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INVESTIGATION OF $UO_4 \cdot 2NH_3 \cdot 2HF$ BY SIMULTANEOUS THERMOGRAVIMETRY-DIFFERENTIAL THERMAL ANALYSIS-MASS SPECTROMETRY TECHNIQUE

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ABSTRACT

Thermal decomposition of $UO_4 \cdot 2NH_3 \cdot 2HF$ was studied under high vacuum and in different gas atmospheres (N_2, O_2, synth. air). Gaseous decomposition products were analyzed and recorded using a quadrupole mass spectrometer.

By discussing TG and MS data as well as X-ray analysis of intermediate products an attempt is made, to explain decomposition mechanisms under varied experimental conditions.

Thermal decomposition strongly supports the results of X-ray analysis leading to the formula $UO_4 \cdot 2NH_3 \cdot 2HF$.

INTRODUCTION

Until now, uraniumperoxide compounds of the type $UO_4 \cdot x$ are rather unknown and there are even authors, who doubt their mere existence. Duval[1] supports the opinion that the compound $UO_4 \cdot 2H_2O$ should be written as $UO_3 \cdot H_2O_2 \cdot H_2O$, since the IR spectra indicated no difference to that of UO_3.

More recent investigations by Gordon and Taube[2] prove by labeling with ^{18}O, that a real uraniumperoxide exists. Cordfunke and Aling[3] have been studying the thermal decomposition of hydrated uraniumperoxides: They state, that $UO_4 \cdot 4H_2O$ loses $2H_2O$ between 40 and 200°C and another $2H_2O + \frac{1}{2}O_2$ between 200 and 350°C.

The compound $UO_4 \cdot 2NH_3 \cdot 2HF$, which has been investigated in our laboratory, is isomorphic with $UO_4 \cdot 4H_2O$, in which the H_2O molecules are substituted by $2NH_3$ and $2HF$.

EXPERIMENTAL

Simultaneous TG–DTA

The simultaneous TG–DTA measurements of $UO_4 \cdot 2NH_3 \cdot 2HF$ were performed on a Mettler thermoanalyzer TA1. High vacuum as well as various media were used to vary experimental conditions for thermal decomposition. Pt/PtRh-type thermocouples were used for temperature and differential temperature (DTA) signal.

Typical sample weight was 20 mg, placed in platinum crucible.

Mass spectrometric analysis

As a selective and very rapid analytical method for gaseous decomposition products mass spectrometry is especially suitable. From Fig. 1 it is clearly seen, that the mass analyzer is directly placed into the cooling trap of the thermobalance.

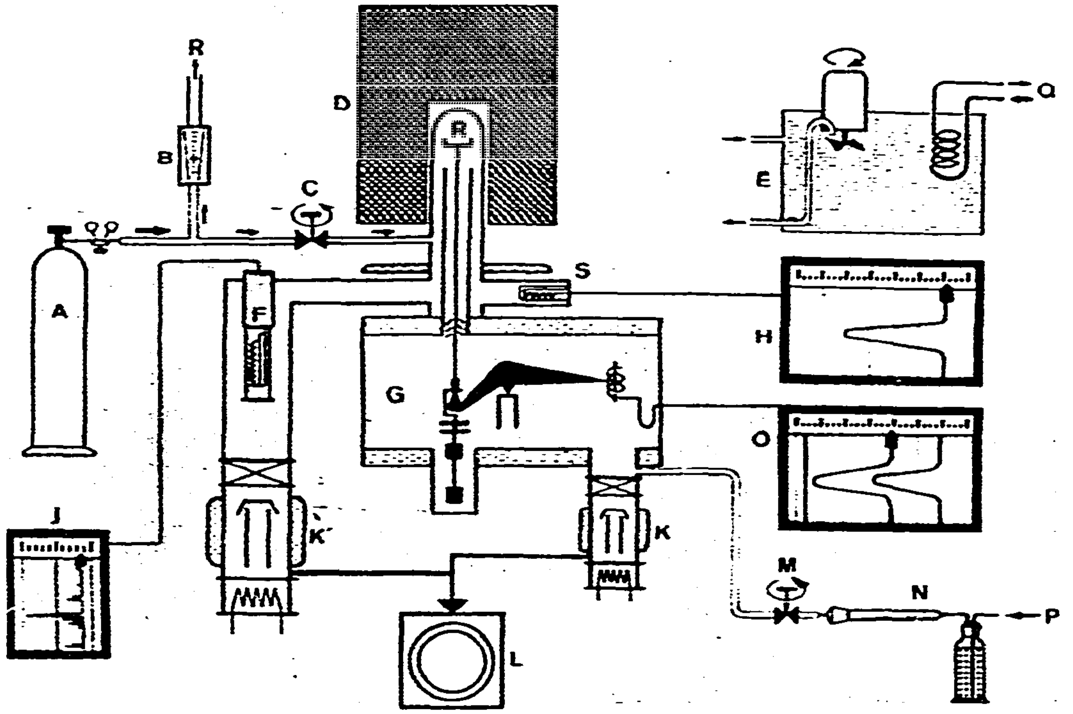

Fig. 1. Schematic illustration of the combination of a Mettler TA-1 thermoanalyzer with the Balzers QMG 101 quadrupole mass spectrometer.

Mass spectrometric analysis is possible in a pressure range of 10^{-5} to 10^{-4} Torr. using the high vacuum system of the thermobalance. Mass spectrometric analysis was performed using a Balzers quadrupole mass spectrometer QMG101 with a peak selector. Simultaneous TG–DTA–MS analysis is described in more detail by Wiedemann[4].

X-ray analysis

Stable intermediate and end products were subjected to X-ray analysis.

Preparation of $UO_4 \cdot 2NH_3 \cdot 2HF$

The preparation of $UO_4 \cdot 2NH_3 \cdot 2HF$ was described by Muller et al.[5].

RESULTS

TG, DTG and DTA information

The thermal decomposition of $UO_4 \cdot 2NH_3 \cdot 2HF$ occurs in two—more or less overlapping—steps, which are not very much dependent on atmospheric or high vacuum conditions (Figs. 2 to 6).

Separation of the weight steps is possible for the experiments in air, nitrogen and oxygen by means of peak separation in the DTG curve. The first step occurs in the temperature range from 130 to 220°C, the second from 220 to 350°C. Decomposition temperatures for both decomposition reactions are not influenced by the different gas media. Between 400 and 600°C only a very small weight loss is measured.

The enthalpies of both reaction steps under high vacuum are endothermic. Contrary to this, we obtain during the first step two much smaller exothermic DTA peaks using normal pressure and air, nitrogen or oxygen atmospheres.

It seems that overlapping endothermic and exothermic phenomena produce this effect (see also the complex reaction mechanism!). The second step, however, is

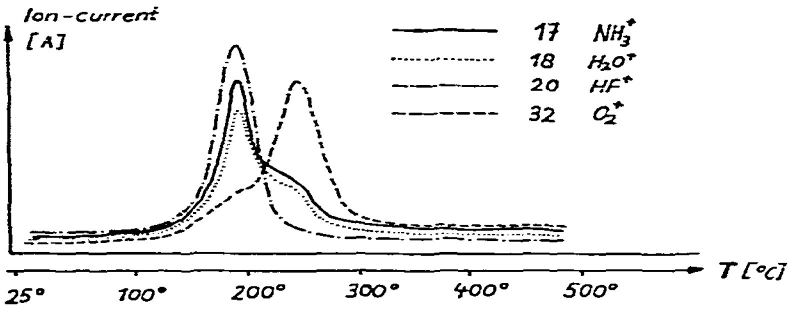

Fig. 2. Mass spectrum of $UO_4 \cdot 2NH_3 \cdot 2HF$. Ion current of different partial pressures as a function of the temperature.

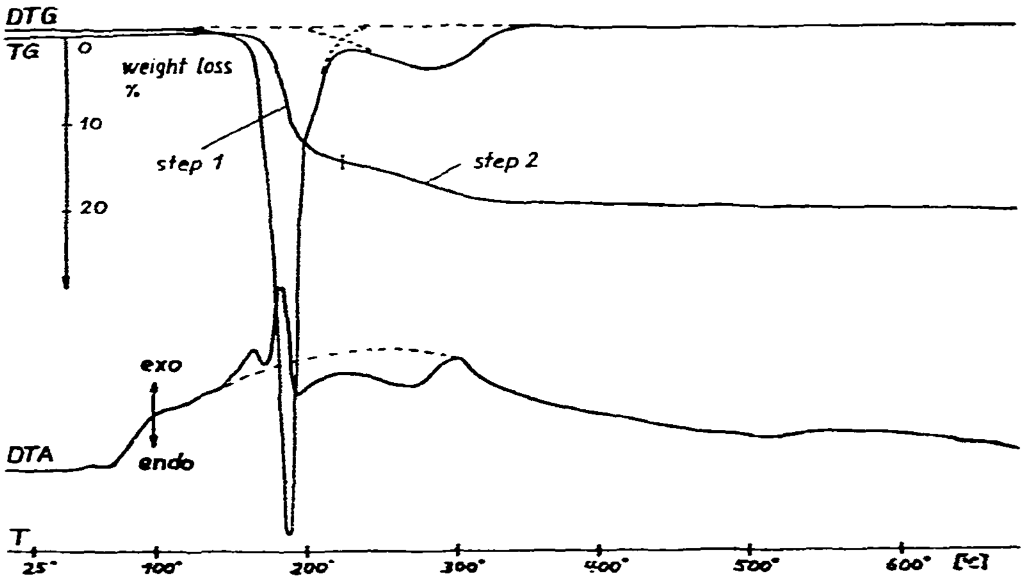

Fig. 3. TG, DTG and DTA curves of $UO_4 \cdot 2NH_3 \cdot 2HF$ measured simultaneously in air.

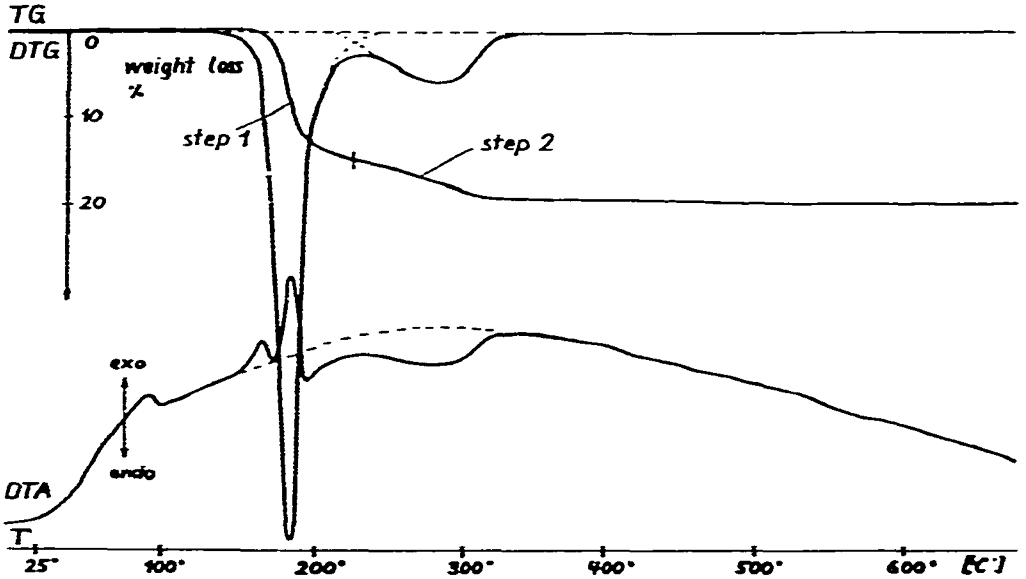

Fig. 4. TG, DTG and DTA curves of $UO_4 \cdot 2NH_3 \cdot 2HF$ measured simultaneously in nitrogen.

TABLE 1

TG, DTA, TEMPERATURE INFORMATION OF THE DECOMPOSITION OF $UO_4 \cdot 2NH_3 \cdot 2HF$ IN DIFFERENT GAS ATMOSPHERES UP TO 600°C

The data are the mean values of 4 measurements.

Experiment	*Atmosphere*	*Weight loss step 1*			*Weight loss step 2*			*Weight loss (%) steps 1 and 2*
		Temp. region (°C)	*DTA*	*%*	*Temp. region (°C)*	*DTA*	*%*	
1	high vacuum ~10^{-5} Torr	90–165 165–225	endo	—	225–380	endo	—	21.4
2	synth. air ~730 Torr	135–220	exo	14.7	220–350	endo	4.9	19.6
3	N_2 ~730 Torr	130–220	exo	14.8	220–350	endo	4.8	19.6
4	O_2 ~730 Torr	135–220	exo	14.6	220–340	endo	4.5	19.1

again correlated with an endothermic DTA peak under atmospheric conditions (air, N_2, O_2). The most important TG and DTA data are listed in Table 1.

Mass spectrometric information

In order to study the thermal decomposition and the related reaction mechanisms in more detail, interesting mass numbers (17; 18; 20; 32 etc.) were recorded

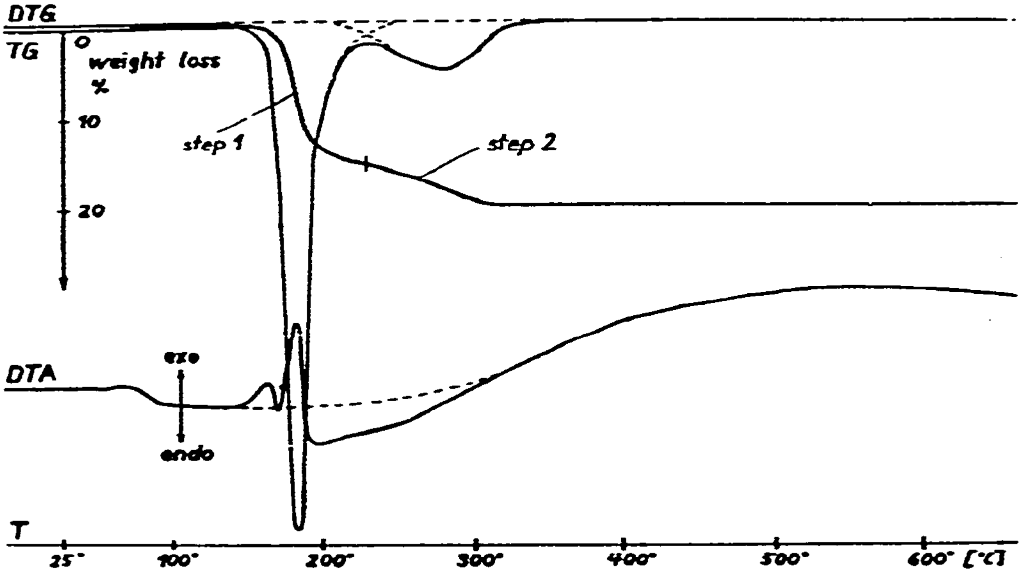

Fig. 5. TG, DTG and DTA curves of $UO_4 \cdot 2NH_3 \cdot 2HF$ measured simultaneously in oxygen.

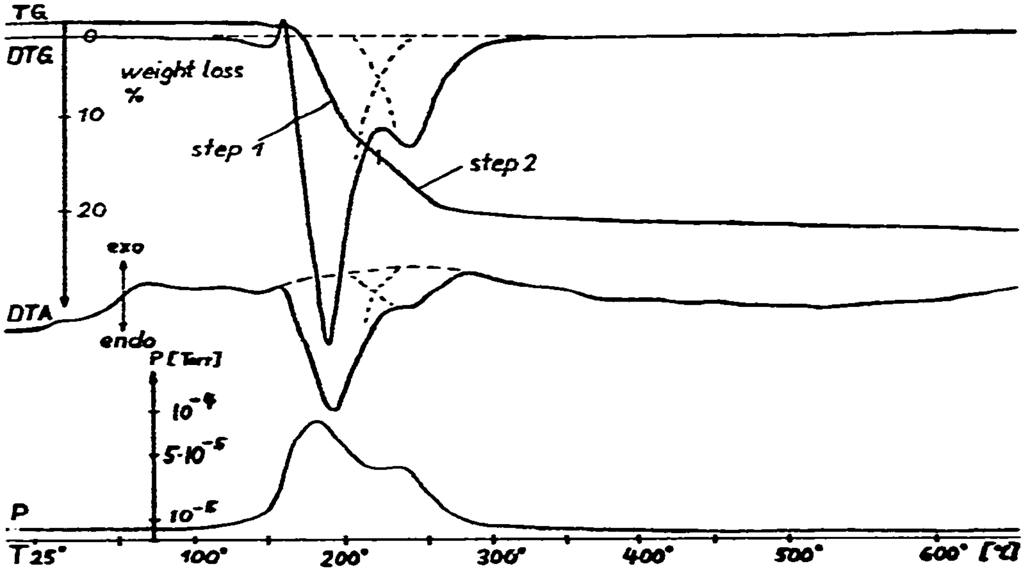

Fig. 6. TG, DTG, DTA and *P* curves of $UO_4 \cdot 2NH_3 \cdot 2HF$ measured simultaneously in high vacuum in combination with mass spectrometer.

simultaneously as a function of temperature. Figures 2 and 6 show the results of such a simultaneous TG–DTA–MS analysis of $UO_4 \cdot 2NH_3 \cdot 2HF$ under high vacuum conditions. It is evident (Fig. 2) that mass numbers 17 $(NH)_3^+$, 18 (H_2O^+) and 20 (HF^+) with their maximum at approx. 190 °C must be correlated with the first step.

Runs with higher mass spectrometric sensitivity show that decomposition starts at 100 to 120 °C with evolution of NH_3 followed by H_2O and HF at 120–130 °C.

Mass number 32 (O_2^+) contributes only little to the first step whereas it is the main component of the second step (maximum at 230–250 °C) together with NH_3 and H_2O partial pressures.

X-ray information

The results of the X-ray analysis are listed in Table 2.

Identification of phases A, B and C, formed after the first weight step was not yet possible. A listing of the most important X-ray reflexes of the reaction products,

TABLE 2

X-RAY DETERMINATION OF THE DECOMPOSITION PRODUCTS OF $UO_4 \cdot 2NH_3 \cdot 2HF$

Exp.	*After weight step*	*Results*	*Remarks*
high vac. (1)	1	phase A unknown	diffuse diagram
hv (2)	2	UO_2F_2	very diffuse diagram, nearly identical with air (1)
air (1)	1	phase B unknown	diffuse diagram
air (2)	2	UO_2F_2	diffuse diagram, nearly identical with hv (2)
N_2 (1)	1	phase C unknown	very diffuse diagram
N_2 (2)	2	phase D unknown	less diffuse diagram

TABLE 3

X-RAY SPECTRA OF THE INTERMEDIATE PRODUCTS AFTER THE 1ST WEIGHT STEP OF THE DECOMPOSITION OF $UO_4 \cdot 2NH_3 \cdot 2HF$

hv (1), phase A		*air (1), phase B*		*N_2 (1), phase C*	
d (Å)	*d* (Å)	*d* (Å)	*d* (Å)	*d* (Å)	*d* (Å)
7.93	3.03	7.93	3.07	8.04	—
6.10 df.	2.72	6.07	2.71	6.06	2.72
5.85	2.46 df.	5.78	2.46	—	—
—	2.05 df.	5.59	2.05	5.60	2.08
4.31 df.	1.93	4.30	1.95	4.23	1.95
4.24	1.84 df.	4.16	1.83	4.23	—
3.66	1.67	3.65	1.66	3.64	—
3.47 df.	1.62	3.43	1.62	3.43	—

isolated from high vacuum, air and nitrogen experiments (Table 3), shows however, that there is a common but unknown compound present in phases A, B and C (see also reaction mechanism). After the second step mainly UO_2F_2 is formed. Secondary products are UO_3 and little U_3O_8.

DISCUSSION

Based on the quantitative evaluation of thermograms, mass spectrometric analysis of gaseous decomposition products and X-ray analysis of intermediates, the thermal decomposition of $UO_4 \cdot 2NH_3 \cdot 2HF$ can be described by the following reactions:

Main reaction (100–400 °C)

step 1 $UO_4 \cdot 2NH_3 \cdot 2HF \xrightarrow{T} UO_4 \cdot 2HF + 2NH_3(g)$

$UO_4 \cdot 2HF \xrightarrow{T} UO_3F_2 + H_2O(g)$

step 2 $UO_3F_2 \xrightarrow{T} UO_2F_2 + \frac{1}{2}O_2(g)$

Secondary reaction I (100–400 °C)

step 1 $UO_4 \cdot 2NH_3 \cdot 2HF \xrightarrow{T}$ "UO_4" $+ 2NH_3(g) + 2HF(g)$

step 2 "UO_4" $\xrightarrow{T} UO_3 + \frac{1}{2}O_2(g)$

Secondary reaction II (400–800 °C)

$3UO_3 \xrightarrow{T} U_3O_8 + \frac{1}{2}O_2(g)$

The main reaction leads to the formation of NH_3 and H_2O during the first step. HF production during this period in the high vacuum experiment has to be explained with secondary reaction I.

Evolution of O_2 during the second step occurs in all of the proposed reaction types. Theoretical weight losses for all of these reaction types have been calculated and listed in Table 4.

TABLE 4

THEORETICAL WEIGHT LOSS, CALCULATED FOR THE 1ST STEP, 2ND STEP AND TOTAL OF STEPS 1 AND 2 OF $UO_4 \cdot 2NH_3 \cdot 2HF$

	Weight loss (%) in		
	Step 1	*Step 2*	*Steps 1+2*
Main reaction	13.83	4.25	18.08
Second reaction I	19.70	4.25	23.95

By comparison of experimental (Table 1) and theoretical weight losses relative proportions of main and secondary reactions have been estimated as well as amounts and nature of intermediates.

Under normal pressure (air, N_2, O_2) the decomposition follows to 85% the main reaction path and a compound of the type UO_3F_2 must be formed (probably identical with the unknown in phases A, B and C). After the second step, where oxygen is lost, a mixture containing approx. 75% UO_2F_2 is obtained. Maximum UO_2F_2 content is observed in an oxygen atmosphere, whereas the minimum of approx. 45% UO_2F_2 was stated in high vacuum experiments, due to high HF formation. (See Table 5.)

TABLE 5

CALCULATION OF THE INTERMEDIATE AND ENDPRODUCTS BY COMBINATED CALCULATION OF THE WEIGHT STEPS 1 AND 2 AND THE THEORETICAL VALUES

Exp.	*Atmosph.*	*After the 1st step*		*After the 2nd step*	
		% UO_3F_2	*% "UO_4"*	*% UO_2F_2*	*% UO_3*
1	high vacuum	—	—	43	57
2	synth. air	84	16	74	26
3	N_2	84	16	74	26
4	O_2	88	12	83	17

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