Journal of Thermal Analysis, Vol. 6 (1974) 145–157

THERMOGRAVIMETRIC STUDY OF URANIUM PHOSPHATES

PART I: URANYL AMMONIUM PHOSPHATE AND ACID URANYL PHOSPHATE*

J. M. SCHAEKERS**

Atomic Energy Board, Physical Metallurgy Division, Pretoria, South Africa

(Received 16 July, 1972)

The thermal decomposition of $UO_2NH_4PO_4 \cdot 3H_2O$ and $UO_2HPO_4 \cdot 4H_2O$ was studied in the temperature range 25 - 1600°C. Both compounds gave $U_2O_3P_2O_7$ around 900°C after a two step dehydration and an orthophosphate-pyrophosphate transformation.

$UO_2NH_4PO_4 \cdot 3H_2O$ did not form any pure intermediates, but $(UO_2)_2P_2O_7$ could be prepared from $UO_2HPO_4 \cdot 4H_2O$. In air, $U_2O_3P_2O_7$ lost phosphorus above 1250°C. In argon, $(UO)_2P_2O_7$ was first formed between 1000 and 1290°C and this product only lost phosphorus at still higher temperatures.

$(UO)_2P_2O_7$ was also obtained by reduction of $(UO_2)_2P_2O_7$ or $U_2O_3P_2O_7$ at 700°C in H_2 or with carbon black in argon above 1000°C. It oxidised in air above 250°C with the formation of $U_2O_3P_2O_7$.

Interest recently revived in uranium phosphates when phosphate containing ores had to be processed [1–4].

This led to the discovery that the uranyl ion, UO_2^{2+}, could be removed completely from acid solutions as uranyl ammonium phosphate, $UO_2NH_4PO_4 \cdot 3H_2O$ or UAP [5, 6]. This product was consequently used for chemical analysis as it was believed to decompose to $(UO_2)_2P_2O_7$ between 700° and 1000° [6–8].

More recently however, it was found that $U_2O_3P_2O_7$ will be formed if UAP is heated above 800° [9, 10].

A possible contaminant during the precipitation of UAP is the dibasic uranyl phosphate, $UO_2HPO_4 \cdot 4H_2O$, which is normally called acid uranyl phosphate or AUP. The thermal stability of this product in air has been discussed in a few papers [6, 11, 12]. However, a detailed study of the decomposition reactions and thermal stability of the different decomposition products under various conditions is not available.

The monobasic uranyl phosphate, $UO_2(H_2PO_4)_2 \cdot XH_2O$, has also been reported in the literature [4, 13, 14]. Its thermal decomposition was studied thoroughly by Kamo et al. [14], who found that no definite intermediate products were formed. The endproduct was UP_2O_7, which seems to be the only stable uranium phosphate,

---

* Some of the results in this paper were taken from a thesis, submitted in partial fulfilment of the requirements for an M. Sc. degree in Inorganic Chemistry.

** Present address: Department of Inorganic and Analytical Chemistry, University of Pretoria, Hillcrest, Pretoria, South Africa.

above 1000°, with a U : P ratio of 1 : 2, even in an oxidising atmosphere. These results could be verified and a detailed study was therefore not necessary.

Experimental

Thermogravimetric experiments were carried out with a Mettler automatic recording thermoanalyser. A suitable crucible holder (type TD_2), which allowed simultaneous DTA measurements, was used for most of the experiments. The capacity of the crucibles, made of Al_2O_3, was 0.03 cm^3.

The experiments were carried out at atmospheric pressure (88.0 kPa average) and under static conditions, which were achieved by using a continuous gas stream of 5 l/h. All gasses were purified and dried before use. The desired gas was introduced in the furnace after it had been evacuated to a pressure of 6.7 Pa.

The weight of the samples, which had always been ground in an agate ball mill, was normally 30 mg, but sometimes had to be increased or decreased, depending on the weight changes involved.

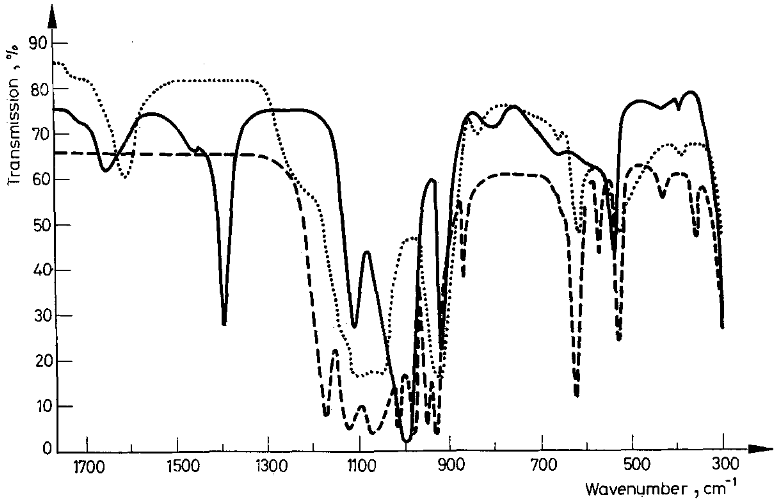

Fig. 1. IR absorption spectra: ———: Spectrum of $UO_2NH_4PO_4 \cdot 3H_2O$; ------- Spectrum of $U_2O_3P_2O_7$; ·······: Spectrum of $(UO_2)_2P_2O_7 \cdot H_2O$

Activation energies were calculated from at least four TG curves, obtained with different heating rates, using the differential method described by other authors [15, 16]. The reported values are always for the 50% completed reaction.

IR spectra were recorded with a Perkin Elmer 221 instrument using a sample concentration of 0.25% in a KBr matrix.

X-ray diffraction patterns were obtained with a Debye camera or a Siemens diffractometer, using Cu Kα radiation and a Ni filter.

Uranium and phosphate contents were determined gravimetrically as $U_2O_3P_2O^7$ [10]. NH_3 was estimated by an indirect Kjeldahl method and water of crystallisation was obtained by difference. The U(IV) content was determined by titrating with $KMnO_4$ after dissolving the sample with diluted H_2SO_4, in an inert atmosphere.

UAP was prepared from 0.01 M $UO_2(NO_3)_2$ solutions. Suitable amounts of H_3PO_4 were first added and, if necessary, some HNO_3 to obtain a clear solution. Precipitation was then brought about by neutralising with an ammonia solution. The results of a typical analysis were: UO_2^{2+} 61.9% (61.78% theor.), PO_4^{3-} 21.8% (21.74% theor.), NH_4^+ 4.1% (4.12% theor.) and H_2O 12.2% (12.36% theor.). Identification of the product was also possible by means of X-ray diffraction [17]. The IR spectrum was identical with that of AUP [12] apart from the strong peak, around 1400 cm^{-1}, due to NH_3 (Fig. 1).

AUP can be prepared from pure $UO_2^{2+} - PO_4^{3-}$ mixtures. However, the U : P ratio must be kept ≤ 1 to avoid contamination with neutral uranyl phosphate, $(UO_2)_3(PO_4)_2 \cdot XH_2O$, [13,18–20]. Precipitation of the tetrahydrate was therefore brought about by adding 24 cm^3 1.0 M UO_2^{2+} to 100 cm^3 of a 0.25 M H_3PO_4 solution. Chemical analysis, by the gravimetric method, gave the following results: UO_2^{2+} 61.8% (61.64% theor.), HPO_4^{2-} 21.7% (21.92% theor.) and H_2O 16.5% (16.44% theor.). The product could also be identified by means of X-ray diffraction [17] and IR analysis [12].

Results and discussion

Decomposition in air

UAP: A representative TG curve is reproduced in Fig. 2, together with the corresponding DTA trace (only up to 1000°) which showed that all the decompositions were endothermic. The experimental weight changes, given in Table 1, are compatible with the following reactions:

Step I $UO_2NH_4PO_4 \cdot 3H_2O \rightarrow UO_2NH_4PO_4 \cdot 0.5H_2O + 2.5H_2O$
Step II $UO_2NH_4PO_4 \cdot 0.5H_2O \rightarrow UO_2NH_4PO_4 + 0.5H_2O$
Step III $UO_2NH_4PO_4 \rightarrow UO_2HPO_4 + NH_3$
Step IV $2UO_2HPO_4 \rightarrow (UO_2)_2P_2O_7 + H_2O$
Step V $2(UO_2)_2P_2O_7 \rightarrow 2U_2O_3P_2O_7 + O_2$

Table 1

Thermal decomposition of UAP in air

Step	% Weight loss (theoretical)	% Weight loss (exper., 4°/min)	Temp. range (°C, 4°/min)	Activation energy (J/mole)
I	10.30	10.00(8.50 + 1.50)	25 – >114	(72.0 ± 0.8) 10^3
II	2.06	2.38	<114 – 148	(69.0 ± 5.0) 10^3
III	3.89	4.34	250 – >473	(143 ± 8) 10^3
IV	2.06	2.05	<473 – 590	(260 ± 12) 10^3
V	1.83	1.56	730 – 864	(583 ± 71) 10^3

The difference between the theoretical and experimental weight changes is mainly due to the large amount of overlapping between consecutive reactions. A good separation was only obtained between step II and step III. A weight loss of approximately 1.5% had to be added to the experimental value for step I to allow for the dehydration which had already taken place during the process of changing the atmosphere to dry air.

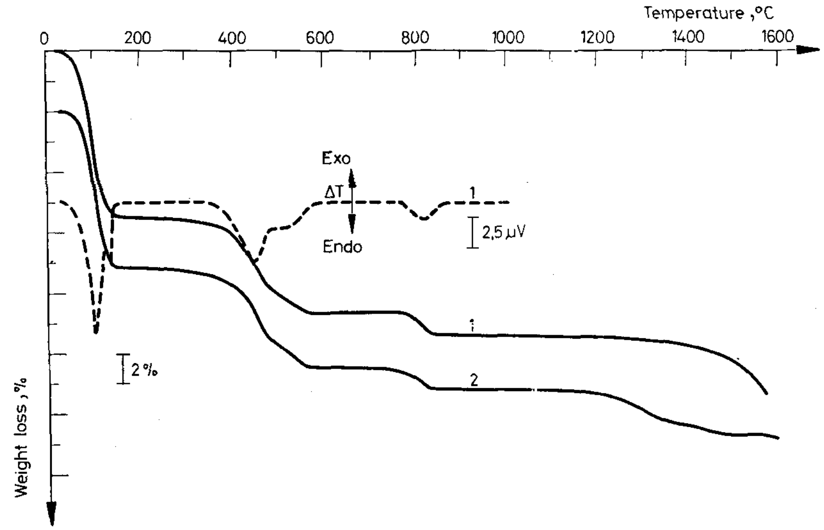

Fig. 2. Decomposition of $UO_2NH_4PO_4 \cdot 3H_2O$: 1) TG at 4°/min in air (with DTA - - - - - - -); 2) TG at 4°/min in argon

Between step IV and step V a slight weight increase of 0.10% was found, which was not observed in an inert atmosphere and was probably due to the oxidation of $(UO)_2P_2O_7$. Some of this product could have been formed by the reduction of UO_2HPO_4 with NH_3, which was volatilised in step III. The reduction may have taken place according to the following reactions.

$$2UO_2HPO_4 \xrightarrow[T > 400°]{NH_3} U_2O_3P_2O_7$$

$$U_2O_3P_2O_7 \xrightarrow[T > 400°]{NH_3} (UO)_2P_2O_7$$

This is also consistent with the experimental weight loss for step V, which was much smaller than the theoretical expected value.

The endproduct at 900° was $U_2O_3P_2O_7$. Chemical analysis showed that both the U : P and U(VI) : U(IV) ratios were 1 : 1. Its IR spectrum (Fig. 1) was identical with that of $(UO_2)_2P_2O_7$ reported in the literature [12]. The latter, however, had been prepared by heating either UAP or AUP in air to 700° and strong contamination with $U_2O_3P_2O_7$ had probably taken place.

$U_2O_3P_2O_7$ is not hygroscopic. It was stable in air and oxygen up to 1250–1300°. At still higher temperatures a further decomposition, due to a loss in phosphorus, was observed.

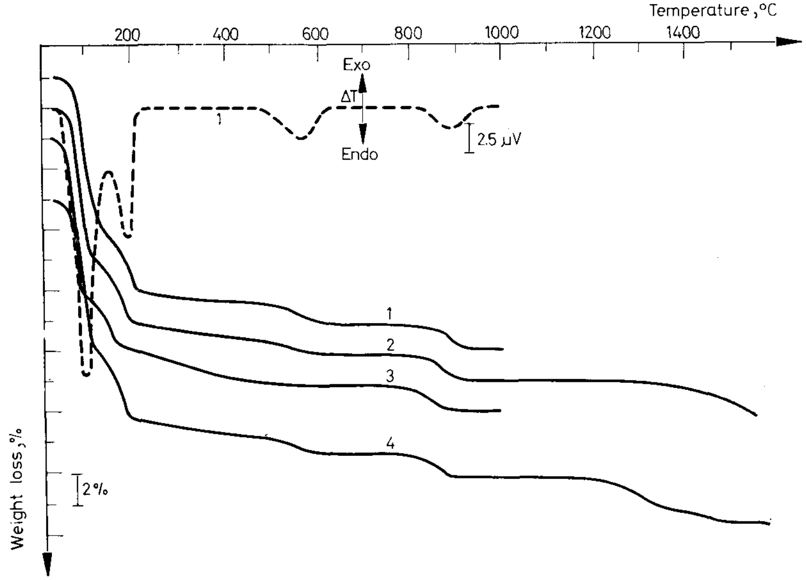

Fig. 3. Decomposition of $UO_2HPO_4 \cdot 4H_2O$: 1) TG at 8°/min in air (with DTA - - - - - - - -); 2) TG at 4°/min in air; 3) TG at 2°/min in air; 4) TG at 4°/min in argon

Activation energies for the five decompositions are given in Table 1.

True endpoint temperatures were derived by linearly extrapolating the experimental values, obtained with different heating rates, to a theoretical heating rate of 0°/min. These were combined with the incipient temperatures to give the true temperature ranges given in Table 2. The results of a few other authors were also given for comparison. An explanation for the appreciable differences cannot be given, as the experimental conditons were not reported in detail.

AUP: Some TG curves are given in Fig. 3, together with a DTA curve which showed that the four decomposition reactions were endothermic. The experimental weight losses (Table 3) indicated that the following reactions had probably taken place.

Step I $UO_2HPO_4 \cdot 4H_2O \rightarrow UO_2HPO_4 \cdot H_2O + 3H_2O$

Step II $UO_2HPO_4 \cdot H_2O \rightarrow UO_2HPO_4 + H_2O$

Step III $2UO_2HPO_4 \rightarrow (UO_2)_2P_2O_7 + H_2O$

Step IV $2(UO_2)_2P_2O_7 \rightarrow 2U_2O_3P_2O_7 + O_2$

Table 2

Comparison of decomposition temperatures for UAP

Step	Reference [6]	Reference [9]	Reference [7]	Own results
I	40 - 130	20 - 120	20 - 130	25 – > 83
II	160 - 170		180 - 200	< 83 – 107
III	410 500	275 - 350	410 - 510	250 – >424
IV	560 - 580	500 - 700	625 - 700	<424 - 560
V	not <850	700 - 1000	—	720 - 820

The large difference between the theoretical and experimental weight loss for step I (2.10%) was again due to a dehydration which occurred while the furnace was evacuated.

The endproduct at 950° could be identified as $U_2O_3P_2O_7$.

The part of the TG curves representing the third step, was rather unusual in that its shape changed when different heating rates were used (Fig. 3). The decomposition rate always changed around 425°, being slow below this temperature and much faster above, and this was thought to be due to a structural change from $2UO_2HPO_4$ to $(UO_2)_2P_2O_7 \cdot H_2O$.

It is apparent that this possibility could be verified by IR analysis of samples taken between 200 and 650° when AUP was heated at 8°/min. The spectra of all the samples taken below 425° still showed the typical orthophosphate peak at 900 cm^{-1}, which was absent, however, in those of the samples taken above 425°. The spectra of the latter were identical with that of $(UO_2)_2P_2O_7$ which had adsorbed some water (Fig. 1).

Therefore it was concluded that the decomposition mechanism for step III depends on the temperature and its probable reaction scheme is given below.

$$\begin{tikzcd}
2UO_2HPO_4 \arrow[r, "T < 425^\circ"] \arrow[d, "T = 425^\circ"] & (UO_2)_2P_2O_7 + H_2O \\
(UO_2)_2P_2O_7 \cdot H_2O \arrow[ur, "T > 425^\circ"'] &
\end{tikzcd}$$

The decomposition of $U_2O_3P_2O_7$, obtained from AUP, was identical with that obtained from UAP and was discussed above.

Table 3

Thermal decomposition of AUP in air

Step	% Weight loss (theoretical)	% Weight loss (exper., 4°/min)	Temp. range (°C, 4°/min)	Activation energy (J/mole)
I	12.33	12.25(10.15 + 2.10)	25 - >122	$(54.4 \pm 1.5)\ 10^3$
II	4.11	4.11	<122 - 192	$(80.4 \pm 9.6)\ 10^3$
III	2.05	2.14	192 - 610	—
IV	1.83	1.70	800 - 931	$(385 \pm 50)\ 10^3$

No activation energy could be calculated for step III. The values for the other steps are given in Table 3. True end point temperatures were calculated and the resulting true temperature ranges are compared with a few results from the literature in Table 4. The dehydration temperatures differ somewhat, but the other end point values agree fairly well.

Table 4

Comparison of decomposition temperatures for AUP

Step	Reference [11]	Reference [12]	Reference [6]	Own results
I	25 - 160	25 - 160	30 - 180	25 - >97
II	160 - 200	160 - 220	230 - 250	<97 - 170
III	500 - 550	550 - 620	560 - 600	170 - 550
IV	max = 700	810 - 900	not <850	800 - 880

Decomposition in other atmospheres

The thermal stability of UAP and AUP was also studied in oxygen, nitrogen and argon. The decomposition pattern in oxygen was very much the same as the one in air over the entire temperature range. However, the end point temperatures for the formation of $U_2O_3P_2O_7$ were approximately 50° higher.

The weight increase found for UAP between steps IV and V was also larger.

The decomposition pattern, below 1000°, in argon and nitrogen did not differ much either. No weight increase was found between steps IV and V in the TG curve of UAP (Fig. 2) which was further evidence for the reduction-oxidation process described above.

The end point temperatures for the formation of $U_2O_3P_2O_7$ were about 25° lower than the ones observed in air. This indicated that, although $U_2O_3P_2O_7$ cannot be reoxidised in air at atmospheric pressure, its formation reaction is nevertheless reversible.

$U_2O_3P_2O_7$ decomposed further in an inert atmosphere above 1000° (Figs 2 and 3). At 1200° the decomposition was appreciable and an inflection point was observed in the TG curve at 1340°. The weight loss of 1.82% at this temperature indicated that the following reaction may have taken place:

$$2U_2O_3P_2O_7 \rightarrow 2(UO)_2P_2O_7 + O_2$$

Chemical analysis of the product showed that the U : P ratio had remained constant at 1 : 1 and that only U(IV) was present. The IR spectrum was not well defined (Fig. 4) but it was identical with that of a product, prepared by heating a 2 : 1 mixture of UO_2 and P_2O_5 in argon above 1000°, which could be identified as $(UO)_2P_2O_7$ by means of X-ray diffraction [21].

A true temperature range of 1000 – 1290° and an activation energy of (462 ± 23) 10^3 J/mole were eventually derived for this reaction.

Further decomposition, which was accompanied by a loss in phosphorus, occurred above 1340° (Figs 2 and 3). The reaction product melted around 1480°, which was probably the reason why a nearly constant weight was observed at this temperature. The IR spectrum of a sample taken at this point was hardly recognisable, although it still resembled the spectrum of $(UO)_2P_2O_7$ (Fig. 4) indicating that no definite intermediate had formed.

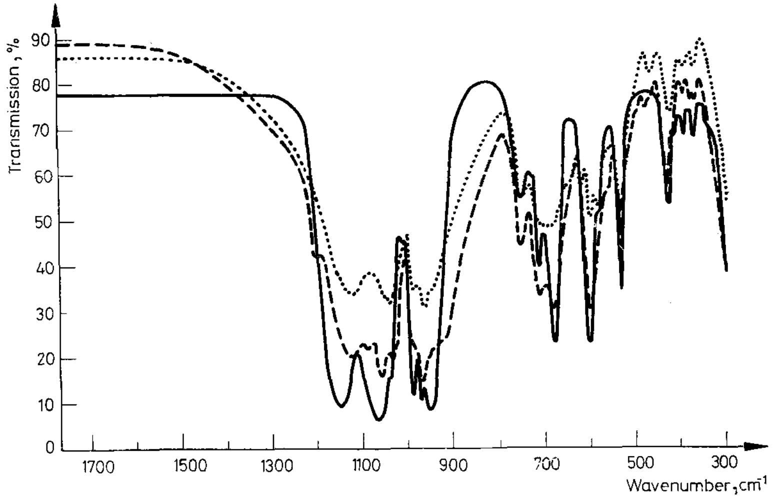

Fig. 4. IR absorption spectra: ———— : $(UO)_2P_2O_7$ heated in argon between 1000 and 1200°; - - - - - - -: $(UO)_2P_2O_7$ by decomposition of UAP in argon at 1350°; · · · · · · ·: $(UO)_2P_2O_7$ heated in argon at 1480°

Reduction of $U_2O_3P_2O_7$ and $(UO_2)_2P_2O_7$ in hydrogen

UAP and AUP were first dehydrated in the usual way when they were heated in a stream of hydrogen. Reduction commenced during the third decomposition step, around 425°, with the formation of $(UO)_2P_2O_7$ at 670° and UO_2 at 1000°. Similar results have been reported in the literature [22, 23].

$U_2O_3P_2O_7$: The starting material for these tests was prepared by heating UAP in air to 1000°. The TG and DTA curves (Fig. 5) showed that a single step exothermic reduction had taken place between 400 and 680°. The experimental weight loss of 2.39% agrees fairly well with the reaction below:

$$U_2O_3P_2O_7 \xrightarrow{H_2} (UO)_2P_2O_7 + H_2O$$

The true temperature range for this reaction was 350 – 636°. An activation energy of (165 ± 5) 10^3 J/mole could also be calculated.

Above 700°, a further weight decrease indicated the start of a reductive decomposition with the formation of UO_2.

$(UO_2)_2P_2O_7$: This product was prepared by heating AUP to 590° in air for 30 minutes. The product was hygroscopic but all the adsorbed water was volatilised again well below 350° and it did therefore not interfere with the reduction reactions.

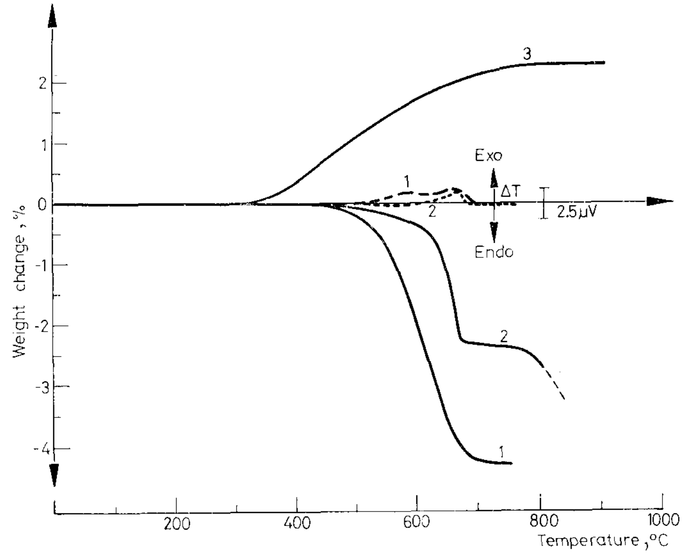

Fig. 5. Thermal analysis of $(UO_2)_2P_2O_7$, $U_2O_3P_2O_7$ and $(UO)_2P_2O_7$: 1) TG for $(UO_2)_2P_2O_7$ at 4°/min in H_2 (with DTA — — — -); 2) TG for $U_2O_3P_2O_7$ at 4°/min in H_2 (with DTA - - - - - - -); 3) TG for $(UO)_2P_2O_7$ at 4°/min in air

The TG curve (Fig. 5), with a weight loss of 4.27%, suggested a single step reduction to $(UO)_2P_2O_7$ between 350 and 700°, but DTA proved it to be a much overlapping two step reduction, probably according to the reactions given below:

$$\text{Step I} \qquad (UO_2)_2P_2O_7 \xrightarrow{H_2} U_2O_3P_2O_7 + H_2O$$

$$\text{Step II} \qquad U_2O_3P_2O_7 \xrightarrow{H_2} (UO)_2P_2O_7 + H_2O$$

The overall true temperature range was 350–652°. An activation energy of $(135 \pm 5)\ 10^3$ J/mole for step I was calculated, but a meaningful value for step II could not be obtained.

The end product of both reduction experiments was characterised by chemical analysis, giving a 0% U(VI) content and an unchanged U : P ratio of 1 : 1. A well-defined IR spectrum (Fig. 4) was only obtained after heating the product in argon to 1000°.

Reduction of $U_2O_3P_2O_7$ and $(UO_2)_2P_2O_7$ with carbon black in argon

The carbon black employed was "Durex O", a finely divided powder. The adsorbed volatile matter was first removed by heating it for three hours to 1000° at a pressure of 1.34 Pa. No weight change could be detected below 1200° when this product was then reheated in an inert atmosphere. Intimate carbon mixtures were obtained by grinding the different materials together in a small ball mill.

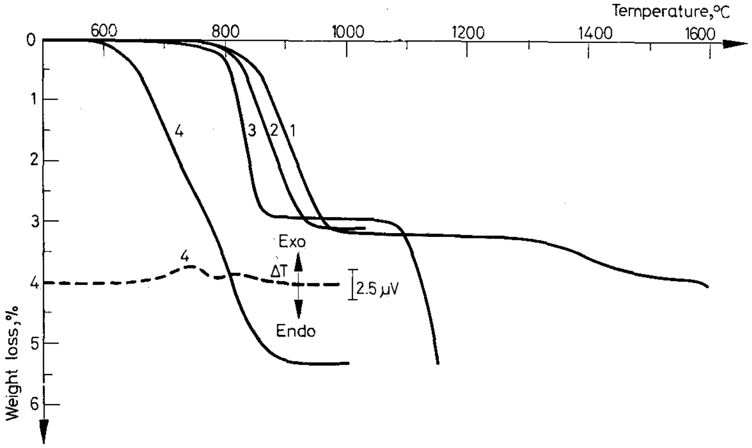

Fig. 6. Thermal analysis of $(UO_2)_2P_2O_7$ and $U_2O_3P_2O_7$ mixed with carbon black: 1) TG for $[U_2O_3P_2O_7 + 0.5\ C]$ mixture at 4°/min in argon; 2) TG for $[U_2O_3P_2O_7 + 2.0\ C]$ mixture at 4°/min in argon; 3) TG for $[U_2O_3P_2O_7 + 10\ C]$ mixture at 4°/min in argon; 4) TG for $[(UO_2)_2P_2O_7 + 11\ C]$ mixture at 4°/min in argon (with DTA - - - - - -)

$U_2O_3P_2O_7$: The complete reduction of $U_2O_3P_2O_7$ was studied with a mixture containing 10 carbon atoms for each pyrophosphate molecule. The weight loss of 2.79% between 600 and 873° (Fig. 6) suggested a reduction to $(UO)_2P_2O_7$, probably according to the reaction below:

$$2U_2O_3P_2O_7 \xrightarrow{C} 2(UO)_2P_2O_7 + CO_2$$

No obvious DTA signal was observed during the reaction for which a true temperature range of 600–840° could be derived as well as an activation energy of (384 ± 26) 10^3 J/mole.

A reductive decomposition took place above 1050°, giving UO_2 at 1250° and if sufficient carbon was still present U-metal or U-carbides were formed at 1600°. These results are similar to those reported for the reduction of Ca-phosphates [24, 25]. It has also been reported that Ca_3P_2 may be obtained under certain conditions [26]. No UP could, however, be detected at any stage of the reaction.

It was also observed that the temperature ranges and activation energies changed when the carbon content of the samples was varied and a sample containing only two carbon atoms for each pyrophosphate molecule gave an activation energy of (317 ± 8) · 10^3 J/mole and an endpoint temperature of 962° (Fig. 6), compared with (384 ± 26) · 10^3 J/mole and 873° for the sample discussed above.

$(UO_2)_2P_2O_7$: The reduction in argon was studied with a mixture containing 11 carbon atoms for each pyrophosphate molecule. TG and DTA (Fig. 6) indicated that a two step exothermic reduction occurred between 500 and 920°. The experimental weight losses of 2.75 and 2.62% indicated that the two following reactions may have taken place:

$$\text{Step I} \quad 2(UO_2)_2P_2O_7 \xrightarrow{C} 2U_2O_3P_2O_7 + CO_2$$

$$\text{Step II} \quad 2U_2O_3P_2O_7 \xrightarrow{C} 2(UO)_2P_2O_7 + CO_2$$

The endproduct was again characterised by means of IR and chemical analysis. Although a certain amount of overlapping occurred between the two reactions, it was still possible to derive true temperature ranges of 500 – >716° and <716 – 895° and activation energies of (192 ± 19) · 10^3 J/mole and (390 ± 20) · 10^3 J/mole for step I and II respectively.

Stability of $(UO)_2P_2O_7$

Pure samples of $(UO)_2P_2O_7$ were prepared by heating stoichiometric mixtures of $U_2O_3P_2O_7$ and carbon black (U : C ratio 4 : 1) in argon to 1000°. In argon the compound only started decomposing above 1250°. The TG curve (Fig. 6) above 1350° was identical with the TG curve for the decomposition of UAP or AUP in argon, in the same temperature range, and this was discussed above.

$(UO)_2P_2O_7$ was not hygroscopic and oxidation was only observed above 250° when it was heated in air (Fig. 5). The oxidation product was $U_2O_3P_2O_7$ and was obtained at 800°.

Conclusions

UAP decomposed when it was heated in air giving $U_2O_3P_2O_7$ at 1000° after five endothermic reactions. Ammonia, which was volatilised in the third step, partly reduced the remaining product to $(UO)_2P_2O_7$, but the final endproduct was still $U_2O_3P_2O_7$.

The same product was obtained when AUP was heated in air to 1000°, but only after four decomposition steps. At 425° a structural change from $2UO_2HPO_4$ to $(UO_2)_2P_2O_7 \cdot H_2O$ occurred. The decomposition of the anhydrous product UO_2HPO_4 to $(UO_2)_2P_2O_7$ therefore was temperature dependent.

Pure $(UO_2)_2P_2O_7$ could be prepared from AUP but not from UAP.

$U_2O_3P_2O_7$ was stable in air up to 1250–1300°. Above this temperature a loss of phosphorus was observed. It was, however, less stable in argon and decomposed to $(UO)_2P_2O_7$ between 1000 and 1290°. A loss of phosphorus was again observed at higher temperatures.

$U_2O_3P_2O_7$ and $(UO_2)_2P_2O_7$ could be reduced to $(UO)_2P_2O_7$ with either hydrogen or with carbon black in argon at 650° and 1000° respectively. This product was still further reduced to UO_2 at higher temperatures.

$(UO)_2P_2O_7$ was not hygroscopic. It started oxidising above 250° in air.

*

I should like to thank Miss Cynthia Bennett for the assistance with the laboratory work, Mr. L. A. Goold for recording the many IR spectra and Mr. W. G. Greybe for obtaining the X-ray diffraction patterns.

I also wish to thank the Atomic Energy Board of South Africa for permission to publish this paper.

References

1. I. Ingelsrud, et al., Report BMI-JDS-212 (1949).
2. H. W. Adam, et al., Report BMI-JDS-214 (1949).
3. R. G. d'Arcy, Report ACCO-22 (1952).
4. C. F. Baes, Jr., J. M. Schreyer and J. M. Lesser, Report AECD-3596 (1953).
5. W. W. Harris and Reberta H. Scott, Report AECD-2746 (1949).
6. V. I. Karpov and Ts. L. Ambartsumyan, Russ. J. Inorg. Chem. English Transl., 7 (1962) 949.
7. C. Duval, "Inorganic Thermogravimetric Analysis", Elsevier Publishing Company, Amsterdam, Sec. Ed., 1963, p. 666.
8. G. W. C. Milner, D. H. Rowe and G. Phillips, Report AERE-A4906 (1965).
9. A. E. Klygin, et al., J. Anal. Chem. USSR, English Transl., 15 (1960) 311.
10. J. M. Schaekers, Anal. Chem., 44 (1972) 1873.
11. V. Pekarek and M. Benosova, J. Inorg. Nucl. Chem., 26 (1964) 1743.
12. V. Pekarek and V. Veseley, J. Inorg. Nucl. Chem., 27 (1965) 1151.
13. J. M. Schreyer and C. F. Baes, Jr., J. Am. Chem. Soc., 76 (1954) 354.
14. M. Kamo and S. Ohashi, Bull. Chem. Soc. Japan, 43 (1970) 84.
15. J. H. Flynn and L. A. Wall, J. Res. Nat. Bur. Std., A. 70A (1966).
16. H. G. Wiedeman, A. van Tets and H. P. Vaughan, Paper presented at the Pittsburg Conference on Analytical Chemistry and Applied Spectroscopy, Feb., 1966.
17. H. W. Dunn, Report ORNL-2092 (1956).
18. N. Pavkovic, M. Branica and B. Tezak, Croat. Chem. Acta, 40 (1968) 117.
19. N. Pavkovic, M. Wrischer and M. Branica, Croat. Chem. Acta, 40 (1968) 127.
20. A. D. Ryon and D. W. Kuhn, Report Y-315 (1949) and Y-381 (1949).
21. A. Burdese and M. L. Borlera, Ann. Chim. Rome, 53 (1963) 344.
22. H. A. Bernhardt, W. Davis, Jr. and R. J. Heus, Report K-383 (1949).
23. H. A. Bernhardt, et al., Report K-429 (1949).
24. D. A. Patrushev and A. S. Mikulinskii, J. Appl. Chem. USSR, English Transl., 33 (1960) 781.
25. K. D. Jacob and D. S. Reynolds, Ind. Eng. Chem., 20 (1928) 1240.
26. H. W. Ross, A. L. Mehring and R. M. Jones, Ind. Eng. Chem., 16 (1924) 563.

Zusammenfassung — Die thermische Zersetzung von $UO_2NH_4PO_4 \cdot 3H_2O$ und $UO_2HPO_4 \cdot 4H_2O$ wurde im Temperaturbereich von 25 bis 1600° untersucht. Beide Verbindungen ergaben nach einer zweistufigen Dehydratation und einer Ortophosphat-Pyrophosphat-Umlagerung um 900° $U_2O_3P_2O_7$.

$UO_2NH_4PO_4 \cdot 3H_2O$ bildete keine reinen Zwischenprodukte, doch konnte aus $UO_2HPO_4 \cdot 4H_2O$ $(UO_2)_2P_2O_7$ hergestellt werden. In der Luft verlor $U_2O_3P_2O_7$ über 1250° Phosphor. In Argon entstand zuerst zwischen 1000 und 1290° $(UO)_2P_2O_7$ und dieses Produkt gab bei noch höheren Temperaturen Phosphor ab. $(UO)_2P_2O_7$ wurde auch durch Reduktion von $(UO_2)_2P_2O_7$ oder $U_2O_3P_2O_7$ bei 700° in H_2 oder mit Kohle in Argon über 1000° erhalten. Es wurde in Luft bei Temperaturen über 250° unter Bildung von $U_2O_3P_2O_7$ oxydiert.

Résumé — Etude de la décomposition thermique de $UO_2NH_4PO_4 \cdot 3H_2O$ et de $UO_2HPO_4 \cdot 4H_2O$ entre 25 et 1600°C. Ces deux composés donnent $U_2O_3P_2O_7$ à 900°C environ, après une déshydratation en deux étapes et la transformation de l'orthophosphate en pyrophosphate.

Dans le cas de $UO_2NH_4PO_4 \cdot 3H_2O$, il ne se forment pas de composés intermédiaires purs alors qu'on peut obtenir $(UO_2)_2P_2O_7$ à partir de $UO_2HPO_4 \cdot 4H_2O$. Dans l'air, le départ du phosphore de $U_2O_3P_2O_7$ s'effectue au-dessus de 1250°C. Dans l'argon, il se forme d'abord $(UO)_2P_2O_7$ entre 1000 et 1290°C, aux température plus elevees ce produit perd encore du phospore. Il est également possible d'cbtenir $(UO)_2P_2O_7$ en réduisant $(UO_2)_2P_2O_7$ ou $U_2O_3P_2O_7$ à 700°C par l'hydrogène ou bien par le carbone en opérant dans l'argon au-dessus de 1000°C. Ce produit, chauffé dans l'air, s'oxyde au-dessus de 250°C avec formation de $U_2O_3P_2O_7$.

Резюме — Изучен термораспад $UO_2\text{И}H_4PO_4 \cdot 3H_2O$ и $UO_2HPO_4 \cdot 4H_2O$ в области температур 25—1600°. Оба соединения, после двухступенчатой дегидратации и превращения отрофосфат — пирофосфат, дают около 900° $U_2O_3P_2O_7$

UO_2 $H_4PO_4 \cdot 3H_2O$ не образует чистых промежуточных продуктов, однако из $UO_2HPO_4 \cdot 4H_2O$ можно получить $(UO_2)_2P_2O_7$. $U_2O_3P_2O_7$ в атмосфере воздуха теряет фосфор при температурах выше 1250°. $(UO)_2P_2O_7$ в аргоне образуется первым между 1000 и 1290° и теряет фосфор при еще более высоких температурах. $(UO)_2P_2O_7$ также был получен восстановлением $(UO_2)_2P_2O_7$ или $U_2O_3P_2O_7$ при 700° в водороде или с помощью сажи в аргоне выше 1000°. На воздухе он окисляется выше 250° с образованием $U_2O_3P_2O_7$.