HETEROGENEOUS CHEMICAL REACTIONS IN THE SILENT ELECTRIC DISCHARGE. XIII.* REACTIONS BETWEEN HYDROGEN AND SOLID INORGANIC COMPOUNDS.

By **Susumu MIYAMOTO.**

Received February 27th, 1935. Published May 28th, 1935.

Investigations on the reduction of a number of solid inorganic substances by hydrogen under the silent electric discharge were carried out;

* Heterogeneous chemical reactions in the silent electric discharge. XII; *Kolloid-Z.*, **69** (1934), 179.

there follows an account of the results obtained since the publication of the previous papers.[1] The apparatus and the method of investigation are essentially the same as those mentioned in the previous papers.[1]

(1) **Selenious acid.** The quantity of selenious acid, H_2SeO_3, employed = 2 g. Time of silent electric discharge = 2 hours. The white powder became yellowish red soon after the electric current was passed, and the wall of the discharge tube was gradually covered with a thin yellow film of metallic selenium.

The reaction product was dissolved in water; red metallic selenium remained. The formation of a thin metallic film on the wall of the discharge tube suggests that hydrogen selenide is produced first, and the reactions in the discharge tube seem to be expressed by the following equations:

$$H_2SeO_3 + 3H_2 = SeH_2 + 3H_2O,$$
$$SeH_2 = Se + H_2.$$

(2) **Selenic acid.** Selenic acid, H_2SeO_4, employed = 2 g. Time of silent electric discharge = 2 hours. As selenic acid is an extremely hygroscopic compound, it had absorbed a small quantity of water, which was not determined. The white powder became red, showing the liberation of metallic selenium. The reduction products were shaken with water, and filtered. Red powder of metallic selenium remained. The presence of selenious acid in the filtrate was proved in the normal manner.[2]

The reaction products are selenious acid and metallic selenium, and the reactions in the discharge tube are expressed by the following equations:

$$H_2SeO_4(\text{solid}) + H_2 = H_2SeO_3 + H_2O,$$
$$H_2SeO_3 + 2H_2 = Se + 3H_2O.$$

(3) **Sodium selenate.** Sodium selenate, $Na_2SeO_4 \cdot 10H_2O$, employed = 3 g. Time of silent electric discharge = 3 hours. The powder became red, showing the liberation of metallic selenium. Water was added to the discharge tube, well shaken and filtered. Red metallic selenium remained. The presence of selenite in the filtrate was proved quite the same way as in the case of selenic acid.

---

(1) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 724, 788, 914, 933; **54** (1933), 85, 202, 705, 1223; **55** (1934), 320.

(2) Treadwell-Hall, "Analytical Chemistry", 8th Edition, Vol. I, p. 541.

The principal reaction products are selenite and metallic selenium, and the reactions in the discharge tube are expressed by the following equations:

$$Na_2SeO_4(solid) + H_2 = Na_2SeO_3 + H_2O,$$
$$Na_2SeO_3 + 2H_2 = Se + 2NaOH + H_2O.$$

(4) **Tellurous acid.** Tellurous acid, H_2TeO_3, employed = 2 g. Time of silent electric discharge = 2 hours. Not only the white powder became black, but the wall of the discharge tube was also covered with a thin film of metallic tellurium, forming a beautiful mirror.

The formation of tellurium mirror suggests that hydrogen telluride is first produced, and the reactions in the discharge tube are expressed by

$$H_2TeO_3(solid) + 3H_2 = TeH_2 + 3H_2O,$$
$$TeH_2 = Te + H_2.$$

It is an interesting fact that when selenious or tellurous acid is reduced under the silent electric discharge, metallic hydride is first produced, quite in the same way as in the case of the reduction of arsenic[3] or antimony compounds.[4]

(5) **Sodium tellurite.** Sodium tellurite, Na_2TeO_3, employed = 2 g. Time of silent electric discharge = 4 hours. White powder became black soon after the electric current was passed, showing the liberation of metallic tellurium. In this case no appreciable amount of metallic tellurium was deposited on the wall of the discharge tube. The reaction in the discharge tube is expressed by

$$Na_2TeO_3(solid) + 2H_2 = Te + 2NaOH + H_2O.$$

(6) **Telluric acid.** Telluric acid, $H_2TeO_4 2H_2O$, employed = 3 g. Time of silent electric discharge = 4 hours. White powder became black soon after the electric current was passed, and the wall of the discharge tube was gradually covered with a thin film of metallic tellurium.

Alkaline solution was added to the discharge tube, well shaken, and filtered. Metallic tellurium remained. The filtrate contained tellurite.[5] The principal reaction products are tellurous acid and metallic tellurium, and the reactions in the discharge tube seem to be expressed by

---

(3) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 734, 735.
(4) *Ibid.*, **53** (1932), 789, 790, 791.
(5) Treadwell-Hall, "Analytical Chemistry", 8th Edition, Vol. I., p. 545.

$$H_2TeO_4(\text{solid}) + H_2 = H_2TeO_3 + H_2O,$$
$$H_2TeO_3 + 3H_2 = TeH_2 + 3H_2O,$$
$$TeH_2 = Te + H_2.$$

(7) **Potassium thiosulphate.** Exp. 1. The production of potassium sulphate, hydrogen sulphide, and sulphur was proved quite in the same way as in the case of sodium thiosulphate.[6]

Exp. 2. The quantity of hydrogen sulphide produced was determined. The quantity of potassium thiosulphate employed = 7.0 g. Time of silent electric discharge = 7 hours. Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 3.82 c.c.

It seems that the principal reactions in the discharge tube are expressed by the following equations:

$$K_2S_2O_3 + H_2 = K_2SO_3 + H_2S,$$
$$4K_2S_2O_3 = 3K_2SO_4 + K_2S_5,$$
$$K_2S_5 = K_2S + 4S,$$
$$K_2S + 2H_2O = 2KOH + H_2S,$$
$$S + H_2 = H_2S.$$[7]

(8) **Silver carbonate.** Silver carbonate, Ag_2CO_3, employed = 2 g. Time of silent electric discharge=4 hours. On leaving the discharge tube the gas was passed through an absorption bottle, containing barium hydroxide solution.

Soon after the electric current was passed, the powder in the discharge tube became black, and in the absorption bottle white precipitate was produced, showing the production of metallic silver and carbon dioxide. The reaction products in the discharge tube were shaken with hot dilute sulphuric acid to dissolve silver carbonate remained and silver oxide produced. A small quantity of white powder remained. On rubbing the powder with a glass rod, it manifested metallic lustre, showing that it is metallic silver.

The principal reactions in the discharge tube are expressed by

$$Ag_2CO_3(\text{solid}) = Ag_2O + CO_2,$$
$$Ag_2O + H_2 = 2Ag + H_2O.$$[8]

---

(6) S. Miyamoto, *J. Chem. Soc. Japan*, **55** (1934), 1145.
(7) *Ibid.*, **53**
(8) *Ibid.*, **53** (1932), 796.

According to Losanitsch,[9] the following reaction is also possible in the present case.

$$CO_2 + H_2 = HCOOH.$$

(9) **Lithium chlorate.** Exp. 1. The formation of lithium chloride was proved quite in the same way as in the case of potassium chlorate.[10]

Exp. 2. The quantity of lithium chloride produced was determined by Volhard's method.[11] Lithium chlorate, $LiClO_3 \cdot \frac{1}{2} H_2O$, employed = 7.0 g. Time of silent electric discharge = 6 hours. Volume of silver nitrate solution of 0.01000 normal, equivalent to the quantity of lithium chloride produced = 26.10 c.c.

The reaction in the discharge tube is expressed by

$$LiClO_3(solid) + 3H_2 = LiCl + 3H_2O.$$

(10) **Sodium bromate.** Exp. 1. Sodium bromate, $NaBrO_3$, employed =4 g. Time of silent electric discharge = 6 hours. No appreciable change was observed in the appearance of the powder.

The reaction product was dissolved in water and the solution was acidified with dilute sulphuric acid. The solution became yellow and it decolourizes methylorange, showing the liberation of free bromine:

$$HBrO_3 + 5HBr = 3Br_2 + 3H_2O.$$

It proves the formation of potassium bromide in the the discharge tube.

Exp. 2. The quantity of sodium bromide produced was calculated by the determination of the quantity of sodium bromate remained. Sodium bromate employed = 6.1851 g. Time of silent electric discharge = 5 hours. Volume of arsenious acid solution of 0.1000 normal, equivalent to the quantity of sodium bromide produced = 58.5 c.c.

The reaction in the discharge tube is expressed by

$$NaBrO_3(solid) + 3H_2 = NaBr + 3H_2O.$$

Summary.

The chemical reactions under the silent electric discharge were studied when hydrogen reacts with the following inorganic solid substances.

---

(9) *Ber.*, **30** (1897), 135.
(10) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 731.
(11) Treadwell-Hall, "Analytical Chemistry", 7th Edition, Vol. II, p. 603.

	Reacting substance	Reaction products
(1)	Selenious acid	Selenium
(2)	Selenic acid	Selenium and selenious acid
(3)	Sodium selenate	Selenium and sodium selenite
(4)	Tellurous acid	Tellurium
(5)	Sodium tellurite	Tellurium and sodium hydroxide
(6)	Telluric acid	Tellurium and tellurous acid
(7)	Potassium thiosulphate	Potassium sulphite, hydrogen sulphide, and sulphur
(8)	Silver carbonate	Silver and carbon dioxide
(9)	Lithium chlorate	Lithium chloride
(10)	Sodium bromate	Sodium bromide

The author acknowledges with thanks the receipt of a grant from the Japanese Imperial Academy.

Laboratory of Physical Chemistry,
Hiroshima University.