HETEROGENEOUS CHEMICAL REACTIONS IN THE SILENT ELECTRIC DISCHARGE. IX.

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Investigations of the reduction of a number of inorganic solid substances by hydrogen in the silent electric discharge have been carried out over a considerable period: there follows an account of the results obtained since the publication of the previous papers.[1] The apparatus and method of procedure are essentially the same as previously mentioned.[1]

Experimental.

(1) **Potassium Sulphite.** Exp. 1. A qualitative experiment was first carried out, 8.00 gr. of anhydrous potassium sulphite being employed. The result was exactly the same as in the case of sodium sulphite.[2] The evolution of hydrogen sulphide was proved.

Exp. 2. The quantity of hydrogen sulphide produced was determined in the normal manner.

Potassium sulphite employed = 8.00 gr.
Time of silent electric discharge = 5 hours.
Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 3.55 c.c.

From these experimental facts it is concluded that the principal reactions in the discharge tube are expressed by the following equations:

$$K_2SO_3(s)+3H_2 = K_2S(s)+3H_2O,$$
$$K_2S(s)+2H_2O(l) = 2KOH+H_2S,$$
$$K_2S(s)+H_2 = 2K(s)+H_2S,$$
$$2K+2H_2O = 2KOH+H_2.$$

(2) **Cadmium Bromide.** Exp. 1. Seven grams of the powdered crystals of cadmium bromide, $CdBr_24H_2O$, were employed. On leaving

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

(2) Miyamoto, ibid., **54** (1933), 1231.

discharge tube, the gas was passed through a small absorption bottle, containing about 5 c.c. of distilled water. The absorption bottle employed is shown by Fig. 1. The white powder in the discharge tube gradually became black and small drops of water were found condensed on the wall of the discharge tube. After the lapse of 6 hours the electric current was stopped. The water drops formed on the wall of the discharge tube were proved to be acidic. The solid reaction products were shaken with water and filtered. A small quantity of greyish black powder remained. The filtrate was acidic, which was undoubtedly due to the presence of hydrogen bromide. On rubbing with a glass rod, the greyish black powder showed metallic lustre, and it dissolved in hydrochloric acid with the evolution of fine gas bubbles. The solution produced was proved to contain cadmium chloride. It is therefore certain that the insoluble greyish black powder is metallic cadmium.

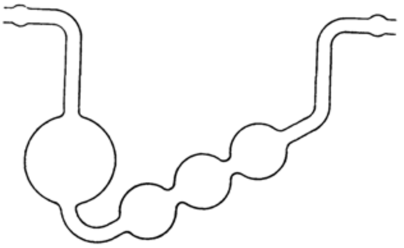

Fig. 1.

The water in the absorption bottle was weakly acidic, and on adding silver nitrate solution, a small quantity of silver bromide precipitated.

From these experimental results it is concluded that the principal reaction in the discharge tube is

$$CdBr_2(s) + H_2 = Cd + 2HBr.$$

(3) **Potassium Perchlorate.** Exp. 1. The quantity or potassium perchlorate, $KClO_4$, employed = 8.00 gr. Time of silent electric discharge = 5 hours. No appreciable change was observed in the appearance of the powder in the discharge tube. The solid reaction product was shaken with water and filtered. On adding silver nitrate solution to the filtrate, white precipitate was produced, proving the presence of chloride.

Exp. 2. The quantity of chloride produced was determined by Volhard's method.[3]

Potassium perchlorate employed = 7.00 gr.
Time of silent electric discharge = 5 hours.
Volume of silver nitrate solution of 0.01000 normal, equivalent to the quantity of potassium chloride produced = 20.10 c.c.

(3) Treadwell, "Kurzes Lehrbuch der analytischen Chemie," 10th ed., Vol. II, p. 614.

From these facts it is concluded that the principal reaction in the discharge tube is expressed by

$$KClO_4(s)+4H_2 = KCl(s)+4H_2O.$$

(4) **Mercuric Cyanide.** Exp. 1. The quantity of mercuric cyanide, $Hg(CN)_2$, employed $= 7.00$ gr. Time of silent electric discharge $= 7$ hours. On leaving the discharge tube, the gas was passed through a gas absorption bottle, containing about 5 c.c. of potassium hydroxide solution. The powder in the discharge tube became slightly grey. The solid reaction product was shaken with water. Fine drops of metallic mercury were found on the bottom of the container.

The alkaline solution in the absorption bottle was placed in a test tube, heated with a few drops of ferrous sulphate solution, and acidified. The solution coloured blue, and, on standing, a small quantity of Prussian blue precipitated, proving the presence of cyanide.[4]

It was thus proved that the principal reaction products are metallic mercury and hydrogen cyanide.

Exp. 2. Two absorption bottles, containing potassium hydroxide solutions were connected with the discharge tube, and the quantity of hydrogen cyanide absorbed was determined by Liebig's method.[5]

Mercuric cyanide employed $= 7.00$ gr.
Time of silent electric discharge $= 7$ hours.
The quantity of hydrogen cyanide produced $= 0.00452$ gr.

From these experimental results it is concluded that the principal reaction in the discharge tube is expressed by

$$Hg(CN)_2(s)+H_2 = Hg(l)+2HCN(g).$$

(5) **Mercuric Thiocyanate.** Exp. 1. The quantity of mercuric thiocyanate, $Hg(SCN)_2$, employed $= 7.00$ gr. Time of silent electric discharge $= 5$ hours. On leaving the discharge tube the gas was passed first through distilled water and then through potassium hydroxide solution. The white powder in the discharge tube gradually became yellowish red and after the lapse of a few hours the powder became black. A part of the wall of the discharge tube was covered with a thin film of metallic mercury, forming a mirror. The reaction product in the discharge tube was shaken with water and filtered. The filtrate was

(4) Treadwell, "Kurzes Lehrbuch der analytischen Chemie," 13th ed., Vol. I, p. 306.

(5) Ibid., 10th ed., Vol. II, p. 617.

acidic. The insoluble substance was well washed with water, placed in a test tube, and heated with hydrochloric acid of about 8 normal. The evolution of hydrogen sulphide was proved.

The liquid in the first absorption bottle was examined. It had the following properties.

(1) It was acidic. (2) The solution was placed in a test tube, and a small quantity of ferric chloric solution was added. The solution became red, proving the presence of thiocyanic acid. (3) The presence of hydrocyanide was proved exactly as in the case of mercuric cyanide.

The alkaline solution in the second absorption bottle had the following properties.

(1) The presence of cyanide was proved. (2) The presence of sulphide was proved.

From these facts it is certain that the principal reaction products are metallic mercury, mercuric sulphide, hydrogen cyanide, hydrogen sulphide, and thiocyanic acid.

Exp. 2. The quantity of hydrogen sulphide evolved was determined.

Mercuric thiocyanate employed = 7.00 gr.
Time of silent electric discharge = 5 hours.
Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 7.60 c.c.

From these facts it seems that the principal reactions in the discharge tube are expressed by the following equations:

$$Hg(SCN)_2+2H_2 = HgS+H_2S+2HCN,$$
$$HgS+H_2 = Hg+H_2S,^{(6)}$$
$$Hg(SCN)_2+H_2 = Hg+2HSCN.$$

(6) **Silver Cyanide.** Exp. 1. The quantity of silver cyanide, AgCN, employed = 7.00 gr. Time of silent electric discharge = 5 hours. On leaving the discharge tube, the gas was passed through an absorption bottle, containing about 5 c.c. of potassium hydroxide solution. The white powder in the discharge tube gradually became black. A part of the black powder in the discharge tube had metallic lustre, showing the formation of metallic silver. It was proved exactly as in the case of mercuric cyanide that hydrogen cyanide was one of the reaction products.

Exp. 2. The quantity of hydrogen cyanide produced was determined exactly as in the case of mercuric cyanide.

(6) Miyamoto, *J. Chem. Soc. Japan,* **53** (1932), 794.

Silver cyanide employed = 7.00 gr.
Time of silent electric discharge = 5 hours.
The quantity of hydrogen cyanide produced = 0.00138 gr.

It is concluded that the reaction in the discharge tube is expressed by

$$2AgCN(s) + H_2 = 2Ag + 2HCN.$$

(7) **Sodium Thiocyanate.** Exp. 1. The quantity of sodium thiocyanate, NaSCN, employed = 7.00 gr. Time of silent electric discharge = 7 hours. As sodium thiocyanate is a very hygroscopic substance, the quantity of water included in the reacting substance was considerable. The powder in the discharge tube gradually coloured light yellow and a part became moist. The formation of hydrogen cyanide and hydrogen sulphide was proved exactly as in the case of mercuric thiocyanate.

The solid reaction product was dissolved in water. Light yellow solution was produced. The solution was alkaline. The solution was placed in a test tube, and a small quantity of sodium hydroxide solution and a few drops of sodium nitroprusside solution were added. The solution coloured reddish violet, proving the presence of sulphide.[7]

It was thus proved that the principal reaction products are sodium sulphide, hydrogen cyanide, and hydrogen sulphide.

Exp. 2. The quantity of hydrogen sulphide produced was determined.

Sodium thiocyanate employed = 7.00 gr.
Time of silent electric discharge = 6 hours.
Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 1.10 c.c.

From these experimental facts it seems that the principal reactions in the discharge tube are expressed by the following equations:

$$2NaSCN(s) + H_2 = Na_2S_2(s) + 2HCN,$$
$$Na_2S_2 + H_2 = Na_2S + H_2S,$$
$$Na_2S + 2H_2O = 2NaOH + H_2S,$$
$$Na_2S + H_2 = 2Na + H_2S,$$
$$2Na + 2H_2O = 2NaOH + H_2.$$

(8) **Lead Thiocyanate.** Exp. 1. The quantity of lead thiocyanate, $Pb(SCN)_2$, employed = 7.00 gr. Time of silent electric discharge = 6

(7) Treadwell, "Kurzes Lehrbuch der analytischen Chemie," 13th ed., Vol. I, p. 391.

hours. The evolution of hydrogen cyanide and hydrogen sulphide was proved exactly as in the case of mercuric thiocyanate. The powder in the discharge tube gradually became black. The solid reaction product was shaken with water, filtered, and washed. The filtrate was acidic. The insoluble substance was placed in a test tube, and heated with hydrochloric acid. The evolution of hydrogen sulphide was proved.

It was thus proved that the principal reaction products are lead sulphide, hydrogen cyanide, and hydrogen sulphide.

Exp. 2. The quantity of hydrogen sulphide evolved was determined.

Lead thiocyanate employed = 7.00 gr.
Time of silent electric discharge = 6 hours.
Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 1.20 c.c.

From these experimental facts it is concluded that the principal reaction in the discharge tube is expressed by

$$Pb(SCN)_2(s) + 2H_2 = PbS + H_2S + 2HCN.$$

As it was proved that lead sulphide is reduced further,[8] the following reaction must have occurred in the discharge tube:

$$PbS + H_2 = Pb + H_2S.$$

(9) **Potassium Cyanide.** The quantity of potassium cyanide, KCN, employed = 7.00 gr. Time of silent electric discharge = 7 hours. The alkaline solution, through which the gas had been passed on leaving the discharge tube, was analyzed. No cyanide was detected. The powder in the discharge tube was analyzed. No appreciable change was observed.

It was thus proved that potassium cyanide was hardly reduced under the conditions of this experiment.

Summary.

The chemical reactions in the silent electric discharge were studied when hydrogen reacted on the following inorganic solid substances.

(1) Potassium sulphite. Reaction products:—hydrogen sulphide and potassium hydroxide.

(2) Cadmium bromide. Reaction products:—metallic cadmium and hydrogen bromide.

(8) Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 795.

(3) Potassium perchlorate. Reaction products:—potassium chloride and water.

(4) Mercuric cyanide. Reaction products:—metallic mercury and hydrogen cyanide.

(5) Mercuric thiocyanate. Reaction products:—mercuric sulphide, metallic mercury, hydrogen cyanide, hydrogen sulphide, and thiocyanic acid.

(6) Silver cyanide. Reaction products:—metallic silver and hydrogen cyanide.

(7) Sodium thiocyanate. Reaction products:—sodium sulphide, hydrogen sulphide, and hydrogen cyanide.

(8) Lead thiocyanate. Reaction products:—lead sulphide, hydrogen sulphide, and hydrogen cyanide.

(9) Potassium cyanide. It was proved that potassium cyanide was hardly reduced under the conditions of this experiment.

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