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PREPARATION OF ANHYDROUS PLUTONIUM TRICHLORIDE

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CHEMISTRY--TRANSURANIC ELEMENTS

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CHEMISTRY - TRANSURANIC ELEMENTS

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INTRODUCTION AND SUMMARY

In September 1951, a request was received from ORNL for several batches of anhydrous plutonium trichloride. This compound has been prepared by the reaction of gaseous HCl with plutonium III oxalate(1) and several small batches were made in this manner preparatory to the production of larger lots for ORNL.

At the suggestion of F. N. Case and H. C. McCurdy of ORNL it was decided to investigate the possibility of using hexachloropropene as a chlorinating agent because such a method would be more satisfactory for them to use in the future.

Accordingly, some exploratory tests were made using hexachloropropene with various plutonium compounds as starting material. This led to a method of preparation of anhydrous $PuCl_3$ of 98% purity by heating hexachloropropene with Pu III oxalate at 180 to 190°C for 18 hours.

By this method 628.7 grams of the trichloride were prepared and were sent to ORNL.

EXPERIMENTAL WORK

A number of exploratory runs were made in which hexachloropropene was heated at 185°C for 6 hours with various plutonium compounds. The solids were separated from the organic liquid by filtration on sintered

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(1) C. S. Garner, "The Preparation of Plutonium Trichloride," LA-112 (1944).

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glass and were examined for the extent of conversion to the chloride. Results with various starting materials are discussed below.

Plutonium dioxide - Samples of plutonium dioxide were made by ignition of Pu III oxalate at 600°C for 2 hours. After heating with hexachloropropene the oxide made from oxalate showed no conversion to chloride.

Aqueous plutonium chloride solution - These solutions proved unsatisfactory as starting material because of the lengthy evaporation time required and the hydrolytic formation of oxides which, under the conditions of the experiments, are not chlorinated by hexachloropropene. After the solution had been evaporated to a slurry, extended heating periods ($\sim$48 hours) were required to approach 95% conversion, with the impurities being mostly oxides of plutonium.

Plutonium peroxide - A sample of plutonium peroxide precipitated from a sulfate-free nitrate solution gave only a 10% conversion to $PuCl_3$ after heating with hexachloropropene. The remaining 90% consisted of plutonium oxides.

Plutonium nitrate - Solid plutonium nitrate was obtained by vacuum evaporation of a nitrate solution. Chlorination of this material with hexachloropropene gave a solid containing 70% $PuCl_3$ and 30% Pu III chloro-nitrate. Longer heating periods (18 to 24 hours) did not appreciably increase the $PuCl_3$ yield.

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Aqueous plutonium nitrate solutions - During the evaporation considerable spattering took place. The material that lodged on the side of the flask was converted to the oxide which remained unchanged after 8 hours of heating. The product contained 70% PuO_2 and 30% $PuCl_3$.

Plutonium III oxalate - Plutonium III oxalate was precipitated from a nitrate solution to which HI had been added as reductant. This material gave a product containing 86% plutonium trichloride after heating the oxalate with hexachloropropene for 6 hours. The remaining 14% was a mixture of unchanged oxalate and Pu III chloro-oxalate. Microscopic examination by Eugene Staritzky of CMR-1 showed that these impurities were in the center of the larger $PuCl_3$ crystals and suggested that longer heating periods would possible increase the $PuCl_3$ content of the product.

With heating periods of 18 hours the $PuCl_3$ content of the product was 98%, and the remainder was either unchanged oxalate or organic solids of unknown composition. Heating periods longer than 18 hours did not appreciably increase the percentage of $PuCl_3$.

The molar ratio of hexachloropropene to plutonium was not important except where the ratio was less than 10 to 1, in which case the volume of hexachloropropene was too small to allow efficient mixing of constituents.

Extremely vigorous stirring increased the yield of $PuCl_3$ and, when coupled with longer heating periods, products containing 98% $PuCl_3$ were obtained.

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The highest yields were obtained with liquid temperatures ranging from 180 to 190°C. Below 180°C the per cent conversion was low and above 190°C considerable amounts of organic impurities were formed.

<u>Preparation of four 100-gram batches of $PuCl_3$</u> - The hexachloropropene was added, at room temperature, to the Pu III oxalate in a three neck, 3 liter round bottom flask equipped with magnetic stirrer and reflux condenser. After 18 hours of heating, the solid material was collected in a sintered glass funnel and washed with several portions of anhydrous carbon tetrachloride. The product was dried by pulling moisture-free argon through the filter cake for 3 or 4 hours. Analytical data are given below.

Samples of each lot were examined both by X-ray diffraction and optical microscopy. The $PuCl_3$ content was determined by its solubility in water.

Lot 1:
(Runs 1 and 2)

$PuCl_3$ content 98%
X-ray diffraction - only $PuCl_3$ discernible
Pu found, 226.75 grams; Pu calculated, 227.86 grams
Microscopic examination -
- < 5% impurities
- < 5% of the $PuCl_3$ hydrated
- The impurities -
  - Pu III oxalato-chloride (50%) and
  - unidentified organic solids (50%)

Lot 2:
(Runs 3 and 4)

$PuCl_3$ content 96%
X-ray diffraction - predominantly $PuCl_3$ and a small amount of unidentified material
Pu found, 201.64 grams, Pu calculated, 207.18 grams
Microscopic examination -
- < 5% impurities
- < 5% of the $PuCl_3$ hydrated
- The impurities -
  - Pu III oxalato-chloride (70%) and
  - unidentified organic solids (30%)

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DISCUSSION

The procedure developed consists of heating hexachloropropene with freshly prepared Pu III oxalate for 18 hours at 180 to 190°C with extremely vigorous stirring. This method gave products containing 98% $PuCl_3$. The products may be further purified by sublimation in a stream of dry HCl.

The Pu III oxalate must be used shortly after preparation since it will slowly decompose at room temperature to form PuO_2 which is not chlorinated by hexachloropropene under these conditions. It was noted in this investigation that when the oxalate was allowed to stand for 3 or 4 days before treatment the yield of anhydrous $PuCl_3$ in the product was decreased by as much as 2 or 3%.

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APPENDIX

Materials and Reagents

Carbon tetrachloride: C. P. grade. Used as obtained.

Hexachloropropene: b.p. 209 to 210°C at 760 mm Hg. Usually used as obtained from Columbia Organic Chemicals, Inc., Charleston, S.C. This material contained 95% C_3Cl_6, 5% lesser halogenated chloropropenes. For several preliminary runs the material was purified by vacuum distillation, but no increase in per cent conversion was noted.

Plutonium oxide: Prepared by igniting Pu III oxalate for 2 hours at 600°C.

Plutonium peroxide: Prepared by addition of 30% H_2O_2 to a sulfate-free plutonium nitrate solution.

Plutonium chloride-plutonium oxychloride mixture: Prepared by passing dried gaseous HCl and H_2 over Pu III oxalate for 8 hours at 600°C.

Plutonium nitrate: Prepared by vacuum evaporation of an aqueous nitrate solution. Probable formula: $Pu(OH)(NO_3)_3 \cdot 6\ H_2O$.

Plutonium III oxalate: This material was prepared from a nitrate solution which had been purified by two peroxide precipitations. 47% HI was used to reduce the Pu to Pu III. 0.67M oxalic acid solution was added to precipitate the $Pu_2(C_2O_4)_3 \cdot 6\ H_2O$ which was then collected on a medium sintered glass funnel, washed with three portions of 0.1M oxalic acid, rinsed with two portions of 95% C_2H_5OH, and dried by pulling air through filter cake for 2 or 3 hours.

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