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Studies of the Chemical Reactions of Uranium Iodide with Oxygen and Iodine at High Temperatures

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Uranium tetraiodide is oxidized to triuranium octoxide through three intermediates, which are deposited on silica powder heated to temperatures of about 400, 300 and 200°C respectively. The intermediates are produced by the action of oxygen contained in small amounts in a helium stream (1/100—1/10000 atm.) on uranium tetraiodide. The intermediates are considered to be compounds consisting of uranium, iodine and oxygen. Chemical analysis, the measurement of the melting point and X-ray analysis show that the compound deposited at the temperature of 400°C is uranium triiodide, while the compounds deposited at 300 and 200°C are both uranium tetraiodides. Three hypotheses have been formulated to interpret the above phenomenon, in which the reaction of uranium iodides with iodine has been studied.

In the author's previous studies of the chemical behavior of fission products captured in graphite powder, it was found that fission iodine diffusing out of the uranium dioxide and graphite is not an elementary iodine but a chemical form of uranium tetraiodide.[1-2] Uranium tetraiodide attracts moisture and is oxidized in air to triuranium octoxide and iodine; therefore, it should be handled in a dry, inert atmosphere. The graphite and beryllia used as moderators for a high-temperature gas-cooled reactor have many gaseous impurities, such as hydrogen, oxygen, and water vapor, adsorbed on the surface.[3] These gaseous impurities are released gradually as the reactor operates. In order to ascertain the chemical behavior of fission iodine in a reactor fuel, the reactions between uranium tetraiodide and these gaseous impurities must be studied carefully.

As has already been reported in a previous paper,[4] the reactions between uranium tetraiodide and oxygen were studied by using a thermochromatograph. It was found that uranium tetraiodide was oxidized to triuranium octoxide through three intermediates, which deposited on silica powder heated to temperatures of about 400, 300 and 200°C.

These intermediates were produced by the action of oxygen contained in small amounts in a helium stream (1/100—1/10000 atm.) on uranium tetraiodide. The intermediates were considered to be compounds consisting of uranium, iodine and oxygen, although the existence of these compounds in their solid state has not been reported in the literature.

The present work was undertaken in order to estimate the chemical form of these intermediates. Chemical analysis, melting-point measurements and X-ray analysis were carried out for these intermediates. The results of these experiments showed that these intermediates were not compounds consisting of uranium, iodine and oxygen; the compound deposited at the temperature of 400°C was uranium triiodide, while the compounds deposited at 300°C and at 200°C both consisted of uranium tetraiodide. These results indicate that uranium triiodide and tetraiodide moved to positions in the thermochromato-tube at which the temperatures were much lower than the melting points. Three hypotheses were made in order to interpret the above phenomenon; by means of these hypotheses, the reaction of uranium iodides with iodine was studied.

As a result, the following mechanism was found to account for the above phenomenon. First, the oxygen reacts with uranium tetraiodide and produces an elementary iodine. Then this iodine reacts with adjacent uranium tetraiodide, producing a compound of uranium tetraiodide to which iodine has been added. This addition compound has a low melting point, and so moves to a lower temperature in the thermochromato-tube and is decomposed to uranium triiodide, tetraiodide and iodine.

Experimental and Results

Sample Preparation. — *Uranium Tetraiodide Packed in Silica Breakable.*—Uranium tetraiodide

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1) S. Yajima, K. Shiba and M. Handa, This Bulletin, **36**, 253 (1963).

2) S. Yajima, K. Shiba and M. Handa, ibid., **36**, 258 (1963).

3) J. P. Redmond and P. L. Walker, Jr., *Nature*, **186**, 73 (1960).

4) S. Yajima, K. Shiba and M. Handa, This Bulletin, **38**, 278 (1965).

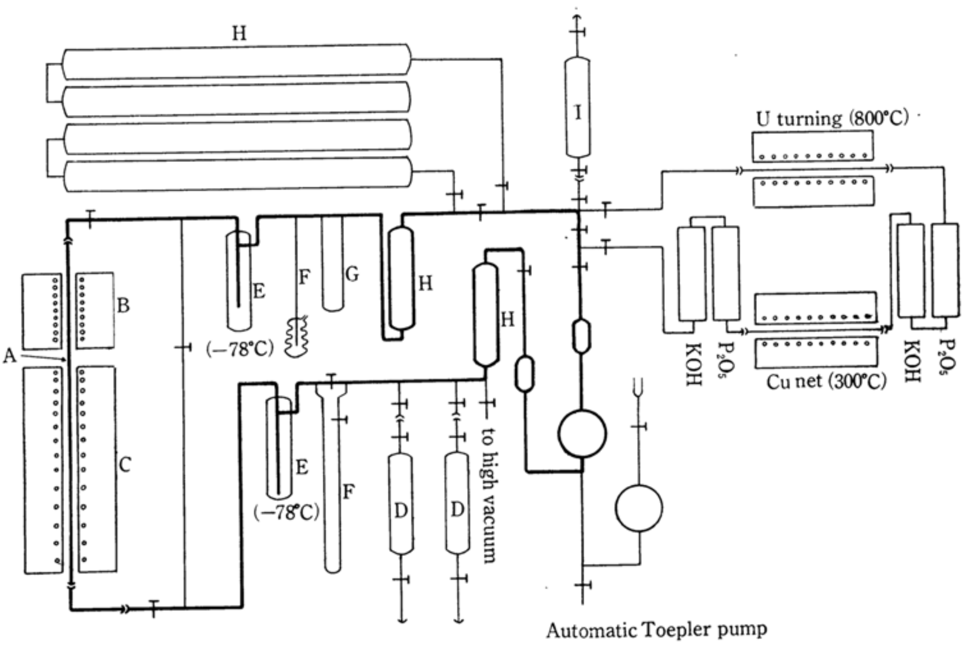

Fig. 1. Flow system of thermochromatograph.

A: Thermochromato-tube
B: Sample heating furnace (600°C)
C: Thermochromato-furnace (600°C to room-temperature)
D: Carrier gas vessel
E: Mercury trap
F: Mano-meter
G: Flow-meter
H: Buffer tank
I: Vessel for trapping carrier gas

was prepared by the direct combination of uranium and iodine, as has been described in the literature.5) From 0.2 to 10 g. of the uranium tetraiodide was packed in a silica breakable with a ball joint, which was in turn placed in a glove box filled with purified helium gas. Then a cock was attached to the breakable with a ball-joint holder, and the entire assembly was taken out of the glove box. The helium gas in the breakable was evacuated, and the part of the breakable containing the sample was sealed off by an oxy-hydrogen flame.4)

Apparatus.—The apparatus used is shown schematically in Fig. 1. The apparatus had an automatic Toepler pump, making possible experiments with oxygen of various concentrations as the carrier gas. Buffer tanks were installed at the entrance and exit of the automatic Toepler pump, in order to stabilize the flow rate of the carrier gas; the volumes of these buffer tanks were 0.5 and 25.0 l. respectively. These large-volume buffer tanks can be used to keep the concentration of oxygen constant when some of it is consumed in the oxidation of the sample material.

The experimental apparatus also had a bypass gas purification system which made possible experiments with purified helium carrier gas. The thermochromato-tube, made of transparent silica, was 1.2 cm. in inner diameter and 100 cm. long. An empty silica tube was used as the thermochromato-tube, and so the sample packed in the silica breakable was held by silica wool packed in the tube. The tube was heated by the thermochromato-furnace so as to produce a linear temperature gradient of 600°C to room-temperature along its axis.

Procedure.—The entire apparatus was evacuated with a rotary pump, and then arbitrary volumes of helium and oxygen were introduced into the apparatus to a one-tenth atmosphere. The gases were completely mixed together by circulating them for 5 hr. through the apparatus with the automatic Toepler pump.

However, when the experiment was carried out in an inert atmosphere, only helium was introduced; the gas was purified by circulation for 5 hr. through the gas purification system with the automatic Toepler pump. After the apparatus had been filled with the carrier gas, the breakable containing the sample was broken, with an iron bar sealed in the silica tube, from outside the thermochromato-tube. Then the thermochromato-furnace was started in order to heat the tube. After the temperature of the furnace had reached 600°C, the circulation of the carrier gas was continued for a further 5 to 10 hr. The thermochromato-tube was then cooled, and the top and bottom of the tube were sealed by an oxy-hydrogen flame. The sealed tube was transferred to a glove box

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5) N. W. Gregory, UCRL, RL-4, 6, 272 (1944).

filled with purified helium, and the compounds deposited on the wall of the silica tube, which had been heated at 400, 300 and 200°C, were taken out of the tube by cutting it with a baby grinder. These compounds were weighed and packed in silica breakables for chemical analysis and for measurement of the melting point; they were also packed in capillary tubes for X-ray analysis.

The Determination of the Uranium and Iodine in the Compounds Deposited on Silica Tubes Heated at 400, 300 and 200°C.—The breakable containing a sample was broken above a beaker of water and rapidly immersed. The three samples were completely dissolved in water. A reddish-purple solution was obtained from the compound deposited at 400°C, while a green solution was obtained from the compounds deposited at 300 and 200°C. The reddish-purple solution immediately turned green. Each solution was placed in a 100-ml. measuring flask and was diluted with water to 100 ml. A few milliliters of the solution were then put in a separating funnel and nitric acid was added. The iodine was extracted by carbon tetrachloride. The iodine in the carbon tetrachloride, which turned reddish-purple, was directly determined by colorimetry at the wavelength of 575 mμ. Sulfuric acid was added to the residue solution, from which the iodine had been extracted, and the solution was heated almost to dryness. After the nitric acid had been expelled by repeating the above procedure three times, the pH of the solution was adjusted with ammonium hydroxide (not containing the carbonate radical) and the uranium was extracted by an oxine-chloroform solution. The uranium content of the chloroform was determined by colorimetry at 380 mμ. The analytical results are shown in Table III.

The Determination of Oxygen in the Compounds Deposited at 400 and 300°C.—The method of determining oxygen by subtracting the weights of uranium and iodine from the total weight of the sample is inferior to the method of determining oxygen directly. Therefore, the oxygen was determined directly. The compounds of uranium, iodine and oxygen were oxidized to triuranium octoxide and iodine when heated in the air at 600°C. From the determinations of the uranium and iodine in these compounds, it was shown that the iodine/uranium ratio was 3.0 for the compound deposited at 400°C and 4.0 for the compounds deposited at 300 and 200°C. If oxygen is present in these compounds, the amount consumed in their oxidation should decrease in proportion to that which they already contain. This is because these compounds, like the oxidation products, must consist of stoichiometric compositions of uranium, iodine or oxygen. The calculated volumes of oxygen consumed in the oxidation of 1 g. of various compounds are shown in Table I.

TABLE I. OXYGEN VOLUMES CONSUMED TO OXIDIZE 1 g. OF COMPOUND ($U_xI_yO_z$) TO URANIUM OXIDE AND IODINE

Compound	Oxygen volumes consumed for reaction ml. at S.T.P.	Chemical equation
U	130.0	$3U+4O_2=U_3O_8$
UI_2	69.9	$3UI_2+4O_2=U_3O_8+3I_2$
UI_3	48.3	$6UI_3+8O_2=2U_3O_8+9I_2$
UI_4	40.2	$3UI_4+4O_2=U_3O_8+6I_2$
UOI_3	29.9	$6UOI_3+5O_2$ $=2U_3O_8+9I_2$
UOI_4	24.5	$6UOI_4+5O_2$ $=2U_3O_8+12I_2$
UO_2I_3	11.4	$6UO_2I_3+2O_2$ $=2U_3O_8+9I_2$
UO_2I_4	9.7	$3UO_2I_4+O_2=U_3O_8+6I_2$

The oxygen consumed for the reactions was measured by means of a B. E. T. apparatus.⁶⁾ The B. E. T. apparatus can measure amounts of oxygen as small as 0.02 ml. at S. T. P. The results obtained are shown in Table II.

TABLE II. DETERMINATION OF OXYGEN IN THE COMPOUNDS DEPOSITED AT THE TEMPERATURES OF 400 AND 300°C

Compound	Sample weight g.	Oxygen consumed ml. at S.T.P.	Oxygen consumed to oxidize 1 g. of sample ml. at S.T.P.	Ref.
Compound deposited at 400°C	0.356	16.6	46.5	
	0.692	31.5	45.5	UI_3(1 g.)
	1.117	56.1	47.9	48.3 ml.
	0.319	14.7	46.2	
Compound deposited at 300°C	0.643	25.3	39.4	UI_4(1 g.)
	0.377	15.5	41.1	40.2 ml.

The Measurement of the Melting Point.—The melting point was measured in an inert gas atmosphere, using a fused salt bath (lithium chloride - potassium chloride eutectic mixture). The apparatus for measuring the melting point is shown in Fig. 2. The melting point of the compound deposited at 400°C was found to be 788±10°C, while that for the compound at 300°C, was 506±10°C.

Discussion

Before the experiment, it was thought that the compounds depositing at 400, 300 and 200°C would all consist of uranium, iodine and oxygen. However, the results of their chemical analyses, which are given in Table III, show that the deposit at 400°C was uranium triiodide, while the deposits at 300 and 200°C were uranium tetraiodide.

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6) S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).

TABLE III. CHEMICAL FROM OF THE COMPOUNDS DEPOSITED AT 400, 300 AND 200°C

Compound	Sample No.	Iodine g. atom	Uranium g. atom	Oxygen g. atom	Ratio of I/U	Result
Compound deposited at 400°C	1	2.86×10^{-3}	9.86×10^{-4}	0	2.90	UI_3
	2	2.69×10^{-3}	9.19×10^{-4}	0	2.93	
	3	4.33×10^{-3}	1.44×10^{-3}	0	2.90	
	4	1.73×10^{-3}	5.76×10^{-4}	0	2.95	
Compound deposited at 300°C	1	3.48×10^{-3}	8.64×10^{-4}	0	4.03	UI_4
	2	2.00×10^{-3}	5.19×10^{-4}	0	3.85	
Compound deposited at 200°C	1	8.66×10^{-5}	2.09×10^{-5}	—*	4.14	UI_4
	2	8.27×10^{-5}	2.17×10^{-5}	—*	3.81	
	3	9.29×10^{-5}	2.30×10^{-5}	—*	4.04	

* The oxygen was not analyzed since only a small amount of sample could be obtained.

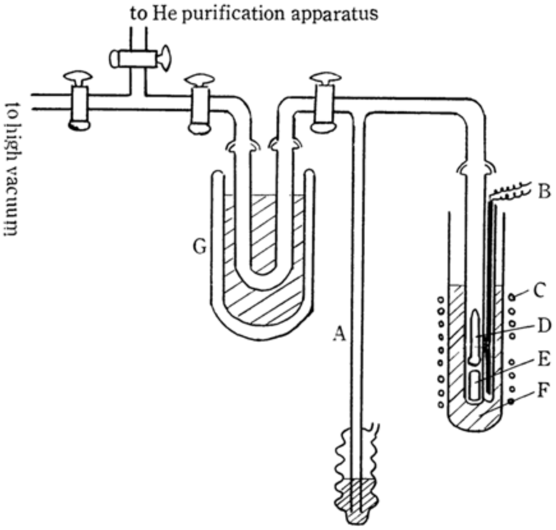

Fig. 2. Apparatus for measuring the melting point.
A: Mercury bubbler
B: Pt-PtRh thermocouple
C: Nichrome heater
D: Sample
E: Sample breaker
F: Mixed fused bath (KCl-LiCl eutectic)
G: Iodine trap (cooled with liquid nitrogen)

Further, the melting points of the compounds deposited at 400 and 300°C were 788 and 506°C, nearly equal to those of uranium triiodide (780°C) and uranium tetraiodide (508°C), as reported by other workers.7-8) The X-ray patterns (powder method) obtained for the compounds deposited at 400 and 300°C also agreed with those for the uranium triiodide and tetraiodide prepared in the laboratory. When the compound deposited at 400°C was dissolved in water, the reddish-purple color characteristic of the uranium ion (III) appeared. The compounds deposited at 300 and 200°C, on the other hand, exhibited a green color characteristic of the uranium ion (IV).

On the basis of these data, it may be reasonable to conclude that the compound deposited at 400°C is uranium triiodide and that the compound deposited at 300 and 200°C is uranium tetraiodide.

Using a thermochromatograph, the deposition temperature was determined for many metal iodides in an inert gas atmosphere using an experimental time of 2 hr. It was found that many metal iodides deposited at temperatures near their melting points.9)

When purified helium was used as the carrier gas, uranium tetraiodide deposited on the wall of a silica tube heated at 550°C. When the carrier gas contained a small amount of oxygen (1/10000 to 1/10 atm.), uranium triiodide and uranium tetraiodide deposited at 400, 300 and 200°C.

The above observations indicate that there must be a metastable compound present with a low melting point. The discussions below will deal with mechanisms for the movement of uranium tetraiodide and triiodide toward temperatures lower than the melting points.

Three possible mechanisms may be considered in accounting for the above phenomenon:

1) A metastable compound, consisting of uranium, iodine and oxygen, is produced by the action of oxygen on uranium tetraiodide. The compound moves toward lower temperatures, being carried by the helium gas, and decomposes to uranium triiodide, uranium tetraiodide, iodine and oxygen. The chemical equation postulated is as follows:

$$aUI_4+bO_2 \rightarrow cU_xI_yO_z \begin{array}{l} \nearrow dUI_4+eI_2+fO_2 \\ \searrow gUI_3+hI_2+iI_2 \end{array} \tag{1}$$

2) A metastable compound, produced similarly, disproportionates to uranium triiodide, uranium tetraiodide, uranium oxide and iodine:

$$aUI_4+bO_2 \rightarrow cU_xI_yO_z \begin{array}{l} \nearrow dUI_4+eU_3O_8+fI_2 \\ \searrow gUI_3+hU_3O_8+iI_2 \end{array} \tag{2}$$

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

8) M. M. Popov and M. D. Senin, *Zh. Neorgan. Khim.*, 2, 1479 (1957).

9) S. Yajima, K. Shiba and M. Handa, unpublished work.

3) In the first step of a third mechanism, oxygen reacts with uranium tetraiodide, producing elementary iodine and uranium oxide. Then this iodine reacts with uranium tetraiodide, present nearby, and the addition compound which is produced moves toward lower temperatures, decomposing to uranium triiodide, uranium tetraiodide and iodine:

$$3UI_4+4O_2 \rightarrow U_3O_8+6I_2 \qquad (3)$$

$$aUI_4+bI_2 \rightarrow cUI_{4+x} \begin{array}{l} \nearrow dUI_4+eI_2 \\ \searrow fUI_3+gI_2 \end{array} \qquad (4)$$

The first mechanism appears unreasonable in explaining the phenomenon because of the reported heats of formation for uranium iodides and uranium oxides:⁷⁾

$$U(\text{solid})+3/2I_2(\text{gas})=UI_3(\text{solid}) \qquad (5)$$

$$\varDelta H_{298^\circ K}=-136.9\pm0.6 \text{ kcal. per mol.}$$

$$U(\text{solid})+2I_2(\text{gas})=UI_4(\text{solid}) \qquad (6)$$

$$\varDelta H_{298^\circ K}=-156.6\pm0.6 \text{ kcal. per mol.}$$

$$U(\text{solid})+O_2(\text{gas})=UO_2(\text{solid}) \qquad (7)$$

$$\varDelta H_{298^\circ K}=-256.6 \text{ kcal. per g. of U}$$

$$U(\text{solid})+4/3O_2(\text{gas})=1/3U_3O_8(\text{solid}) \qquad (8)$$

$$\varDelta H_{298^\circ K}=-281.7 \text{ kcal. per g. of U}$$

The heats of formation for uranium oxides are much greater than those for uranium iodides. In other words, the binding energy of uranium with oxygen is much greater than that with iodine. Therefore, the postulated metastable compound, $U_xI_yO_z$, which decomposes to uranium iodides, iodine and oxygen, cannot be considered seriously.

In view of the heats of formation mentioned above, it seems that the disproportionation reaction of the metastable compound is probable, as has been suggested in the second mechanism. The binding energy of uranium with oxygen is much greater than that with iodine. Uranium oxide is isolated first, from the metastable compound; the chemical bond between uranium and iodine is left as it is, and the excess iodine is released as elementary iodine. Since the uranium oxide is isolated as a compound with a high melting point, it cannot move in the thermochromato-tube once it separates from the metastable compound. Consequently, uranium oxide must deposit near the uranium iodide if the intermediate is present and moves toward lower temperatures. However, uranium oxide could not be found at any positions of the thermochromato-tube except where the sample had been packed. Therefore, it is not reasonable to assume this mechanism for the phenomenon mentioned above.

Two kinds of experiments were carried out in attempting to confirm the third mechanism. In one experiment, an amount of elementary iodine equal to that produced when a sample is completely oxidized was sealed in a silica breakable in a similar manner. The silica breakable containing this elementary iodine was placed on a sample in the thermochromato-tube, the temperature there being about 60°C. The helium carrier gas was purified and the thermochromato-furnace was heated to produce a linear temperature gradient from 600°C to room-temperature. Both of the silica breakables were broken, and then the sample heating furnace was started. The temperature was maintained for 2 hr. after it reached 600°C. The iodine sublimate passed through the sample, flowing down the tube. Iodine from the tube was trapped in a liquid nitrogen-cooled trap. Then the reactions of iodine with uranium tetraiodide and triiodide were examined. The results obtained for the reactions were the same as those obtained for the oxygen-helium mixed carrier gas; that is, uranium triiodide deposited at 400°C and uranium tetraiodide at 300 and 200°C. The amount of uranium tetraiodide deposited at 200°C was very small. From these facts, it may be considered that the uranium tetraiodide deposited at 200°C is formed by the action of iodine on the uranium iodides already deposited at 400 and 300°C, through the mechanism by which uranium iodides move and deposit at 400 and 300°C.

In the second experiment, stoichiometric amounts of iodine, required to produce uranium hexaiodide (UI_6) and uranium decaiodide (UI_{10}), were mixed with uranium tetraiodide in a helium gas atmosphere; these mixtures were sealed in silica vessels after the helium gas had been evacuated. Then the silica vessels were heated for 10 hr. at 600 to 700°C. After the vessels, had been cooled, the substances obtained were taken out, weighed, and placed in silica breakables. These materials were unstable compounds, releasing iodine vapor even when they were taken out in a helium gas atmosphere.

The experimental results obtained for both the samples with a purified helium carrier were the same as those obtained when iodine was placed on the uranium tetraiodide.

The results in the first experiment indicate that there exists a compound, UI_{4+x}, with a much lower melting point than that of uranium tetraiodide. In the second experiment, because the materials release iodine in the helium gas atmosphere, they exist only under a certain iodine vapor pressure. The results obtained for the uranium hexaiodide and uranium decaiodide show that these compounds decompose to uranium triiodide, uranium tetraiodide and iodine in an inert gas atmosphere.

From the foregoing experiments and discussions, it seems reasonable to conclude that the phenomenon in which uranium triiodide and uranium tetraiodide move toward temperatures lower than their melting points and deposit there takes place via the formation of an iodine addition compound of uranium tetraiodide.

Foster and Tvrzicky have reported that, when uranium tetraiodide is left in air, uranyl iodide (UO_2I_2) and uranous oxyiodide (UOI_2) are produced.[6] However, the results of the present studies on the oxidation of uranium tetraiodide have shown that such compounds are too unstable to be produced by the direct oxidation of uranium tetraiodide.

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