HETEROGENEOUS CHEMICAL REACTIONS IN THE SILENT ELECTRIC DISCHARGE. VIII.

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Investigations of the reduction of inorganic solid substances by hydrogen in the silent electric discharge were carried out.(1)

The apparatus and method of procedure are essentially the same as previously mentioned.(1)

Experimental.

(1) **Cupric Nitrate.** Exp. 1. Powdered crystals of cupric nitrate, $Cu(NO_3)_2 3H_2O$, employed = 8.00 gr. Time of silent electric discharge = 5 hours. A gas absorption apparatus, which is exactly the same as that employed in the case of calcium nitrate,(2) was connected to the discharge tube. Nitrogen peroxide contained in the gaseous reaction products is absorbed by alkaline solution in absorption bottle (1), nitric oxide is then oxidized and absorbed by alkaline solution in absorption bottle (2), and ammonia is absorbed by dilute sulphuric acid in absorption bottle (3).

Water was produced during the reaction and small drops of condensed water were formed on the wall of the discharge tube. A part of the powder in the discharge tube became black and a part reddish brown. A small part of the wall of the discharge tube was covered with a thin film of metallic copper, forming a mirror.

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

(2) Ibid., **54** (1933), 89.

Water was added into the discharge tube, well shaken, filtered and washed. A small quantity of insoluble reddish brown powder remained. Most part of the insoluble matter dissolved in hydrochloric acid, producing cupric chloride solution. It is clear that the insoluble substance is principally copper oxide. The filtrate had the following properties.

(1) It was acidic. (2) The solution was placed in a test tube, made alkaline, and heated. The evolution of ammonia was proved. (3) The solution was placed in a test tube, made alkaline, and added to Fehling's solution. On heating, no reduction took place, which proved the absence of hydroxylamine. (4) Sodium hydroxide solution was added to the solution, and the precipitated copper hydroxide was filtered. Potassium iodide solution was added to the filtrate, and the solution was acidified with dilute sulphuric acid, and a few drops of starch solution was added. The solution coloured blue, proving the presence of nitrite.

The alkaline solution in absorption bottle (1) was placed in a test tube and the presence of nitrite was proved. It is therefore certain that nitrogen peroxide is one of gaseous reaction products.

By analyzing the alkaline solution in absorption bottle (2), it was similarly proved that a small quantity of nitric oxide had been produced during the reaction.

The sulphuric acid solution in absorption bottle (3) was placed in a test tube, made alkaline, and heated. The evolution of a small quantity of ammonia was proved.

From these experimental facts it is certain that the principal reaction products are ammonium salt, copper oxide, copper nitrite, nitrogen peroxide nitric oxide, and ammonia.

Exp. 2. The quantity of nitrite produced was determined. The solid reaction products were shaken with water, sodium hydroxide solution sufficient to precipitate the total amount of copper ion was added, and the solid was filtered and washed. The quantity of nitrite contained in the filtrate was determined in the normal manner.

Cupric nitrate employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

Volume of potassium permanganate solution of 0.01000 normal, equivalent to the quantity of nitrite produced = 1.52 c.c.

Exp. 3. The quantity of ammonium salt produced was determined in the normal manner.(3)

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(3) Treadwell, "Kurzes Lehrbuch der analytischen Chemie," 10th ed., Vol. II, p. 483.

Cupric nitrate employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 4.54 c.c.

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

$$Cu(NO_3)_2(s)+8H_2(g) = CuO(s)+2NH_3(g)+5H_2O(l),$$
$$Cu(NO_3)_2(s)+2NH_3(g)+2H_2O(g) = Cu(OH)_2(s)+2NH_4NO_3(s),$$
$$Cu(NO_3)_2xH_2O(l)+2H_2(g) = Cu(NO_2)_2yH_2O(l)+(x+2-y)H_2O(l),$$
$$Cu(NO_2)_2yH_2O(l)+2NH_3(g) = Cu(OH)_2(s)+2NH_4NO_2(y-2)H_2O(l),$$
$$NH_4NO_3(s)+H_2(g) = NH_4NO_2(s)+H_2O(l),^{(4)}$$
$$NH_4NO_2(s) = N_2(g)+2H_2O(l),$$
$$Cu(NO_3)_2(s)+2H_2 = CuO(s)+NO_2(g)+NO(g)+2H_2O(l),$$
$$CuO+H_2 = Cu(s)+H_2O(l).^{(5)}$$

(2) **Zirconium Nitrate.** Exp. 1. Zirconium nitrate, $Zr(NO_3)_45H_2O$, employed = 7.00 gr. Time of silent electric discharge = 5 hours. A gas absorption apparatus, similar to that employed in the previous case, was connected with the discharge tube. Soon after the electric current was passed, a brown gas, undoubtedly nitrogen peroxide, evolved. Water was produced during the reaction and a part of the powder became moist. Water was added to the discharge tube, well shaken, and filtered. Insoluble white powder is undoubtedly zirconium hydroxide. The filtrate had the following chemical properties.

(1) It was acidic. (2) The absence of hydroxylamine was proved. (3) The presence of nitrite was proved. (4) The presence of ammonium salt was proved.

By analyzing the solutions in absorption bottles (1), (2), and (3), it was proved that nitrogen peroxide and nitric oxide evolved during the reaction, but no ammonia.

From these experimental facts it is certain that the principal reaction products are ammonium salt, zirconium oxide, nitrite, nitrogegn peroxide, and nitric oxide.

Exp. 2. The quantity of nitrite produced in the solid reaction products, that of nitrogen peroxide, and that of nitric oxide, were determined.

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(4) Miyamoto, *J. Chem. Soc. Japan,* **54** (1933), 715.

(5) Ibid., **53** (1932), 792.

Zirconium nitrate employed = 7.00 gr.

Time of silent electric discharge = 5 hours.

Volume of potassium permanganate solution of 0.01000 normal equivalent to the quantity of nitrite produced in the discharge tube = 3.26 c.c.

Volume of $KMnO_4$-solution of 0.01000 normal, equivalent to the quantity of nitrite produced by the absorption of NO_2 = 153.8 c.c.

Volume of $KMnO_4$-solution of 0.01000 normal, equivalent to the quantity of nitrite produced by the absorption of the oxidation product of nitric oxide = 526.6 c.c.

Exp. 3. The quantity of ammonium salt produced was determined.

Zirconium nitrate employed = 7.00 gr.

Time of silent electric discharge = 5 hours.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 9.45 c.c.

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

$$Zr(NO_3)_4(s)+16H_2(g) = ZrO_2(s)+4NH_3(g)+10H_2O(l),$$

$$Zr(NO_3)_4(s)+4NH_3(g)+4H_22O(l) = Zr(OH)_4+4NH_4NO_3(s),$$

$$Zr(NO_3)_4(s)+4H_2(g) = ZrO_2(s)+2NO_2(g)+2NO(g)+4H_2O(l),$$

$$NO_2(g)+H_2(g) = NO(g)+H_2O(l),$$

$$NH_4NO_3(s)+H_2(g) = NH_4NO_2(s)+H_2O(l),$$

$$NH_4NO_2(s) = N_2(g)+2H_2O(l).$$

(3) **Thallous Nitrate.** Exp. 1. The quantity of thallous nitrate, $TlNO_3$, employed = 7.00 gr. Time of silent electric discharge = 5 hours. The white powder in the discharge tube became greyish black. Hot water was added to the discharge tube, well shaken, and filtered. A small quantity of insoluble greyish black powder remained. The powder did not dissolve in boiling water. It dissolved in nitric acid or sulphuric acid, forming thallium salt solution. It is therefore certain that the black powder insoluble in boiling water is metallic thallium. The solution, produced by dissolving the solid reaction products in hot water, had the following properties.

(1) It was alkaline, which is undoubtedly due to the presence of thallous hydroxide. (2) It was proved that nearly no ammonium salt was present in the solution. (3) The absence of hydroxylamine was proved. (4) The presence of nitrite was proved.

By analyzing the solutions in absorption bottles (1), (2), and (3), it was proved that nitrogen peroxide and ammonia were gaseous reaction products.

It was thus proved that the principal reaction products are nitrite, thallous hydroxide, metallic thallium, nitrogen peroxide, and ammonia.

Exp. 2. The quantity of nitrite produced was determined. The solid reaction product was dissolved in hot water, thallous ion precipitated by adding acidified sodium chloride solution, and the precipitate was filtered and washed. The quantity of nitrite contained in the filtrate was determined in the normal manner.

Thallous nitrate employed = 7.00 gr.
Time of silent electric discharge = 5 hours.
Volume of $KMnO_4$-solution of 0,01000 normal, equivalent to the quantity of nitrite produced = 31.50 c.c.

Exp. 3. The quantity of ammonia evolved was determined.

Thallous nitrate employed = 7.00 gr.
Time of silent electric discharge = 4 hours.
Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonia absorbed by sulphuric acid solution = 1.13 c.c.

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

$$TlNO_3(s) + H_2(g) = TlNO_2(s) + H_2O(l),$$
$$TlNO_3(s) + 4H_2(g) = TlOH(s) + NH_3(g) + 2H_2O(l),$$
$$TlNO_2(s) + 3H_2(g) = TlOH(s) + NH_3(g) + H_2O(l),$$
$$2TlOH(s) + H_2 = 2Tl(s) + 2H_2O(l).$$

(4) **Uranyl Nitrate.** Exp. 1. The quantity of uranyl nitrate, $UO_2(NO_3)_2 6H_2O$, employed = 7.00 gr. Time of silent electric discharge = 5 hours. A part of the yellow powder in the discharge tube became reddish brown. Distilled water was added into the discharge tube, well shaken, and filtered. Brown powder remained. It seems that the insoluble substance is principally uranium hydroxide. The filtrate had the following properties.

(1) It was acidic. (2) The solution contained ammonium salt. (3) The solution contained a minute quantity of nitrite. It seems that the nitrite produced is ammonium nitrite. (4) The absence of hydroxylamine was proved. (5) The solution was added to a dilute $KMnO_4$-solution and sulphuric acid added. The solution became colourless. As

it was proved that the quantity of nitrite produced is negligible, it is clear that the decolouration is due to the presence of uranous compound, which had been produced during the discharge.

By analyzing the solutions in the absorption bottles (1), (2), and (3), it was proved that neither ammonia nor nitric oxide had been produced during the discharge, but a minute quantity of nitrogen peroxide.

Exp. 2. The quantity of uranous salt produced was determined in the normal manner.(6)

Uranyl nitrate employed = 7.00 gr.

Time of silent electric discharge = 5 hours.

Volume of $KMnO_4$-solution of 0.01000 normal, equivalent to the quantity of uranous salt produced = 10.10 c.c.

As it was proved that nitrite produced is negligible, the value obtained was taken as the quantity of uranous salt.

Exp. 3. The quantity of ammonium salt was determined.

Uranyl nitrate employed = 7.00 gr.

Time of silent electric discharge = 5 hours.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 7.28 c.c.

From these experimental facts it seems that the principal reaction products are ammonium salt, uranous salt, uranium hydroxide, nitrite, and nitrogen peroxide, and that the reactions in the discharge tube are expressed by the following equations:

$$\begin{gathered}
UO_2(NO_3)_2(s)+8H_2 = UO_2(OH)_2(s)+2NH_3(g)+4H_2O(l),\\
2UO_2(NO_3)_2(s)+6NH_3(g)+6H_2O(l) = 4NH_4NO_3(s)+(NH_4)_2U_2O_7+3H_2O,\\
2UO_2(NO_3)_2(s)+2H_2 = U(NO_3)_4(s)+U(OH)_4(s),\\
U(NO_3)_4(s)+16H_2 = U(OH)_4+4NH_3+8H_2O(l),\\
U(NO_3)_4+4NH_3+4H_2O = U(OH)_4(s)+4NH_4NO_3(s),\\
NH_4NO_3(s)+H_2 = NH_4NO_2(s)+H_2O(l),\\
NH_4NO_2(s) = N_2+2H_2O,\\
UO_2(NO_3)_2(s)+H_2 = UO_2(OH)_2+2NO_2(g).
\end{gathered}$$

(5) **Ferric Nitrate.** Exp. 1. The quantity of ferric nitrate, $Fe(NO_3)_3 6H_2O$, employed = 8.00 gr. Time of silent electric discharge = 5 hours. A part of the powder gradually became reddish brown, and

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(6) Treadwell, "Kurzes Lehrbuch der analytischen Chemie," 10th ed., Vol. II, p. 531.

water was found condensed on the wall of the discharge tube. The solid reaction products were well shaken with water and filtered. Insoluble reddish brown powder was proved to be ferric hydroxide. The filtrate had the following properties.

(1) It was acidic. (2) The solution contained ammonium salt. (3) The solution contained nitrite. (4) The absence of hydroxylamine was proved.

By analyzing the solutions in the absorption bottles (1), (2), and (3), it was proved that nitrogen peroxide and nitric oxide were produced during the discharge, but no ammonia.

It was thus proved that the principal reaction products are ferric hydroxide, ammonium salt, nitrite, nitrogen peroxide, and nitric oxide.

Exp. 2. The quantity of nitrite, that of nitrogen peroxide, and that of nitric oxide produced were determined exactly as in the case of zirconium nitrate.

Ferric nitrate employed = 8.00 gr.
Time of silent electric discharge = 5.5 hours.
Volume of $KMnO_4$-solution of 0.01000 normal, equivalent to the quantity of nitrite produced = 15.80 c.c.
Volume of $KMnO_4$-solution, equivalent to the quantity of nitrite produced by the absorption of nitrogen peroxide = 235.60 c.c.
Volume of $KMnO_4$-solution of 0.01000 normal, equivalent to the quantity of nitrite produced by the absorption of the oxidation product of nitric oxide = 816.30 c.c.

Exp. 3. The quantity of ammonium salt produced was determined.

Ferric nitrate employed = 8.00 gr.
Time of silent electric discharge = 5 hours.
Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 1.27 c.c.

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

$$\begin{aligned}
&2Fe(NO_3)_3(s)+6H_2 = 2Fe(OH)_3(s)+3NO_2(g)+3NO+3H_2O,\\
&Fe(NO_3)_3(s)+12H_2 = Fe(OH)_3+3NH_3+6H_2O(l),\\
&Fe(NO_3)_3(s)+3NH_3+3H_2O = Fe(OH)_3+3NH_4NO_3(s),\\
&NH_4NO_3+H_2 = NH_4NO_2(s)+H_2O,\\
&NH_4NO_2(s) = N_2+H_2O(l),\\
&NO_2(g)+H_2 = NO(g)+H_2O.
\end{aligned}$$

(6) **Chromic Nitrate.** Exp. 1. The quantity of chromic nitrate, $Cr(NO_3)_3 9H_2O$, employed = 8.00 gr. Time of silent electric discharge

= 5 hours. Water was produced during the reaction and a part of the powder became moist. The solid reaction products were shaken with water and filtered. A small quantity of dark brown powder remained. The insoluble substance was principally chromium hydroxide. The filtrate had the following properties.

(1) It was acidic. (2) The presence of nitrite was proved. (3) The solution contained ammonium salt. (4) The absence of hydroxylamine was proved.

By analyzing the solutions contained in absorption bottles (1), (2), and (3), it was proved that no appreciable amount of nitrogen peroxide, nitric oxide, and ammonia, were produced.

It was thus proved that the principal reaction products are ammonium salt, chromium hydroxide and nitrite.

Exp. 2. The quantity of nitrite was determined.

Chromic nitrate employed = 8.00 gr.
Time of silent electric discharge = 5.5 hours.
Volume of $KMnO_4$-solution of 0.01000 normal, equivalent to the quantity of nitrite produced = 1.95 c.c.

Exp. 3. The quantity of ammonium salt produced was determined.

Chromic nitrate employed = 8.00 gr.
Time of silent electric discharge = 5 hours.
Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 19.23 c.c.

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

$$Cr(NO_3)_3(s)+12H_2 = Cr(OH)_3(s)+3NH_3+6H_2O,$$
$$Cr(NO_3)_3(s)+3NH_3+3H_2O = Cr(OH)_3+3NH_4NO_3(s),$$
$$NH_4NO_3(s)+H_2 = NH_4NO_2(s)+H_2O,$$
$$NH_4NO_2(s) = N_2+2H_2O.$$

(7) **Calcium Sulphite.** Exp. 1. The quantity of calcium sulphite, $CaSO_32H_2O$, employed = 8.00 gr. Time of silent electric discharge = 5 hours. No appreciable change was observed in the appearance of the white powder in the discharge tube. The solid reaction products were shaken with water. White turbid solution was obtained. It had the following properties.

(1) The solution was alkaline. (2) The solution was placed in a test tube and heated. The evolution of hydrogen sulphide was proved. It is therefore certain that the solution contained sulphide.

$$CaS + 2H_2O = Ca(OH)_2 + H_2S.$$

The alkaline solution, through which the gas had been passed on leaving the discharge tube, was placed in a test tube, acidified with hydrochloric acid, and heated. Hydrogen sulphide evolved.

It was thus proved that calcium sulphide, calcium hydroxide, and hydrogen sulphide are the principal reaction products.

Exp. 2. On leaving the discharge tube the gas was passed through two absorption bottles, containing alkali solutions, and the quantity of hydrogen sulphide absorbed was determined in the normal manner.

Calcium 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 = 1.20 c.c.

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

$$CaSO_3(s) + 3H_2 = CaS(s) + 3H_2O,$$
$$2CaS + 3H_2O = Ca(OH)_2(s) + Ca(HS)_2(s),$$
$$Ca(HS)_2(s) = CaS + H_2S.$$

(8) **Sodium Sulphite.** Exp. 1. The quantity of anhydrous sodium sulphite, Na_2SO_3, 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 products were dissolved in water. Light brown solution obtained had the following properties.

(1) It was alkaline. (2) The solution was placed in a test tube, sodium hydroxide solution and a few drops of sodium nitroprusside solution added. The solution coloured orange, proving the absence of sulphide.

The alkaline solution, through which the gas had been passed on leaving the discharge tube, was placed in a test tube, acidified, and heated. The evolution of hydrogen sulphide was proved.

Exp. 2. The quantity of hydrogen sulphide was determined exactly as in the case of calcium sulphite.

Sodium sulphite employed = 8.00 gr.
Time of silent electric discharge = 6 hours.
Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of H_2S produced = 0.99 c.c.

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

$$Na_2SO_3(s)+3H_2 = Na_2S(s)+3H_2O,$$
$$Na_2S+2H_2O = 2NaOH+H_2S,$$
$$Na_2S+H_2 = 2Na+H_2S,$$
$$2Na+2H_2O = 2NaOH+H_2.$$

Further experiment will be necessary to decide the occurrence of the third reaction.

Summary.

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

(1) Cupric nitrate. Reaction products:—ammonium salt, copper oxide, metallic copper, nitrite, nitrogen peroxide, nitric oxide, and ammonia.

(2) Zirconium nitrate. Reaction products:—ammonium salt, zirconium oxide, nitrite, nitrogen peroxide, and nitric oxide.

(3) Thallous nitrate. Reaction products:—Nitrite, thallous hydroxide, metallic thallium, nitrogen peroxide, and ammonia gas.

(4) Uranyl nitrate. Reaction products:—ammonium salt, uranous salt, uranium hydroxide, nitrite, and nitrogen peroxide.

(5) Ferric nitrate. Reaction products:—ammonium salt, ferric hydroxide, nitrite, nitrogen peroxide, and nitric oxide.

(6) Chromic nitrate. Reaction products:—ammonium salt, chromium hydroxide, and nitrite.

(7) Calcium sulphite. Reaction products:—Calcium sulphide, calcium hydroxide, and hydrogen sulphide.

(8) Sodium sulphite. Reaction products:—Sodium hydroxide, and hydrogen sulphide.

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