Journal of Thermal Analysis, Vol. 18 (1980) 99—109

THE THERMAL DECOMPOSITION OF PLUTONIUM (IV) OXALATE HEXAHYDRATE*

D. A. NISSEN

Sandia Laboratories Livermore, California 94550, USA

(Received February 8, 1979)

The thermal decomposition of $Pu(C_2O_4)_2 \cdot 6H_2O$ has been studied in both argon and oxygen using a combination of thermogravimetry and infrared spectroscopy. Decomposition in an inert atmosphere involves reduction of the cation to the trivalent state and its subsequent reoxidation to form PuO_2. In an oxidizing atmosphere, with unrestricted access of oxygen, reduction of the cation does not take place and decomposition to PuO_2 is through the oxycarbonate. The reduction of Pu(IV) appears to take place by a carbon monoxide catalyzed mechanism and the presence of carbon in the PuO_2 decomposition product is attributed to the disproportionation of CO.

Of the several processes used to prepare plutonium metal the most widely used involves the thermal decomposition of $Pu(C_2O_4)_2 \cdot 6\,H_2O$ to the oxide (PuO_2), fluorination of the oxide to PuF_4 and the subsequent reduction of the fluoride to the metal with calcium. One particular disadvantage of this process is that the carbon which apparently arises as a consequence of the thermal decomposition of the oxalate, is carried through the process and appears as an impurity in the plutonium metal product. To aid in the removal of this carbon impurity the thermal decomposition of $Pu(C_2O_4)_2 \cdot 6\,H_2O$ is done in air at 300 to 400°.

Several earlier studies have been done on this process [1–6]. However, the interpretations were at variance with each other and as Glasner points out [7], the thermogravimetric results have had little support by other experimentation or observation.

The present study makes use of both infrared spectroscopy and thermogravimetric techniques to follow the thermal decomposition of $Pu(C_2O_4)_2 \cdot 6\,H_2O$ in both argon and oxygen to try to define explicitly the source of the carbon and to determine the effect, if any, of oxygen on the mechanism of the thermal decomposition of $Pu(C_2O_4)_2 \cdot 6\,H_2O$ itself.

Experimental

The starting material, $Pu(C_2O_4)_2 \cdot 6\,H_2O$, was prepared by the method described by Harmon and Reas [8]. Briefly, this involved adding 1 *M* $H_2C_2O_4$ and H_2O_2, for valence adjustment, to a $Pu(NO_3)_4$ solution (~ 4 *M* HNO_3) held at 50 – 55°

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* Work supported by U.S. Department of Energy, DOE, under Contract AT(29-1)-789

The resulting precipitate was allowed to digest for ~ 1 hour at this temperature and then filtered. Dry air was pulled through the precipitate for 3–4 hours. An elementary analysis of the product $Pu(C_2O_4)_2 \cdot 6\,H_2O$ showed 45.2 w/o Pu and 33.3 w/o C_2O_4 compared to the theoretical values of 45.7 and 33.7.

In accordance with the findings of Jenkins, et al. [9], the plutonium oxalate was used within three days of precipitation in order to minimize any radiation damage due to alpha radiation from the plutonium. Within this time period less than 5% of the oxalate was converted to the oxide.

Samples of oxalate weighing approximately 30 mg were placed in a quartz pan and suspended by a quartz chain from a Cahn Model RG electrobalance. The weight of the sample was continuously recorded while it was being heated at a controlled, constant rate. The temperature was measured by a chromel-alumel thermocouple positioned next to the quartz pan and was recorded separately. The sample pans were designed so that the maximum possible amount of sample was exposed to the atmosphere.

A flowing atmosphere of either argon, oxygen, or air, was continuously in contact with the sample. To insure that thermal gradients were minimized the entering gas was preheated to the furnace temperature. All of the gases used in these experiments passed over magnesium perchlorate to remove any water.

The desired linear heating rate was provided by an F&M Model 240-M temperature programmer. Continuous monitoring of the furnace temperature showed it to be within ±3° C of the control temperature.

The nature of various intermediate compounds formed during thermal decomposition of the starting material was determined by examination of their infrared spectrum. A sample of the desired intermediate was obtained by simply running a duplicate experiment and rapidly cooling the sample by raising it from the furnace. By cooling the sample while it was still enclosed in the balance, the integrity of the atmosphere was insured. The cooled sample was mulled in Nujol, the mull placed between sodium chloride plates, and the spectrum run on a Perkin–Elmer Model 21 spectrophotometer.

Results

A typical thermogravimetric curve for the decomposition of plutonium (IV) oxalate hexahydrate, heated at a linear rate of 2 °C/min in argon is shown in Figure 1. For reference, the calculated weights of various plutonium compounds are also shown.

The hexahydrate begins to decompose at ~50°. This reaction appears to be complete at ~130° with the formation of a brick-red material which has a molecular weight corresponding to the monohydrate. Its infrared spectrum, curve 2, Figure 2, is very similar to that of the hexahydrate starting material. This is particularly evident in the region between 1300 and 1359 cm^{-1}.

At ~185° the first intermediate material begins to decompose to form a blue-green colored material which is stable over the temperature range 210–375° and whose molecular weight corresponds closely to the anhydrous trivalent oxalate. The infrared spectrum of this second intermediate is shown in Figure 2, curve 3, and is very similar to that of $Pu(C_2O_4)_{3/2} \cdot 10\,H_2O$ [10]. The small peak at 3200 cm^{-1} is due to traces of water picked up during preparation of the Nujol mulls.

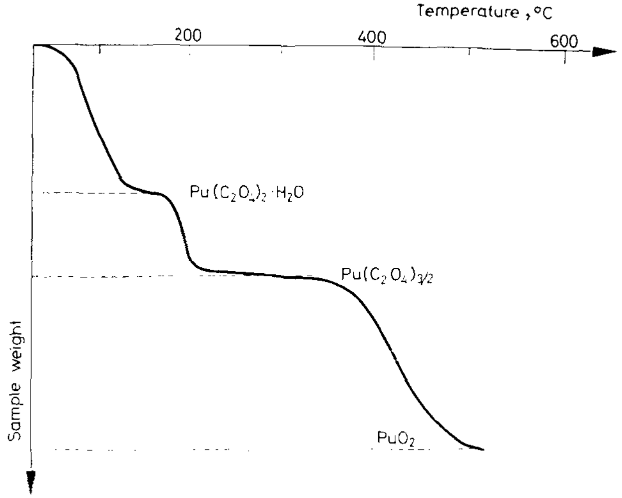

Fig. 1. Weight-temperature curve for the thermal decomposition of $Pu(C_2O_4)_2 \cdot 6H_2O$ in argon. Heating rate 20 °C/min

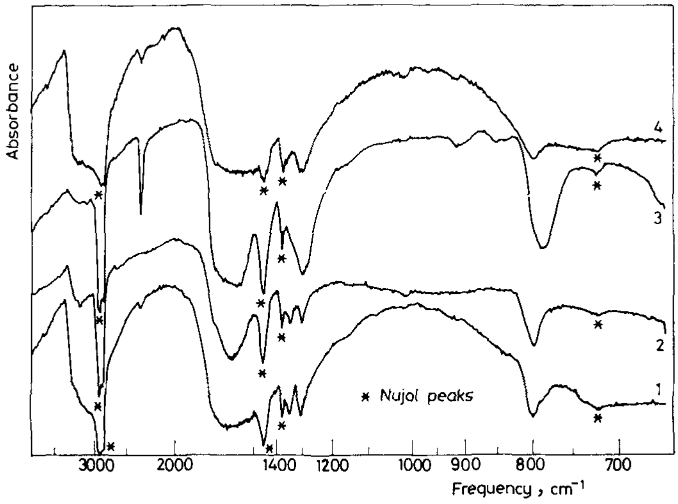

Fig. 2. Infrared spectra of residues obtained on heating $Pu(C_2O_4)_2 \cdot 6H_2O$ to various temperatures in argon. Spectrum 1. 25°, 2. 120°, 3. 215°, 4. $Pu(C_2O_4)_{3/2} \cdot 10H_2O$ – 25°

The decomposition of this second intermediate to PuO_2 begins at ~375° and is complete at 525°.

Figure 3 shows the results which are obtained when $Pu(C_2O_4)_2 \cdot 6\ H_2O$ is heated in a flowing air or oxygen atmosphere at a linear rate of 2°C/min. These results are different in some particulars from the case where the same starting material was heated in an argon atmosphere. As in Figure 1, the calculated weights for various plutonium compounds are shown.

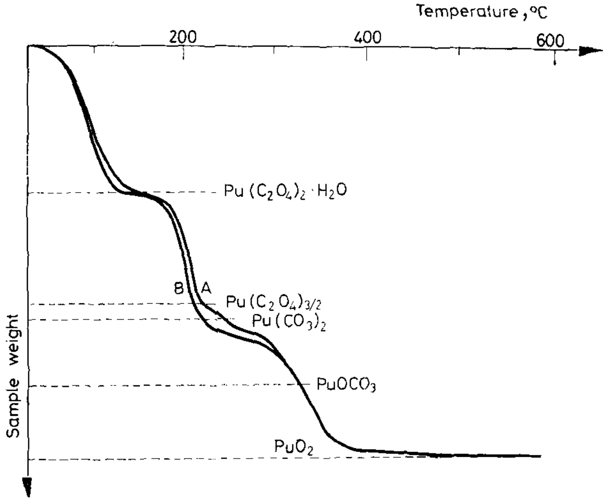

Fig. 3. Weight-temperature curves for the thermal decomposition of $Pu(C_2O_4)_2 \cdot 6H_2O$ in air (A) and oxygen (B). Heating rate 20 °C/min

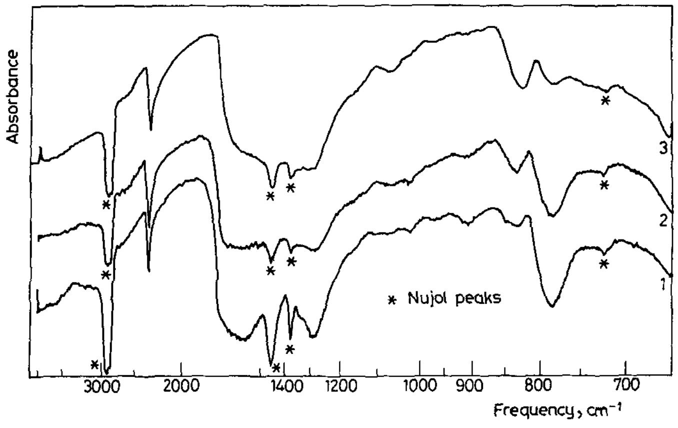

Fig. 4. Infrared spectra of residues obtained on heating $Pu(C_2O_4)_2 \cdot 6H_2O$ to various temperatures in air. Spectrum 1. 225°, 2. 250°, 3. 275°

That portion of the thermogravimetric curves which extends from 25° to 175° parallels the analogous region in Figure 1 in every way. As the temperature is raised, the weight-versus-temperature curves exhibit regions of decreased slope which extends between 225° and 300°. As the temperature is raised above 300°, decomposition directly to PuO_2 follows and is complete by 500°.

Figure 4 shows the spectra of samples taken at various temperatures along the plateau which extends from 225 to 300°. The spectrum labeled 1 is that of the green colored product which results when a sample of $Pu(C_2O_4)_2 \cdot 6\,H_2O$ heated to 225° at a rate of 2 °C/min in a flowing air atmosphere.

The spectrum labeled 2 is that of the yellow-colored material which results when $Pu(C_2O_4)_2 \cdot 6\,H_2O$ is heated in air to 250° at a rate of 2 °C/min and spectrum 3 is of material which is produced when $Pu(C_2O_4)_2 \cdot 6\,H_2O$ is carefully heated in air to 275° at a rate of 2 °/min and rapidly cooled as previously indicated.

If a sample of $Pu(C_2O_4)_2 \cdot 6\,H_2O$ is held at 250° in an oxygen atmosphere until constant weight has been reached the yellow-brown-colored residue which results has a molecular weight corresponding to $PuOCO_3$. When this material is added to concentrated hydrochloric acid, the solid decomposes with the evolution of gas from which one infers the presence of carbonate. Sokhina and Gelman [11] have proposed that $PuOCO_3$ is formed as a result of the radiolytic decomposition of Pu(IV) oxalate.

Discussion

Irrespective of the stoichiometry of the intermediate products formed during the thermal decomposition of $Pu(C_2O_4)_2 \cdot 6\,H_2O$ one thing is readily apparent, regardless of the composition of the atmosphere the final product of this decomposition is PuO_2.

Based on the thermogravimetric evidence, supported by infrared spectra of the intermediate compounds which are formed, we propose the following sequence of reactions to represent the thermal decomposition of $Pu(C_2O_4)_2 \cdot 6\,H_2O$ in an inert atmosphere:

$$Pu(C_2O_4)_2 \cdot 6\,H_2O \rightarrow Pu(C_2O_4)_2 \cdot H_2O + 5\,H_2O \qquad (1)$$

$$Pu(C_2O_4)_2 \cdot H_2O \rightarrow Pu(C_2O_4)_{3/2} + H_2O + CO_2 \qquad (2)$$

$$Pu(C_2O_4)_{3/2} \rightarrow PuO_2 + 2\,CO + CO_2. \qquad (3)$$

That the formation of a stable monohydrate, reaction (1), represents the first step in the thermal decomposition of $Pu(C_2O_4)_2 \cdot 6\,H_2O$ is supported by both the close similarity of spectra 1 and 2 of Fig. 2 and by the agreement between the experimentally determined molecular weight of this product and that of the monohydrate, Fig. 1.

As the sample temperature increases beyond 175° the monohydrate begins to lose its water of hydration and the plutonium itself is reduced from Pu (IV) to Pu (III). This second step in the thermal decomposition appears complete at ~350° with the conversion of $Pu(C_2O_4)_2 \cdot 6\,H_2O$ to $Pu(C_2O_4)_{3/2}$, reaction (2).

We see that the infrared spectrum of the compound which we have identified as $Pu(C_2O_4)_{3/2}$ from thermogravimetric data is identical with that of $Pu(C_2O_4)_{3/2} \cdot \cdot 10\,H_2O$ which was prepared independently [10], Fig. 2. This is particularly evident in the region of 1300 cm^{-1} where the pronounced doublet associated with Pu (IV) has changed. Either it has merged into a single peak or one of the peaks of the doublet has become greatly reduced in intensity. From the fact that spectrum 3, Fig. 2, shows no indication of the presence of carbonate, the absence of a peak in the region of 850 cm^{-1}, we infer that the oxalate anion is itself unchanged.

Reduction of the cation during thermal decomposition is not a situation unique to plutonium. Analogous behavior has been shown for several transition metal oxalates and investigated in some detail for europium oxalate [12, 13].

Several investigators have used data from thermogravimetric experiments to show that Pu (III) is formed during the thermal decomposition of $Pu(C_2O_4)_2$ in an inert atmosphere [14]. However, the exact composition of the Pu (III) compound formed was not unequivocally defined.

Studies of the thermal decomposition of the trivalent plutonium oxalate compound $Pu(C_2O_4)_{3/2} \cdot 10\,H_2O$ under the same experimental conditions have shown that the decahydrate decomposes in one step to the anhydrous oxalate which is stable over the range 150–300°. At 300° PuO_2 begins to be formed and the reaction is complete at 500°. No intermediate compounds were observed [2, 10]. In the final stage of the decomposition Pu (III) is reoxidized to PuO_2, reaction (3).

From thermogravimetric data taken in an oxidizing atmosphere, the initial part of the thermal decomposition sequence appears to be identical with that observed in an inert atmosphere, reaction (1). Following this, however, the situation becomes somewhat more complex.

Both the thermogravimetric results and infrared spectra seem to indicate that the product of the thermal decomposition of the monohydrate is the trivalent plutonium oxalate, (2). However, this compound has only a very limited stability in an oxidizing atmosphere; in pure oxygen there is no indication whatever for the formation of the trivalent plutonium intermediary, Fig. 3, curve B.

Comparison of the spectra shown in Fig's. 2 and 4 indicate that, in contrast to thermal decomposition in an inert atmosphere, the oxalate anion itself is undergoing a change. Specifically, there appears to be a gradual transformation of the oxalate to carbonate.

In spectrum 1 of Fig. 4 a small peak appears at about 830 cm^{-1} which is not seen on the spectra of Fig. 2 and which grows larger as the temperature increases. This peak is indicative of the presence of carbonate [15]. While we are unable to present the spectrum of plutonium carbonate for comparison because the dry compound is not stable [14] the 830 cm^{-1} peak occurs in approximately the same position as one of the carbonate peaks in the spectra of a number of other carbonates [12, 13, 15]. Unfortunately, the principal carbonate band which is centered at about 1450 cm^{-1} [15] is obscured by two strong oxalate bands at 1300 and 1600 cm^{-1} as well as one of the Nujol peaks. However, the gradual transition from oxalate to carbonate illustrated by the spectra of Fig. 4; and in particular, the decrease in the 780 cm^{-1} peak, is identical to that obtained by Glasner for the transformation of europium oxalate to carbonate [12, 13]. These results coupled with the thermogravimetric data indicate that the change in slope of the weight-temperature curve around 200°, Fig. 3, is due not to a stoichiometric compound but rather to a mixed material composed of plutonium oxalate in the bulk and some plutonium carbonate species, possibly $PuOCO_3$ on the surface. As the temperature increases more and more of the plutonium oxalate is converted to the oxy-carbonate.

The final step of the decomposition is the conversion of the carbonate-oxalate mixture to PuO_2 which is complete at ~400°.

The general features of the thermal decomposition sequence of $Pu(C_2O_4)_2 \cdot 6\,H_2O$ in oxygen shown below are similar to those proposed by Myers [4]

$$Pu(C_2O_4)_2 \cdot 6\,H_2O \rightarrow Pu(C_2O_4)_2 \cdot H_2O + 5\,H_2O \tag{4}$$

$$Pu(C_2O_4)_2 \cdot H_2O \begin{cases} \rightarrow Pu(C_2O_4)_{3/2} + H_2O + CO_2 & (5) \\ \xrightarrow{O_2} PuOCO_3 + 3\,CO_2 & (6) \end{cases}$$

$$Pu(C_2O_4)_{3/2} + O_2 \rightarrow PuOCO_3 + 2\,CO_2 \tag{7}$$

$$PuOCO_3 \rightarrow PuO_2 + CO_2. \tag{8}$$

The extent of reactions (5) and (7) is dependent upon the oxygen partial pressure as well as the accessibility of the bulk material to oxygen.

It is entirely possible that the heterogeneous nature of the decomposing solid in the 200–300° range may account for the large number of intermediate compounds reported to have been formed during the thermal decomposition of $Pu(C_2O_4)_2 \cdot 6\,H_2O$ in an oxidizing atmosphere [14]. This is particularly true where the identification of intermediate compounds was limited to a simple assignment of molecular weights to various inflections in the weight-temperature curve.

We are unable to explain the peak at 2300 cm^{-1}, Figs 2 and 4, except to note that Glasner observed the same peak in infra-red spectra of the decomposition products of europium oxalate [12].

The plutonium dioxide product of the thermal decomposition of $Pu(C_2O_4)_2 \cdot 6\,H_2O$ in either air (oxygen) or argon was found to contain significant amounts of carbon. The quantity varied depending upon the atmosphere over the sample; ranging from about 10000 ppm for a sample decomposed in argon to 5000–6000 ppm in air and 1500 ppm in oxygen. Carbon analysis was done by heating the PuO_2 in the thermobalance to 800° in oxygen until the sample weight remained constant, usually 30 minutes, and then determining the weight loss of the sample of PuO_2. Infrared spectra of PuO_2 prior to the carbon analysis showed the absence of both oxalate and carbonate. These data merely confirm the earlier results of Jenkins and Waterman [1].

Elementary carbon is often found in the decomposition products of oxalates [12, 13, 16] and its formation during the decomposition of calcium oxalate has been studied by Simons and Newkirk [16]. The explanation offered is that the carbon monoxide formed during the thermal decomposition, e.g. reaction (3), is subsequently decomposed *via* the disproportionation reaction

$$2\,CO \rightarrow CO_2 + C. \tag{9}$$

This conclusion is disputed, however, by Jenkins and Waterman [1] who maintain that the disproportionation reaction (9) would not be expected to take place at measurable rates at temperatures around 200–300 °C because the rate of disproportionation of carbon monoxide in the gas phase is known to be very slow at temperatures below 700°. They propose instead the reaction

$$Pu(C_2O_4)_2 \rightarrow Pu(CO_3)_2 + C + CO_2. \tag{10}$$

The infrared spectra of the intermediates formed during the thermal decomposition of $Pu(C_2O_4)_2 \cdot 6\,H_2O$ in an inert atmosphere do not show the presence of carbonate. Since we find as much as 10000 ppm carbon in PuO_2 formed in argon our results do not support Jenkins and Waterman's proposed reaction (10) but favor instead the disproportionation of carbon monoxide (9) as the mechanism for the formation of elementary carbon in the PuO_2 product.

Crude differential thermal analysis measurements made during the thermal decomposition of $Pu(C_2O_4)_2 \cdot 6\,H_2O$ in various atmospheres show a large exothermic peak at ~250° in an oxidizing atmosphere, the magnitude varying with the oxygen partial pressure [10]. This same phenomena was observed and discussed by Simons and Newkirk [16] and was attributed to the reaction

$$CO + 1/2\,O_2 \rightarrow CO_2 \tag{11}$$

which liberates 67.7 kcal/mole CO at 700 K [17].

By analogy with his studies of the thermal decomposition of europium oxalate [12, 13] Glasner has postulated a carbon monoxide catalyzed mechanism to explain the reduction of $Pu(C_2O_4)_2 \cdot 6\,H_2O$ [7].

$$Pu(C_2O_4)_2 \rightarrow Pu(C_2O_4)_{2-x}(CO_3)_x + xCO \tag{12}$$

$$Pu(C_2O_4)_2 + CO \rightarrow Pu(C_2O_4)_{3/2} + CO_2 + CO \tag{13}$$

where reaction (12) is very slow so that no measurable amount of carbon monoxide is evolved.

As the oxygen partial pressure increases the carbon monoxide that is released in the initial reaction (12) is oxidized to CO_2 thus preventing the reduction of Pu(IV). Our data suggest that $PuOCO_3$ is formed as a result of the thermal decomposition of $Pu(C_2O_4)_2$ in oxygen. This situation is complicated by the simultaneous exothermic oxidation of CO, (11), which causes the sample temperature to rise in an uncontrolled manner with a consequent acceleration in the decomposition reaction. Because oxygen has only a limited access to the bulk of the sample, decomposition there proceeds as if the sample were in an inert atmosphere (2) and (3). As a consequence, even in an oxygen atmosphere some elementary carbon is formed by the disproportionation of CO (9). However, the carbon concentration is much lower since a large portion of the CO has been oxidized to CO_2.

Conclusions

By using a combination of thermogravimetric analysis and infra-red spectroscopy we have identified the products of the thermal decomposition of $Pu(C_2O_4)_2 \cdot 6\,H_2O$ in both an inert and oxidizing atmosphere.

In a flowing inert atmosphere (argon) the thermal decomposition can be represented by the following sequence of reactions:

$$\begin{aligned} Pu(C_2O_4)_2 \cdot 6\,H_2O &\rightarrow Pu(C_2O_4)_2 \cdot H_2O + 5\,H_2O \\ Pu(C_2O_4)_2 \cdot H_2O &\rightarrow Pu(C_2O_4)_{3/2} + CO_2 + H_2O \\ Pu(C_2O_4)_{3/2} &\rightarrow PuO_2 + 2\,CO + CO_2. \end{aligned}$$

The decomposition sequence is more complex in an oxidizing atmosphere. The nature and stability of the intermediate products are a strong function of the oxygen partial pressure and accessibility of oxygen gas to the bulk material. In contrast to the inert gas case, in an oxidizing atmosphere the oxalate anion decomposes to the carbonate and plutonium is not reduced to the trivalent state. As a consequence, during the decomposition the bulk material is composed of a complex mixture of the oxalate and carbonate whose composition is continually changing. At about 300° the whole mixture is converted to PuO_2.

In a flowing oxidizing atmosphere this whole decomposition sequence is summarized by the following reactions:

$$Pu(C_2O_4)_2 \cdot 6\,H_2O \rightarrow Pu(C_2O_4)_2 \cdot H_2O + 5\,H_2O$$

$$\begin{tikzcd} & Pu(C_2O_4)_{3/2} + H_2O + CO_2 \\ Pu(C_2O_4)_2 \cdot H_2O \arrow[ur] \arrow[dr, "O_2"] & \\ & PuOCO_3 + 3\,CO_2 \end{tikzcd}$$

$$\begin{aligned} Pu(C_2O_4)_{3/2} + O_2 &\rightarrow PuOCO_3 + 2\,CO_2 \\ PuOCO_3 &\rightarrow PuO_2 + CO_2. \end{aligned}$$

By analogy with his work on Eu (III) oxalate [12, 13], Glasner has postulated a mechanism to explain the cyclic reduction-oxidation behaviour of Pu (IV) [7]; the reduction of Pu (IV) is due to a carbon monoxide catalyzed mechanism

$$Pu(C_2O_4)_2 \rightarrow Pu(C_2O_4)_{2-x}\,(CO_3)_x + x\,CO$$

$$Pu(C_2O_4)_2 + CO \rightarrow Pu(C_2O_4)_{3/2} + CO_2 + CO.$$

The experimental data do not permit a detailed explanation for the oxidation of Pu(III) to PuO_2 in an inert atmosphere but we suspect that it may be caused by carbon dioxide formed by the disproportionation of carbon monoxide released during thermal degradation of the oxalate, i.e.,

$$\begin{aligned} \mathrm{Pu(C_2O_4)_{3/2}} &\rightarrow \mathrm{PuC_2O_4(CO_3)_{1/2}} + 1/2\,\mathrm{CO} \\ &\qquad\qquad\qquad\qquad\hookrightarrow 1/4\,\mathrm{CO_2} + 1/4\,\mathrm{C} \end{aligned}$$

$$\mathrm{Pu(C_2O_4)_{3/2}} + \mathrm{CO_2} \rightarrow \mathrm{PuO_2} + 2\,\mathrm{CO_2} + 2\,\mathrm{CO}.$$

From the presence of a carbon residue in the PuO_2, we infer the production of CO during the decomposition and its subsequent disproportionation:

$$2\,\mathrm{CO} \rightarrow \mathrm{CO_2} + \mathrm{C}.$$

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RÉSUMÉ — On a étudié la décomposition thermique de $Pu(C_2O_4)_2 \cdot 6\,H_2O$ dans l'argon et dans l'oxygène à la fois par thermogravimétrie et par spectroscopie infrarouge. La décomposition dans une atmosphère inerte met en jeu la réduction du cation à l'état trivalent et sa réoxydation subséquente pour donner PuO_2. En atmosphère oxydante, avec accès nonlimité d'oxygène, la réduction du cation n'a pas lieu et la décomposition en PuO_2 s'effectue par l'intermédiaire de l'oxycarbonate. La réduction de Pu(IV) semble avoir lieu par un mécanisme catalysé par le monoxyde de carbone et on attribue la présence du carbone dans le produit de décomposition PuO_2 à la dismutation de CO.

ZUSAMMENFASSUNG — Die thermische Zersetzung von $Pu(C_2O_4)_2 \cdot 6\,H_2O$ wurde sowohl in Argon als auch in Sauerstoff unter Anwendung einer Kombination der Thermogravimetrie und der Infrarotspektroskopie untersucht. Die Zersetzung in einer inerten Atmosphäre umfaßt die Reduktion des Kations zur Dreiwertigen Form und seiner darauffolgenden Reoxidation zu PuO_2. In einer oxidierenden Atmosphäre mit unbeschränktem Sauerstoffzutritt findet die Reduktion des Kations nicht statt und die Zersetzung in PuO_2 erfolgt über das Oxycarbonat. Die Reduktion von Pu(IV) scheint durch einen kohlenmonoxidkatalysierten Mechanismus zu erfolgen und die Gegenwart von Kohle in dem PuO_2-Zersetzungsprodukt wird der Disproportionierung von CO zugeschrieben.

Резюме — Изучено термическое разложение $Pu(C_2O_4)_2 \cdot 6H_2O$ в атмосфере аргона и кислорода, используя комбинированную технику термогравиметрии и ИК спектроскопии. Разложение в инертной атмосфере протекает с восстановлением катиона до трехвалентного состояния и с последующим реокислением до PuO_2. В окислительной атмосфере с неограниченным доступом кислорода восстановление катиона не имеет место, а разложение протекает через оксикарбонат с образованием PuO_2. Восстановление Pu(IV) обусловлено каталитическим действием моноокиси углерода, а присутствие углерода в продуктах разложения PuO_2 обусловлено диспропорционированием CO.