SHORT COMMUNICATIONS

The Formation of Uranium Trioxide by the Oxidation of Uranium Iodides at Low Temperatures

By Muneo HANDA

Division of Fuel Research and Development, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki

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The oxidations of uranium tetraiodide and triiodide by oxygen were studied using a special experimental apparatus, in which the column of a gas chromatograph was replaced with an electric furnace and traps of water vapor, oxygen, and iodine. With this apparatus, studies can be made easily and accurately of chemical reactions between gases and solids, even when such solids cannot be treated in the air. This is because measurements can be made on the gases consumed or released during the reaction. The heating curves (the rate of temperature increase: 2°C/min.) obtained for the reactions between uranium iodides and oxygen are shown in Fig. 1. The peaks appearing in the heating curves correspond to the

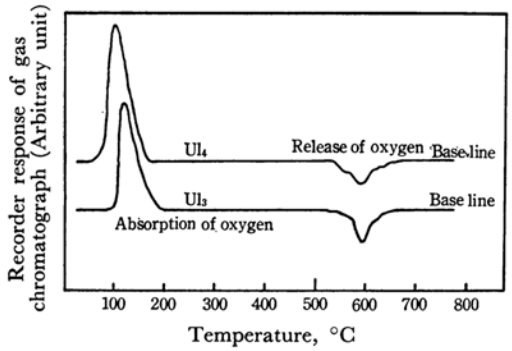

Fig. 1. Heating curves of uranium iodides.
Sample weight UI_4: 0.152 g.
UI_3: 0.141 g.
Partial pressure of oxygen: 1/10 atm.
Rate of temperature increase: 2°C/min.

absorption of oxygen, while the valleys correspond to the release of oxygen during the reaction. The oxidations of uranium tetraiodide and of uranium triiodide by oxygen, whose partial pressure was one-tenth of the atmosphere, started at temperatures of about 60 and 100°C respectively. When the temperatures were raised to about 600°C, the products resulting from the oxidations of uranium iodides released oxygen; the volume of oxygen released was about one-tenth of that absorbed in the oxidation. The colors of the compounds obtained by the oxidations of uranium tetraiodide and triiodide were both brown. When these brown-colored compounds were heated to about 600°C, oxygen was released and they turned black at the same time. The brown and the black compounds were then taken out from the apparatus for chemical and X-ray analyses; these analyses showed that the brown compounds were uranium trioxide and the black compounds, triuranium octoxide. Therefore, the peaks of the absorption of oxygen in the heating curves for uranium iodides appeared when the uranium iodides were oxidized to uranium trioxide; the valleys of the release of oxygen, on the other hand, were caused by the decomposition of uranium trioxide to triuranium octoxide. The reactions involved are as follows:

$$\xrightarrow{60^\circ C} \quad 2UI_4 + 3O_2 = 2UO_3 + 4I_2 \qquad (1)$$

$$\xrightarrow{100^\circ C} \quad 2UI_3 + 3O_2 = 2UO_3 + 3I_2 \qquad (2)$$

$$\xrightarrow{600\text{—}700^\circ C} \quad 3UI_4 + 4O_2 = U_3O_8 + 6I_2 \qquad (3)$$

$$\xrightarrow{600\text{—}700^\circ C} \quad 6UI_3 + 8O_2 = 2U_3O_8 + 9I_2 \qquad (4)$$

It has been reported by Foster and Tvrzicky[1] that oxygen or dry air converts uranium iodides to triuranium octoxide at elevated temperatures, and to uranyl iodide (UO_2I_2) or uranous oxyiodide (UOI_2) at room temperature. An attempt was therefore made by the present author to obtain the same compounds at various temperatures and at various oxygen partial pressures using the same method; however, his experiments all failed to produce such compounds. In the course of the experiments, however, he observed the reaction in which the oxidation proceeded in two stages as the temperature was raised. The oxidations of uranium iodides at low temperatures, represented by the two chemical equations, 1 and 2, may be useful for the preparation of pure uranium trioxide.

1) In J. J. Katz and E. Rabinowitch, ed., "The Chemistry of Uranium: The Element, Its Binary and Related Compounds," Dover Publications, New York (1951) p. 538.