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Solidification of Iodide Ion by Reaction with Bi_2O_3

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α-Bi_2O_3 is a candidate material for the immobilization of radioactive iodine. The present paper discusses a method for removing radioactive iodide ion by fixing it into α-Bi_5IO_7 by a direct reaction with α-Bi_2O_3; it also reports on experimental conditions under which aqueous iodide reacts with α-Bi_2O_3 to form a single phase of α-Bi_5IO_7. α-Bi_2O_3 was reacted with aqueous iodide in LiI, NaI, KI, and NH_4I solutions. Although a previous paper reported that the concentration of aqueous iodide ion was the most important factor to form a single phase of α-Bi_5IO_7, the present result shows that it is not an important factor. The α-Bi_5IO_7 single phase can be obtained regardless of the concentration of iodide ion when the ratio of the gram molecular number of the bismuth oxide and the gram ion number of the radioactive iodide ion is adjusted in the range 5 : 2 to 1 : 2 in a LiI solution, 4 : 1 to 1 : 2 in a NaI solution, and 4 : 1 to 1 : 4 in a KI solution. A reaction in a NH_4I solution does not produce a single phase of Bi_5IO_7 at any ratio.

Bi_2O_3 (α-Bi_2O_3) is a candidate material for the immobilization of radioactive iodine, such as iodine-129, which has a very long half-life of 16 million years. Bi_2O_3 reacts with iodine to form bismuth iodide oxides. Until now, five kinds of bismuth iodide oxides have been reported. The phase diagram of a Bi_2O_3–BiI_3 system was studied by Klemakov et al.,[1] in which three phases, (BiIO, $Bi_7I_3O_9$, and Bi_5IO_7 (α-Bi_5IO_7)) were reported. After this, Krämer found an additional compound, $Bi_4I_2O_5$.[2] Moreover, in addition to these compounds, a polymorph of Bi_5IO_7 (called "β-Bi_5IO_7") was reported by Ketterer et al.;[3] it has not yet been confirmed by other researchers.

From the viewpoint of the immobilization of radioactive iodide, Bi_5IO_7 is the most promising compound among these bismuth iodide oxides, since it is the most stable at high temperature,[2,4,5] and it is seven orders of magnitude more stable than BiIO and fourteen orders of magnitude more stable than BiI_3 toward hydrolysis.[6]

Many methods for preparing Bi_5IO_7 have been reported: The chemical reaction of Bi_2O_3 and BiI_3 at high temperature;[1,7] the thermal decomposition of BiIO or BiI_3;[2,4] the hydrolysis of BiI_3 or BiIO using KOH solution;[3] and the direct reaction of Bi_2O_3 with aqueous iodide in solution.[5,8]

The last one, reported by Tayler et al.,[8] is the most appropriate for adaptation to the immobilization of radioactive iodine from an aqueous solution. The reaction can be represented as

$$5Bi_2O_3 + 2I^- + H_2O \longrightarrow 2Bi_5IO_7 + 2OH^-.$$

They studied the reaction of Bi_2O_3 with aqueous iodide at various concentrations in a NaI solution, finding that only at low iodide concentration ($<5\times10^{-2}$ mol dm^{-3}), was Bi_5IO_7 formed as the sole product. At high iodide concentration ($\geqq 5\times10^{-2}$ mol dm^{-3}), products other than Bi_5IO_7 (such as $Bi_4I_2O_5$ or $Bi_7I_3O_9$) are formed.

In the present study, the reaction of Bi_2O_3 with aqueous iodide was studied in NaI solution, yielding a new result. Moreover, a similar reaction was also studied in LiI, KI, and NH_4I solutions. On the basis of these experimental results, a new condition is proposed to form Bi_5IO_7 as the sole product.

Experimental

Tayler et al.[8] reported that there is a big variation in both the rate and extent of the reactions with Bi_2O_3 from different sources. This was again confirmed in the present experiments with the Bi_2O_3 samples supplied by four different sources. Although two of them showed good reactivity, another two showed poor reactivity. The former were supplied from two sources, Iwaki Seiyaku and Johnson & Matthey. Their purities were 2N and 5N. Bi_2O_3 supplied from Iwaki Seiyaku was usually used in the present study.

The reaction of Bi_2O_3 powder with aqueous iodide was carried out without any agitation in a plastic test tube stopped tightly with a lid, and placed in a thermostatic container. The airtightness of the test tube was confirmed by measuring its weight both before and after the reaction.

The reaction products were identified by their powder X-ray diffraction patterns. The iodide ion concentration was determined by ion chromatography, using DIONEX 4500i. A scanning electron micrograph was obtained using an Akasi-130 microscope.

Results and Discussion

Extent of Reaction: The extent of the reaction of Bi_2O_3 with aqueous iodide was examined as a function of time. The experimental conditions were as follows: Temperature, 50 °C; weight of Bi_2O_3, 233 mg; concentration of NaI solution, 0.2 mol dm^{-3}; and volume of NaI solution, 1000 µl. The results are given in Fig. 1. Curves 1 and 2 are the results with Bi_2O_3 supplied by Iwaki Seiyaku and by Johnson & Matthey, respectively. There is little difference between them, suggesting that those have the same reactivity to aqueous iodide. The reaction came to completion within almost 48 h; more than 95% of the iodide ion was removed as a solid. Bi_5IO_7 was the sole product in all reactions given in Fig. 1.

A similar experiment was carried out under different

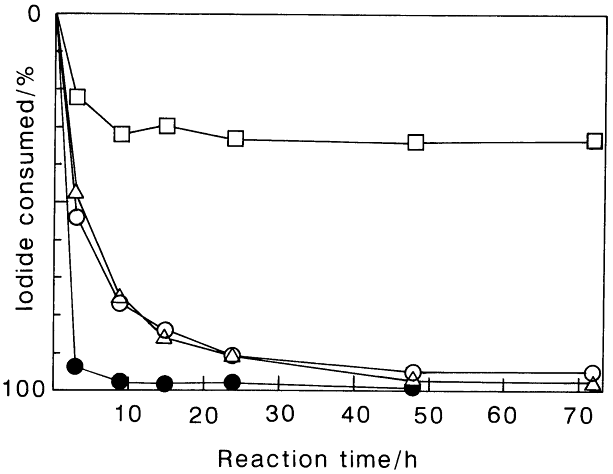

Fig. 1. Extent of reaction, iodide consumed vs. reaction time. (temperature: 50°C; weight of Bi_2O_3: 233 mg) ○: curve 1 (Iwaki Seiyaku Bi_2O_3 in 0.2 mol dm^{-3} NaI solution, volume of NaI solution: 1000 μl), △: curve 2 (Johnson & Matthey Bi_2O_3 in 0.2 mol dm^{-3} NaI solution, volume of NaI solution: 1000 μl), ●: curve 3 (Iwaki Seiyaku Bi_2O_3 in 0.8 mol dm^{-3} NaI solution, volume of NaI solution: 250 μl), □: curve 4 (Iwaki Seiyaku Bi_2O_3 in 0.2 mol dm^{-3}. NH_4I solution, volume of NH_4 I solution: 1000 μl).

conditions, as follows: Concentration of NaI solution, 0.8 mol dm^{-3}; volume of NaI solution, 250 μl. These new conditions were established while keeping a ratio of Bi_2O_3 and iodide ion at the same value, as in the first two experiments. All of the other experimental conditions were the same as described above. The experimental result is expressed as curve 3 in Fig. 1. In this case, the reaction ended within 9 h; this reaction time became shorter than in a 0.2 mol dm^{-3} NaI solution. Aqueous iodide of more than 99% was removed and Bi_5IO_7 was the sole product in all reactions.

Similar experiments at the same two concentrations were curried out for KI solutions; the results were almost the same as in NaI solutions.

It is concluded from these experimental results, that when Bi_2O_3 reacts with various concentrations of aqueous iodide without changing a ratio of the gram molecular number of Bi_2O_3 and the gram ion number of iodide ion, the reaction proceeds faster and more iodide ion is solidified, along with an increase in the concentration of iodide ion, that is, a decrease in the solution volume.

The extent of the reaction of Bi_2O_3 with aqueous iodide was also examined in NH_4I solutions as a function of time. The experimental conditions were the same as for curve 1 in Fig. 1. The results are given as curve 4 in Fig. 1, which shows very low reactivity compared with another curves. The reason is discussed in the following section.

Reaction at Various Concentrations: The reaction of Bi_2O_3 with iodide ion was studied at various concentrations between 0.05 and 4 mol dm^{-3} in LiI, NaI, KI, and NH_4I solutions.

Table 1. Reaction of Bi_2O_3 in NaI Solution

Concentration mol dm^{-3}	Ratio[a)]	Reaction product
0.05	10:1	Bi_5IO_7+n.i.p.[b)]
0.1	5:1	Bi_5IO_7+n.i.p.
0.2	5:2	Bi_5IO_7
0.5	1:1	Bi_5IO_7
1.0	1:2	Bi_5IO_7
2.0	1:4	$Bi_5IO_7+Bi_4I_2O_5$
3.0	1:6	$Bi_5IO_7+Bi_4I_2O_5$
4.0	1:8	$Bi_5IO_7+Bi_4I_2O_5$

a) Ratio of gram molecule (ion) number of Bi_2O_3 and I^-.
b) Not identified peaks.

Table 2. Reaction of Bi_2O_3 in NaI Solution

Concentration mol dm^{-3}	Ratio[a)]	Reaction product
0.2	10:1	Bi_5IO_7+n.i.p.[b)]
0.5	4:1	Bi_5IO_7
0.8	5:2	Bi_5IO_7
1.0	2:1	Bi_5IO_7
2.0	1:1	Bi_5IO_7
3.0	2:3	Bi_5IO_7
4.0	1:2	Bi_5IO_7

a) Ratio of gram molecule (ion) number of Bi_2O_3 and I^-.
b) Not identified peaks.

Table 1 shows the experimental results obtained in NaI solutions. The experimental conditions were as follows: Temperature, 50°C; weight of Bi_2O_3 sample, 233 mg; volume of NaI solution, 1000 μl; and reaction time, 96 h.

Table 2 shows another result also obtained in NaI solutions under different conditions. Here, the volume of the solution was not 1000 μl, but 250 μl. All of the other experimental conditions were the same as those in Table 1.

These results are not consist with the results obtained by Taylar et al.[8)] According to their method, when the iodide ion concentration in NaI solution exceeds 5× 10^{-2} mol dm^{-3}, other compounds than Bi_5IO_7 are formed; the iodide ion concentration must therefore be maintained below the above-mentioned value. On the contrary, as shown in Tables 1 and 2, Bi_5IO_7 can be formed as the sole product at iodide ion concentrations exceeding 5×10^{-2} mol dm^{-3}. The iodide ion concentration is thus not the most suitable factor in controlling the phases formed in NaI solutions. Instead of the concentration, the ratio of the gram molecular number of Bi_2O_3 and the gram ion number of iodide ion is important in forming Bi_5IO_7 as the sole product. As shown in Tables 1 and 2, in the range from 4 : 1 to 1 : 2 Bi_5IO_7 was formed as the sole product, independent of the concentration.

Reactions in KI solutions were also observed at various concentrations. The results are given in Tables

Table 3. Reaction of Bi_2O_3 in KI Solution

Concentration mol dm^{-3}	Ratio[a)]	Reaction product
0.05	10:1	Bi_5IO_7+n.i.p.[b)]
0.1	5:1	Bi_5IO_7+n.i.p.
0.2	5:2	Bi_5IO_7
0.5	1:1	Bi_5IO_7
1.0	1:2	Bi_5IO_7
2.0	1:4	Bi_5IO_7
3.0	1:6	$Bi_5IO_7+Bi_4I_2O_5$
4.0	1:8	$Bi_5IO_7+Bi_4I_2O_5$

a) Ratio of gram molecule (ion) number of Bi_2O_3 and I^-.
b) Not identified peaks.

Table 4. Reaction of Bi_2O_3 in KI Solution

Concentration mol dm^{-3}	Ratio[a)]	Reaction product
0.2	10:1	Bi_5IO_7+n.i.p.[b)]
0.5	4:1	Bi_5IO_7
0.8	5:2	Bi_5IO_7
1.0	2:1	Bi_5IO_7
2.0	1:1	Bi_5IO_7
3.0	2:3	Bi_5IO_7
4.0	1:2	Bi_5IO_7

a) Ratio of gram molecule (ion) number of Bi_2O_3 and I^-.
b) Not identified peaks.

Table 5. Reaction of Bi_2O_3 in LiI Solution

Concentration mol dm^{-3}	Ratio[a)]	Reaction product
0.05	10:1	Bi_5IO_7+n.i.p.[b)]
0.1	5:1	Bi_5IO_7+n.i.p.
0.2	5:2	Bi_5IO_7
1.0	1:2	Bi_5IO_7
2.0	1:4	$Bi_5IO_7+Bi_4I_2O_5$

a) Ratio of gram molecule (ion) number of Bi_2O_3 and I^-.
b) Not identified peaks.

Table 6. Reaction of Bi_2O_3 in NH_4I Solution

Concentration mol dm^{-3}	Ratio[a)]	Reaction product
0.05	10:1	Bi_5IO_7+n.i.p.[b)]
0.1	5:1	Bi_5IO_7+n.i.p.
0.2	5:2	$Bi_5IO_7+Bi_4I_2O_5$
0.5	1:1	$Bi_4I_2O_5$+BiIO
1.0	1:2	$Bi_4I_2O_5$+BiIO
2.0	1:4	$Bi_4I_2O_5$+BiIO
3.0	1:6	$Bi_4I_2O_5$+BiIO

a) Ratio of gram molecule (ion) number of Bi_2O_3 and I^-.
b) Not identified peaks.

3 and 4. The experimental conditions regarding Tables 3 and 4 were the same as those for Tables 1 and 2, respectively. These results show that the Bi_5IO_7 single phase can be obtained when the ratio of the gram molecular number of the bismuth oxide and the gram ion number of the iodide ion is adjusted so as to range from 5 : 2 to 1 : 4.

Table 5 shows the results of the reactions in LiI solutions. The experimental conditions are same as of those of Table 1. In this case, over the range of the mole ratios from 5 : 1 to 1 : 2 the Bi_5IO_7 single phase could be obtained.

Reactions in NH_4I solutions showed different results from those of solutions. Over any range of ratios iodide ion in NH_4I could not produce pure Bi_5IO_7, and the products contained unknown phases or $Bi_4I_2O_5$ or BiIO (Table 6).

The results obtained concerning reactions in LiI, NaI, and KI solutions lead to the conclusion that the concentration of aqueous iodide is not the most important factor to produce a single phase of Bi_5IO_7; rather, the ratio of gram molecular number of Bi_2O_3 and the gram ion number of the iodide ion is the dominant factor in the formation of products. This can be explained as follows:

As described in the previous section, the preparation of Bi_5IO_7 is represented by

$$5Bi_2O_3 + 2I^- + H_2O \longrightarrow 2Bi_5IO_7 + 2OH^-. \qquad (1)$$

When this reaction begins to proceed, the formation of Bi_5IO_7 also begins. During an early step, formed Bi_5IO_7 coexists with free (not reacted) iodide ions. When the concentration of the free iodide ions is greater than some value a new phase begins to form according to the following equations:

$$4Bi_5IO_7 + 6I^- + 3H_2O \longrightarrow 5Bi_4I_2O_5 + 6OH^-$$

or

$$7Bi_5IO_7 + 8I^- + 4H_2O \longrightarrow 5Bi_7I_3O_9 + 8OH^-.$$

The range of the ratio in which Bi_5IO_7 can be present as the sole product is influenced by various factors, such as coexisting cations and anions, temperature, and pH.

In a NH_4I solution, Bi_5IO_7 cannot be present as a stable phase. This is because although Bi_5IO_7 is formed, it soon changes into other phases by reacting with neighboring iodide ions.

Figures 2 and 3 show scanning electron micrographs of Bi_2O_3 samples supplied from Iwaki Seiyaku and Johnson & Matthey, respectively. The former is needle-like; the latter is plate-like. The difference in the shapes did not influence the shape of the Bi_5IO_7 crystals formed. A scanning electron micrograph of the Bi_5IO_7 crystals produced Johnson & Matthey (Bi_2O_3) is shown in Figure 4, and is almost the same as that from Iwaki Seiyaku. Since these crystals are needle-like, it would not be difficult for the surface of a Bi_2O_3 crystal to maintain contact with iodide ions through the openings in them, although the needle-like crystals cover the surface gradually with proceeding of the reaction.

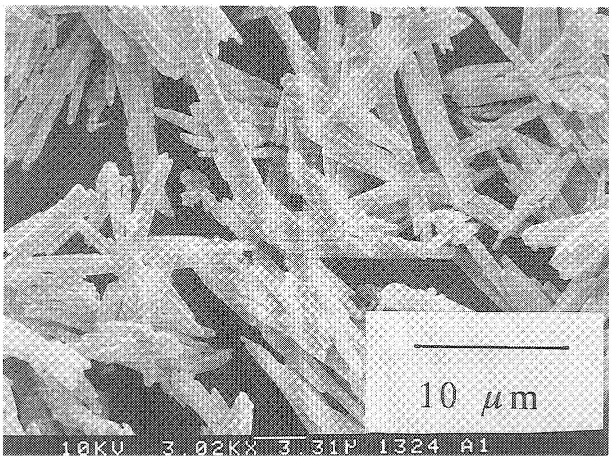

Fig. 2. Scanning Electron Micrograph of Iwaki Seiyaku Bi_2O_3.

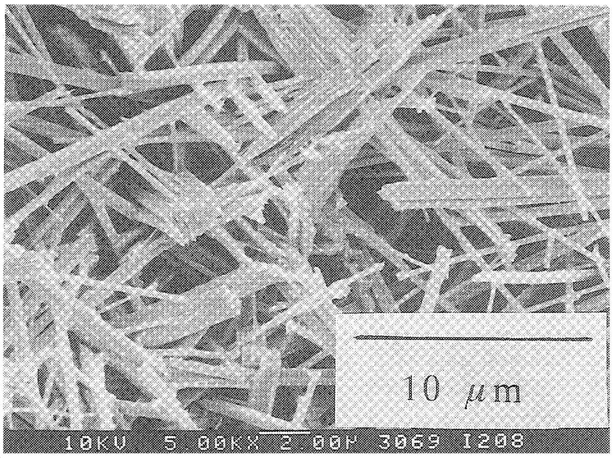

Fig. 4. Scanning Electron Micrograph of Bi_5IO_7 grown from Johonson & Matthey Bi_2O_3 in a NaI solution.

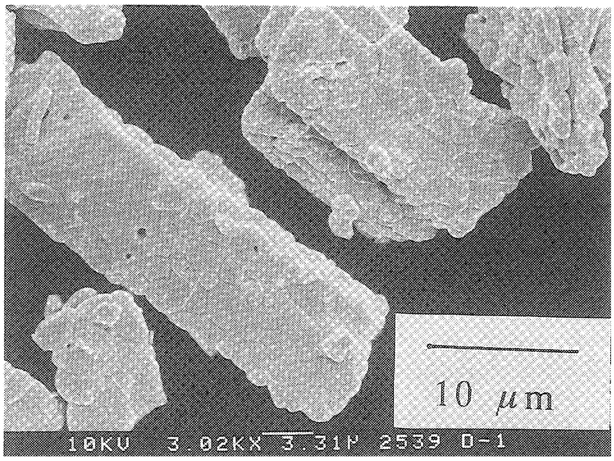

Fig. 3. Scanning Electron Micrograph of Johonson & Matthey Bi_2O_3.

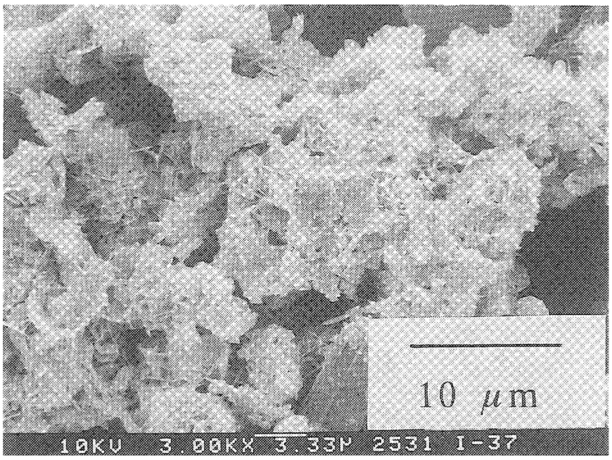

Fig. 5. Scanning Electron Micrograph of $Bi_4I_2O_5$ grown in a NaI solution.

Figure 5 shows a scanning electron micrograph of $Bi_4I_2O_5$ crystals, fine platelets; if they densly cover the surface of the Bi_2O_3 crystal during an early step of the reaction, the free surface of Bi_2O_3 becomes smaller and the rate and extent of the reaction become low. This is the reason why Bi_2O_3 shows such a low extent of reaction in NH_4I solutions.

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