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[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

The Preparation of PuP_2O_7 and $PuPO_4$[1]

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Methods for the preparation of two new plutonium phosphates, $PuPO_4$ and PuP_2O_7, are described. Monoclinic $PuPO_4$ was prepared by the precipitation and high temperature dehydration of hexagonal $PuPO_4 \cdot [0.5H_2O(?)]$ and by the decomposition of a crystalline plutonium(IV) oxalatophosphate which contained a P/Pu atomic ratio of 1/1. Plutonium(IV) oxalatophosphates of variable composition with P/Pu ratios ranging from 1/1 to 2/1 were prepared. Cubic PuP_2O_7 was obtained by the decomposition of the plutonium(IV) oxalatophosphate with a P/Pu ratio of 2/1 and by the decomposition of phosphorus-deficient oxalatophosphates mixed with sufficient solid $NH_4H_2PO_4$ to restore the over-all P/Pu ratio to 2/1. Both compounds, $PuPO_4$ and PuP_2O_7, were characterized by X-ray, microscopic and chemical analyses.

Introduction

Several crystalline plutonium phosphates have been obtained in the course of work done at this Laboratory, but very few compounds of this type have been reported.[2-5] The gelatinous compound usually obtained when phosphoric acid is added to acid solutions of plutonium(IV) has been identified as $Pu(HPO_4)_2 \cdot xH_2O$.[3] Crystalline $Pu_2H(PO_4)_3 \cdot yH_2O$ and $Pu_3(PO_4)_4 \cdot zH_2O$ were obtained[3,4] by heating gelatinous $Pu(HPO_4)_2 \cdot xH_2O$ in the presence of different mother liquors in sealed tubes at 70–110° for periods up to two weeks. Hexagonal $PuPO_4 \cdot [0.5H_2O(?)]$[5] was prepared in a similar manner by starting with a gelatinous plutonium(III) phosphate precipitate. All preparations were made on a micro scale, and, with the exception of $PuPO_4 \cdot [0.5H_2O(?)]$, the identifications were based on chemical analyses.

This paper will be concerned with methods for the preparation of the new compounds, $PuPO_4$ and PuP_2O_7, primarily from plutonium(IV) oxalatophosphates as intermediates, and with the examination of some of the properties of $PuPO_4$ and PuP_2O_7. The designation "plutonium oxalatophosphate" will be used for crystalline precipitates containing plutonium with variable oxalate and phosphate compositions without intending to imply that the preparations necessarily are discrete compounds. Wherever any compositions are expressed as ratios of two or more components, atomic or mole ratios are implied.

Early in this investigation it was found that crystalline plutonium(IV) oxalatophosphates could be precipitated from solutions of plutonium(IV) in 85% orthophosphoric acid. Plutonium(IV) oxalatophosphates of variable composition with P/Pu ratios from 1/1 to 2/1 were prepared. Chemical analyses, optical properties and X-ray diffraction powder patterns were obtained for a series of sixteen precipitates, but identification of specific compounds could not be made from the available data. Although minute single crystals were isolated from several of the precipitates, single crystal X-ray patterns could not be obtained because partial decomposition occurred during the required exposure time. The products obtained by thermal decomposition of members of the series of plutonium(IV) oxalatophosphates were either the pure compounds, $PuPO_4$ and PuP_2O_7, or mixtures of these two compounds, depending upon the ratio of phosphorus to plutonium in the parent material.

Experimental

Materials.—Three stock solutions of plutonium(IV) phosphate in orthophosphoric acid were prepared. The valence state of plutonium in each solution was confirmed by spectrophotometric analysis.

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(1) This work was done under the auspices of the Atomic Energy Commission.

(2) G. T. Seaborg and J. J. Katz, "The Actinide Elements," Nat. Nuclear Energy Ser. IV, 14A, McGraw-Hill Book Co., Inc., New York, N. Y., 1954, pp. 414–417.

(3) E. L. King, Paper 6.01 in "The Transuranium Elements," Nat. Nuclear Energy Ser. IV, 14B, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, pp. 638–664.

(4) C. Smith, ref. 3, paper 6.34, p. 850.

(5) C. Smith, University of Chicago Metallurgical Laboratory Progress Report, CK-1587, May 1, 1944, p. 12.

Solution I.—Freshly precipitated plutonium(IV) peroxide was decomposed by heating for several hours at 150°, and the product was dissolved in 85% phosphoric acid at approximately 75°. The concentration of plutonium after centrifugation was approximately 180 g./l. (0.75 *M*).

Solution II.—Plutonium(IV) dioxalate was dissolved in 85% phosphoric acid by slowly heating to 200°. The loss of water at the elevated temperatures concentrated the solution to approximately 95% phosphoric acid. The concentration of plutonium in solution after centrifugation was 160 g./l. (0.67 *M*).

Solution III.—Plutonium(IV) peroxide, decomposed at 150°, was dissolved in 85% phosphoric acid at 25–30°. The small amount of residue which remained was dissolved in additional 85% phosphoric acid at 120°. The combined solutions, after centrifugation, were diluted with 85% phosphoric acid to adjust the plutonium concentration to approximately 160 g./l. (0.67 *M*). In this solution 20–30% of the plutonium was found to be present as plutonium(VI). Reduction to plutonium(IV) was accomplished electrolytically, using platinum electrodes and a cathode current density of 0.02 amp./cm.^{2}.

Analytical Procedures.—A 30-min. sodium carbonate fusion of plutonium phosphate compounds made possible the quantitative separation of plutonium and phosphorus by extraction with 1 *M* hydrochloric acid. The residue was dried at 400° and weighed as PuO_2. Phosphorus was determined in the filtrate by a double precipitation of $MgNH_4PO_4$ followed by ignition to $Mg_2P_2O_7$.

Oxalate in plutonium(IV) oxalatophosphates was determined separately by the following procedure. Excess standard $Ce(SO_4)_2$ solution was added to a slurry of the sample in 2 *M* sulfuric acid, and the mixture was heated until all of the solid had dissolved. The excess $Ce(SO_4)_2$ in the cooled solution was titrated with standard H_2O_2 solution, using *o*-phenanthroline ferrous sulfate as an indicator. A correction was made for the quantitative oxidation of plutonium(IV) to plutonium(VI) by the $Ce(SO_4)_2$.

Preparation of PuP_2O_7.—Relatively pure PuP_2O_7 was prepared by the thermal decomposition of plutonium(IV) oxalatophosphates with P/Pu ratios ranging in value from 1/1 to 2/1. Prior to decomposition, those samples with ratios less than 2/1 were mixed with sufficient $NH_4H_2PO_4$ to increase the total P/Pu ratio to 2/1. The following two procedures illustrate the limiting cases, *i.e.*, preparation and decomposition of plutonium(IV) oxalatophosphates with P/Pu ratios of 2/1 and 1/1, respectively.

Procedure A.—An aliquot of stock solution I containing 20 g. of plutonium was added slowly, with stirring, to a 0.9 *M* solution of $H_2C_2O_4 \cdot 2H_2O$ in 85% phosphoric acid at 90–100°. The final proportions of all reactant concentrations were $[Pu]/[H_2C_2O_4]/[H_3PO_4] = 1/5/100$. A pink precipitate began to form shortly before the addition of stock solution had been completed. The precipitate was digested at 90–100° for 2.5 hr., with continuous stirring, and for an additional period of 65 hr. at 25–30°, without stirring, before it was centrifuged and transferred to a Pyrex Buchner-type fritted funnel of medium porosity. It was washed successively with 0.1 *M* $H_2C_2O_4$–0.1 *M* H_3PO_4 solution, water and absolute ethanol. The residue was dried in a stream of air at 25–30° for 18 hr. Microscopic examination of a sample revealed tiny, pink, crystalline, rectangular plates and blades with an absorption spectrum characteristic of plutonium(IV) compounds. A complex X-ray diffraction pattern was obtained.

Anal. $Pu/C_2O_4/PO_4 = 1.00/1.00/1.99$.

A portion of the plutonium(IV) oxalatophosphate contained in a platinum crucible with a loosely fitting lid was decomposed in an air atmosphere in an electric muffle furnace by slowly increasing the temperature from 25° to 950° over a 5-hr. period. After ignition to constant weight at 950°, the product was identified as PuP_2O_7 by X-ray diffraction analysis.

Anal. Calcd. for PuP_2O_7: Pu, 57.88; P, 15.00. Found: Pu, 58.4; P, 14.9; P/Pu = 1.97.

Procedure B.—An aliquot of stock solution II containing 40 g. of plutonium was added slowly, with stirring, to a 5 *M* aqueous solution of $H_2C_2O_4 \cdot 2H_2O$ at 90–100°. The final proportions of all reactant concentrations were $[Pu]/[H_2C_2O_4]/[H_3PO_4] = 1/10/20$. The pink precipitate, which began to form almost immediately, was digested with continuous stirring for 5 hr. at 70–100°. After an additional period of 65 hr. at 25–30°, without stirring, the precipitate was filtered, washed and dried as described under Procedure A. The product consisted of pink crystalline aggregates of individual crystals measuring up to 5 to 15 μ in the largest dimension. The absorption spectrum was characteristic of plutonium(IV) compounds. The X-ray pattern was complex but different from the pattern of the material prepared by Procedure A.

Anal. $Pu/C_2O_4/PO_4 = 1.00/1.55/0.99$.

This plutonium(IV) oxalatophosphate was mixed intimately with sufficient $NH_4H_2PO_4$ to increase the total P/Pu ratio to 2.02/1. The mixture was decomposed and ignited in the manner described under Procedure A. At temperatures of 550, 750 and 875°, the crucible was removed from the furnace and the contents were stirred with a platinum rod. The product was finally ignited to constant weight at 950°, cooled, leached with hot water, filtered and dried. The residue, after ignition to constant weight at 950°, was identified as PuP_2O_7 by X-ray diffraction analysis.

Anal. Found: Pu, 57.9; P, 15.2. P/Pu = 2.02.

Preparation of $PuPO_4$.—$PuPO_4$ was prepared by the thermal decomposition of a plutonium(IV) oxalatophosphate with a P/Pu ratio of 1/1 and also by dehydration of $PuPO_4 \cdot [0.5H_2O(?)]$. Whenever samples of plutonium oxalatophosphate prepared by Procedure B of the preceding section were decomposed without the addition of $NH_4H_2PO_4$, the product was $PuPO_4$ instead of PuP_2O_7. The first of the following two procedures illustrates an alternative preparation of a plutonium(IV) oxalatophosphate with a P/Pu ratio of 1/1.

Procedure A.—An aliquot of stock solution III containing 24 g. of plutonium and a 0.65 *M* aqueous solution of $H_2C_2O_4 \cdot 2H_2O$ were added simultaneously to an aliquot of 85% orthophosphoric acid stirred rapidly at 100°. The addition rates of the stock and oxalic acid solutions were 0.5 and 5 ml./min., respectively. The final proportions of all reactant concentrations were $[Pu]/[H_2C_2O_4]/[H_3PO_4] = 1/10/37$. A pink precipitate began to form within the first hour. The temperature was kept at 80–100° during the 5-hr. period required for addition of the reagents and during an additional digestion period of 16 hr. Stirring was continued for 24 hr. longer at 25–30°, after which the precipitate was transferred to a Pyrex Buchner-type fritted funnel of medium porosity. The residue was washed and dried in the manner described under Procedure A in the preceding section. Microscopic examination of a sample of the residue revealed aggregates of pink, crystalline, rectangular plates of various sizes up to *ca.* 15 μ in the largest dimension. The absorption spectrum was characteristic of plutonium(IV) compounds. The complex X-ray diffraction powder pattern was somewhat different from that obtained for the plutonium oxalatophosphate described under Procedure B in the preceding section.

Anal. $Pu/C_2O_4/PO_4 = 1.00/1.58/1.03$.

Thermal decomposition and ignition of this plutonium oxalatophosphate by the usual procedure gave a product which was identified as monoclinic $PuPO_4$ by X-ray diffraction analysis.

Anal. Calcd. for $PuPO_4$: Pu, 71.56; P, 9.28. Found: Pu, 71.3; P, 9.41; P/Pu = 1.02.

Procedure B.—A 0.4 *M* solution of $PuCl_3$ was prepared by dissolving pure plutonium metal in 12 *M* hydrochloric acid, filtering and diluting the filtrate with water to approximately 1 *N* acidity. Simultaneous additions of 200 ml. of this $PuCl_3$ solution and 400 ml. of 0.5 *M* $(NH_4)_2HPO_4$ solution to 400 ml. of 0.07 *M* hydrochloric acid at 80–90° were made at rates of approximately 5 and 9 ml./min., respectively. A pale blue precipitate began to form almost immediately. The precipitate was digested for 1 hr. at 80–90° with continued stirring and for 64 hr. at 25–30° without stirring, after which it was filtered, washed with water, and dried to approximately constant weight at 100–150°. The product was identified as hexagonal $PuPO_4 \cdot [0.5H_2O(?)]$ by X-ray diffraction analysis.

Anal. Calcd. for $PuPO_4 \cdot 0.5H_2O$: Pu, 69.68; P, 9.03; H_2O, 2.63. Found: Pu, 68.4; P, 9.61; H_2O (by diff.), 2.1; P/Pu = 1.08.

A portion of the $PuPO_4 \cdot [0.5H_2O(?)]$ was ignited to constant weight at 950° in air. The product was identified as monoclinic $PuPO_4$ by X-ray diffraction analysis. The P/Pu ratio was found to be 1.09, indicating that no phosphorus had been lost during the ignition. The high value of the P/Pu ratio is believed to have been caused by the presence of an impurity containing excess phosphorus carried down during the precipitation of $PuPO_4 \cdot [0.5H_2O(?)]$ and retained in subsequent operations. A likely impurity would be an empirical compound such as $Pu_2(HPO_4)_3 \cdot xH_2O$ which might be expected to decompose to $Pu_4(P_2O_7)_3$ during ignition, leaving the P/Pu ratio unchanged.

Anal. Calcd. for $PuPO_4$: Pu, 71.56; P, 9.28. Found: Pu, 70.2; P, 9.86.

Separation of $PuPO_4$ from $PuPO_4$–PuP_2O_7 Mixtures.—The thermal decomposition of plutonium(IV) oxalatophosphates with P/Pu ratios greater than 1/1 but less than 2/1 gave mixtures of $PuPO_4$ and PuP_2O_7. In order to determine whether or not these mixtures might be separated by selective dissolution of one of the two components, the information in Table I was obtained. One-gram samples of each of the pure compounds were stirred with 25 ml. of each of the reagents in Table I at 25–30° and at 90–100°. The relative proportions of the compounds in solution after 4–5 hr. are compared in the table.

TABLE I

DISSOLUTION OF $PuPO_4$ AND PuP_2O_7[a]

Reagent	$PuPO_4$ 25–30°	$PuPO_4$ 90–100°	PuP_2O_7 25–30°	PuP_2O_7 90–100°
HCl, concd.	Slight	Complete	Complete	Complete
HNO_3, concd.	Incomplete	Complete	Slight	Incomplete
H_2SO_4, concd.	....	Complete[b]	Complete[b]	Complete[b]
H_3PO_4, 85%	Negligible	Incomplete	Complete	Complete
$HC_2H_3O_2$, 100%	....	No reaction	....	Negligible
NaOH, 6 *N*	....	Incomplete[c]	....	Complete[c]

[a] 1-g. sample stirred 4–5 hr. with 25 ml. of each reagent. [b] Metathesis occurred. Product insoluble in concd. acid; soluble in dilute acid. [c] Metathesis occurred. Product insoluble in 6 *N* NaOH or water; soluble in acid solution.

Hydrochloric, phosphoric and nitric acids were selected for further dissolution experiments with a mixture containing 62% PuP_2O_7 and 38% $PuPO_4$, by weight. The mixture was prepared by thermal decomposition and ignition at 950° of a plutonium(IV) oxalatophosphate with a P/Pu ratio of 1.56/1.00. The $PuPO_4$ occurred both as separate aggregates and as inclusions in PuP_2O_7 grains. The dissolution procedure was the same as that used for experiments with the pure compounds. Both concentrated hydrochloric acid and 85% orthophosphoric acid at 25–30° effectively dissolved the PuP_2O_7 component, leaving practically all of the $PuPO_4$ as a residue containing only a few per cent. by volume of microscopically resolved impurities. No impurities were detected by X-ray diffraction. Concentrated nitric acid failed to dissolve $PuPO_4$ preferentially from the mixture as had been hoped. Even after 60% of the sample had been dissolved, the proportions of the two components in the residue were still unchanged.

X-Ray and Optical Properties.—The lattice constants of the hexagonal unit cell of $PuPO_4 \cdot [0.5H_2O(?)]$ were: a = 7.011 ± 0.002 Å., c = 6.401 ± 0.002 Å. The calculated density of $PuPO_4 \cdot 0.5H_2O$ (three molecules of $PuPO_4$ per unit cell) was 6.27 g./cm.^{3}. Samples of this compound were homogeneous and optically isotopic, probably because they were non-crystalline on the scale of optical microscopy. Consequently, microscopic detection of small amounts of impurities was not possible. The mean refractive index determined for sodium light was 1.76, and the absorption spectrum was characteristic of plutonium(III) compounds.

The lattice constants of the monoclinic unit cell of $PuPO_4$ were: a = 6.73 ± 0.02 Å.; b = 7.00 ± 0.02 Å.; c = 6.42 ± 0.02 Å.; β = 103.8 ± 0.4. The calculated density was 7.55 g./cm.^{3}. Most samples of this compound consisted of dark blue, birefringent aggregates of minute crystals with barely resolved grain size and a mean refractive index of 1.87. The three principal refractive indices determined for samples of $PuPO_4$ ignited at 1400° were: 1.855, 1.86 and 1.905. The absorption spectrum was characteristic of plutonium(III) compounds. Unidentified impurities representing less than an estimated 5% by volume of a sample prepared from plutonium(IV) oxalatophosphate and 5–10% of a sample prepared from $PuPO_4 \cdot [0.5H_2O(?)]$ were indicated by small inclusions of lower refringence.

The lattice constant of the simple cubic unit cell of PuP_2O_7 was 8.560 ± 0.006 Å.; the calculated density was 4.37 g./cm.^{3}. The refractive index of the isotropic crystals was 1.676. Samples prepared by both procedures normally consisted of very fine-grained colorless aggregates which preserved the crystal shape of the parent material. Quite frequently these pseudomorphs exhibited an appreciable, though irregular, birefringence (possibly due to the structure of the aggregates), and were occasionally characterized by lower and variable indices, 1.63–1.66, suggesting the possible presence of unresolved impurities. The absorption spectra were characteristic of plutonium(IV) compounds.

Discussion

The formation of plutonium(IV) oxalatophosphate precipitates offers convenient methods for the preparation of crystalline $PuPO_4$ and PuP_2O_7 of relatively high purity. Other methods for these preparations were attempted with less success. $PuPO_4$ obtained by the precipitation and dehydration of $PuPO_4 \cdot [0.5H_2O(?)]$ contained excess phosphate as an impurity. The attempted precipitation of plutonium from solution as a pyrophosphate, or as an acid phosphate which could be ignited to a pyrophosphate, involved non-crystalline intermediates which were difficult to handle. The products of solid phase reactions between PuO_2 and H_3PO_4, $NH_4H_2PO_4$ or $Na_4P_2O_7$, at temperatures up to 1000°, contained relatively large proportions of impurities. Crystalline plutonium oxalatophosphates, on the other hand, could be prepared in any quantity and could be converted readily to the corresponding $PuPO_4$ or PuP_2O_7.

The plutonium(IV) oxalatophosphate with a P/Pu ratio of 1/1 was the most reproducible member of the series. Two variations of the method for its preparation by precipitation with aqueous solutions of oxalic acid have been given. In other experiments the temperature, concentration, rate of addition and order of addition of reagents were changed with resultant variations in crystal size of the precipitate but with no significant effect on the composition. The final product of the decomposition of any plutonium(IV) oxalatophosphate preparation with a P/Pu ratio of 1/1 was always $PuPO_4$.

When phosphoric acid solutions of varying oxalic acid concentrations were substituted for the aqueous oxalic acid solutions, plutonium oxalatophosphates with P/Pu ratios ranging in values from 1/1 to 2/1 were obtained. The final products of the decomposition of these intermediates were mixtures of PuP_2O_7 and $PuPO_4$; the proportion of PuP_2O_7 increased with increasing P/Pu ratio in the parent material. The proportion of PuP_2O_7 obtained from a given intermediate oxalatophosphate could be increased by the admixture of solid $NH_4H_2PO_4$ prior to decomposition. As the total P/Pu ratio was made to exceed 2/1 by such additions, however, increasing proportions of an unidentified crystalline pink compound were formed at the expense of the PuP_2O_7 component. Pure PuP_2O_7 was obtained only when the total P/Pu ratio was very close to 2/1.

When the conditions of the precipitation with phosphoric acid solutions of oxalic acid were suitably controlled, a plutonium(IV) oxalatophosphate with a P/Pu ratio of 2/1 was obtained. The final product of the decomposition and ignition of such an intermediate material was always PuP_2O_7.

The thermal stability of $PuPO_4$ and PuP_2O_7 was found to be much greater in air than *in vacuo*. Both compounds could be ignited at 950–1000° in air with no detectable loss in weight. At 950° and 5×10^{-5} mm. pressure, however, PuP_2O_7 slowly decomposed to $PuPO_4$. The decomposition rate *in vacuo* was accelerated at 1200–1400°. Significant crystal growth without decomposition resulted when samples of $PuPO_4$ were heated momentarily to 1400° in an induction furnace at 10^{-4} mm. pressure. Longer periods of heating, *e.g.*, 20 min. at 1400–1500°, caused a large proportion of the $PuPO_4$ to decompose, without evidence of melting, to the more stable compound, PuO_2.

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LOS ALAMOS, NEW MEXICO

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

The Kinetics of the Disproportionation of Plutonium(V)[1]

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A study has been made of the kinetics of the disproportionation of plutonium(V) in perchlorate solutions of unit ionic strength in which the PuO_2^+ was prepared by the reduction of the plutonyl ion with iodide ion. With this method of preparation, the disproportionation of plutonium(V) was studied in the absence of significant quantities of plutonium(III) and (IV) in the initial phases of the experiments. The rate of disproportionation of plutonium(V) has been found to be directly proportional to the first power of the hydrogen ion concentration, which suggests that the slow step is probably $PuO_2^+ + Pu(O)OH^{++} \rightarrow PuO_2^{++} + Pu(O)OH^+$. An activation energy of 19.6 kcal. has been computed from the temperature dependence of the specific reaction rate constants for the slow step of the disproportionation reaction. The disproportionation of plutonium(V) has also been studied in deuterium oxide to note the influence of a change in solvent upon the reaction rates. It appears from the kinetic results obtained that no evidence has been found which would support the hydrogen atom transfer mechanism in the plutonium(V) disproportionation reaction. Plutonium(V) also has been prepared from the plutonyl ion by the spontaneous α-reduction process. The kinetic data appear to be adequately described by a consideration of previously determined rate and equilibrium constants and the rate constant for the Pu(V)–Pu(V) reaction which was obtained from the experiments in which the plutonyl ion was reduced with iodide.

Introduction

The kinetics of the disproportionation of plutonium(V) has been the subject of previous studies[2,3] in which it was observed that the mechanism of the disproportionation reaction consisted of the slow reaction, $Pu(V) + Pu(III) \rightarrow 2Pu(IV)$, together with the rapid equilibrium reaction, $Pu(V) + Pu(IV) \rightleftarrows Pu(III) + Pu(VI)$. Plutonium(V) is also thermodynamically unstable in moderately acid solution, with respect to the reaction $2Pu(V) \rightarrow Pu(VI) + Pu(IV)$, as has been pointed out[2] and as can be shown from a consideration of the formal potentials[4,5] of the Pu(IV)–Pu(V) and the Pu(V)–Pu(VI) couples. In studies[2] of the disproportionation of plutonium(V) in which the PuO_2^+ was prepared by the electrolytic reduction of plutonyl ion, it appears that the solutions initially contained significant amounts of plutonium in the trivalent state. Connick concluded that the bimolecular rate constant for the disproportionation of plutonium(V) by the Pu(III)–Pu(V) mechanism is at least 35 times greater than that for the Pu(V)–Pu(V) path at room temperature in 0.5 *M* hydrochloric acid; hence, it is somewhat difficult to study the disproportionation of plutonium(V) through the latter reaction in the presence of moderate amounts of plutonium(III). In the present work use was made of the observation[5,6] that plutonium(V) can be prepared by the quantitative reduction of plutonyl ion with iodide ion. Thus, the disproportionation of plutonium(V) could be studied, at least in the initial phases of the reaction, in the absence of significant quantities of plutonium(III). In another series of experiments the PuO_2^+ was prepared by the alpha particle radiation from the plutonium. In these studies, which were of longer duration, it was necessary to consider the disproportionation of plutonium(V) by the Pu(III)–Pu(V) mechanism. An attempt was made to examine some of the details of the disproportionation of plutonium(V) by the proposed Pu(V)–Pu(V) mechanism by noting the influence on the rate of reaction of the substitution of deuterium oxide for ordinary water as the solvent.

Experimental

The apparatus and procedure were essentially those previously described.[7] Neutral solutions of Merck reagent grade sodium iodide were standardized against dried samples of Mallinckrodt reagent grade silver nitrate using a potentiometric method of analysis. After the addition of a given weight of neutral sodium iodide solution to the plutonyl solution, sufficient quantities of standardized perchloric acid and sodium perchlorate were added to maintain the desired acidity and ionic strength. This procedure was used to avoid the air oxidation of the iodide ion which proceeds rapidly in moderately acid solutions. Usually from 25 to 50% of the plutonyl solution was reduced with iodide to PuO_2^+. The sodium perchlorate salt was the recrystallized product obtained by the neutralization of Mallinckrodt reagent grade sodium carbonate with this manufac-

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[1] This work was done under the auspices of the U. S. Atomic Energy Commission. Presented in part at the 131st Meeting of the American Chemical Society, Miami, Florida, April 10, 1957.

[2] R. E. Connick, THIS JOURNAL, **71**, 1528 (1949).

[3] R. E. Connick, "The Transuranium Elements," Natl. Nuclear Energy Ser., Div. IV, Vol. 14-B, 1949, p. 268.

[4] K. A. Kraus, F. Nelson and G. L. Johnson, THIS JOURNAL, **71**, 2510 (1949).

[5] S. W. Rabideau, *ibid.*, **78**, 2705 (1956).

[6] K. A. Kraus and G. E. Moore, ref. 3, p. 550.

[7] S. W. Rabideau, THIS JOURNAL, **75**, 798 (1953).