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THERMAL BEHAVIOR OF THE PRODUCTS ISOLATED IN URANIUM COMPOUND-HYDRAZINE SYSTEMS*

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Products obtained via precipitation from the reactions of uranium compounds with hydrazine were characterized by thermal analysis and other methods.

Precipitates of uranium oxides were isolated from the reactions with hydrazine at 60 and 100 °C. Upon heating in an inert atmosphere, the samples underwent dehydration, accompanied by decomposition of the hydrazine. Hydrazine and its decomposition products, ammonia and hydrogen, partially reduced the uranium(VI) to uranium(IV) oxide. The products obtained by precipitation at 60 °C were stable in air. In contrast, the products obtained on reduction at 100 °C exhibited pronounced sensitivity toward oxidation by air.

The precipitation of uranium concentrates from uranyl solutions is a frequently encountered process in the technology of uranium ore processing. Although a large number of chemicals have been proposed for the precipitation reactions, only a few concentrates thus prepared have industrial significance. Both ammonia and hydrogen peroxide reagents are commercially used to obtain uranium concentrates. Hydrazine may be regarded as a derivative of ammonia in which a hydrogen atom is substituted by the NH_2 group, or as a nitrogen analogue of hydrogen peroxide. Depending on the experimental conditions, reactions between uranyl solutions and a solution of hydrazine hydrate yielded two different products.

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At lower temperature (60°), a yellow powder was isolated [2], which was identified by chemical analysis, IR and Raman spectroscopy and X-ray powder diffraction as uranium(VI) oxide hydrazine hydrate. At higher temperatures (around 100°), the hydrazine acted as a reducing agent and a dark-gray product was obtained, which was identified, by chemical analysis and X-ray powder diffraction studies, as uranium sesquioxide with varying proportions of uranium(IV). A study of the thermal behavior of both products by means of TG, DTG, DTA and DSC measurements revealed the thermal properties of the products and helped to clarify questions regarding their composition.

Experimental

Uranium(VI) oxide hydrazine hydrate was prepared via the reaction of uranyl nitrate solution with a solution of hydrazinium hydrate at 60°. The contents of uranium and hydrazine in the product and in the intermediates were determined volumetrically: uranium(VI) by titration with potassium bichromate [3], uranium(IV) by titration with ferroammonium sulfate [4, 5] and hydrazine by potentiometric titration [6].

Infrared spectra of the solids pressed between CsBr discs were obtained by using a Perkin-Elmer 521 spectrometer. The Raman spectra of samples in a Pyrex tube were recorded on a Spex 1401 double monochromator, using exciting radiation from the 5682 Å line of a Coherent Radiation Laboratories (model Kr) ion laser.

X-ray powder diffraction data were obtained with a Phillips-Debye camera and CuK radiation.

For thermal analysis, Mettler TA1 and TA3000 systems were used. Experimental conditions: sample weights: 30-100 mg; heating rate: 4 deg min^{-1}; flow rate: 5-18 l h^{-1} of dry argon, argon-hydrogen or air atmospheres.

The volatiles and gases evolved during the thermal analysis were determined with a Varian Aerograph Series 1400 gas chromatograph connected to a Hewlett-Packard 3385A Integrator. The flow rate of helium carrier gas was 50 ml min^{-1}, and the heating rate was 2.5 deg min^{-1}.

Results and discussion

The compositions of the products used in these thermoanalytical studies are given in Table 1. The thermal properties were studied in several atmospheres: inert argon, a mixture of 4 per cent hydrogen in argon, and dry air.

Table 1. Composition of starting materials, %

Sample	U (tot)	U(IV)	Hydrazine	Water
$UO_3.0.4N_2H_4.H_2O$	73.7	–	3.8	7.6
Uranium oxide	78.5	49.6	0.8	

Thermal analysis in dry argon atmosphere

The results of thermal analysis of the uranium(VI) oxide hydrazine hydrate are given in Fig. 1. The onset of thermal decomposition in a dry argon purge occurs at 50°. Up to 143°, the sample loses 7.4 per cent of its initia l weight.

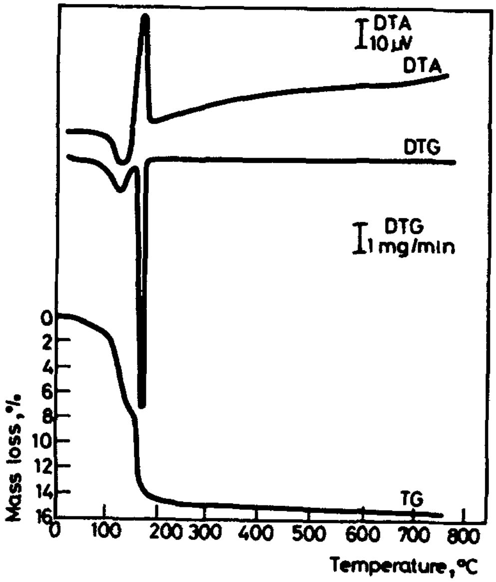

Fig. 1 TG, DTG and DTA curves of uranium(VI) oxide hydrazine hydrate in argon

This first step of thermal decomposition, with DTG peak at 123°, is endothermic. With increasing temperature, the sample decomposes further, with the second DTG peak at 167°, which DTA reveals to be an exothermic process. Above 200° the rate of weight loss markedly diminishes, but the sample continually loses weight up to 750°, with a final cumulative mass loss of 15.4 per cent.

Table 2 Chemical analysis of the intermediates, %

Sample	U(tot.)	U(IV)	N_2H_4
Start (25°C)	73.7	–	3.8
I (136°C)	80.1	9.4	1.0
II (173°C)	85.5	39.1	0
III (400°C)	88.0	–	–
IV (750°C)	88.1	–	–

The thermal decomposition was also studied by isolation of the intermediates and their chemical analysis (Table 2). The temperatures of the stages of thermal decomposition in these experiments differed somewhat, due to the fact that macroscopic sample weights were used.

Chemical analysis revealed that the thermal decomposition of uranium(VI) oxide hydrazine hydrate starts with dehydration, beginning at 50°. The weight loss in the first stage of thermal degradation of the sample (7.4 per cent) closely corresponds to the calculated value for dehydration of the sample (7.6 per cent), but chemical analysis of the intermediate obtained at 136° showed that hydrazine is also partially evolved or decomposes simultaneously. As the hydrazine decomposes in this stage, uranium(VI) is partially reduced to uranium(IV); this can be caused by hydrazine itself or by its decomposition products, ammonia and hydrogen [7].

In the second exothermic step (the temperature interval from 143° to 200°), the hydrazine completely decomposes and is not found in the intermediate isolated at 173°. The uranium(IV) content of the intermediate rises from 9.4 to 39.1 per cent. The reduction of uranium(VI) oxide to uranium(IV) oxide can follow the reaction

$$UO_3 + H_2 \rightarrow UO_2 + H_2O \qquad \Delta H^{o}_{25^{\circ}} = -105.9 \text{ kJ/mol}$$

It is known to proceed through several stages [8]:

$$UO_3 + H_2 \rightarrow U_3O_{8+x} + H_2O$$

$$U_3O_8 + H_2 \rightarrow U_3O_{8-x} + H_2O$$
$$U_3O_8 + H_2 \rightarrow UO_{2+x} + H_2O$$

The changes in the sample during the thermal analysis can be assigned to one or more of the above reactions. One possible scheme for the sample decomposition is the partial reduction of uranium(VI) oxide by hydrazine to the oxides with uranium in lower oxidation states. A second possible scheme is the decomposition of the hydrazine to ammonia, nitrogen and hydrogen and the interaction of these evolved gases with the solid sample in the crucible. It was not possible to distinguish which reactions take place, but it is known [9] that in the thermal decomposition of ammonium diuranate the residual ammonia in the sample can cause the reduction of uranium(VI).

In the sample of uranium(VI) oxide hydrazine hydrate, the ratio of uranium and hydrazine was 1:0.383 [10, 11]. Assuming that all of the hydrazine reacts during the reaction, 0.5 mol of hydrazine would suffice for the complete reduction of uranium(VI) to uranium(IV). The ratio of uranium and hydrazine being smaller than this, it could theoretically reduce only 76.6 per cent of the uranium(VI).

The results of chemical analysis of the intermediates obtained at 136° and 173° show the reduction of uranium in the low-temperature region. The uranium(IV) content in the intermediate is 9.4 per cent at 136° and 39.1 per cent at 173°. The total concentration of uranium in the sample (85.5 per cent) means that at 173° 39.1 per cent of the uranium is reduced.

Thermal analysis in argon containing 4 per cent hydrogen

The expectation that uranium(VI) oxide hydrazine hydrate does not contain enough hydrazine for total reduction of the uranium in oxidation state (IV) was the reason for also carrying out the thermal analysis in an argon atmosphere containing 4 per cent hydrogen (Fig. 2).

The results are similar to those obtained in a dry argon atmosphere (Table 3). The initial temperature under these conditions is 40°. The weight loss up to 200° is 13.52 per cent, with two DTG peaks, at 123° and 170°. In the temperature region from 450° to 600°, further weight loss occurs. The final weight loss is 16.6 per cent.

The results of chemical analysis of the intermediates show that in this case the dehydration of the sample is accompanied by a lowering of its hydrazine content. The uranium content at 340° is 88.1 per cent, which corresponds to the uranium oxide $UO_{2.01}$. Thermal analysis in a mixture of

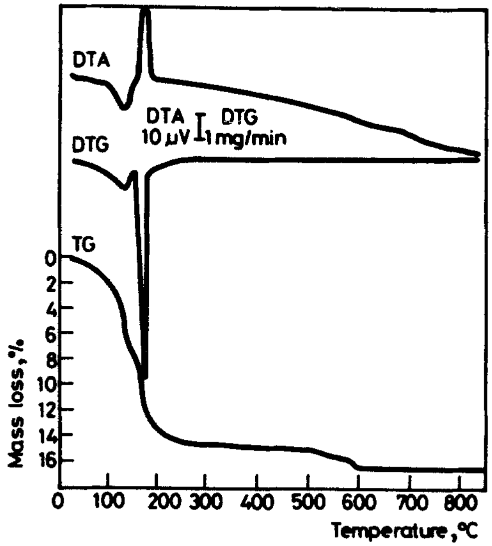

Fig. 2 TG, DTG and DTA curves of uranium(VI) oxide hydrazine hydrate in argon-hydrogen

argon and 4 per cent hydrogen reveals a more complete reduction of the uranium(VI) to uranium(IV) than in an argon atmosphere.

Table 3 Chemical analysis of the intermediates, %

Sample	U(tot.)	U(IV)	N_2H_4
Start (25°C)	73.7	–	3.8
I (130°C)	82.0	7.3	1.2
II (340°C)	88.1	42.2	0
III* (860°C)	88.3	83.2	–

*) the concentration of uranium was determined on the basis of the TG curve

Thermal analysis in air

The sample starts to lose weight at 50° in a dry air purge atmosphere (Fig. 3). In the temperature interval from this temperature up to 156°, the sample loses 6.7 per cent of its initial weight. Above this temperature, the sample loses further weight, but after 650° the weight loss is 13.7 per cent, and up to 800° it loses only another 0.1 per cent.

The intermediate obtained at 156° (Table 4) has a higher uranium content (83.9 per cent) than that for uranium(VI) oxide (83.31 per cent). At

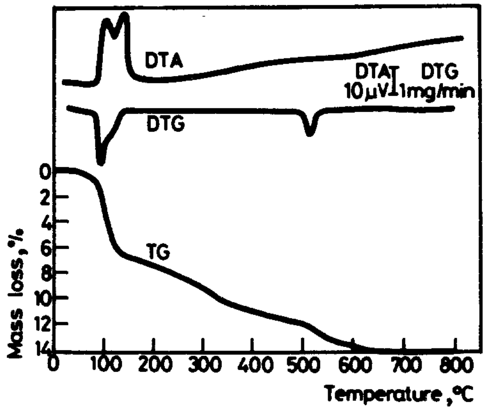

Fig. 3 TG, DTG and DTA curves of uranium(VI) oxide hydrazine hydrate in air

460°, the uranium content (84.3 per cent) approaches the calculated value for U_3O_8 (84.80 per cent), which is further confirmed by chemical analysis of the intermediate for uranium(IV) (31.6 per cent), the calculated value being 33.3 per cent.

Table 4 Chemical analysis of the intermediates, %

Sample	U (tot.)	U (IV)	N_2H_4
Start (25°C)	73.7	–	3.8
I (156°C)	83.9	–	0.3
II (460°C)	84.3	31.6	0
III (800°C)	84.3	39.0	0

Thermal analysis of uranium oxide precipitated by hydrazine at higher temperatures

The product obtained by precipitation of uranium oxides from uranyl solutions heated up to around 100° differed markedly from that obtained by precipitation at 60°. Chemical analyses are given in Table 1. The product is unstable in air.

Uranium oxide precipitated at the higher temperature starts to decompose at 40° and in the first step, up to 169°, it loses 4.5 per cent of its initial weight (Fig. 4). In the temperature interval between 169° and 279°, a further weight loss (6.5 per cent) is observed. The cumulative weight loss up to 465° is 8.6 per cent, and up to the end temperature it is 9.3 per cent.

Table 5 Total uranium content and proportion between U(IV)/U(tot) in intermediates obtained during thermal analysis in different atmospheres

Temp., Ar		Ar + 4% H_2		Air		
°C	U(tot) %	U(IV)/U(tot)	U(tot) %	U(IV)/U(tot)	U(tot) %	U(IV)/U(tot)
25	73.7		73.7		73.7	
130			82.0	0.079		
136	80.1	0.0944				
156					83.9	
173	85.5	0.391				
340			88.1	0.422		
400	88.0					
460					84.3	0.316
750	88.1					

Table 6 Intermediates of thermal decomposition of uranium (VI) oxide hydrazine hydrate in different atmospheres as different uranium oxigen ratios

Temp., Ar °C	Ar + 4% H_2	Air	
25	–	–	–
130	–	$UO_{2.92}$	–
136	$UO_{2.91}$	–	–
156	–	–	$UO_{2.85}$
173	$UO_{2.52}$	–	–
340	–	$UO_{2.01}$	–
400	$UO_{2.03}$	–	–
460	–	–	$UO_{2.77}$
750	$UO_{2.03}$	–	–

The first step can be attributed to the dehydration of the sample and the subsequent steps to the decomposition of hydrazine and the simultaneous partial reduction of uranium(VI) to uranium(IV).

The results in the argon + hydrogen atmosphere are similar to those in argon, but the total weight loss between 50° and 897° is 10.7 per cent. The higher weight loss can be attributed to the greater extent of reduction of uranium(VI) to uranium(IV) by the hydrogen present in the purge gas.

The thermal decomposition of the sample in air differs markedly from the first two decompositions: in the first step, between 30° and 287.4°, the sample loses 4.0 per cent of the starting weight. Upon heating to 373.8°, an increase in weight of 0.4 per cent is observed. In the last steps, the sample decomposes further, and up to 897° the cumulative weight loss is 6.6 per cent.

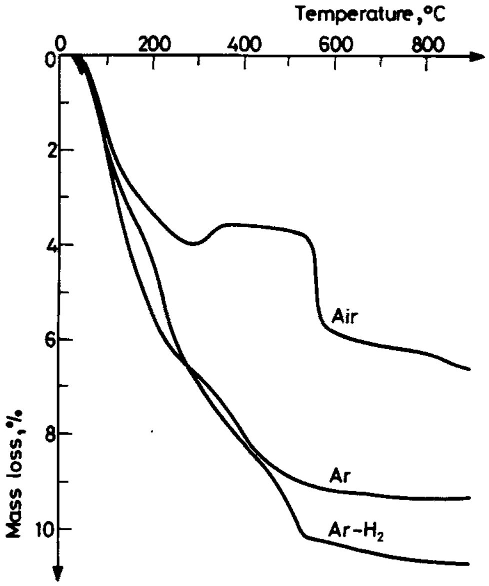

Fig. 4 TG curves of uranium oxide in argon, argon - hydrogen and air

The weight loss in the first step is a consequence of the dehydration and the decomposition of the hydrazine. In the next two steps, partial oxidation occurs, prior to decomposition to uranium(IV) oxide. In the DSC curves (Fig. 5), endothermic effects are obtained in all atmospheres for the first step of thermal decomposition. In air, a strong endothermic effect occurs at 560°, which is not found in the other atmospheres.

Analysis of the end-products revealed that the U:O ratio corresponds to the following compositions for the residues: Ar - $UO_{2.31}$, Ar/H2 - $UO_{2.05}$, and air - $UO_{2.82}$.

Study of the thermal decompositions of the investigated uranium compounds demonstrated that the hydrazine bound in the starting materials causes (either itself or its decomposition products) the reduction of uranium(VI) to lower oxidation states. The degree of reduction depends on several factors: the hydrazine content, the purity of the atmosphere, the residence time and the composition of the evolved gases.

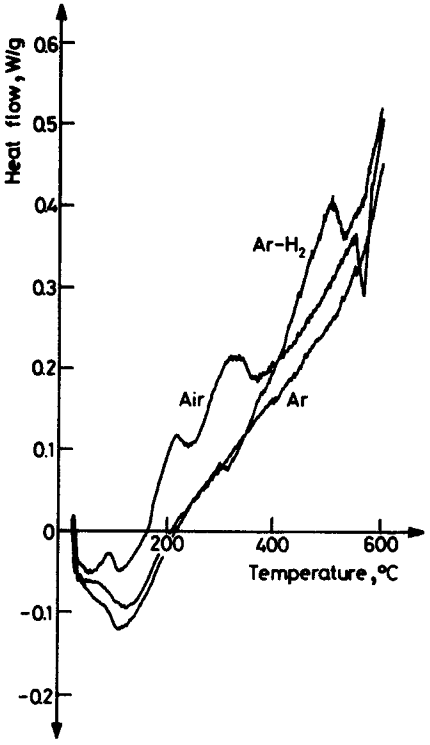

Fig. 5 DSC curves of uranium oxide in argon, argon - hydrogen and air

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Zusammenfassung — Aus Uranverbindungen mit Hydrazin gefällte Produkte werden mittels Thermoanalyse und anderen Methoden beschrieben.

Niederschläge von Uranoxiden wurden aus der Reaktion mit hydrazin bei 60 und 100°C isoliert. Bei Erhitzen in inerter Atmosphäre werden die Proben unter gleichzeitiger Zersetzung des hydrazins dehydratiert. Hydrazin und seine Zersetzungsprodukte Ammoniak un Wasserstoff reduzieren Uran(VI)-oxide teilweise zu Uran(IV)-oxiden. Die beim Fällen bei 60°C erhaltenen Produkte sind an Luft stabil. Im Gegensatz dazu besitzen die bei der Reduktion bei 100°C erhaltenen Produkte gegenüber der Oxydation an Luft eine gesteigerte Empfindlichkeit.