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Thermal Decomposition of Uranyl Dihydrogen Orthophosphate Trihydrate

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The thermal decomposition of uranyl dihydrogen orthophosphate trihydrate was studied by means of paper chromatography, X-ray diffractometry, differential thermal analysis, thermogravimetric analysis, infrared spectroscopy and chemical analysis. From these studies, it was revealed that in the thermal decomposition of the uranyl salt the following reactions take place. 1) The formation of condensed phosphates with relatively small polymerization degrees such as di- and triphosphates takes place below 300°C, accompanied by the elimination of water. 2) A uranyl salt of long-chain metaphosphate, $[UO_2(PO_3)_2]_n$ is produced bewteen 300 and 840°C. 3) The metaphosphate is melted at about 900°C, while uranium(VI) is reduced to uranium(IV) at the same time. 4) As a result of the reduction, the formation of uranium(IV) diphosphate, UP_2O_7, starts. 5) Finally, almost pure uranium(IV) diphosphate is produced at 1200°C.

Condensed phosphates of uranium prepared hitherto are di- and triphosphates of uranium(VI), di- and metaphosphates of uranium(IV) and diphosphates of uranium(IV and VI).[1-3] It has not been decided whether uranium(IV) metaphosphate is a cyclic or linear phosphate. Uranyl diphosphate is only one condensed phosphate of uranium(VI) which has so far been prepared by dehydration condensation. It appears that uranyl ion is not stable against heating. When uranyl salts are heated with orthophosphoric acid or phosphorus pentoxide, uranium(VI) is reduced to uranium(IV).[3] Uranyl diphosphate, $(UO_2)_2P_2O_7$ is also reduced to diuranium(IV and VI) trioxide diphosphate, $U_2O_3P_2O_7$ at 1020°C.[4] The purpose of the present investigation is to determine what chemical reactions take place and what kinds of condensed phosphates of uranium are produced during the process of the thermal decomposition of uranyl dihydrogen orthophosphate trihydrate (UDOT).

When dihydrogen orthophosphate of a certain metal ion with a charge n, M^{n+} is heated until all water of constitution is lost, metaphosphate, $[M(PO_3)_n]_x$ is produced by the reaction

$$x\cdot M(H_2PO_4)_n \longrightarrow [M(PO_3)_n]_x + x\cdot n\cdot H_2O \quad (1)$$

Metaphosphates are usually divided into two groups, cyclic and linear metaphosphates. Cyclic metaphosphates have ring structures, and their molecular weights are usually not very high. Linear metaphosphates have open-chain structures, and their molecular weights are considerably high.

Thilo and Grunze have found a certain relation between the structure of metaphosphate and the

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1) "Gmelins Handbuch der anorganischen Chemie," 8 Auflage, System-Nummer **55**, Verlag Chemie, Berlin (1936), s. 181.

2) Y. Shibata, "Mukikagakuzensho," XVII-1, Maruzen Co., Ltd., Tokyo (1953), p. 263.

3) Y. Baskin, *J. Inorg. Nucl. Chem.*, **29**, 383 (1967).

4) V. Pekárek and V. Vesely, *ibid.*, **27**, 1151 (1965).

size and charge of metal ion. If metal ions with the same charge are considered, metaphosphates of the metal ions with medium sizes are the cyclic ones, while those of the metal ions with smaller or larger sizes are the linear ones.[5,6]

It is of principal interest to determine which kind of metaphosphate of uranium(VI) will be produced when UDOT is heated. According to the rule mentioned above, the formation of a linear metaphosphate is expected for the uranyl salt because of the big size of uranyl ions. The present studies were carried out by means of paper chromatography, X-ray diffractometry, differential thermal analysis, thermogravimetric analysis, infrared spectroscopy and chemical analysis.

Experimental

Preparation of Uranyl Dihydrogen Orthophosphate Trihydrate (UDOT), $UO_2(H_2PO_4)_2 \cdot 3H_2O$.[7] Before the preparation of UDOT, uranyl monohydrogen orthophosphate tetrahydrate was first prepared from uranyl nitrate hexahydrate and orthophosphoric acid by the usual method.[8] UDOT was prepared by shaking a mixture of 10 g of the uranyl monohydrogen orthophosphate tetrahydrate and 35 m*l* of 85% orthophosphoric acid for 2—3 weeks at 20°C and then by filtering the resulting solid with a glassfilter (yield 3.5 g). By addition of another 10 g of the uranyl monohydrogen orthophosphate tetrahydrate to the filtrate UDOT was prepared with yield higher than that of the first procedure (yield 12.7 g). The wet solid was washed with acetone and then carbon tetrachloride and dried in a vacuume desiccator over calcium chloride for 12 hr. Analytical results of the UDOT thus prepared are as follows.

Found: UO_3, 55.2%; P_2O_5, 28.0%; H_2O, 16.8% (by difference). Calcd for $UO_2(H_2PO_4)_2 \cdot 3H_2O$: UO_3, 55.22%; P_2O_5, 27.40%; H_2O, 17.38%.

The X-ray diffraction pattern (Fig. 4) was identical with the one reported by Dunn.[9]

Analysis of Uranium. A volumetric method with dichromate[10] was used for the analysis of uranium in uranium phosphate samples obtained by heating the UDOT. A sample was dissolved in a mixed solution of sulfuric acid and orthophosphoric acid. Uranium(VI) in the solution was then reduced to uranium(IV) with Jone's reductor. After the addition of iron(III) chloride solution, the resulting iron(II) was titrated with a standard solution of potassium dichromate.

Analysis of Phosphorus. A pH titration method was used for the determination of phosphorus in the uranium phosphate samples. Since uranium disturbs the determination of phosphorus by this method, uranium should be removed from a sample solution before titration.

A sample was dissolved in a 1 M hydrochloric acid solution. The solution was passed through a cation-exchange resin column of Dowex 50W-X 8 of hydrogen form. The column was then washed with water until the washings were neutral to litmus. After condensed phosphates in the effluent mixed with the washings were completely hydrolyzed, the resulting orthophosphate was titrated with a standard solution of sodium hydroxide with a Hirama automatic recording titrator.

Preparation of Sample Solutions for Paper Chromatography. Paper chromatography was used to determine the distribution of condensed phosphate species in the uranium phosphate samples. Thus, the samples must be dissolved in a nearly neutral solution without heating in order to prevent condensed phosphates from hydrolysis. Since uranium interferes with the normal behavior of condensed phosphates in paper chromatography, it must be removed from sample solutions. It was found that the following method is suitable for this purpose.

For the dissolution of a sample containing approximately 0.1 mmol of uranium, about 10 m*l* of a 0.6 M sodium hydrogen carbonate solution was used. Three 15 m*l* portions of a mixed benzene solution of TTA (thenoyltrifluoroacetone) and TBP (tributyl phosphate), with concentrations 0.2 M and 0.1 M, respectively, were used to extract uranium from the solution. When the extraction of uranium was performed, no phosphate species were extracted into the organic phase.

The samples heated in the temperature range between 100 and 750°C were dissolved by the simultaneous use of the aqueous solution of sodium hydrogen carbonate and the benzene solution of TTA and TBP. However, the samples heated at higher temperature than 750°C were not dissolved by this procedure. Thus, these samples were first dissolved in the aqueous solution of sodium hydrogen carbonate, and then the extraction of uranium was carried out with the benzene solution of TTA and TBP. For the most insoluble samples which were produced by heating the UDOT at 1000, 1100 and 1200°C, it took about a month to dissolve them in the sodium hydrogen carbonate solution.

Paper Chromatographic Separation and Determination of Phosphates. For one-dimensional paper chromatography fifter paper of Toyo Roshi No. 51A, 20×18 cm was used. A developing solvent was prepared by mixing 250 m*l* of a 20% trichloroacetic acid solution (100 g of trichloroacetic acid and 7 m*l* of 28% aqueous ammonia per 500 m*l* of the solution), 100 m*l* of water and 650 m*l* of acetone.[11] Development was performed at 20°C for about 4 hr by the ascending method.

An acidic molybdate solution was sprayed to detect phosphates on the filter paper. The paper was then dried and placed under ultraviolet rays until blue spots of phosphates appeared.[12]

Determination of phosphate species on the paper chromatogram was performed by a colorimetric meth-

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[5] E. Thilo and I. Grunze, *Z. Anorg. Allg. Chem.*, **290**, 209 (1957).

[6] E. Thilo and I. Grunze, *ibid.*, **290**, 223 (1957).

[7] J. M. Schreyer and C. F. Baes, Jr., *J. Amer. Chem. Soc.*, **76**, 354 (1954).

[8] T. Moeller, "Inorganic Syntheses," V. McGraw-Hill Book Co., Inc., New York (1957), p. 150.

[9] H. W. Dunn, "X-ray Diffraction Data for Some Uranium Compounds," ORNL-2092, (1956), p. 13.

[10] J. M. Schreyer and C. F. Baes, Jr., *Anal. Chem.*, **25**, 644 (1953).

[11] D. N. Bernhart and W. B. Chess, *ibid.*, **31**, 1026 (1959).

[12] C. S. Hanes and F. A. Isherwood, *Nature*, **164**, 1107 (1949).

od.[13] Each phosphate species on the paper was leached with an aqueous ammonia and treated with a Mo(V)–Mo(VI) reagent.[14] The absorbance of the sample solution was measured at 830 mμ.

Two-dimensional paper chromatography[15] was carried out to identify phosphate species which were contained in oily substances derived from the heating products of the UDOT between 800 and 940°C. Filter paper of Toyo Roshi No. 51A, 40×40 cm was used. The first development was carried out at 5°C for 40 hr with the basic solvent[15] which was a mixture of 20 m*l* of 2-propanol, 20 m*l* of *N*,*N*-dimethylformamide, 20 m*l* of methyl ethyl ketone and 1 m*l* of 28% aqueous ammonia. After developing with the basic solvent and then drying, the second development was performed at 5°C for 16 hr at a right angle to the direction of the first development with the acidic solvent[15] which was prepared by mixing 60 m*l* of methanol, 10.3 m*l* of a trichloroacetic acid solution (20 g of trichloroacetic acid and 4.6 m*l* of 28% aqueous ammonia in 100 m*l* of water), 5 m*l* of acetic acid and 10 m*l* of water.

Instruments. X-Ray diffraction patterns for powder samples were obtained with a Rigaku-denki X-ray diffractometer Model D-3F, nickel-filtered Cu*K*α radiation being used.

Thermal analyses were carried out at a heating rate of 12°C/min in static air with a Shimazu thermoanalyzer DT-2A. As a reference material, α-alumina was used. Samples were not diluted.

Infrared spectra were measured with a Hitachi EPI-S2 spectrophotometer by the usual KBr-disk method.

Results and Discussion

A thermogravimetric analysis (TGA) curve and differential thermal analysis (DTA) curves for the UDOT are given in Figs. 1 and 2, respectively. From the TGA curve, it seems that the first two water molecules are eliminated up to 120°C, the additional two water molecules are eliminated between 120 and 200°C and the last one is gradually eliminated between 200 and 700°C. An explanation for the weight loss observed at nearly 900°C will be mentioned later.

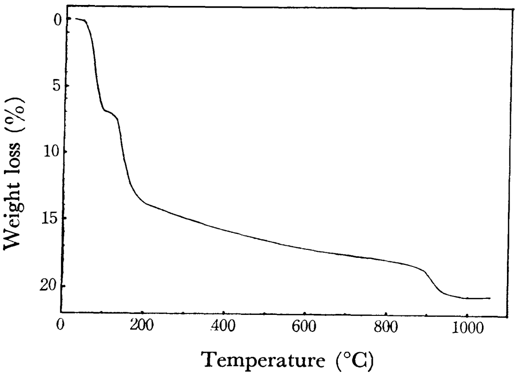

Fig. 1. Thermogravimetric analysis of $UO_2(H_2PO_4)_2\cdot3H_2O$.

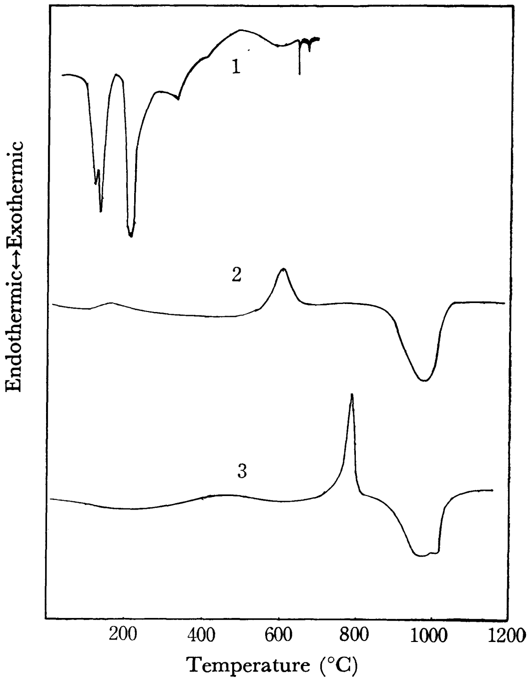

Fig. 2. Differential thermal analysis.
1) $UO_2(H_2PO_4)_2\cdot3H_2O$
2) The sample produced by heating $UO_2(H_2PO_4)_2\cdot3H_2O$ at 600°C
3) The sample produced by heating $UO_2(H_2PO_4)_2\cdot3H_2O$ at 800°C

When the UDOT was heated in a cell for the DTA measurement, the sample fused and overflowed the cell at about 650°C. Thus two samples which had been heated at 600 and 800°C in an electric furnace were used for the observation of the behavior in DTA at temperatures higher than 600°C.

The two endothermic peaks in the temperature range lower than 300°C in curve 1 of Fig. 2 correspond to the two-step change of the weight loss in the temperature range in the TGA curve of Fig. 1. Thus, they are due to the evaporation of water. There is no sufficient data to discuss thoroughly the exothermic peaks at 600 and 800°C in curves 2 and 3 of Fig. 2, respectively. However, these exothermic peaks seem to be due to the transformation of amorphous substances from an unequilibrium state to an equilibrium state and/or the crystallizaton of amorphous substances. The endothermic peaks observed at about 1000°C will be discussed later.

From these curves, fifteen points of heating temperature were selected in order to investigate the distribution change of phosphate species during the process of the thermal decomposition; they were

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[13] M. J. Smith, *Anal. Chem.*, **31**, 1023 (1959).

[14] F. Lucena-Conde and L. Prat, *Anal. Chim. Acta*, **16**, 473 (1957).

[15] E. Thilo and U. Schülke, *Z. Anorg. Allg. Chem.*, **341**, 293 (1965).

[16] E. Steger and G. Leukroth, *ibid.*, **303**, 169 (1960).

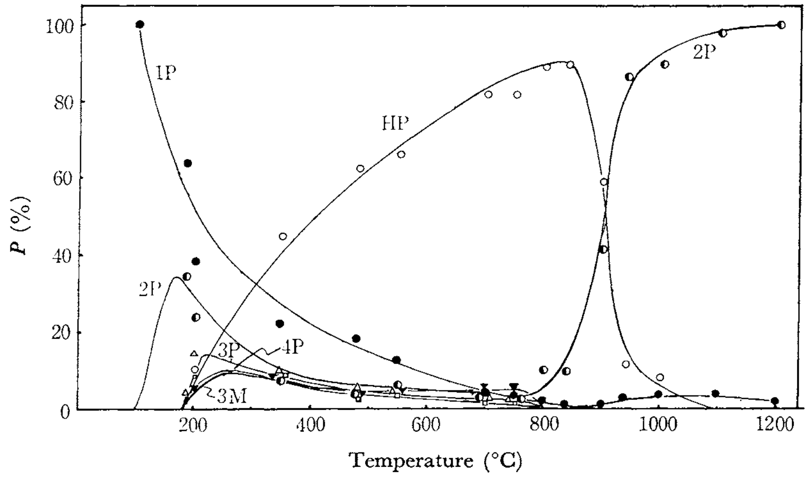


Fig. 3. Distribution of condensed phosphate species in heating products of $UO_2(H_2PO_4)_2 \cdot 3H_2O$. 1P(●): Orthophosphate, 2P(◐): Diphosphate, 3P(△): Triphosphate, 4P(□): Tetraphosphate, HP(○): Highpolyphosphate, 3M(▲): Trimetaphosphate

100, 180, 205, 350, 480, 550, 700, 750, 800, 840, 900, 940, 1000, 1100 and 1200°C. Phosphate species in the samples heated in air at these temperatures were analyzed by the dissolution procedure and paper chromatography. The distribution of the phosphate species thus obtained are given in Fig. 3, where the "high polyphosphate" means both the linear phosphates longer than tetraphosphate and the cyclic phosphates larger than trimetaphosphate.

In the case of samples heated at 800, 840, 900 and 940°C, when extraction was carried out, oily substances resulted at the bottom of the aqueous solutions. The oily substances were separated from the aqueous and benzene solutions and dissolved in water. The phosphate species in these aqueous solutions were proved to be highly polymerized phosphate (probably metaphosphate with a long-chain structure) by two-dimensional paper chromatography. The $P\%$ values of the high polyphosphate in Fig. 3 represent the amount of phosphorus in the oily substances.

Figure 3 shows that di-, tri-, tetra- and trimetaphosphates are formed in the temperature range between 180 and 350°C. At temperatures higher than 350°C, the amount of orthophosphate and these condensed phosphates except for diphosphate decreases with temperature and approaches nearly zero at 840°C. On the other hand, the amount of high polyphosphate increases with temperature and reaches about 90% at 840°C. At nearly 900°C, an abrupt change takes place, *i.e.*, the high polyphosphate undergoes decomposition, while diphosphate is formed again. At 1200°C the amount of diphosphate become almost 100%. Since the dissolution of the samples heated at a higher temperature than 900°C took a long time, the hydrolytic degradation of the samples during the dissolution must be taken into consideration. However, it can be concluded that the extent of this hydrolytic degradation was not large, because only small

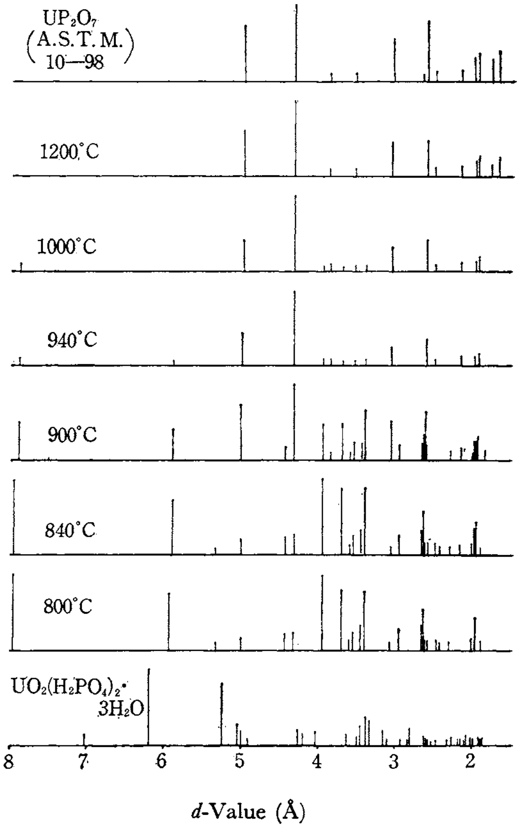


Fig. 4. X-Ray diffraction patterns of $UO_2(H_2PO_4)_2 \cdot 3H_2O$ and its heating products.

amounts of orthophosphate were observed in the solutions of the samples in question.

The results of the X-ray diffractometric analysis are given in Fig. 4. The uranium phosphate samples heated at temperatures higher than 750°C are crystalline, while those obtained in the temperature range between 100 and 750°C are amorphous. The diffraction pattern for the sample heated at 1200°C is in good agreement with that of uranium(IV) diphosphate, UP_2O_7, which is described in an A.S.T.M. card 10—98. The diffraction pattern for the sample heated at 800°C, which was confirmed to be the uranyl salt of long-chain metaphosphate by the paper chromatographic analysis, has not so far been reported.

The X-ray diffraction patterns for the samples producted in the temperature range between 800 and 1200°C show the gradual increase of the content of the uranium(IV) diphosphate and the gradual decrease of that of the uranyl salt of long-chain metaphosphate with temperature. This fact essentially agrees with the results of paper chromatographic analysis.

An infrared spectrum for the sample heated at 1200°C is similar to that for silicon, tin, titanium and zirconium diphosphates.[16] The composition of the sample heated at 1200°C is as follows.

Found; UO_2, 67.0; P_2O_5, 34.6%. Calcd for UP_2O_7; UO_2, 65.55; P_2O_5, 34.45%.

These data also indicate that the sample in question is uranium(IV) diphosphate.

We see that the most reasonable reactions which take place in the process of the thermal decomposition of the UDOT are as follows.

In the temperature range between room temperature and 100°C the reaction

$$UO_2(H_2PO_4)_2\cdot 3H_2O \longrightarrow UO_2(H_2PO_4)_2\cdot H_2O + 2H_2O \qquad (2)$$

is expected to take place, because no condenced phosphates appear in the products, and the TGA curve indicates the elimination of two water molecules.

In the temperature range between 100 and 180°C, one more molecule of crystallization water may be eliminated.

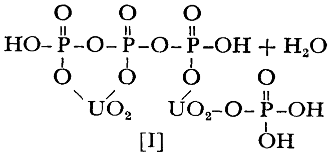
$$UO_2(H_2PO_4)_2\cdot H_2O \longrightarrow UO_2(H_2PO_4)_2 + H_2O \qquad (3)$$

However, the formation of diphosphate was confirmed by means of paper chromatography. Thus, the reaction

$$UO_2(H_2PO_4)_2 \longrightarrow UO_2H_2P_2O_7 + H_2O \qquad (4)$$

also occurs. In the temperature range between 180 and 200°C, further dehydration reaction takes place. Until the temperature reaches 200°C, four water molecules were eliminated as a whole. Thus, if reactions (2), (3) and (4) are completed, there might be no orthophosphate in the product. However, a considerable amount of orthophosphate was observed in the sample heated at 200°C by means of paper chromatography. Thus in addition to reactions (3) and (4), condensation reactions may take place in the temperature range between 100 and 200°C:

$$UO_2H_2P_2O_7 + UO_2(H_2PO_4)_2 \longrightarrow$$



$$HO-\overset{O}{\overset{\|}{P}}-O-\overset{O}{\overset{\|}{P}}-O-\overset{O}{\overset{\|}{P}}-OH + H_2O \qquad (5)$$

$$\underbrace{O\quad O}_{UO_2}\qquad O-UO_2-O-\overset{O}{\overset{\|}{P}}(OH)-OH$$

[I]

$$n\cdot UO_2H_2P_2O_7 \longrightarrow (UO_2)_nH_2P_{2n}O_{6n+1} + (n-1)H_2O \qquad (6)$$

Here n is relatively small in this temperature range.

At nearly 300°C, the contents of tri-, tetra- and trimetaphosphates reach their maxima. When the temperature rises from 300 to 800°C, the contents of ortho-, di-, tri-, tetra- and trimetaphosphates decrease, while the content of the high polyphosphate still increases. Accordingly, in this temperature range the condensation reactions such as reactions (5) and (6) mainly occur, and the intermediates such as product [I] in reaction (5) seem to be the sources of ortho-, di-, triphosphate, *etc.* in the sample solutions.

At 800°C the condensation reactions are over, and the main component of the sample is the uranyl salt of long-chain metaphosphate, *i.e.*, uranyl metaphosphate, $[UO_2(PO_3)_2]_n$.

$$(UO_2)_nH_2P_{2n}O_{6n+1} \longrightarrow [UO_2(PO_3)_2]_n + H_2O \qquad (7)$$

It was confirmed by visual observation that the melting of the sample occurs at about 900°C, and the product swells at the same time. The wide endothermic peak at 900—1000°C in the DTA curve might be due to the melting of the sample and the reduction of uranium(VI) to uranium(IV) accompanied by the formation of oxygen gas. The reduction of uranium(VI) to uranium(IV) was ascertained by the titration of the sample solutions with dichromate. This titration did not give quantitative data for uranium(IV) because a part of it was oxidized during the dissolution of the samples. Owing to the reduction of uranyl ions, UO_2^{2+} to uranium(IV) ions, U^{4+}, the positive charge of the cations increases from 2 to 4. Since the balance between the positive charge of the uranium(IV) cations and the negative charge of the phosphate anions should be kept, the degradation of the long-chain metaphosphates occurs to form finally uranium(IV) diphosphate.

$$[UO_2(PO_3)_2]_n \longrightarrow n\cdot UP_2O_7 + n/2\cdot O_2 \qquad (8)$$

However, it must be noted that the thermal decomposition of reaction (8) occurred in air. Thus, the weight loss at about 900°C on the TGA curve is due to the escape of oxygen gas from the sample. The total weight loss of the UDOT exactly coincides

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[16] E. Stege and G. Leukroth, *ibid.*, **303**, 169 (1960).

with the calculated value, 20.6% which is derived on the assumption that the UDOT, $UO_2(H_2PO_4)_2 \cdot 3H_2O$ is completely changed into uranium(IV) diphosphate, UP_2O_7.

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