to stand with excess of cold water some of the liquid selenium monobromide remains undecomposed at the end of several days.

Dry Sulfur Dioxide and Dry Carbon Monoxide do not react with fused selenium oxybromide. **Hydrogen Sulfide** causes slight decomposition.

Hydrocarbons.—The saturated aliphatic hydrocarbons are only slowly attacked by selenium oxybromide at a high temperature.

The unsaturated aliphatic hydrocarbons react with selenium oxybromide with great energy. Amylene, turpentine and isoprene react with great violence with selenium oxybromide.

The aromatic hydrocarbons such as benzene, toluene, and xylene form physical mixtures with selenium oxybromide from which the hydrocarbons can be recovered by hydrolysis of the mixture with water.

Naphthalene, anthracene, phenanthrene and retene dissolve readily in selenium oxybromide with chemical change.

Separation of the Hydrocarbon Series by Selenium Oxybromide.—It is possible to separate the various hydrocarbon series from one another. Benzene and toluene dissolve in selenium oxybromide and can be separated from such hydrocarbons as heptane which is immiscible with selenium oxybromide and is immiscible with a solution of the benzene or toluene in the oxybromide. The lighter heptane floats. Such unsaturated hydrocarbons as amylene can also be separated from heptane by selenium oxybromide. Naphthalene and heptane are readily separated by this reagent.

Carbohydrates and Proteins.—Selenium oxybromide when just melted dissolves with ease such proteins as hair, silk, leather, gliadin from wheat, zein from corn, glutenin from wheat, elastin, gelatin, blood albumen and egg albumen.

Its action on cellulose is not appreciable. The melted substance can be filtered through filter paper, as has been frequently done in this laboratory.

Vegetable and Fish Oils.—The action of selenium oxybromide toward the vegetable and fish oils is similar to the behavior of sulfur monochloride or selenium oxychloride. With oils having a high iodine number the action is vigorous while with the oils which are of a more saturated character the

action is more moderate. The oils are changed into a rubber-like mass which contains selenium and bromine. The oils examined were raw and boiled linseed, china wood, soy bean, corn, cotton, sesame, peanut, castor, olive, palm, coconut, menhaden, cod liver, whale, sperm, lard and neat's foot oil.

The "Insoluble" Phenolic condensation products, Redmanol and Bakelite, dissolve readily in melted selenium oxybromide. The reaction is accelerated by heat. The substances are changed chemically.

Gums, resins, dried paints, lacquers, baked organic enamels, glues, and insoluble casein glues dissolve readily in melted selenium oxybromide. The natural asphalts, bitumens and resins, when of unsaturated character dissolve readily in melted selenium oxybromide. Saturated substances such as ozocerite form 2- component systems in which the lighter melted substance floats on the heavier selenium oxybromide layer.

Coals and Carbons.—When melted selenium oxybromide is brought into contact with coals of the bituminous variety, reaction takes place with the resinic and bituminous parts of the coal, solution of a part of the coal is effected, and at the same time an insoluble carbonaceous residue is left behind.

Anthracite coal containing no volatile combustible matter is unaffected, as are thoroughly ignited coke and graphite.

Amorphous forms of carbon containing hydrocarbons lose their hydrocarbon content when treated with selenium oxybromide. Thus, ordinary lampblack yields a black extract with melted selenium oxybromide, leaving behind carbon.

Activation of Charcoal by selenium oxybromide can be accomplished readily. "Retorted" nut carbon when treated with melted selenium oxybromide loses hydrocarbons and actually effervesces in the cold from the heating effect produced in the chemical reaction.

Similarly, a solution of selenium oxybromide in carbon tetrachloride or benzol, extracts hydrocarbons from "unactivated" nut charcoal leaving behind activated carbon which does not react with selenium oxybromide.

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Summary

Selenium oxybromide is a reddish-yellow solid melting at $+1.5$ – $+1.7^{\circ}$. It can readily be prepared by any reaction in which pure selenium dioxide and tetrabromide are brought in contact.

When heated, selenium oxybromide slowly begins to dissociate just above its melting point, while at higher temperatures the dissociation is so great that it is impracticable to use distillation, even under reduced pressure, as a means of purification.

Its chemical properties are similar to those of the oxychloride. In liquid form, above 42°, it is a powerful solvent, deporting itself in general as an oxidizing and brominating agent.

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THE EFFECT OF SUCROSE ON THE ACTIVITIES OF THE CHLORIDE AND HYDROGEN IONS

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I. The Effect of Sucrose on the Activity of the Chloride Ion in Tenth and Half Normal Solutions of Potassium Chloride

In recent years, the measurement of the individual activity of an ion has been rendered possible by certain assumptions, first made by MacInnes.¹

The first postulate was that the activities of the anion and cation in the same solution of an electrolyte may differ from one another; the second, that in solutions of potassium chloride, the activities of the anion and cation are equal; and the third, that in solutions of univalent chlorides of the same concentrations, the chloride ion has the same activity in every case. The second and third assumptions have been shown by Harned,² to be true experimentally.

Noyes and MacInnes³ have utilized the values of the e.m.f.'s of the cells with and without transport containing potassium chloride, obtained by MacInnes and Parker,⁴ to calculate the activities of potassium chloride in solutions of different concentration, varying from 0.001 to 0.5 *M*. As a basis for the calculation of these relative activities the assumption was made that the activity coefficient was identical with the conductivity-viscosity ratio in very dilute solutions, and on this basis the activities in solutions up to 0.5 *N* potassium chloride were computed. By means of the second postulate of MacInnes, the activities of potassium chloride become identical with those of the chloride ion.

The present investigation consists of measurements of the activity of the chloride ion when the environment is changed by the use of sucrose solutions of different concentrations as solvent in place of pure water. The reason for the use of sucrose is that it is proposed to extend the measurements of the activities of ions, when the environment is changed, to the

¹ MacInnes, *THIS JOURNAL*, **41**, 1086 (1919).

² Harned, *ibid.*, **42**, 1808 (1920).

³ Noyes and MacInnes, *ibid.*, **42**, 239 (1920).

⁴ MacInnes and Parker, *ibid.*, **37**, 1445 (1915).