Chemical Reactions in the Silent Electric Discharge. XVI. Reactions between Hydrogen and Solid Inorganic Compounds.

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Studies on the reduction of a number of solid inorganic substances by hydrogen under the silent electric discharge were carried out; there follows an account of the results obtained since the publication of the previous papers.⁽¹⁾

(1) Potassium chromate. It was proved that chromic oxide is a principal reaction product. Potassium chromate employed $= 5 \,\mathrm{g}$. Time of silent electric discharge $= 12 \,\mathrm{hours}$. The quantity of chromic oxide produced $= 0.1083 \,\mathrm{g}$.

The principal reaction in the discharge tube is expressed by $2K_2CrO_4 + 3H_2 = 4KOH + Cr_2O_3 + H_2O$.

(2) Potassium bichromate. Potassium bichromate is reduced to chromic oxide also. Potassium bichromate employed = $5 \, \text{g}$. Time of silent electric discharge = $12 \, \text{hours}$. The quantity of chromic oxide produced = $0.0463 \, \text{g}$.

The principal reaction in the discharge tube is expressed by $K_2Cr_2O_7 + 3H_2 = 2KOH + Cr_2O_3 + 2H_2O$.

(3) Ammonium chromate. A gas absorption bottle, containing dilute sulphuric acid solution, was connected to the discharge tube, and the quantity of ammonia absorbed was determined in the normal manner. Ammonium chromate employed = $5 \, \mathrm{g}$. Time of silent electric discharge = $8 \, \mathrm{hours}$. Volume of the sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonia absorbed = $6.68 \, \mathrm{c.c.}$ The quantity of chromic oxide produced = $0.0357 \, \mathrm{g.}$

The principal reaction in the reaction tube is expressed by

$$2(NH_4)_2CrO_4 + 3H_2 = 4NH_3 + Cr_2O_3 + 5H_2O$$
.

(4) Ammonium bichromate. Ammonium bichromate employed = $5 \,\mathrm{g}$. Time of silent electric discharge = $12 \,\mathrm{hours}$. Volume of the sulphuric acid solution of $0.1000 \,\mathrm{normal}$, equivalent to the quantity of ammonia absorbed = $3.21 \,\mathrm{c.c.}$ The quantity of chromic oxide produced = $0.0210 \,\mathrm{g.}$

⁽¹⁾ S. Miyamoto, J. Chem. Soc. Japan, **53** (1932), 724, 788, 914, 933; **54** (1933), 85, 202, 705, 1223; **55** (1934), 320, 1143; **56** (1935), 521; this Bulletin, **9** (1934), 139, 165, 175, 505; **10** (1935), 199.

The principal reaction is expressed by

$$(NH_4)_2Cr_2O_7 + 3H_2 = 2NH_3 + Cr_2O_3 + 4H_2O$$
.

(5) Calcium chlorate. Calcium chlorate is reduced to chloride in the discharge tube. The quantity of chloride produced was determined in the normal manner. Calcium chlorate employed = 7.0 g. Time of silent electric discharge = 6 hours. Volume of the silver nitrate solution of 0.01000 normal, equivalent to the quantity of calcium chloride produced = 37.40 c.c.

The reaction in the discharge tube is expressed by

$$Ca(ClO_3)_2 + 6H_2 = CaCl_2 + 6H_2O$$
.

(6) Sodium chlorate. Sodium chlorate employed = 7 g. Time of silent electric discharge = 6 hours. Volume of the silver nitrate solution of 0.01000 normal, equivalent to the quantity of sodium chloride produced = 28.50 c.c.

The reaction in the discharge tube is expressed by

$$NaClO_3 + 3H_2 = NaCl + 3H_2O$$
.

(7) Barium sulphite. It was proved that barium sulphide and hydrogen sulphide are the principal reaction products. The reactions in the discharge tube will be expressed by

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\begin{split} BaSO_3 + 3H_2 &= BaS + 3H_2O \text{ ,} \\ BaS + 2H_2O &= Ba(OH)_2 + H_2S \text{ ,} \\ BaS + H_2 &= Ba + H_2S \text{ .} \end{split}
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- (8) Thorium nitrate. Exp. 1. The formation of thorium hydroxide, ammonium salt and nitrite was proved.
- Exp. 2. The quantity of ammonium salt produced was determined in the normal manner. Thorium nitrate, $Th(NO_3)_4\cdot 12H_2O$, employed = 5 g. Time of silent electric discharge = 6 hours. Volume of the sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 8.12 c.c.
- Exp. 3. The quantity of nitrite produced was determined. Thorium nitrate employed = $5 \, \text{g}$. Time of silent electric discharge = $6 \, \text{hours}$. Volume of the potassium permanganate solution of $0.0100 \, \text{normal}$, equivalent to the quantity of nitrite produced = $7.78 \, \text{c.c.}$

The reactions in the discharge tube will be expressed by

$$\begin{split} Th(NO_3)_4 + 16H_2 &= Th(OH)_4 + 4\,NH_3 + 8H_2O \text{ ,} \\ Th(NO_3)_4 + 4NH_3 + 4H_2O &= 4NH_4NO_3 + Th(OH)_4 \text{ ,} \\ NH_4NO_3 + H_2 &= NH_4NO_2 + H_2O \text{ .} \end{split}$$

(9) Ammonium persulphate. It was proved that sulphate and hydrogen sulphide are the principal reaction products. The reactions in the reaction tube will be expressed by

$$\begin{array}{l} (NH_4)_2S_2O_8+5H_2=(NH_4)_2SO_4+H_2S+4H_2O \ , \\ (NH_4)_2S_2O_8+H_2=(NH_4)_2SO_4+H_2SO_4 \ . \end{array}$$

(10) Potassium persulphate. The formation of sulphate and hydrogen sulphide was proved. The velocity of the reaction was very small. The reactions in the discharge tube will be expressed by

$$\begin{split} &K_2S_2O_8+5H_2=K_2SO_4+H_2S+4H_2O\text{ ,}\\ &K_2S_2O_8+H_2=K_2SO_4+H_2SO_4\text{ .} \end{split}$$

Summary.

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

Reacting substance	Reaction products
(1) Potassium chromate	Chromic oxide and potassium hydroxide
(2) Potassium bichromate	Chromic oxide and potassium hydroxide
(3) Ammonium chromate	Chromic oxide and ammonia gas
(4) Ammonium bichromate	Chromic oxide and ammonia gas
(5) Calcium chlorate	Calcium chloride
(6) Sodium chlorate	Sodium chloride
(7) Barium sulphite	Barium sulphide and hydrogen sulphide
(8) Thorium nitrate	Thorium hydroxide, nitrite and ammonium salt.
(9) Ammonium persulphate	Sulphate and hydrogen sulphide,
(10) Potassium persulphate	Sulphate and hydrogen sulphide.

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