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SOME PROPERTIES OF SELENIUM OXYCHLORIDE. II

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Further studies on the chemistry of selenium oxychloride have shown that it is essential to have the substance in a high degree of purity in order that its behavior may not be confused with reactions other than those of the oxychloride itself. In many of the reactions it is essential that the product be anhydrous, inasmuch as a small amount of moisture in some instances materially modifies its deportment.

A small amount of water present in selenium oxychloride, as has been shown by A. P. Julien in this laboratory, increases its conductivity enormously and, as has been demonstrated in the experiments of A. K. Brewer in this laboratory, its reactivity toward the carbonates is largely dependent on the amount of water present.

Anhydrous selenium oxychloride can be prepared on a small scale in the laboratory only when the most elaborate precautions are taken to avoid the presence of moisture. One of the ideal methods would be to bring together dry selenium dioxide and fused selenium and treat with of dry chlorine. Both fused selenium and chlorine can readily be obtained anhydrous, but selenium dioxide even when repeatedly sublimed, adheres tenaciously to a small amount of water, as has been shown in this laboratory by Julien, Muehlberger and others. Production of the dioxide by burning elementary selenium in oxygen is a simple method of obtaining very pure and dry material but the transfer of the dry oxide from the receiver in which it is condensed must be carried out with the usual care in handling so hygroscopic a body.

Repeated distillation of selenium oxychloride under reduced pressure will give a very good product with proper fractionation.

Thus far, the best qualitative test for water in selenium oxychloride is with cobalt carbonate. It has been developed with the assistance of A. K. Brewer and is a modification of a reaction previously described.¹ When cobalt carbonate which has been dried at 200° for 3 hours in a current of dry carbon dioxide is treated with the purest selenium oxychloride that we have been able to obtain and immediately sealed in dry glass tubes, no action is apparent after the tubes have been standing for months. The cobalt carbonate preserves its original pink color and the liquid selenium oxychloride has not changed in color. Tests which have been made on a number of tubes show that there is no increased pressure such as would be the case were carbon dioxide given off. When perfectly dry cobalt carbonate is treated with selenium oxychloride which contains a mere

¹ This Journal, **43**, 32 (1922).

trace of water, or when a tube containing the dried cobalt carbonate and material repeatedly fractioned under diminished pressure is opened and exposed to the air for only a few seconds and again sealed, in a few hours the nearly colorless liquid selenium oxychloride becomes a quite pronounced blue and the tube develops a strong internal pressure due to evolved carbon dioxide. A number of such sealed tubes, in which the selenium oxychloride showed a blue color, when allowed to stand for several months exploded from the pressure of carbon dioxide which is continuously produced.

Only a very small amount of water in the selenium oxychloride will cause the dried cobalt carbonate to become blue instantly while the liquid itself quickly assumes a blue color. The carbonates of calcium, strontium, copper, nickel, cobalt and ferrous iron, as shown in the experiments of A. K. Brewer in this laboratory, when entirely dry, are not attacked by anhydrous selenium oxychloride during contact for many hours and showed no loss of carbon dioxide that could be detected by weighing a potash absorption bulb. In these experiments, which were conducted in gas evolution flasks, after testing the action of selenium oxychloride alone, water was added and in a few minutes the theoretical amount of carbon dioxide was collected and weighed.

The anhydrous carbonates of barium and of magnesium give off carbon dioxide slowly with selenium oxychloride while dry zinc carbonate evolves carbon dioxide more rapidly. Dry lithium carbonate is acted upon very slowly by anhydrous selenium oxychloride, while the fused carbonates of sodium and potassium react with anhydrous selenium oxychloride, giving off considerable heat and evolving carbon dioxide.

Action of Reducing Gases. Sulfur Dioxide is without action on dry selenium oxychloride even when heated to the boiling point of the latter. When water is present, however, elementary selenium is precipitated.

Dry Hydrogen Sulfide on contact with selenium oxychloride causes at first a red-brown color, after which hydrogen chloride is evolved and yellow selenium sulfide is produced. At the same time heat is evolved, which dissociates the selenium sulfide into sulfur and red selenium.

Liquid Hydrogen Disulfide reacts vigorously with selenium oxychloride in the cold, producing sulfur and the same order of products as is formed with hydrogen sulfide.

Dry Carbon Monoxide made by the action of warm sulfuric acid on sodium formate, has no action on selenium oxychloride either at room temperatures or up to the boiling point of selenium oxychloride, 177.2°

Iodic Acid, Iodine Pentoxide and Potassium Iodate, when brought in contact with selenium oxychloride, give at first chlorine and later chloride of iodine.

Per-iodic Acid, with selenium oxychloride, evolves chlorine, and when the mixture is warmed chloride of iodine is produced.

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Potassium Bromate with selenium oxychloride in the cold gives at first chlorine followed quickly by a mixture of bromine and chlorine.

Potassium Persulfate, when warmed with selenium oxychloride, slowly evolves chlorine, while the persulfate-sulfuric acid mixture evolves chlorine with effervescence in the cold.

Telluric Acid, and Anhydrous Solid Selenic Acid evolve chlorine when gently warmed with selenium oxychloride.

Metals.—In attempting to dehydrate selenium oxychloride in this laboratory by means of metallic sodium, A. P. Julien has verified the previous experiments of Lenher,² but in addition has shown that after continued contact for some hours, the two react slightly to form a small amount of selenium monochloride. When this reaction commences, as is evidenced by the production of a red-brown color, reactions of unknown character in the system begin to proceed very rapidly, sometimes being accompanied by violent explosions.

Of the metals, tungsten, tantalum and titanium (with A. I. Andrews) are very resistant to the action of selenium oxychloride.

TUNGSTEN WIRE heated with selenium oxychloride in a sealed tube to 105° shows no tarnish until after 28 days and there is no appreciable change in weight at 105° until after 46 days. At higher temperatures, $140-200^{\circ}$, a week's time is required for the development of the black tarnish, while at 375° , experiments showed about 10% corrosion in 2 hours.

TANTALUM, kindly furnished by C. W. Balke, showed no corrosion with selenium oxychloride at $105-110^{\circ}$ in 6 months' time. At 200° there was no loss of weight in 2 hours and at 375° only 0.65% loss in 2 hours.

TITANIUM after 12 months' contact with selenium oxychloride at ordinary temperature in a sealed tube was unaffected. When the two are heated to 375° for 2 hours the action is not appreciable.

Phosphorus.—The reactions between phosphorus and selenium oxychloride have been studied further by A. I. Andrews. Both red and yellow phosphorus react energetically with selenium oxychloride at the ordinary temperature. In our work, it has been found most convenient to bring together ordinary phosphorus and selenium oxychloride in an evacuated flask maintained at the temperature of melting ice in order to moderate the action and to prevent formation of various oxides from the oxygen of the air. In all of the experiments conducted, the selenium oxychloride was in excess and the products of the reaction were always phosphorus pentoxide and the chlorides of selenium, Se_2Cl_2 and $SeCl_4$.

Michaelis³ has worked on the reactions between the various chlorides of phosphorus and selenium oxychloride, and states that phosphorus trichlo-

² Ref. 1, p. 39.

³ Michaelis, Jenaische Z., 6, 79, 86, 93 (1871).

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ride reacts with evolution of heat forming a red solution and a white residue, the products of the reaction being selenium mono- and tetrachloride, together with phosphorus oxychloride. This we have verified. He also states that when selenium and phosphorus oxychlorides are brought together, phosphorus pentoxide and selenium tetrachloride are formed. In our experiments, we find no such action; on the other hand, the two liquids are completely miscible, which would not be the case were selenium tetrachloride formed. Possible impurities in the reagents may explain this error, particularly since phosphorus pentachloride with selenium oxychloride yields insoluble selenium tetrachloride together with phosphorus oxychloride.

Carbon Tetrachloride is an excellent solvent for selenium oxychloride, as has been noted, but in time they react, producing selenium tetrachloride and phosgene. This is particularly true when the two are heated together for some hours.

Protein material in pure condition, such as gliadin from wheat, zein from corn, glutenin from wheat, and elastin, as well as albumen, from egg and from blood, have been found to be readily attacked and dissolved by selenium oxychloride.

Activated Carbon.—It has been shown previously that pure carbon in its various forms does not react with selenium oxychloride even when heated to moderate temperatures. At or above red heat, when considerable dissociation of selenium oxychloride takes place, both amorphous and graphitic carbon are oxidized.

That one of the essential differences between the absorbent properties of "retorted" carbon and "activated carbon" is due to the presence of hydrocarbons in the unactivated carbon can be readily demonstrated by extraction of retorted nut shells with selenium oxychloride. After such extraction at the ordinary temperature and subsequent removal of the selenium oxychloride and extractive matter, the carbon then shows the same adsorptive properties toward such substances as chloropicrin as does the carbon which has been activated by the action of steam at high temperatures.

Summary

It has been observed that selenium oxychloride containing a small amount of water deports itself differently in many ways from the anhydrous material. The best test so far known for traces of water in selenium oxychloride is the reaction with dry cobalt carbonate.

The general chemical behavior of selenium oxychloride is that of an acid chloride of oxidizing character. In its various actions, it chlorinates and oxidizes.

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