Acknowledgment

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Summary

In the reaction between selenium and oxygen in the glow discharge, the effects of the variables, pressure, current, electrode distance, shape of tubes, were studied. From these studies, optimum conditions for the production of selenium dioxide and trioxide were ascertained. The characterization of these products, by means of chemical analysis, was supplemented by X-ray diffraction studies.

The reaction is best initiated in the negative glow and is completed by the deposition of product on the cold tube walls.

MADISON, WIS. RECEIVED AUGUST 28, 1936

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

The Oxidation of Selenium in the Glow Discharge. III. Striated Deposits and Possible Mechanism[1]

BY EARL OLSON AND V. W. MELOCHE

Although the glow discharge may be said to comprise a rather complex field for chemical reaction, the use of solid selenium as one of the reactants and the cooling of the walls of the tube in liquid air greatly reduce the complexity of the system. In a homogeneous system, it is difficult to determine the nature of the reaction in the various parts of the discharge column. Since the products of the oxidation of selenium are solids, it has been possible to study the deposits which formed as striations *in the column* and to study the effect of the change of pressure and power on these striations. We propose to describe the results of this study and use these data together with results published in a previous paper in support of a proposed mechanism for the oxidation of selenium in the glow discharge.

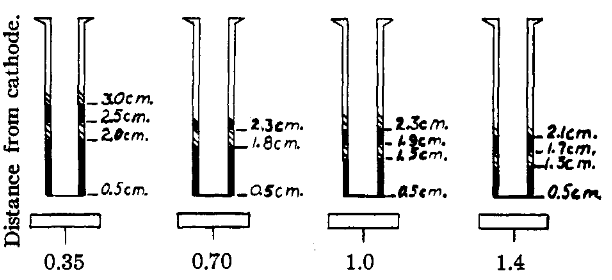

Fig. 1.—▨, Oxides of selenium; █, elementary selenium.

Apparatus.—The apparatus used in this research was the same as that described in previous papers.[2,3] The data to be presented were obtained with the discharge tube III, illustrated in the second paper, having a distance of 10 cm. between the electrodes. Direct current was used.

Striated Deposits in the Discharge

Selenium was fused on the bottom of a glass suspension 0.5 cm. from the cathode as shown in Fig. 1. The basket was suspended in the center of the discharge column. After subjecting the selenium to the glow discharge for an hour and a half, it was found that oxides and elementary selenium deposited not only on the walls of the tube but also on the vertical glass supports directly in the path of the discharge. Distinct striations of white selenium oxide and elementary selenium were sharply defined if the pressure were held constant during the run. The striation dimensions of four constant pressure runs are given in Fig. 1. The lined areas represent deposits of oxides, while the solid black areas represent deposits of elementary selenium. For example, the striations occurring at 0.35 mm. pressure consisted of a 1.5-cm. deposit of black elementary selenium, then 0.5 cm. of white oxide of selenium, 0.5 cm. of red elementary selenium, and above this another selenium oxide deposit of 0.4 cm. No deposit was detectable higher on the glass support. It is well known that red selenium is transformed to the black variety byheat. In agreement with this is the fact that the black selenium deposited close to the cathode where the temperature was relatively high and the red selenium deposited farther away from the cathode where the temperature was undoubtedly lower.

It is believed that this is the first report of striated depositions occurring directly in the discharge column. Brewer[4] has reported a well defined band of deposit on the wall of the tube in the region of the negative glow; also, under special conditions, striated deposits on the wall in the positive column region. The above figure represents striated deposits in the head of the positive column. The lower black area is in the region of the negative glow and Faraday's dark space. The two oxide deposits (lined areas) and the upper black area are in the region of the head of the

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[1] This investigation was supported in part by the Wisconsin Alumni Research Foundation. This paper is presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Kramer and Meloche, THIS JOURNAL, **56**, 1081 (1934).

(3) Olson and Meloche, *ibid.*, **58**, 2511 (1936).

(4) Brewer, *et al.*, *J. Phys. Chem.*, **34**, 153, 2343 (1930); **35**, 1281, 1293 (1931).

positive column. These striated deposits must have been produced by the luminous and non-luminous regions of the discharge. It is well known that these regions move away from the cathode with decreasing pressure. Figure 1 shows that the deposits of selenium and of selenium oxide were affected in a similar manner, supporting the conclusion that the deposits are regulated by the striations of the discharge.

In order to determine whether the oxides of selenium were deposited in a luminous or non-luminous region, the potential drop between two probes was measured with an electrostatic voltmeter. The two probes were placed at distances 2 and 2.5 cm. from the cathode and the discharge moved past them by varying the pressure. Figure 2 shows the variation of potential drop between the probes as the discharge was moved past them.

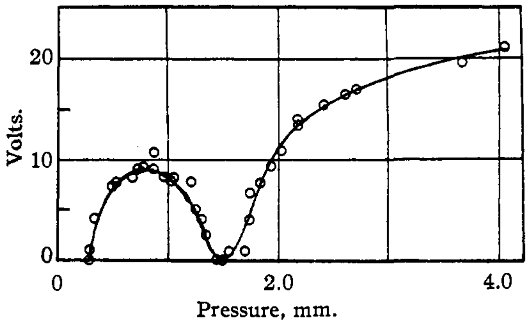

Fig. 2

Figure 3 shows a continuous graph of the striated deposits in Fig. 1.

From the voltage measurements, it can be seen that a non-luminous stratum existed between the probes at pressures of 0.3 and of 1.5 mm. Also, a luminous region filled the space between the probes at a pressure of 0.9 mm. Now, upon inspection of Figure 3, it may be definitely concluded that selenium was deposited in luminous regions and selenium oxide in the non-luminous. This fact gives an indication as to the mechanism of the oxidation of selenium in the glow discharge; the selenium was activated in the negative glow or other luminous regions and then combined with oxygen in a dark space or outside of the discharge column. If any combination of activated selenium and oxygen takes place in a luminous region, decomposition immediately follows.

Facts Pertinent to Mechanism

1. Using a glass suspension located in the d. c. discharge, selenium metal was deposited in luminous portions and selenium oxide deposited in the dark spaces, indicating that selenium was activated in the luminous regions and combined with oxygen in the dark regions.

2. Using a discharge tube with rod electrodes and employing alternating current, higher concentrations of selenium trioxide were found behind the electrodes. This indicated that selenium trioxide was formed near or behind the electrodes; also, the particles were propelled parallel to the electric field.

3. Using the same rod electrodes but employing direct current, larger weights of product and higher percentages of selenium trioxide were found behind the cathode than behind the anode. The larger amount of product behind the cathode indicates that the selenium was attracted toward the cathode and, therefore, was positively charged. Deposition of product in other parts of the tube does not contradict the above for it is certainly feasible that gas neutralization may also take place and, therefore, mere diffusion of product to all parts of the walls.

The higher percentage of selenium trioxide behind the cathode indicates that the selenium was more highly activated in the negative glow, thereby producing a higher concentration of selenium trioxide. This is also indicated by the effect of pressure upon the concentration of selenium trioxide in the product; higher concentrations were obtained at that pressure at which the selenium is in or near the negative glow.

4. A higher concentration of selenium trioxide was produced when a steady current of oxygen was passed through the discharge tube than when oxygen was simply allowed to diffuse into the tube from one opening. (2) This supports the view that the oxides of selenium are formed in the dark spaces or outside the discharge column.

5. Selenium was placed 2 cm. from the cathode and a discharge run at 1.4 mm. pressure; no vaporization or oxidation of selenium occurred. (2) When the pressure was reduced to 0.4 mm. vaporization and the oxidation of selenium took place. Evidently the selenium must be in the region of the negative glow or no appreciable reaction will occur. Brewer[4] has also found the negative glow to be the most reactive region.

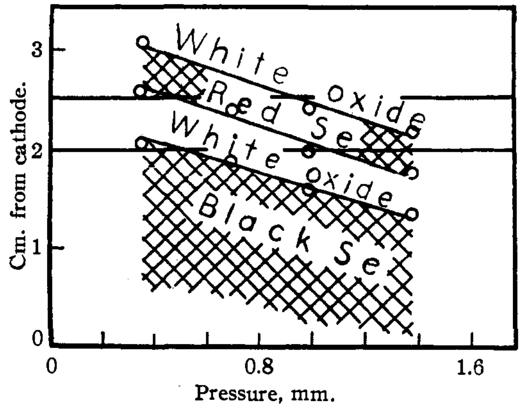

Fig. 3.

6. When pure selenium dioxide was placed in the negative glow, a red coloration developed, indicating reduction to metallic selenium. If selenium dioxide is unstable in the glow, certainly selenium trioxide is unstable and, therefore, only selenium ions exist in the luminous regions, oxides being formed in the dark spaces or outside the discharge column.

7. Increase of power caused an increase of percentage of selenium trioxide and of weight of the product.[3]

8. Previous experiments have shown that selenium trioxide is not formed by the action of ozone on selenium. This fact supports our belief that activated selenium is necessary for the formation of selenium trioxide.

The Mechanism

The selenium is vaporized and activated in the luminous portions of the discharge, the rate being at a maximum in the negative glow. It is highly probable that positive ions are formed and propelled toward the cathode. Once outside the region of the discharge, the activated selenium combines with oxygen forming either the dioxide or trioxide; more trioxide is formed at higher activations of the selenium, as indicated by the effect of current and voltage on the per cent. of selenium trioxide in the product. The particles are positively charged, gas or wall neutralization taking place. Undoubtedly there is decomposition of selenium trioxide occurring. It seems logical that there will be less decomposition of a selenium trioxide particle if it is neutralized on the wall, which is at a low temperature and will take up the heat of neutralization. On the other hand, if gaseous neutralization takes place, the heat cannot be dissipated and therefore might decompose the selenium trioxide molecule. It may be mentioned that only very low percentages of selenium trioxide were found when the tube was at room temperature during the reaction.

Summary

1. Banded deposits of selenium metal and selenium oxide were obtained in the glow discharge column. This afforded a means of determining the region in which the oxidation of selenium takes place. A correlation of voltage measurements and the character of the striated deposits shows that vaporization and activation of selenium takes place in the luminous regions. Combination with oxygen takes place in the dark regions.

2. After considering the experimental facts, a mechanism is suggested.

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The CN Bond in Methyl Cyanide and Methyl Isocyanide

BY L. O. BROCKWAY

The bond between the carbon and nitrogen atoms in methyl cyanide and other organic nitriles has long been regarded as a triple electron pair bond, the structural formula for these compounds, $\mathrm{R{-}C{\equiv}N}$, being considered satisfactory because in it carbon shows its normal valence of four and nitrogen one of its two normal valences, three. The isocyanides, on the other hand, according to the same considerations might have either one of two formulas, $\mathrm{R{-}N{\equiv}C}$ and $\mathrm{R{-}N{=}C}$. In the former the carbon atom is again quadrivalent while the nitrogen is quinquivalent; the latter formula is distinguished by the bivalent carbon atom. This formula, suggested by Nef, was favored because it was thought that the unusual chemical reactivity of the isocyanides was perhaps due to the "unsaturated" bivalent carbon atom.

In 1919 Langmuir[1] considered the possibility of a third formula for the CN radical on the basis of the Lewis theory of valency, namely, $\mathrm{R{-}C}\text{≣}\mathrm{N}$. Langmuir, however, noted the isosterism of cyanide ion and nitrogen molecule and rejected the triple bond structure because of the pronounced chemical differences between nitrogen molecule and acetylene, for which a triple bond structure was accepted. He proposed a structure in which one pair of electrons was shared between the two atoms and the remaining eight formed an octet around the two atoms together. This structure was not generally accepted and Lewis in 1923[2] supported the validity of the triple bond formulation for the cyano radical. In accordance with the octet theory this formula originally considered by Langmuir is preferable to the first two mentioned above since it is the only one of the three in which each of the atoms is surrounded by four electron pairs. This is evident when the formulas are written to show both the shared and the unshared electrons, as follows

$$\mathrm{R:N::::C} \qquad \mathrm{R:\ddot{N}::C:} \qquad \mathrm{R:N:::C:}$$

The interpretation of the octet theory by quantum mechanics in terms of the application of the Pauli exclusion principle to the elements of the first row of the periodic table still excludes the first but admits the second and third structures.

The first direct attempt to decide among these three bond types for methyl isocyanide was made

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[1] I. Langmuir, THIS JOURNAL, **41**, 868, 1543 (1919).

[2] G. N. Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, 1923, p. 127.