Detection of the Atomic Oxygen Evolved in the Decomposition of Some Metallic Oxides*

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Atomic oxygen was found to be evolved from the surface of a platinum ribbon, when it is heated to 1400°C in vacuo, if the ribbon has been treated previously with nitrous oxide or discharged oxygen gas.[1-4] It was believed that platinum dioxide is formed on the platinum surface, and that atomic oxygen is given off by the decomposition of platinum dioxide when the ribbon is heated to a high temperature in vacuo. Afterwards, atomic oxygen was found to be evolved when platinum dioxide prepared from ammonium chloroplatinate and sodium nitrate was decomposed in vacuo at a high temperature.[5] This experimental finding was believed to support the above conclusion. Then, various metallic oxides were examined to determine whether they would similarly evolve atomic oxygen when decomposed at a high temperature in vacuo. It was found that some metallic oxides evolve atomic oxygen, while others do not.[6] In order to clarify these phenomena, oxides of chromium, iron, manganese, cobalt and cadmium will be investigated in the present experiment.

Experimental

Apparatus.—The main part of the apparatus is shown in Fig. 1. **P** is a coil (1 mm.×3.5 mm.×

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[*] Presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, March, 1963.

[1] K. Mitani and Y. Haranō, This Bulletin, 33, 1147 (1960).

[2] K. Mitani and Y. Haranō, ibid., 33, 276 (1960).

[3] Y. Haranō, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 1812 (1960).

[4] Y. Haranō, ibid., **82**, 22 (1961).

[5] Y. Haranō, ibid., **82**, 19 (1961).

[6] Y. Haranō, ibid., **82**, 152 (1961).

12 mm.) made of a platinum ribbon (1.3 mm. × 0.10 mm. × 62 mm.) which is spot-welded to platinum wires sealed into a glass stem. These platinum wires are subsequently connected to copper wires. A sample of metallic oxide placed on a quartz plate ((0.3—0.4) mm. × 2.5 mm. × 8 mm.) is inserted into the platinum coil, and then heated by an electric current. The glass tube A can be taken off from the ground joint, and the samples dropping from P can be removed easily.

D is a thin glass plate hung in the side tube of the reaction vessel. Molybdenum trioxide has been deposited on one side of D. Atomic oxygen is detected by the change in the color of molybdenum trioxide from pale yellow to blue.

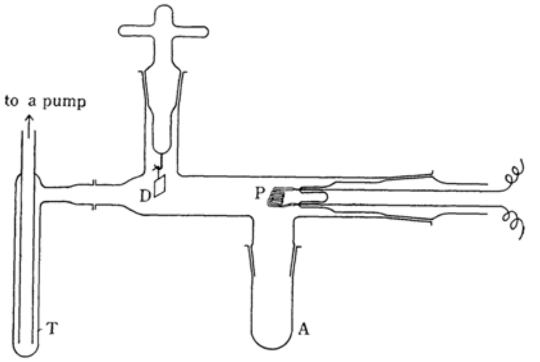

Fig. 1 The main part of the apparatus.

The apparatus can be evacuated by a mercury diffusion pump through a trap cooled by dry ice.

The sensitivity of molybdenum trioxide to atomic oxygen varies with the state of deposition on a glass plate. It seems that the thicker the layer of molybdenum trioxide, the larger its sensitivity. Molybdenum trioxide was deposited uniformly on a thin glass plate in the apparatus shown in Fig. 2. D is a piece of cover-glass for microscopic use, in the middle of one edge of which a small glass hook is attached. When molybdenum wire M is heated by an electric current to red heat, molybdenum is oxidized by air, and the glass bell-jar is filled with the smoke of the molybdenum trioxide thus formed. As tiny lumps of molybdenum trioxide crystals, entangled like cotton, fall to the bottom at first, a glass plate B is placed (as is shown in Fig. 2) in order to catch them. After some time, a uniform smoke is left behind in the bell-jar when the glass plate B is removed. Minute crystals of molybdenum trioxide settle down slowly on pieces of cover-glass, until the required thickness is obtained, whereupon the glass plate B is inserted again to stop further deposition. The molybdenum trioxide deposited on a glass plate by the method mentioned above is white or pale yellow; it changes to blue by atomic oxygen, probably according to the following equation: [7]

$$3MoO_3+O \rightarrow Mo_3O_8+O_2$$

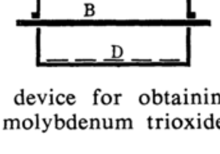

Fig. 2. The device for obtaining a uniform deposit of molybdenum trioxide.

Materials.—Commercial chromic oxide was used at first. Later, chromic oxide was prepared by the following method. Potassium dichromate was heated with sulfur in a porcelain crucible, and the chromic oxide (Cr_2O_3) formed was washed free from potassium sulfate and dried.

Ferric oxide (Fe_2O_3) was made by heating ferrous sulfate, or by heating ferric hydroxide obtained by the action of excess ammonium hydroxide upon ferric chloride.

Manganese dioxide (MnO_2) was prepared by heating manganous nitrate which had been obtained by the action of concentrated nitric acid on manganous carbonate. Manganous nitrate was heated in a porcelain crucible until the evolution of brown gas ceased completely; the residue in the crucible was then boiled with dilute nitric acid, filtered, and washed. The residue was heated again in a crucible to ca. 500°C for an hour. Manganese dioxide was obtained as a black powder.

Cobalt oxide was prepared by heating cobalt nitrate. After being washed with water, the black powder obtained was heated again to 500—600°C in a crucible. The composition of this sample was not definite, but it was supposed to be near Co_3O_4.

Cadmium oxide (CdO) was made by heating cadmium carbonate in a platinum crucible until no further change in weight occurred.

Hydrogen was purified by diffusion through a heated palladium tube.

Procedure.—Whether atomic oxygen is evolved or not is judged in every case by the change in the color of molybdenum trioxide, when the platinum ribbon is heated to 1400°C for 20 min. in vacuo.

After atomic oxygen is once given off in the thermal decomposition of metallic oxide inserted into the platinum coil, atomic oxygen is found to be evolved from the platinum surface heated in vacuo for a long time.[1,2,8] It is believed that platinum dioxide is formed on the platinum surface, and that atomic oxygen is given off by the decomposition of platinum dioxide when the ribbon is heated to a high temperature in vacuo. Therefore, the following preliminary treatment of the platinum ribbon is necessary before every experiment. After the apparatus is sufficiently evacuated, hydrogen is admitted to a pressure of 3 mmHg and the platinum ribbon is heated to 1400°C for 30 min. Subsequently, the ribbon is degassed at 1400°C for 30 min. in

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[7] W. H. Rodebush and W. A. Nichols, *J. Am. Chem. Soc.*, **52**, 3864 (1930).

[8] K. Mitani and Y. Haranō, This Bulletin, **32**, 1386 (1959).

vacuo. Then, whether or not atomic oxygen is still given off from the platinum surface is determined by the change in the color of molybdenum trioxide, the platinum ribbon being heated to 1400°C for 20 min. If molybdenum trioxide changes its color, the above-mentioned treatment is repeated until no atomic oxygen is given off from the platinum ribbon.

The weight of metallic oxide placed at one time on a quartz plate is about 1 mg. The quartz plate once used reacts with the sample placed on it, and substances difficult to be removed completely by most reagents form. As these substances seem to give off atomic oxygen in some cases, a new quartz plate is used in each experiment. A new one does not give off atomic oxygen when heated to high temperatures.[6)]

The sample of metallic oxide placed on a quartz plate is heated in the platinum coil. The temperature of the platinum ribbon is measured with an optical pyrometer. The temperature of the sample, although it can not be determined accurately, is thought to be slightly lower than that of the ribbon.

As the samples appear as powder, it is possible that they adsorb air or water vapor. Therefore, the samples are, in some cases, degassed at 500—700°C for 30 min. in vacuo prior to being heated to 1400°C.

To detect atomic oxygen formed as an intermediate substance of a chemical reaction, a new method has been devised in the authors' laboratory. This method is based upon the fact that a platinum ribbon once in contact with atomic oxygen evolves it for a long time when heated to high temperatures in vacuo. Atomic oxygen has already been confirmed by this method to exist as an intermediate, when nitrous oxide is decomposed at relatively high pressures (10—50 mmHg) on the platinum surface,[1,4)] and when carbon monoxide is oxidized by a platinum catalyst.[9)] Therefore, in the present investigation, after the experiment of heating a sample of metallic oxide in the platinum coil, the sample and the quartz plate were removed and the platinum ribbon alone was heated to 1400°C for 20 min. in vacuo. If atomic oxygen was evolved in the latter case, it was regarded as further confirmation that atomic oxygen was evolved by the decomposition of metallic oxide.

Results and Discussion

Chromic Oxide.—Chromic oxide was heated several times on a quartz plate, as has been mentioned above, and also to 1400°C directly on the surface of the platinum ribbon. Molybdenum trioxide scarcely changed its color in any case. It is believed that chromic oxide does not give off atomic oxygen. The appearance of a sample remained unchanged even after the experiment, so probably chromic oxide was not decomposed by the heating.

Ferric Oxide.—When ferric oxide placed on a quartz plate was heated to 1400°C for 20 min. in the platinum coil, molybdenum trioxide distinctly changed its color from pale yellow to blue. In some cases a sample of ferric oxide was degassed at about 700°C for 30 min. in vacuo before being heated to 1400°C, but the same result was obtained, irrespective of the procedure.

Ferric oxide is red-brown, but a sample after being heated to 1400°C becomes black. It was confirmed that the latter can be attracted by a magnet, while the former can not. From these facts, it is certain that ferric oxide is decomposed by heat, forming ferrosoferric oxide Fe_3O_4.

The portion of a quartz plate with which the sample was in contact became somewhat dark during heating.

Manganese Dioxide.—Molybdenum trioxide turned blue while manganese dioxide placed on a quartz plate was heated to 1400°C in the platinum coil.

After the experiment, the quartz plate, together with the sample, was removed, and the platinum ribbon alone was heated. Molybdenum trioxide turned blue in this case also.

Manganese dioxide was prepared by the dry method and, moreover, heated to about 500°C in air, so that probably it was not hydrated. Therefore, manganese dioxide was usually heated at once to 1400°C, without a preliminary degassing. To make sure, however, a sample of manganese dioxide was degassed at about 500°C in vacuo, and then heated to 1400°C. In this case, molybdenum trioxide turned blue in the same manner.

A sample of manganese dioxide in the platinum coil was observed through a magnifying glass during heating. When manganese dioxide began to be heated to high temperatures, it was decomposed rapidly, violently evolving gas and jumping about, and in a short time almost all the sample fell from the quartz plate.

The portion of the quartz plate with which the sample was in contact became dark during heating.

Cobalt Oxide.—Molybdenum trioxide turned blue in the case of cobalt oxide heated to 1400°C in vacuo.

After the experiment, the quartz plate, together with the sample, was removed, and the platinum ribbon alone was heated. Molybdenum trioxide turned even a deeper blue than when the sample was inserted in the platinum coil.

The sample of cobalt oxide before being heated was black. After the experiment, the surface of the sample was dark brown, while the interior had turned a lighter brown. This

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9) Y. Haranō, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 316 (1961).

brown substance is thought to be cobaltous oxide CoO.

As the composition of the cobalt oxide used in this experiment was not definite, samples of cobalt oxide were heated to various temperatures between 500°C and 800°C in air at 1 atm. in order to oxidize them to the higher oxide Co_3O_4. The results of the experiments using these samples were the same as the above.

Cadmium Oxide.—Molybdenum trioxide turned blue, in the case of cadmium oxide, if the amount of the sample used was very small or if the sample was heated to lower temperatures (700—1100°C). Molybdenum trioxide, however, turned dark gray in a short time if the same amount as the other oxides was heated to 1400°C. Thereafter, the quartz plate was removed, and the platinum ribbon alone was heated. The color of molybdenum trioxide remained unchanged.

Cadmium oxide is easily decomposed by heat. When it is heated to 1400°C in vacuo, it evaporates rapidly and the vapor of the metallic cadmium formed by the decomposition condenses as a metallic mirror with a black tint on the wall of the reaction vessel. Therefore, it appears that the change in the color of molybdenum trioxide is not due to atomic oxygen, but to the vapor of metallic cadmium. Metallic cadmium distilled in vacuo was placed on a quartz plate and inserted into the platinum coil. When the platinum ribbon began to be heated to 1400°C in vacuo, molybdenum trioxide got a bluish tint at first, but in a short time it turned dark gray.

A silver plate was hung up, together with molybdenum trioxide, and cadmium oxide was heated as usual, but the silver plate did not become black.

From the foregoing facts, it is believed that cadmium oxide does not give off atomic oxygen at the time of thermal decomposition, and that the change in the color of molybdenum trioxide is due to the reduction by the vapor of the metallic cadmium produced by the decomposition.

Conclusion

The results of the present investigation show that chromic oxide and cadmium oxide do not give off atomic oxygen, but that ferric oxide, manganese dioxide, and cobalt oxide do give off atomic oxygen when heated strongly in vacuo.

Previously, Haranō[5,6] investigated whether or not atomic oxygen was evolved when various metallic oxides were heated to high temperatures in vacuo. He concluded that alumina (Al_2O_3), silica (SiO_2), magnesium oxide (MgO), cuprous oxide (Cu_2O), lead monoxide (PbO), lead dioxide (PbO_2), silver oxide (Ag_2O), and silver peroxide (Ag_2O_2) do not evolve atomic oxygen, but that zinc oxide (ZnO), mercuric oxide (HgO), cupric oxide (CuO), and platinum dioxide (PtO_2) do evolve atomic oxygen at high temperatures.

When the results of the present investigation are considered together with his results, it is evident that oxides difficult to decompose, i. e., alumina, silica, magnesium oxide, cuprous oxide, and chromic oxide, do not give off atomic oxygen. It can be said at least that atomic oxygen can not be evolved without the decomposition of the sample. This is quite reasonable. On the other hand, atomic oxygen is not found to be given off from lead monoxide, lead dioxide, silver oxide, silver peroxide, and cadmium oxide, though these oxides can be decomposed with ease. After all, atomic oxygen is given off in the thermal decomposition of zinc oxide, mercuric oxide, cupric oxide, platinum dioxide, ferric oxide, manganese dioxide, and cobalt oxide.

Molybdenum trioxide does not turn blue when the platinum ribbon alone is heated to 1400°C in oxygen. Therefore, it is not true that molecular oxygen formed by the decomposition of metallic oxides comes into contact with the platinum ribbon at a high temperature and so is dissociated into atoms.

It is believed that the oxygen given off by the decomposition of metallic oxides at high temperatures is not in equilibrium, and that a part of the oxygen is evolved in the atomic state from the beginning.

As to the detailed mechanism, however, further investigations will be necessary.

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