Evolution of Atomic Oxygen from Platinum Surface Treated Previously with Nitrous Oxide

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In the previous paper[1], it was reported that atomic oxygen is given off when nitrous oxide is decomposed by the platinum catalyst at low pressures ($1\times10^{-3}\sim5\times10^{-4}$ mmHg) by means of the flow method. When the pressure of nitrous oxide is higher (10~50 mmHg), no atomic oxygen is detected in a similar experiment. But evolution of atomic oxygen is detected in vacuo from heated platinum surface treated previously with nitrous oxide at pressures of 10~50 mmHg. The apparatus used is the same as reported in the previous paper[1]. Atomic oxygen given off is detected by the change of color of molybdenum trioxide deposited on a glass plate. Nitrous oxide is introduced into the reaction vessel to an initial pressure of 10~50 mmHg, and the platinum ribbon is heated to 1100°C. After 30 min., the nitrous oxide is considerably decomposed. In this procedure, molybdenum trioxide does not change its color. Then the reaction vessel is evacuated, by a diffusion pump, and, being continuously evacuated, the platinum ribbon is heated to 1400°C. In this case, molybdenum trioxide in the side tube changes its color from pale yellow to deep blue within 30 min. The platinum ribbon thus treated keeps its ability to change the color of molybdenum trioxide even after heating in vacuo at 1400°C for several hours. During the several experiments repeated, a dark brown film is gradually deposited on the glass wall of the reaction vessel. This dark brown substance seems to be not platinum metal, but platinum oxide[2], because it can mostly be dissolved by hydrochloric acid.

Instead of nitrous oxide, air is introduced into the reaction vessel to a pressure of 1 mmHg, and the platinum ribbon is heated to 1100°C for 30 min. After the apparatus being evacuated, the ribbon is heated to 1400°C in vacuo. Molybdenum trioxide does not change its color throughout this experiment. It is concluded from this that oxygen atoms chemisorbed on platinum surface are desorbed as molecular oxygen when heated in vacuo. The first step of the decomposition of nitrous oxide by the platinum catalyst has been believed to be

$$N_2O \rightarrow N_2 + O_{ads}$$

These adsorbed oxygen atoms may dissolve into the interior of the platinum metal, but then they may be evolved gradually in molecular form when heated after evacuation.

In the previous paper[3] it was reported that evolution of atomic oxygen is detected in vacuo from platinum surface treated previously with discharged oxygen gas. The platinum ribbon treated with nitrous oxide behaves in the same manner as the one treated with discharged oxygen, so it is concluded that platinum dioxide PtO_2 is also formed on the platinum surface treated with nitrous oxide, and that this platinum dioxide is the source of atomic oxygen.

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1) K. Mitani and Y. Haranō, This Bulletin, **32**, 1386 (1959).
2) Cf. E. K. Rideal and O. H. Wansbrough-Jones, *Proc. Roy. Soc.*, **A123**, 202 (1929); G. C. Fryburg, *J. Chem. Phys.*, **24**, 175 (1956).
3) K. Mitani and Y. Haranō, This Bulletin, **33**, 276 (1960).