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THE PREPARATION OF PLUTONIUM TRIBROMIDE

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ABSTRACT

A brief description is given of the following methods for preparing plutonium tribromide, together with experimental results:

(1) Hydrobromination of plutonium dioxide,

(2) Hydrobromination of plutonium trichloride,

(3) Hydrobromination of plutonium (III) oxalate.

The latter method appears to offer advantages of relative rapidity and purity of product. Some of the chemical and physical properties of the tribromide are described.

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THE PREPARATION OF PLUTONIUM TRIBROMIDE

The use of plutonium halides in the production of the metal on a large scale has appeared for some time the best approach to that problem, considerable attention having been devoted by the metallurgists to the reduction of plutonium trifluoride and tetrafluoride and, particularly, of plutonium trichloride. As part of this program some efforts have been made to find a simple and quick method for the preparation of plutonium tribromide from material which has been through a purification process. At the time of this writing the research on the tribromide has not been as extensive as that on the trichloride (see LA-112) and the interest of the metallurgists in the tribromide has practically vanished. This report summarizes the results obtained at Los Alamos on attempted preparations of the tribromide.

Since the purification scheme in use at the time (LA-75) gave highly purified plutonium in the form of $PuO_2(NO_3)_2$ solution which could be evaporated and ignited to pure PuO_2 the earliest efforts were made toward the treatment of such PuO_2 with anhydrous hydrogen bromide. The results of these experiments are given in Table 1. In general, the reaction was carried out at a sufficiently high temperature to cause the tribromide (probably containing some oxide or oxybromide) to melt, which resulted in some sublimation of the tribromide. On a scale of 100 mg or less the procedure appeared to give reasonable yields. However, on a 500-mg scale the reaction was very much slower, particularly with PuO_2 ignited to 1000° C, an observation which was also made in the case of the similar preparation of trichloride. It has been

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shown, however, that regulation of the heating cycle and rate of gas flow may shorten materially the time required for the conversion. It is probable that this method could be made to work satisfactorily on a 200-gram scale if this ever becomes necessary.

As a matter of academic interest chiefly, one sample of $PuBr_3$ was made by the action of dry HBr on $PuCl_3$ (see Table 2). Although the conversion was not quantitative it could probably be made so. Since the other methods of preparation are less time-consuming as a whole this method was not investigated further.

When it was found that $PuCl_3$ could be made quickly from $Pu_2(C_2O_4)_3$ by treatment with dry HCl (see LA-112) the analogous reaction of the oxalate with dry HBr was tried. The results (Table 3) indicated rapid and complete reaction on a 100-mg scale, and it appears that the product prepared by this method is in a higher state of purity than is the case for product obtained by the other methods. An opportunity to test this process on a larger scale has not been forthcoming, but it is believed that this process would be readily adaptable to the 200-gram scale of operations. Use of the oxalate as a starting material also fits in with the present purification scheme.

The preparations tabulated have been carried out in platinum containers placed in an electrically-heated quartz tube through which anhydrous hydrogen bromide could be passed. The latter gas was prepared by direct union of hydrogen (purified by passage over hot uranium) and bromine passed over a hot platinum wire, the hydrogen being in slight excess. The HBr was dried by passage over P_2O_5 or $Mg(ClO_4)_2$, some care being necessary to prevent the

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formation of phosphorus bromides which react with the platinum containers. The yields were followed by careful weighings, and occasional X-ray analyses and bromine analyses were carried out by Groups C-8 and C-9. The small amount of sublimation was corrected for by radioactive analysis (Mrs. Maxwell and co-workers).

No serious attempts have been made to sublime the tribromide, but during most of the runs there was some sublimation. Sublimation of the tribromide in high vacuum can certainly be carried out as simply as in the case of the trichloride.

As prepared in this laboratory, plutonium tribromide is a light green crystalline solid, melting at 685 ± 15° C, and volatilizing appreciably from the molten state. It is hydroscopic, hydrating slowly in air (R.H. = 30-40%) to form $PuBr_3 \cdot 6\,H_2O$. Treatment of the hydrate in a stream of dry HBr at about 225° returns the material to its original anhydrous condition. The salt is readily soluble in water. Heating the tribromide in oxygen at 100° readily converts it to dioxide, the same result being found on heating in air to a higher temperature. Attempts to prepare a higher bromide by reaction of the tribromide with Br_2 have been unsuccessful. In a single experiment it has been found that the tribromide can be readily reduced to the metal with calcium.

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Table 1. Preparation of $PuBr_3$ by hydrobromination of PuO_2

Sample No.	Amount of Pu, mg.	Starting Material	Treatment	% Conversion to $PuBr_3$	Remarks
149-18	6	PuO_2 (700°C)	1) Dry HBr, prolonged heating at RT → 550°: incomplete 2) Dry HBr, ~3 hrs. at RT→700°	~99%	Light green color. Turned to light blue powder on exposure to air, giving X-ray pattern similar to complex chloride obtained by H_2 reduction of "$PuCl_4$" (89-45).
149-23	8	PuO_2 (500°)	1) Dry HBr, ~3 hrs. at RT→720°	~99%	Light green, some darker specks. 49.3% Br (theor. for $PuBr_3$ = 50.0% Br).
149-26	15	PuO_2 (1000°)	1) Dry HBr, ~2 hrs. at RT→750°	~98%	Light green. Material was molten at ~720°.
149-32	13	PuO_2 (1000°)	1) Dry HBr, ~4 hrs. at RT→730°	~95%	Ditto
149-36	14	PuO_2 (300°)	1) Dry HBr, ~4 hrs. at RT→760°	~93%	Ditto
149-50	560	PuO_2 (1025°)	1) Dry HBr, over 28 hrs. at 725°	~46%	Returned for recovery. Oxide from the same source gave trouble in the preparation of trichloride.
149-54	550	PuO_2 (350°)	1) Dry HBr, ~54 hrs. at 720°	~97%	Light green. Fair metal yield on reduction with Ca in MgO.
149-64	198	PuO_2 (350°)	1) Dry HBr, ~ 1½ hr. at RT→400° 2) Dry HBr, ~ 1½ hr. at 600°	>97%	Light green. Material not molten.

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Table 2. Preparation of $PuBr_3$ by hydrobromination of $PuCl_3$

Sample No.	Amount of Pu, mg.	Starting Material	Treatment	% Conversion to $PuBr_3$	Remarks
149-35	4	$PuCl_3$ (0.43% O, No. 89-45)	1) Dry HBr, very prolonged heating at ~750°	~80%	Dark material. Starting material probably had appreciable amount of PuOCl in it.

Table 3. Preparation of $PuBr_3$ by hydrobromination of "$Pu_2(C_2O_4)_3\cdot 9H_2O$"

Sample No.	Amount of Pu, mg.	Starting Material	Treatment	% Conversion to $PuBr_3$	Remarks
149-58	105	"$Pu_2(C_2O_4)_3\cdot 9H_2O$"	1) Evap. slurry to dryness in air at ~50° 2) Dry HBr, 2.5 hrs. at RT→450°, 2 hrs. at 570-600°	~100%	Light green. 49.1% Br. X-ray pattern checked Zachariasen's data on $PuBr_3$ made from Pu + pure Br_2; no second phase.
149-66	100	Ditto	1) Ditto 2) Dry HBr, 2 hrs. at 275°: 69% conv. 3) Dry HBr, 1 hr. at 425° : 80% conv. 4) Dry HBr, 1 hr. at 550° : ~ 100% conv.	~100%	Light green.

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