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# Kinetic Studies of the Oxidation of Uranium Iodides by Oxygen

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The kinetics of the oxidations of uranium tetraiodide and of triiodide by oxygen were studied over the temperature ranges from 55.0 to 66.5°C and from 88.5 to 103.5°C respectively. The experiments were carried out with an apparatus in which the column of a gas chromatograph was replaced by an electric furance and traps of water vapor, oxygen and iodine. Most of the experiments were performed with the same partial pressure of oxygen (64 mmHg) and total flow rate (60 ml. per min.). The activation energies for the reaction of oxygen with uranium tetraiodide and triiodide were, respectively, 21.1 and 22.5 kcal. per mole. The rate of the formation of uranium trioxide was in agreement with the kinetics to be expected for reaction between a gas and a solid at a continuously diminishing spherical interface.

A study of the rates of reaction between uranium iodides and various gases, such as oxygen, hydrogen, and water vapor, provides information about the chemical behavior of fission iodine in a reactor fuel.[1-3] Before the present study was made, however, no fundamental data on the kinetics of

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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] S. Yajima, K. Shiba and M. Handa, ibid., **38**, 278 (1965).

the reaction were available, since uranium iodides are very unstable and must be handled in an inert gas atmosphere or in vacuo.[4]

The present work was therefore undertaken in an attempt to elucidate the kinetics and, if possible, the mechanism of the oxidation of uranium iodides by oxygen. The experiment was carried out with an apparatus in which the column of a gas chromatograph was replaced by an electric furnace and traps of water vapor, oxygen and iodine. This apparatus made it possible to carry out easily and precisely kinetic studies of a sample which could not be treated in the atmosphere.

From the X-ray analysis of the oxidation products, it was found that the reactions between uranium iodides and oxygen proceeded according to the following chemical equations:[5]

$$2UI_4 + 3O_2 = 2UO_3 + 4I_2 \qquad (1)$$

$$2UI_3 + 3O_2 = 2UO_3 + 3I_2 \qquad (2)$$

(The reaction temperature was below 200°C.)

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

$$6UI_3 + 8O_2 = 2U_3O_8 + 9I_2 \qquad (4)$$

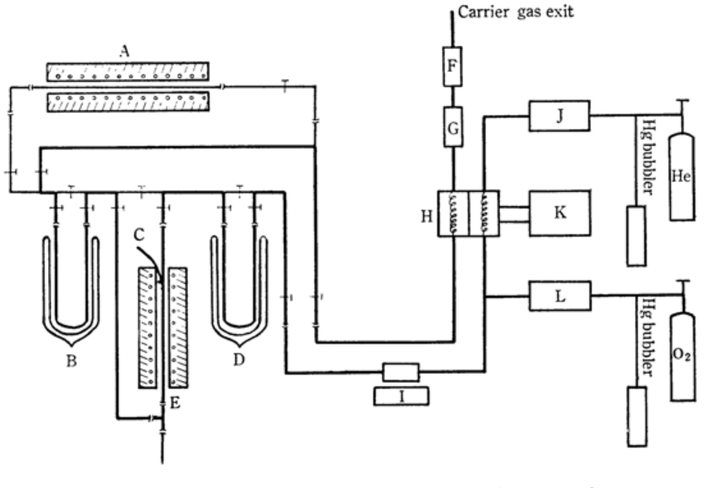
(The reaction temperature was 600°C.)

Reaction 1 occurred with appreciable velocities when the temperature was raised to about 60°C. On the other hand, Reaction 2 proceeded rapidly at about 100°C or above. When uranium iodides were oxidized at 600°C in air, the uranium trioxide produced was decomposed to triuranium octoxide. The chemical reactions are shown in Eqs. 3 and 4. The kinetics of Reaction 1 has been studied over the temperature range from 55.0 to 66.5°C, and that of Reaction 2, over the range from 88.5 to 103.5°C. The rate of the formation of uranium trioxide was in agreement with the kinetics to be expected for a reaction between a gas and a solid at a continuously diminishing spherical interface. The activation energies for Reactions 1 and 2 were 21.1 and 22.5 kcal. per mole respectively.

## Experimental and Results

**The Preparation of the Samples.**—*Uranium Tetraiodide Packed in a Silica Breakable.*—Uranium tetraiodide was prepared by the direct combination of uranium metal and iodine, using the method reported by Gregory.[6] The reaction was slow, but the product prepared in this way was pure uranium tetraiodide. The iodine/uranium ratio in the uranium tetraiodide was 4.00±0.02. The melting point of the uranium tetraiodide measured in an inert gas atmosphere was 506°C, a value approximately agreed with the 508°C reported in the literature.[4,7] The uranium tetraiodide was ground into powder of from 200 to 400 mesh with a glass mortar in a glove box filled with purified helium. About 200 mg. of the uranium tetraiodide was packed in a silica breakable in a way similar to that described in a previous paper.[3]

*Uranium Triiodide Packed in a Silica Breakable.*—Uranium triiodide was prepared by heating a stoichiometic mixture of the uranium tetraiodide and uranium metal powder at 750°C for 24 hr. The product was then purified by using a thermochromatograph[3] with pure helium as the carrier. The uranium triiodide deposited on the wall of the thermochromato-tube heated at 700—800°C



A: Oxygen trap (Uranium turnings: 300°C)
B: Iodine trap (−196°C)
C: Sample
D: Water trap (−196°C)
E: Reaction Furnace
F: Silica gel bed
G: Flow meter
H: Thermal conductivity cell
I: Gas mixing pump
J: Helium purifier
K: Recorder
L: Graphite bed

Fig. 1. Flow diagram of apparatus.

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

[5] M. Handa, This Bulletin, submitted.

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

[7] M. M. Popov and M. D. Senin, *Zhur. Neorg. Khim.*, **2**, 1479 (1957).

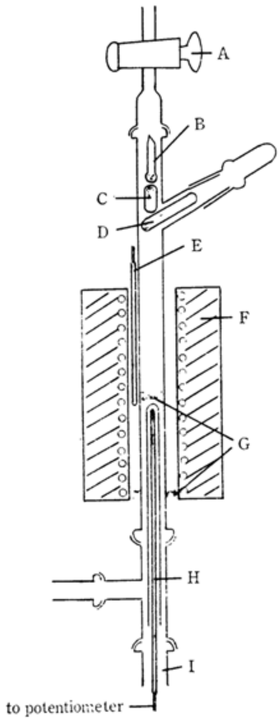
was taken out and transferred into a glove box. The uranium triiodide was then ground into powder of from 200 to 400 mesh and packed in a silica breakable in a way similar to that used for uranium tetraiodide. The iodine/uranium ratio in the uranium triiodide was 3.00±0.02. The melting point measured in an inert gas atmosphere was 788°C, nearly equal to the 780°C reported by other workers.[4,7]

**Apparatus.**—A flow diagram of the experimental apparatus is shown in Fig. 1. The column of a GC-1A Shimadzu-type gas chromatograph was replaced by an assembly of a reaction furnace, a water trap, an iodine trap, and an oxygen trap. Impurities in the helium were eliminated by passing it successively through a potassium hydroxide bed, a magnesium perchlorate bed, a copper gauze heated to 300°C, and uranium turnings heated to 800°C.

Purified helium was first made to flow through a standard thermal conductivity cell, and then oxygen was introduced into the helium stream. The two gases were completely mixed by a glass gas-mixing pump.[8] The water vapor in helium-oxygen gases was further eliminated by passing that gas through a water trap, which had been cooled by a liquid nitrogen at −196°C. After they had passed through the reaction furnace, the gases were introduced into the iodine trap in order to remove the iodine produced by the oxidation of uranium iodides in the reaction furnace. Then the gases were made to flow through a reference thermal conductivity cell, a flow meter, and a silica gel bed, and then released into the atmosphere. The flow rate and the partial pressure of oxygen in the carrier gas were controlled by changing the height of mercury in the bubblers.

The reaction furnace is shown in Fig. 2. A silica breakable containing the sample and a breaker (an iron bar sealed in a silica tube) were suspended in a silica tube in the furnace by a supporter (an iron bar sealed in the silica tube). The temperature of the furnace (a nichrome resistance furnace) was controlled by an S-175-type Chino temperature regulator which was able to maintain the temperature within 0.2% of its full scale and also to heat the sample at the desired rate. The temperature of the sample was measured by a copper-constantan thermocouple connected to a P-31-type Yokogawa potentiometer. A thermocouple to measure the reaction temperature was set beneath the sample in the silica tube.

**The Heating Curves of Uranium Tetraiodide and Triiodide.**—Most of the experiments were performed at the same partial pressure of oxygen (64 mmHg) and total flow rate (60 ml./min.).



A: Glass vacuum cock
B: Sample sealed in a silica breakable
C: Sample breaker
D: Sample supporter
E: Thermocouple (to temperature controller)
F: Reaction furnace
G: Silica wool
H: Thermocouple (copper-constantan)
I: Sealed with electron wax

Fig. 2. Reaction Furnace.

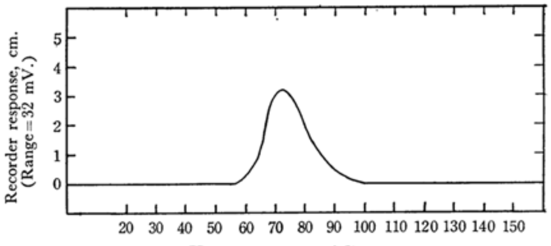


Fig. 3. Heating curve of uranium tetraiodide.
Sample weight: 0.145 g.
Carrier gas flow rate: 60 ml./min.
Partial pressure of oxygen: 64 mmHg
Rate of temperature increase: 2°C/min.

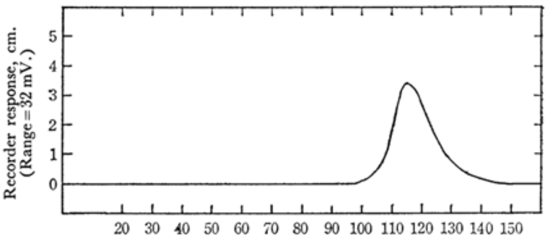


Fig. 4. Heating curve of uranium triiodide.
Sample weight: 0.175 g.
Carrier gas flow rate: 60 ml./min.
Partial pressure of oxygen: 64 mmHg
Rate of temperature increase: 2°C/min.

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[8] M. Handa, Y. Takahashi and K. Shiba, *Bunseki Kagaku (Japan Analyst)*, **13**, 1262 (1964).

When the base line of the recorder became constant, the breakable containing the sample was broken with a magnet and the sample was dropped into the center of the reaction furnace. Then the temperature of the furnace was raised at a constant rate 2°C/min. The heating curves for uranium tetraiodide and triiodide are shown in Figs. 3 and 4 respectively.

**Isotherms for the Oxidation of Uranium Tetraiodide and Triiodide.**—The heating curves of uranium tetraiodide and triiodide have peaks at 75 and 115°C respectively. Consequently, the isotherms for the oxidation of uranium tetraiodide and triiodide were determined in the vicinities of each peak.

The experiments were carried out in a similar way to that used for preparing the heating curves, except that the reaction furnace was kept at the given temperature before the sample was introduced into the furnace. Typical isotherm of uranium tetraiodide at 57.0°C is shown in Fig. 5.

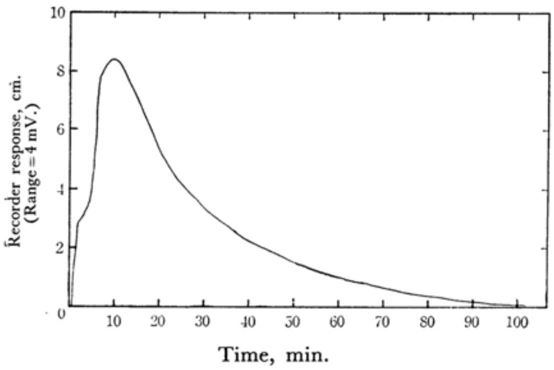

Fig. 5. Rate of oxidation of uranium tetraiodide.
Sample weight: 0.221 g.
Carrier gas flow rate: 60 ml./min.
Partial pressure of oxygen: 64 mmHg
Reaction temperature: 57.0°C

**The X-Ray Analysis of the Oxidation Products.**—A brown-colored material was obtained by isothermal experiments on both uranium tetraiodide and triiodide. The color turned yellow, however, when the material was taken out into the atmosphere. It was not soluble in water. When the brown material was heated in air at 600°C, the color changed from brown to black. The black material was also insoluble in water. An X-ray diffraction analysis indicated the brown material to be uranium trioxide and the black material to be triuranium octoxide.

**The Kinetics of the Reaction.**—A system of a solid and a gas may be idealized by assuming the solid to consist of a spherical particle of a uniform size, with the reaction starting on all particles. In such a reaction the following relationship can be deduced.[9-12]

$$(1 - F)^{1/3} = 1 - k't \tag{5}$$

$$F = (m_0 - m_t)/m_0 \tag{6}$$

where $m_0$ is the initial mass of the particle; $m_t$, the mass of the particle at time $t$, and $k'$, the reaction rate constant. The amount of uranium iodide consumed by oxidation is directly proportional to the amount of oxygen consumed, because the oxidation reaction of uranium iodides proceeds according to Eq. 1 or 2. The amount of oxygen is directly proportional to the area of the recorder chart of the gas chromatograph, and the area is directly proportional to the weight of the piece cut off from the recorder chart. To simplify the calculation of the reaction kinetics, the amount of uranium iodide consumed by oxidation was replaced by the weight of the recorder chart.

All the isotherms reach a peak several minutes after the beginning of the experiment, as the temperature of the sample cannot reach the given temperature immediately after the sample is introduced in the furnace. Therefore, the data obtained before the peak of isothermal curve was reached has been omitted in the calculation of the reaction rate.

The plots of $(1—F)^{1/3}$ against the reaction time for uranium tetraiodide and triiodide are shown in Figs. 6 and 7 respectiveley. The experimental points lie on a straight line for each temperature, which is in agreement with Eq. 5, so that the reactions between uranium iodides and oxygen

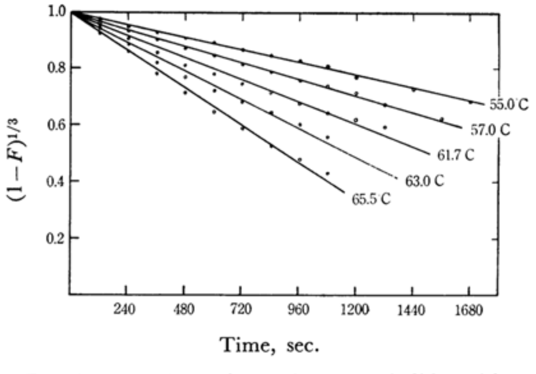

Fig. 6. Reaction of uranium tetraiodide with oxygen $(1-F)^{1/3}$ against time at various temperatures.
Sample weight: 0.223 g. (55.0°C), 0.221 g. (57.0°C), 0.194 g. (61.7°C), 0.143 g. (63.0°C), 0.171 g. (66.5°C)
Carrier gas flow rate: 60 ml./min.
Partial pressure of oxygen: 64 mmHg

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9) V. Y. Labaton and K. D. B. Johnson, *J. Inorg. Nucl. Chem.*, **10**, 74 (1959).

10) C. E. Johnson and J. Fisher, *J. Phys. Chem.*, **65**, 1849 (1961).

11) R. L. Farrar, Jr., and H. A. Smith, ibid., **59**, 763 (1955).

12) J. S. Anderson, *Bull. Soc. Chim.*, **20**, 781 (1953)

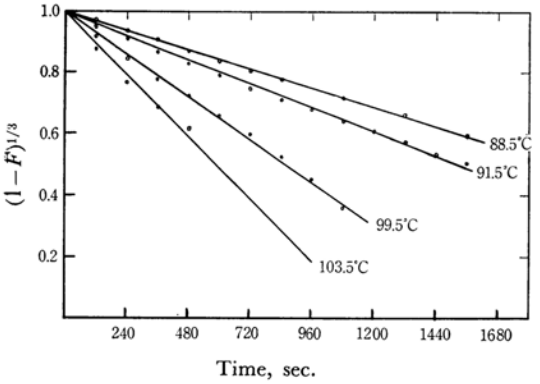

Fig. 7. Reaction of uranium triiodide with oxygen $(1-F)^{1/3}$ against time at various temperatures.
Sample weight: 0.131 g. (88.5°C), 0.098 g. (91.5°C), 0.064 g. (99.5°C), 0.094 g. (103.5°C)
Carrier gas flow rate: 60 ml./min.
Partial pressure of oxygen: 64 mmHg

are governed by the linear law given by Anderson for a gas-solid reaction.[12)]

**The Effect of Oxygen Concentration.**—Most of the runs were carried out with the same partial pressure of oxygen (64 mmHg) and total flow rate (60 ml./min.). In several runs, however, the partial pressure of oxygen was varied, the total flow rate of the carrier gas being kept approximately constant. Table I summarizes the effect of a variation in the partial pressure of oxygen. There is an approximately linear relationship between the reaction rate and the partial pressure of oxygen, as in the case of the fluorination of uranium tetrafluoride with fluorine.[9)]

TABLE I. THE EFFECT OF OXYGEN CONCENTRATION ON THE RATE CONSTANT AT 61.5°C FOR URANIUM TETRAIODIDE

| Oxygen concn. in carrier gas % | Partial pres. ($P_{O_2}$) of oxygen mmHg | $k'$ sec$^{-1}$ | $k' \times 10^6/P_{O_2}$ |
|---|---|---|---|
| 8.50 | 64 | $3.20\times10^{-4}$ | 5.00 |
| 5.74 | 41 | $2.32\times10^{-4}$ | 5.66 |
| 4.50 | 34 | $1.80\times10^{-4}$ | 5.30 |

**The Energy of Activation.**—The reaction rate constant, $k'$, was calculated from the slope in Figs. 6 and 7. The logarithm of the reaction rate constant, $k'$, is plotted against the reciprocal of the absolute temperature, which is shown in Fig. 8. The slopes of the straight line in Fig. 8 are $-4.6\times10^3$ and $-4.9\times10^3$ for uranium tetraiodide and triiodide respectively, from which values the activation energies for their reactions with oxygen were estimated to be 21.1 and 22.5 kcal. per mole.

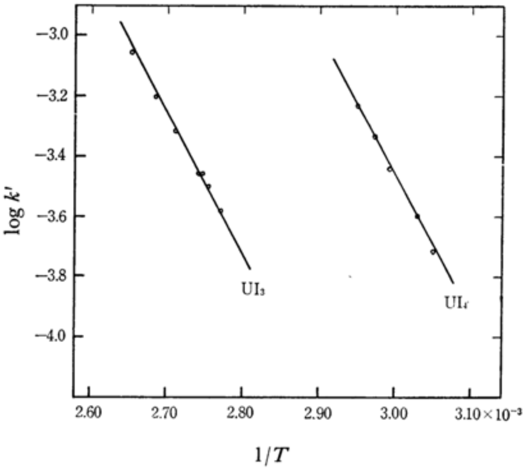

Fig. 8. Arrhenius plot for uranium tetraiodide and triiodide.

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