HETEROGENEOUS CHEMICAL REACTIONS IN THE SILENT ELECTRIC DISCHARGE. XI.

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The results of investigations obtained since the publication of the previous papers[1] are described in this paper. The apparatus and the procedure of the experiments are essentially the same as mentioned previously.

(1) **Potassium Thiocyanate.** Exp. 1. The quantity of potassium thiocyanate KSCN employed = 7.0 g. Time of silent electric discharge = 7 hours. On leaving the discharge tube the gas was passed first through distilled water and then through an alkaline solution.

The solid reaction product was dissolved in water, when a light yellow solution with the following properties was obtained. (1) It was alkaline. (2) The presence of sulphide was proved by means of sodium nitroprusside.[2] By analyzing the distilled water, through which the gaseous reaction product had been passed, the formation of hydrogen cyanide and hydrogen sulphide during the discharge was proved exactly as in the case of mercuric thiocyanate.[3]

Exp. 2. The quantity of hydrogen sulphide produced was determined. The quantity of potassium thiocyanate employed = 7.00 g. Time of silent electric discharge = 5 hours. Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 4.50 c.c.

From these experimental results it seems that the principal reactions in the discharge tube are expressed by the following equations, the reaction products being potassium hydroxide, potassium sulphide, hydrogen sulphide, and hydrogen cyanide.

$$2KSCN+H_2 = K_2S_2+2HCN,$$
$$K_2S_2+H_2 = K_2S+H_2S,$$
$$K_2S+2H_2O = 2KOH+H_2S.$$

(2) **Potassium Silver Cyanide.** Exp. 1. The quantity of potassium silver cyanide $KAg(CN)_2$ employed = 7.0 g. Time of silent electric

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

(2) Treadwell, "Kurzes Lehrbuch der analytischen Chemie," 13th Ed., Vol. 1, p. 391.

(3) S. Miyamoto, this Bulletin, **9** (1934), 177.

discharge = 5 hours. Exactly as in the case of silver cyanide,[4] the formation of metallic silver and hydrogen cyanide was proved.

Exp. 2. The quantity of hydrogen cyanide produced was determined exactly as in the case of silver cyanide.[4] Potassium silver cyanide employed = 7.00 g. Time of silent electric discharge = 5 hours. The quantity of hydrogen cyanide produced = 0.0002 g.

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

$$2KAg(CN)_2+H_2 = 2KCN+2Ag+2HCN\,.$$

(3) **Calcium Thiocyanate.** Exp. 1. The quantity of calcium thiocyanate $Ca(SCN)_2 \cdot 3H_2O$ employed = 7.00 g. Time of silent electric discharge = 6 hours. A gas absorption bottle containing a potassium hydroxide solution was connected with the discharge tube.

The reaction product in the discharge tube was shaken with water; a yellow solution was obtained, which had the following properties.. (1) It was acidic. (2) The absence of sulphide was proved by means of sodium nitroprusside. The evolution of hydrogen cyanide and hydrogen sulphide was proved by analyzing the alkaline solution, through which the gaseous reaction product had been passed on leaving the discharge tube.

Exp. 2. The quantity of hydrogen sulphide produced was determined. Calcium thiocyanate employed = 7.00 g. Time of silent electric discharge = 6 hours. Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 1.50 c.c.

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

$$Ca(SCN)_2+2H_2 = CaS+H_2S+2HCN\,,$$
$$CaS+2H_2O = Ca(OH)_2+H_2S\,.$$

(4) **Ammonium Thiocyanate.** Exp. 1. The quantity of ammonium thiocyanate NH_4SCN employed = 7.00 g. Time of silent electric discharge = 7 hours. On leaving the discharge tube the gas was passed first through an alkaline solution and then through dilute sulphuric acid.

On passing the electric current the powder in the discharge tube became slightly yellow. It was shaken with water and filtered. A small quantity of yellow powder remained, which is supposed to be sulphur. The filtrate was neutral and contained no appreciable quantity of sulphide. By analyzing the alkaline and sulphuric acid solutions through which the gas had been

(4) S. Miyamoto, this Bulletin, **9** (1934), 178.

passed, it was proved that hydrogen sulphide, hydrogen cyanide, and ammonia gas were reaction products.

Exp. 2. The quantity of hydrogen sulphide produced was determined. The quantity of ammonium thiocyanate employed = 7.00 g. Time of silent electric discharge = 6 hours. Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 2.00 c.c.

Exp. 3. The quantity of ammonia gas, absorbed by sulphuric acid, was determined in the usual manner.[5] The quantity of ammonium thiocyanate employed = 7.00 g. Time of silent electric discharge = 7 hours. Volume of sulphuric acid solution of 0.01000 normal, equivalent to the quantity of ammonia produced = 3.02 c.c.

From these experimental facts it seems that the principal reaction products are hydrogen sulphide, hydrogen cyanide, and ammonia gas, and that the reactions in the discharge tube are expressed by the following equations:

$$2NH_4SCN + H_2 = (NH_4)_2S_2 + 2HCN,$$
$$(NH_4)_2S_2 + H_2 = (NH_4)_2S + H_2S,$$
$$(NH_4)_2S = 2NH_3 + H_2S.$$

(5) **Sodium Thiosulphate.** Exp. 1. The quantity of sodium thiosulphate $Na_2S_2O_3 \cdot 5H_2O$ employed = 7.00 g. Time of silent electric discharge = 8 hours. A gas absorption bottle, containing a potassium hydroxide solution, was connected with the discharge tube. On passing the electric current no appreciable change was observed in the appearance of the powder in the discharge tube. Water was added to the solid reaction product, well shaken, and filtered. A small quantity of white powder, undoubtedly sulphur, remained. The filtrate had the following properties. (1) It was alkaline. (2) The absence of sulphide was proved by means of sodium nitroprusside. (3) The presence of sulphite was proved by the method of E. Votocek.[6] By analyzing the alkaline solution in the absorption bottle, it was proved that hydrogen sulphide was a reaction product.

It was thus proved that the principal reaction products are sulphite, sulphur, and hydrogen sulphide.

Exp. 2. The quantity of hydrogen sulphide produced was determined. The quantity of sodium thiosulphate employed = 7.00 g. Time of silent electric discharge = 6 hours. Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 3.82 c.c.

(5) Treadwell, "Kurzes Lehrbuch der analytischen Chemie.," 10th Ed., Vol. 2, p. 483.
(6) Treadwell-Hall, "Analytical Chemistry," 8th. Ed., Vol. 1, p. 416.

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

$$Na_2S_2O_3+H_2 = Na_2SO_3+H_2S,$$
$$4Na_2S_2O_3 = 3Na_2SO_4+Na_2S_5,$$
$$Na_2S_5 = Na_2S+4S,$$
$$S+H_2 = H_2S^{(7)},$$
$$Na_2SO_4+4H_2 = Na_2S+4H_2O^{(8)},$$
$$Na_2SO_3+3H_2 = Na_2S+3H_2O^{(9)}$$
$$Na_2S+2H_2O = 2NaOH+H_2S.$$

(6) **Magnesium Thiosulphate.** Exp. 1. The quantity of magnesium thiosulphate $MgS_2O_3 \cdot 6H_2O$ employed = 7.00 g. Time of silent electric discharge = 7 hours. Exactly as in the case of sodium thiosulphate it was proved that the principal reaction products are sulphite, sulphur, and hydrogen sulphide.

Exp. 2. The quantity of hydrogen sulphide produced was determined. The quantity of magnesium thiosulphate employed = 7.00 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 = 9.04 c.c.

From the results of the experiments it seems that the reactions in the discharge tube are expressed by the following equations:

$$MgS_2O_3+H_2 = MgSO_3+H_2S,$$
$$4MgS_2O_3 = 3MgSO_4+MgS+4S,$$
$$S+H_2 = H_2S,$$
$$MgSO_4+4H_2 = MgS+4H_2O^{(10)},$$
$$MgSO_3+3H_2 = MgS+3H_2O,$$
$$MgS+2H_2O = Mg(OH)_2+H_2S.$$

(7) **Barium Thiosulphate.** Exp. 1. The quantity of barium thiosulphate BaS_2O_3 employed = 7.00 g. Time of silent electric discharge = 6 hours. No appreciable change was observed in the appearance of the powder in the discharge tube. The solid reaction product was shaken with an excess of a sodium carbonate solution and filtered. The presence of sulphide and sulphite in the filtrate was proved exactly as in the case of sodium thiosulphate. It was proved that hydrogen sulphide was contained in the gas which left the discharge tube.

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(7) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 726.
(8) Ibid., **54** (1933), 86.
(9) Ibid., **54** (1933), 1231.
(10) Ibid., **53** (1932), 940.

Exp. 2. The quantity of hydrogen sulphide produced was determined. The quantity of barium thiosulphate employed = 7.00 g. Time of silent electric discharge = 6 hours. Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 1.50 c.c.

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

$$BaS_2O_3+H_2 = BaSO_3+H_2S,$$
$$4BaS_2O_3 = 3BaSO_4+BaS+4S,$$
$$BaSO_4+4H_2 = BaS+4H_2O^{(11)},$$
$$BaSO_3+3H_2 = BaS+3H_2O,$$
$$BaS+H_2 = Ba+H_2S^{(12)},$$
$$S+H_2 = H_2S.$$

(8) **Barium Chlorate.** Exp. 1. The quantity of barium chlorate $Ba(ClO_3)_2$ employed = 7.0 g. Time of silent electric discharge = 6 hours. The formation of chloride was proved in the usual manner.

Exp. 2. The quantity of chloride produced was determined exactly as in the case of potassium chlorate.[13] The quantity of barium chlorate employed = 7.00 g. Time of silent electric discharge = 6 hours. The volume of silver nitrate solution of 0.01000 normal, equivalent to the quantity of barium chloride produced = 15.10 c.c.

It was proved that the principal reaction in the discharge tube is expressed by

$$Ba(ClO_3)_2+6H_2 = BaCl_2+6H_2O.$$

Summary.

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

(1) Potassium thiocyanate. Reaction products: hydrogen cyanide, hydrogen sulphide, and potassium sulphide.

(2) Potassium silver cyanide. Reaction products: silver and hydrogen cyanide.

(3) Calcium thiocyanate. Reaction products: hydrogen cyanide, hydrogen sulphide, and calcium hydroxide.

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(11) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 935.
(12) Ibid., **53** (1932), 936.
(13) Ibid., **53** (1932), 731.

(4) Ammonium thiocyanate. Reaction products: hydrogen cyanide, ammonia, and hydrogen sulphide.

(5) Sodium thiosulphate. Reaction products: sodium sulphite, hydrogen sulphide, and sulphur.

(6) Magnesium thiosulphate. Reaction products: Magnesium sulphite, hydrogen sulphide, and sulphur.

(7) Barium thiosulphate. Reaction products: Barium sulphite, barium sulphide, hydrogen sulphide, and sulphur.

(8) Barium chlorate. Reaction products: barium chloride and water.

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