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THERMOGRAVIMETRIC STUDY OF URANIUM PHOSPHATES

Part II: Neutral uranyl phosphate and U(IV) phosphates*

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The thermal decomposition of $(UO_2)_3(PO_4)_2$ and $U(HPO_4)_2 \cdot xH_2O$ in the temperature range 25—1600 °, was investigated.

$(UO_2)_3(PO_4)_2$ decomposed first to $1/3[U_3O_8 + 3U_2O_3P_2O_7]$ and then to $U_3O_5P_2O_7$ before a loss of phosphorus was observed above 1350°. Decomposition in air and in inert atmospheres was nearly identical.

Reduction with H_2 or with carbon black in argon gave $U_3O_5P_2O_7$ and $[UO_2 + (UO)_2P_2O_7]$ before pure UO_2 was formed.

$U(HPO_4)_2 \cdot xH_2O$ decomposed to UP_2O_7 in argon. It oxidized partly in air before the same product was obtained.

The high temperature stability of UP_2O_7 and $U_3(PO_4)_4$ was also investigated.

The thermal stabilitiy of $UO_2NH_4PO_4 \cdot 3H_2O$ and $UO_2HPO_4 \cdot 4H_2O$ in various atmospheres and their reduction in H_2 or with carbon black in argon was discussed in a previous paper [1].

The existence of neutral uranyl phosphate, $(UO_2)_3(PO_4)_2 \cdot xH_2O$, another compound in the same series, has been reported [2—5]. Its preparation and thermal decomposition in air, O_2, Ar and N_2 between 25 and 1000 °C was reported in another paper [6].

It was found that the tetrahydrate, $(UO_2)_3(PO_4)_2 \cdot 4H_2O$ or NUPT, dehydrates upon heating and that the anhydrous product is stable in air up to 1000°. The same anhydrous product, however, decomposes in Ar and N_2 below 1000° giving the mixture $[U_3O_8 + 3U_2O_3P_2O_7]$.

No information on its stability above 1000° or its reduction with H_2 or carbon black is available, although the compound $(UO)_3(PO_4)_2$, a possible decompositon product, was obtained by Burdese et al. [7] in their study of the system UO_2—P_2O_5.

Some U(IV) orthophosphates also exist. The best known are dibasic uranium phosphate, $U(HPO_4)_2 \cdot xH_2O$ or DUP, [8—13] and tribasic uraniumphosphate, $U_3(PO_4)_4 \cdot xH_2O$ or TUP, [14—16]. Very little is known about the thermal decomposition of these compounds and only a few papers give an indication of their high temperature stability.

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Experimental

Experimental techniques for TG, DTA, IR spectral analysis, X-ray diffraction and chemical analysis were described in the previous paper [1].

$(UO_2)_3(PO_4)_2 \cdot xH_2O$ was prepared as discussed in another paper [6]. The tetrahydrate, $(UO_2)_3(PO_4)_2 \cdot 4H_2O$, was obtained by heating the above product in air to 600° for 30 minutes and cooling in a moist atmosphere. The product was crystalline and could be identified by X-ray diffraction [17].

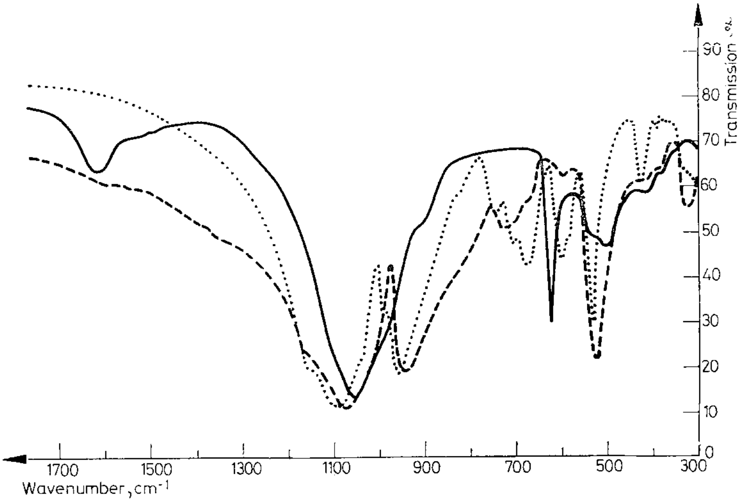

Fig. 1. IR absorption spectra. (———) Spectrum for $U(HPO_4)_2 \cdot xH_2O$; (— — — —) spectrum for UP_2O_7; (........) spectrum for $[(UO)_2P_2O_7 + UP_2O_7]$ mixture

Chemical analysis, by the gravimetric method [18], gave the following results: UO_2^{2+} 75.6%* (75.56% theor.), PO_4^{3-} 17.7% (17.72% theor.) and H_2O 6.7% (6.72% theor).

Dibasic uranium phosphate, $U(HPO_4)_2 \cdot xH_2O$, can be prepared by direct precipitation of U(IV) in acid medium by phosphoric acid. Contamination with TUP is possible and the composition of the gelatinous precipitate depends largely on the pH of the original solution and also on the concentration of strange ions [8–11]. The simple method described by Schreyer and Schreyer and Philips [12, 13] was followed, apart from small modifications in the washing procedure.

The precipitate was slightly hygroscopic and slowly adsorbed sufficient moisture to correspond roughly with the tetrahydrate.

Chemical analysis showed that no U(VI) was present and gave the following composition: U^{4+} (= U total) 48.1%(47.71% theor.) HPO_4^{2-} 37.9% (38.27% theor.) and H_2O 14.0% (14.02% theor.).

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* All % values in this paper are % by weight.

The product was not crystalline and only an IR spectrum could be obtained for further reference (Fig. 1).

Although the direct precipitation of TUP has been reported [14–16], it was not possible to obtain a sufficiently pure product suitable for thermogravimetric experiments. Some tests have therefore been carried out to prepare it by solid state reactions. These will be discussed hereafter.

Results and discussion

Decomposition of NUPT in argon

TG and DTA curves (Fig. 2) showed that, after dehydration below 300°, two endothermic reactions occurred between 770 and 1140°. The weight changes of 2.02% and 0.98% indicated that the two following reactions had probably taken place.

$$\text{Step I}\quad 3(UO_2)_3(PO_4)_2 \rightarrow U_3O_8 + 3U_2O_3P_2O_7 + 2O_2$$

$$\text{Step II}\quad U_3O_8 + 3U_2O_3P_2O_7 \rightarrow 3U_3O_5P_2O_7 + O_2.$$

Step I was already mentioned in a previous paper [6] and it was reported that its true temperature range was 770–932°. The activation energy calculated for this reaction was $(314 \pm 17)\ 10^3$ J/mole.

Chemical analysis of the reaction product at 1140° indicated that the U:P ratio was still 3:2 and that the U(IV):U(VI) ratio was equal to 2:1, which is required for the proposed $U_3O_5P_2O_7$. The IR spectrum (Fig. 3) did not correspond with that of any known U-ortho or pyrophosphate and neither could the typical peaks for U-oxides be detected, indicating that a single product have been formed.

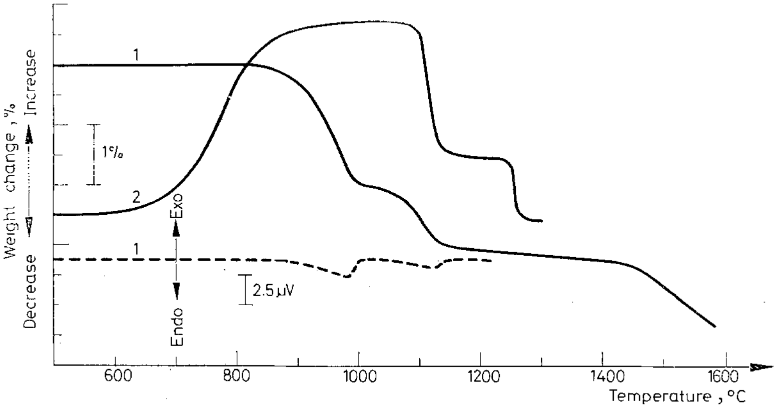

Fig. 2. Thermal analysis of $(UO_2)_3(PO_4)_2$ and $U_3O_5P_2O_7$. 1) TG for $(UO_2)_3(PO_4)_2$ at 6°/min in argon (DTA curve — — — —); 2) TG for $U_3O_5P_2O_7$ at 6°/min in air

X-ray diffraction of a crystalline compound, prepared by heating the mixture [UO_2 + U_3O_8 + $2UP_2O_7$] in argon at 1150° for 20 minutes, which gave the same IR spectrum as the above product also proved that a single product have been formed [19].

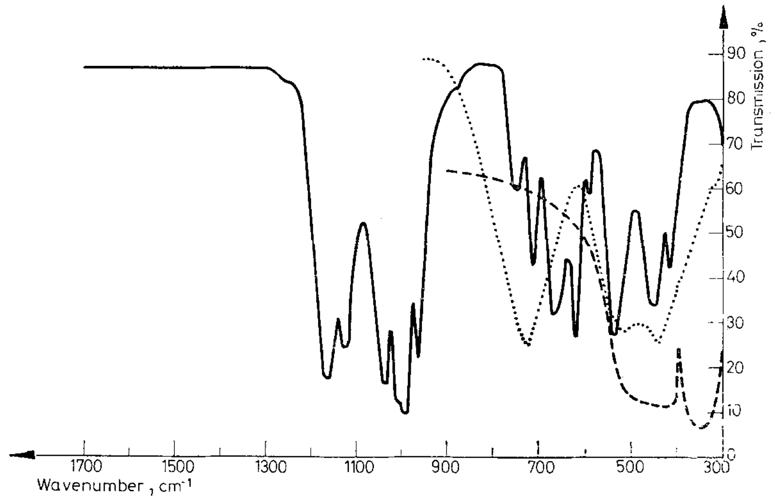

Fig. 3. IR absorption spectra. (———) Spectrum for $U_3O_5P_2O_7$; (— — — —) spectrum for UO_2; (.......) spectrum for U_3O_8

A true temperature range of 1000 – 1074° for step II was derived in the usual way, as well as an activation energy of (455 ± 49) 10^3 J/mole.

It is obvious that the reaction, given as step II, was not a simple decomposition. U_3O_8 and $U_2O_3P_2O_7$ are both stable in the temperature range concerned, and a recombination must therefore have taken place before the decomposition is possible. The following reaction mechanism for step II is therefore proposed:

Step IIa $U_3O_8 + 3U_2O_3P_2O_7 \rightarrow [U_9O_{17}(P_2O_7)_3]$
Step IIb $[U_9O_{17}(P_2O_7)_3] \rightarrow 3U_3O_5P_2O_7 + O_2$.

The decomposition (step IIb) is responsible for the TG curve, but it is much more likely that the recombination reaction is rate determining, in which case the activation energy given above is actually the value for the reaction given as step IIa.

A further weight decrease, due to a loss in phosphorus, was observed when the product was heated above 1140°. The decomposition rate, however, was only appreciable at 1450°. It was also observed that the product melted when it was heated to 1580°.

$U_3O_5P_2O_7$ was not hygroscopic and no obvious oxidation could be observed below 500° when it was heated in air. A single step oxidation occurred above this temperature with the formation of $(UO_2)_3(PO_4)_2$ at 900° (Fig. 2). The latter decomposed again to $U_3O_5P_2O_7$ above 1000°.

Decomposition of NUPT in air

It has been reported that NUPT dehydrates in air below 300 ° and that the anhydrous product is stable up to 1000° [6].

Between 1000 and 1300° a two step decomposition occurred (Fig. 4). Both reactions were endothermic and the experimental weight changes indicated that the same reactions as those given above for the decomposition in argon had probably taken place.

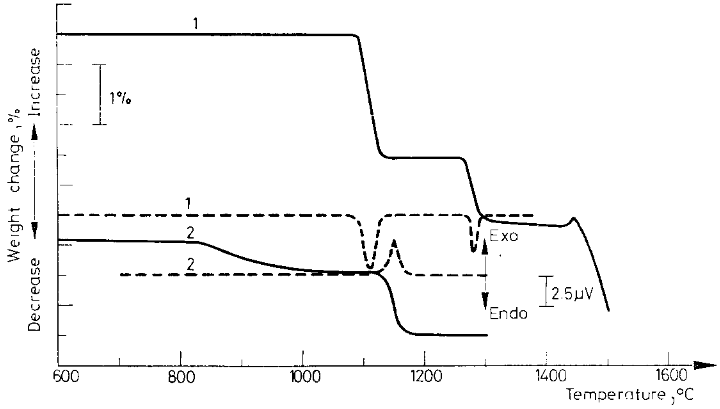

Fig. 4. Thermal analysis of $(UO_2)_3(PO_4)_2$ and $U_3O_5P_2O_7$. 1) TG for $(UO_2)_3(PO_4)_2$ at 6°/min in air (with DTA — — — —); 2) TG for $U_3O_5P_2O_7$ cooling at 6°/min in air (with DTA — — — —)

True temperature ranges of 1060 – 1190° and 1200 – 1282° and activation energies of (1175 ± 125) 10^3 J/mole and (1722 ± 122) 10^3 J/mole were derived for step I and step II, respectively.

Above 1300° a small but steady weight decrease was observed. At 1445° a small apparent weight increase appeared which was probably due to the fast evolution of gas afterwards. It is also possible that a partial reoxidation occurred at this temperature which may have been necessary for the final decomposition which started immediately afterwards. At 1500° the sample had melted.

Samples heated to 1350° reoxidized when they were cooled in air. When cooling at 6°/min, a first oxidation step was observed between 1180 and 1115° (Fig. 4). This reaction was exothermic and was clearly the opposite of the second decomposition step. The second reoxidation was appreciable only at 980° and was not yet complete at 830° when constant weight was obtained.

Comparison of the temperature ranges for the decomposition (1060–1132° for step I and 1220–1298° for step II at 6°/min) and reoxidation reactions (980–830° and 1180–1115°, respectively) gave the equilibrium values at which no change will take place. They were 1020° with either $(UO_2)_3(PO_4)_2$ or $1/3[U_3O_8 + 3U_2O_3P_2O_7]$ and 1200° with either $1/3\ [U_3O_8 + 3U_2O_3P_2O_7]$ or $U_3O_5P_2O_7$. It is obvious, however, that these temperatures will change with other oxygen concentrations.

Reduction of NUPT in H_2

When NUPT was heated in hydrogen the anhydrous product was obtained below 300°. The TG curve above this temperature (Fig. 5) showed a single step reaction between 350 and 657° with a weight loss of 4.50%. This suggested that a product with the composition $(UO_2)_3 \cdot P_2O_5$ have been formed, which could be verified by chemical analysis. A well-defined IR sepctrum was only obtained with a sample that was heated in argon to 1000° after reduction. This indicated that a mixture of UO_2 and $(UO)_2P_2O_7$ have been formed.

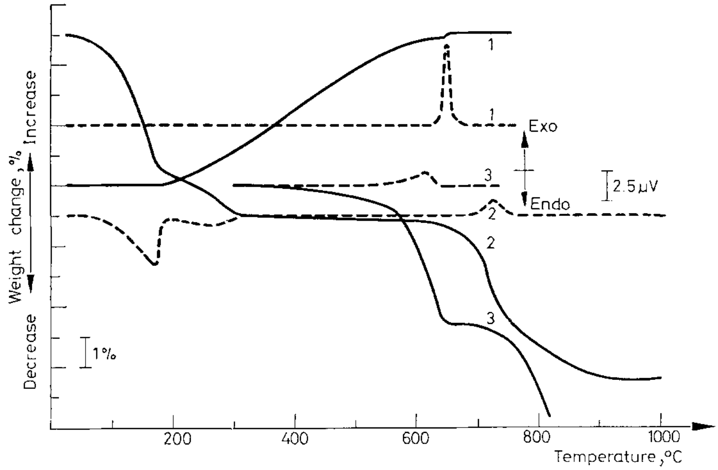

Fig. 5. Thermal analysis of $(UO_2)_3(PO_4)_2 \cdot 4H_2O$ and $[UO_2 + (UO)_2P_2O_7]$. 1) TG for $[UO_2 + (UO)_2P_2O_7]$ mixture at 6°/min in air (DTA curve — — —); 2) TG for $[(UO_2)_3(PO_4)_2 \cdot 4H_2O + 14\ C]$ mixture at 6°/min in argon (DTA curve — — —); 3) TG for $(UO_2)_3(PO_4)_2$ at 6°/min in hydrogen

The corresponding DTA trace (Fig. 5), showed that the reduction was exothermic. However, the exothermic effect ended before the weight change had finished, indicating that a two step reaction had probably taken place.

It was therefore assumed that the reduction in hydrogen followed the same two step mechanism as the one with carbon black in argon, according to the reactions below.

$$\text{Step I} \quad (UO_2)_3(PO_4)_2 \xrightarrow{H_2} U_3O_5P_2O_7 + 2H_2O$$

$$\text{Step II} \quad U_3O_5P_2O_7 \xrightarrow{H_2} UO_2 + (UO)_2P_2O_7 + H_2O.$$

Too much overlapping between the two reactions occurred to determine their individual temperature ranges. A true temperature range of 300–616° for the overall reaction could nevertheless be derived. Realistic figures for activation energies were obtained for step I only, with a value of $(156 \pm 3)\ 10^3$ J/mole.

Above 657° (Fig. 5) a further weight loss was observed and UO_2 was obtained at 950° after a single step reaction.

Oxidation of the mixture $[UO_2 + (UO)_2P_2O_7]$, obtained by reducing NUPT in hydrogen at 657°, started at 175°. The reaction was very slow and constant weight was only obtained at 650° (Fig. 5). Between 645 and 650° a sudden small weight increase occurred, which was accompanied by a sharp exothermic peak. This was believed to be due to a sudden crystallization of the amorphous product, formed after nearly complete oxidation, with the formation of $(UO_2)_3(PO_4)_2$. This product then formed the identified crystalline tetrahydrate on exposing it to a moist atmosphere.

Reduction of NUPT with carbon black in argon

Reduction experiments were carried out with mixtures containing 14 carbon atoms for each NUPT molecule. The complete TG curve, including the two dehydration steps, is reproduced in Figure 5.

Reduction started at 600° and constant weight was again obtained at 920° after a two step reaction. The DTA trace showed an exothermic peak for the first reduction step only. The experimental weight changes indicated that the following reactions may have taken place.

$$\text{Step I} \quad (UO_2)_3(PO_4)_2 \xrightarrow{C} U_3O_5P_2O_7 + CO_2$$

$$\text{Step II} \quad 2U_3O_5P_2O_7 \xrightarrow{C} 2UO_2 + 2(UO)_2P_2O_7 + CO_2$$

The intermediate product was identified by IR analysis of a sample obtained by heating a stoichiometric carbon mixture (U:C ratio = 3:1) to 900°.

True temperature ranges of 600–≥800° and ≤800–892° were derived. An activation energy value of $(287 \pm 26)\ 10^3$ J/mole for step I could be calculated, but no meaningful results were obtained for step II.

A further weight decrease was observed when the reaction mixture containing UO_2, $(UO)_2P_2O_7$ and carbon black, was heated above 1000° in argon. At 1250° constant weight was obtained with UO_2 as the reaction product, which indicated that a reaction, similar to the reduction of $(UO)_2P_2O_7$, had taken place [1]. Burdese and Borlera [7] have reported that, if the mixture $[UO_2 + (UO)_2P_2O_7]$ is heated above 1200° in an inert atmosphere, a recombination takes place with the formation of $(UO)_3(PO_4)_2$ (or $U_3O_4P_2O_7$). These results could not be verified as only UO_2 and $(UO)_2P_2O_7$ could be identified in such a mixture, even after heating to 1350°.

It was, however, observed that the X-ray diffraction pattern of the crystalline sample of $U_3O_5P_2O_7$ [19], described above, was nearly identical with that for $(UO)_3(PO_4)_2$ reported by Burdese and Borlera. It is therefore not impossible that their product was actually $U_3O_5P_2O_7$, which might have been formed by oxidation of the mixture $[UO_2 + (UO)_2P_2O_7]$ by traces of oxygen in the inert gas they used.

Decomposition of DUP in air

The TG curve for the thermal decomposition of DUP in air was reproduced in Figure 6. No thermal effects were observed.

The total weight loss at 960° was 17.8% which corresponds closely with the theoretical value of 17.93% for the overall reaction given below.

$$U(HPO_4)_2 \cdot 4H_2O \rightarrow UP_2O_7 + 5H_2O\ .$$

The end-product could be identified as UP_2O_7 by means of IR [20] (Fig. 1) and X-ray diffraction showed that α-UP_2O_7, the cubic high temperature modification, have been formed [16, 17].

A weight increase was observed between 450 and 700° and this could be attributed to a partial oxidation of the decomposing product. This was confirmed by chemical analysis of a sample taken at 700°, which revealed that about 25% of the uranium had oxidized to U(VI). However, the product was not sufficiently crystalline for X-ray diffraction and identification of the oxidation product by means of IR was not possible either.

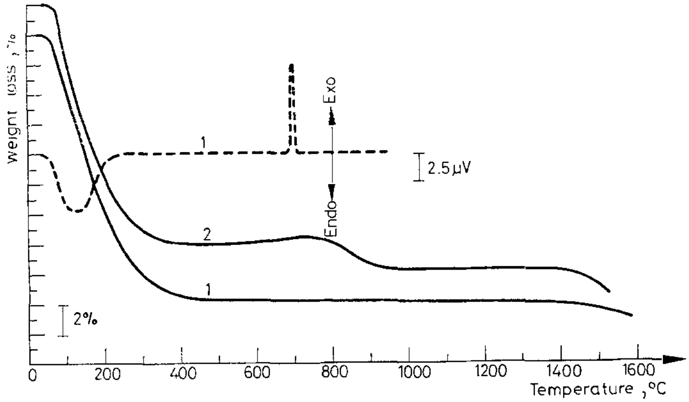

Fig. 6. Thermal analysis of $U(HPO_4)_2 \cdot xH_2O$. 1) TG for $U(HPO_4)_2 \cdot xH_2O$ at 6°/min in argon (DTA curve — — — —); 2) TG for $U(HPO_4)_2 \cdot xH_2O$ at 6°/min in air

The part of the TG curve above 1000° actually represents the stability of UP_2O_7. This compound was stable up to 1350° when a small but steady weight decrease, due to a loss in phosphorus, could be detected. This weight decrease became much faster around 1420° and increased progressively at still higher temperatures.

Decomposition of DUP in argon

The thermal decomposition of DUP in argon was less complicated than in air (Fig. 6). A continuous weight loss was observed up to 460° with a slight discontinuity in the TG curve around 200°. The discontinuity was not very reproducible and did not correspond with any specific decomposition step.

The first part of the TG curve was also accompanied by an exothermic effect which finished more or less at the point where the discontinuity occurred. This indicated that at least a two step decomposition took place, probably according to the reactions given below.

$$U(HPO_4)_2 \cdot 4H_2O \rightarrow U(HPO_4)_2 + 4H_2O$$
$$U(HPO_4)_2 \rightarrow UP_2O_7 + H_2O.$$

There was, however, too much overlapping to justify any definite conclusion.

Above 460°, the weight of the sample remained constant up to 1350°, but a sharp exothermic peak appeared in the DTA trace around 695° (Fig. 6).

Samples heated to just below this temperature could be identified as UP_2O_7 by means of IR, but they were hardly crystalline and only a few diffuse diffraction lines, corresponding with α-UP_2O_7, were obtained with a powder camera.

The samples heated above 695° could be identified as well crystallized α-UP_2O_7. This indicated that the thermal effect at this temperature was due to a sudden crystallization and not a possible β-α transition which normally occurs around 460° [7].

A linear relationship was found between the heating rate and the peak temperature of the exotherm. Extrapolation to a heating rate of 0°/min then gave a true crystallization temperature of 665°.

When UP_2O_7 was heated in argon above 1350° a slow weight decrease was observed, which again could be associated with a loss in phosphorus. The weight change, however, was very small even at 1500°.

Uranium pyrophosphate (UP_2O_7)

UP_2O_7 was formed by decomposing DUP in air or in an inert atmosphere. It is reported that the same compound will be obtained by heating $UO_2(H_2PO_4)_2$ xH_2O [21] or $U(PO_3)_4$ [22] or even a mixture of uranium oxide with phosphate or P_2O_5 [20] above 1000°.

These results were verified experimentally and they indicated that above

1000° UP_2O_7 is the only stable uranium phosphate with a U:P ratio 1:2, even in an oxidizing atmosphere.

UP_2O_7 was not hygroscopic and did not oxidize, not even when heated in a pure oxygen atmosphere to its decomposition temperature.

A decomposition occurred between 700 and 1000° when it was heated in H_2, leaving a residue of UO_2. UO_2 was also formed when it was heated with carbon black in an inert atmosphere at 1250°.

Tribasic uranium phosphate ($U_3(PO_4)_4$)

Anhydrous TUP can be obtained by heating the the precipitated product to 200° in an inert atmosphere [15].

It is reported that it is stable in an inert atmosphere up to 1350°. At higher temperatures a loss in phosphorus may occur [16]. The same authors also claim that the product does not oxidize in air after it has been heated in nitrogen.

As $U_3(PO_4)_4$ could not be obtained by direct precipitation a few attempts were made to prepare it by solid state reactions, using the following mixtures.

$$3UO_2 + 4(NH_4)_2HPO_4$$
$$2UO_2 + 4UP_2O_7$$
$$3(UO)_2P_2O_7 + 2(NH_4)_2HPO_4.$$

All the mixtures were first heated in hydrogen to 600° for 30 minutes to ensure complete reduction to U(IV). X-ray diffraction at this stage showed that all the samples contained only UO_2 and UP_2O_7 as crystalline material, and other compounds could not be detected by means of IR either.

No weight changes could be detected if any of the mixtures was subsequently heated in argon to 1350°. At still higher temperatures a small weight decrease due to a loss in phosphorus was observed.

Samples were taken between 1100 and 1350°. IR (Fig. 1) and X-ray diffraction showed that only mixtures of UP_2O_7 and $(UO)_2P_2O_7$ were obtained in this way and not the compound $U_3(PO_4)_4$. The samples oxidized to $[U_2O_3P_2O_7 + UP_2O_7]$ mixtures when heated in air, even after they had first been heated in argon.

These results were more consistent with those reported by Pannell and Rubino [14] who found that TUP starts dissociating at 600° with the formation of UP_2O_7 and a hardly crystalline product which they thought to be UO_2.

Conclusions

Anhydrous NUPT, $(UO_2)_3(PO_4)_2$, decomposed in argon with the formation of the mixture 1/3 $[U_3O_8 + 3U_2O_3P_2O_7]$ at 932° and $U_3O_5P_2O_7$ at 1070°. A further decomposition, which was accompanied by a loss in phosphorus, occurred at higher temperatures.

A similar decomposition pattern was found in air but the reaction temperatures were about 200° higher than in argon.

The mixture [$UO_2 + (UO)_2P_2O_7$] was formed at 616° when NUPT was heated in hydrogen, with $U_3O_5P_2O_7$ as a possible intermediate. Reduction with carbon black in an inert atmosphere was clearly a two-step reaction starting at 600°. The same mixture [$UO_2 + (UO)_2P_2O_7$] was formed, but only at 892°. Further reduction to pure UO_2 was possible in both cases.

The reported recombination of [$UO_2 + (UO)_2P_2O_7$] to $(UO)_3(PO_4)_2$ above 1200° could not be verified.

$U(HPO_4)_2 \cdot xH_2O$ dehydrated and was partly oxidized when heated in air, but UP_2O_7 was still obtained at 950°.

In argon complete dehydration occurred below 460° with the formation of non-crystalline UP_2O_7 · α-UP_2O_7 was then formed after a sudden crystallization at 690°.

UP_2O_7 was stable in air and argon up to 1350° but lost some phosphorus at higher temperatures. Reduction with hydrogen or with carbon black gave UO_2 as the reaction product.

Pure $U_3(PO_4)_4$ could not be obtained by direct precipitation. Its preparation by solid state reactions was also unsuccessful and only mixtures of UP_2O_7 and $(UO)_2P_2O_7$ could be obtained in argon, even after heating to 1350°.

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References

1. J. M. Schaekers, J. Therm. Anal., 6 (1974) 99.
2. A. D. Ryon and D. W. Kuhn, Report Y-381 (1949).
3. J. M. Schreyer and C. F. Baes, Jr., J. Amer. Chem. Soc., 76 (1954) 354.
4. N. Pavkovic, M. Branica and B. Tezak, Croat. Chem. Acta, 40 (1968) 117.
5. N. Pavkovic, M. Wrischer and M. Branica, Croat. Chem. Acta, 40 (1968) 127.
6. J. M. Schaekers, Proc. 3rd ICTA, Davos, Switzerland, 1971. [AED-conf.-71-247-006.]
7. A. Burdese and M. L. Borlera, Ann. Chim. (Rome), 53 (1963) 344.
8. R. G. d'Arcy, Report ACCO-22 (1952).
9. J. Dasher, Report MITG-420 (1950).
10. W. F. Arendale and C. F. Coleman, Report Y-501 (1949).
11. E. Strandell, Acta Chem. Scand., 11 (1957) 105.
12. J. M. Schreyer, J. Amer. Chem. Soc., 77 (1956) 2772.
13. J. M. Schreyer and L. R. Philips, J. Phys. Chem., 60 (1956) 588.
14. J. H. Pannell and E. M. Rubino, Report MITG-245 (1950).
15. Yu. P. Muromskii, Yu. P. Simanov and O. G. Nemkova, Report ANL-trans-33 p. 326.
16. A. Burdese and M. L. Borlera, Ric. Scient., 29 (1959) 2537.
17. H. W. Dunn, Report ORNL-2092 (1956).
18. J. M. Schaekers, Anal. Chem., 44 (1972) 1873.

19. J. M. SCHAEKERS, J. Appl. Crystall, 6 (1973) 249.
20. R. HUBIN and P. TARTE, Spectrochim. Acta, 23A (1967) 1815.
21. M. KAMO and S. OHASHI, Bull. Chem. Soc. Japan, 43 (1970) 84.
22. A. BURDESE and M. L. BORLERA, Ric. Scient., 30 (1960) 103.

RÉSUMÉ — On a étudié la décomposition thermique de $(UO_2)_3(PO_4)_2$ et de $U(HPO_4)_2 \cdot xH_2O$ entre 25 et 1600°.

$(UO_2)_3(PO_4)_2$ décompose d'abord en 1/3 $(U_3O_8 + 3U_2O_3P_2O_7)$ puis en $U_3O_5P_2O_7$, avant que la perte en phosphore ne s'observe au-dessus de 1350°. Le processus de la décomposition s'effectue à peu près de la même façon dans l'air et en atmosphère inerte.

La réduction par H_2 ou par le noir de carbone dans de l'argon donne $U_3O_5P_2O_7$ et $[UO_2 + (UO)_2P_2O_7]$ avant que UO_2 ne se forme

Dans l'argon, $U(HPO_4)_2 \cdot xH_2O$ se décompose en UP_2O_7. Dans l'air, il subit une oxydation partielle avant la formation du même produit.

On a également étudié la haute stabilité thermique de UP_2O_7 et de $U_3(PO_4)_4$.

ZUSAMMENFASSUNG — Die thermische Zersetzung von $(UO_2)_3(PO_4)_2$ und $U(HPO_4)_2 \cdot xH_2O$ wurde im Temperaturbereich von 25 bis 1600° untersucht.

$(UO_2)_3(PO_4)_2$ wurde zuerst zu 1/3 $[U_3O_8 + 3U_2O_3P_2O_7]$ und darauf zu $U_3O_5P_2O_7$ zersetzt, ehe ein Phosphorverlust oberhalb von 1350° beobachtet wurde. Die Zersetzung verlief in Luft und inerter Atmosphäre nahezu auf gleiche Weise.

Die Reduzierung mit H_2 oder mit Kohlenstoff in Argon ergab $U_3O_5P_2O_7$ und $[UO_2 + (UO)_2P_2O_7]$ vor der Bildung von UO_2. $U(HPO_4)_2 \cdot xH_2O$ wurde in Argon zu UP_2O_7 zersetzt. In Luft wurde es teilweise oxidiert, ehe dasselbe Produkt entstand. Die hohe Temperaturstabilität von UP_2O_7 und $U_3(PO_4)_4$ wurde ebenfalls geprüft.

Резюме — Исследован термораспад $(UO_2)_3(PO_4)_2$ и $U(HPO_4)_2 \cdot xH_2O$ в области температуры 25—1600°C. $(UO_2)_3(PO_4)_2$ распадается сначала до $1/3[U_3O_8 + 3U_2O_3P_2O_7]$ и затем до $U_3O_5P_2O_7$ до потери фосфора выше 1350°C. Распад в воздухе и в инертном газе практически тот же самый.

При восстановлении с водородом или с углеродом в аргоне образовались $U_3O_5P_2O_7$ и $[UO_2 + (UO)_2P_2O_7]$ до образования чистого UO_2. $U(HPO_4)_2 \cdot xH_2O$ распадается в UP_2O_7 в аргоне. Оно окисляется частично в воздухе до получения такого же продукта.

Исследована также высокая. термостабильность UP_2O_7 и $U_3(PO_4)_4$.