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THERMAL DECOMPOSITION OF SULPHATE COMPLEXES OF URANIUM(IV) HYDRATES

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A study was made of the thermal decompositions of the hydrates of 5 neutral sulphate complexes and 5 hydroxy-sulphate complexes of uranium(IV). The hydrates did not yield corresponding stable anhydrous compounds. After dehydration, the complexes decomposed in endothermic reactions involving progressive substitution of sulphur trioxide (that is liberated) by oxygen, giving oxy-sulphates and other compunds.

It is generally accepted [1, 2] that in complexes of uranium(IV) some molecules of water are attached to the central atom, but the exact number of water molecules bound to the uranium is a problem. Thermogravimetric studies of sulphate complexes of uranium(IV) have been made in order to solve this difficulty.

The compounds were heated to 800—900° and the formation of relatively stable intermediates (oxy-sulphate compounds) and end-products (oxy compounds or oxy-sulphate compounds) was observed.

The complexes reported in this paper had not previously been prepared. They are of interest when uranium-containing ores have to be processed; the uranyl sulphates of the mother liquid resulting from acid lixiviation can be converted to uranium(IV) sulphates by photochemical reduction [3, 4]. The photoreduction was carried out in sunlight and this requires the addition of a reducing substance: ethanol.

Experimental

Preparation

A stock solution of uranium(IV) sulphate was prepared by photochemical reduction of U_3O_8 in the presence of ethanol and diluted sulphuric acid. Calculated amounts of another metal sulphate solution were added to an earlier solution. The crystals (or precipitates) that appeared were centrifuged and dried in the air. In most cases the basic salts were observed, due to partial hydrolysis of uranium(IV). The addition of enough acid guarantees the formation of neutral sulphates.

Chemical analysis

The compounds were dissolved for analysis by oxidation with conc. H_2O_2. Uranium and other metals were determined by suitable analytical methods. Sul-

Table 1
Analytical results

	Calc., %				Exptl., %			
	U^{+4}	SO_4^{-2}	$M^{+1,2,3}$	H_2O	U^{+4}	SO_4^{-2}	$M^{+1,2,3}$	H_2O
$ZnU(SO_4)_3.6\,H_2O$	34.02	41.19	9.34	15.45	32.72	39.82	9.00	16.00
$Li_2U(SO_4)_3.7\,H_2O$	35.73	43.26	2.08	18.93	35.64	43.00	1.99	18.23
$MgU(SO_4)_3.9\,H_2O$	33.40	40.44	3.41	22.75	33.21	40.98	3.40	21.30
$Cd_5U(SO_4)_7.14\,H_2O$	13.80	38.99	32.59	14.62	13.56	39.20	33.10	14.96
$Mn_3U_2(SO_4)_7.23\,H_2O$	27.55	38.92	9.54	23.98	27.67	38.59	9.49	21.77
$Ni_2U(SO_4)_3(OH)_2.3\,H_2O$	32.53	39.39	16.05	7.39	33.19	39.09	16.20	7.42
$V_2U(SO_4)_4(OH)_2.5\,H_2O$	28.06	45.30	12.01	10.62	28.81	45.48	12.04	10.96
$Zn_4U(SO_4)_4(OH)_4.9\,H_2O$	21.37	34.50	23.47	14.56	21.69	34.97	23.64	15.18
$V_2U_2(SO_4)_6(OH)_2.10H_2O$	34.79	42.12	7.44	13.16	33.77	43.26	8.12	12.85
$La_2U_2(SO_4)_6(OH)_2.10H_2O$	30.82	37.32	17.99	11.56	30.76	38.12	17.80	11.46

phate was determined gravimetrically as $BaSO_4$. The water content was estimated by Karl Fischer titration or by difference to 100% of the other results. Table 1 lists the observed and calculated percentages.

Thermal analysis

Thermal analyses were carried out with a Mettler automatic recording thermoanalyser. A suitable crucible holder, which allowed simultaneous TG–DTA measurements, was used. The crucible material was Al_2O_3. The specimens, which had been ground in an agate ball mill, weighed about 20 mg. The heating rate was 4°/min. A Pt/Pt-Rh, 10% thermocouple was used.

Results and discussion

Representative TG curves are reproduced in Figs 1–10, together with the corresponding DTA traces (as far ~900°), which showed that all the decompositions were endothermic. The experimental weight changes are compatible with the re-

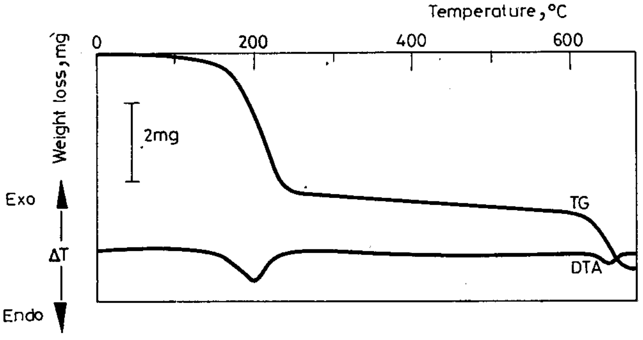

Fig. 1. TG and DTA curves of $ZnU(SO_4)_3.6\,H_2O$

Table 2

1. $ZnU(SO_4)_3 \cdot 6\ H_2O$ 699.688	(a) $\xrightarrow[-6H_2O]{253°}$	$ZnU(SO_4)_3$ 591.598 $dp_t = 15.45\%$ $dp_e = 16.00\%$	(b) $\xrightarrow[-SO_3]{670°}$	$ZnU(SO_4)_2O$ 511.532 $dp_t = 26.89\%$ $dp_e = 26.00\%$	738° (c) $\xrightarrow[-2SO_3]{862°}$	$ZnUO_3$ 351.400 $dp_t = 49.77\%$ $dp_e = 48.00\%$		
2. $Li_2U(SO_4)_3 \cdot 7\ H_2O$ 666.211	(a) $\xrightarrow[-7H_2O]{205°}$	$[Li_2U(SO_4)_3]$ 540.106 $dp_t = 18.93\%$ $dp_e = 18.23\%$	(b) $\xrightarrow[-SO_3]{605°}$	$Li_2U(SO_4)_2O$ .... 460.040 $dp_t = 30.95\%$ $dp_e = 29.51\%$				
3. $MgU(SO_4)_3 . 9\ H_2O$ 712.675	(a) $\xrightarrow[-9H_2O]{231°}$	$MgU(SO_4)_3$ 550.540 $dp_t = 22.75\%$ $dp_e = 21.30\%$	(b) $\xrightarrow[-SO_3]{668°}$	$MgU(SO_4)_2O$ 470.474 $dp_t = 33.98\%$ $dp_e = 34.59\%$	717° (c) $\xrightarrow[-SO_3]{885°}$	$MgU(SO_4)O_2$ .... 390.408 $dp_t = 45.22\%$ $dp_e = 45.63\%$		
4. $Cd_5U(SO_4)_7 . 14\ H_2O$ 1724.702	(a) $\xrightarrow[-14H_2O]{145°}$	$[Cd_5U(SO_4)_7]$ 1490.507 $dp_t = 14.62\%$ $dp_e = 14.96\%$	(b) $\xrightarrow[-2SO_3]{467°}$	$Cd_5U(SO_4)_5O_2$ .... 1392.426 $dp_t = 19.27\%$ $dp_e = 19.47\%$				
5. $Mn_3U_2(SO_4)_7 \cdot 23\ H_2O$ 1727.681	(a) $\xrightarrow[-23H_2O]{168°}$	$[Mn_3U_2(SO_4)_7]$ 1313.336 $dp_t = 23.98\%$ $dp_e = 21.77\%$	(b) $\xrightarrow[-4SO_3]{609°}$	$Mn_3U_2(SO_4)_3O_4$ 993.072 $dp_t = 42.52\%$ $dp_e = 40.64\%$	650° (c) $\xrightarrow[-2SO_3]{795°}$	$[Mn_3U_2(SO_4)O_6]$ 836.970 $dp_t = 51.79\%$ $dp_e = 52.98\%$	(d) $\xrightarrow[-SO_3]{874°}$	Mn_3U_2 752.874 $dp_t = 56.42\%$ $dp_e = 55.55\%$
6. $Ni_2U(SO_4)_3(OH)_2 \cdot 3\ H_2O$ 731.709	$\frac{-3H_2O}{-(H_2O + SO_3)}$ (a) $\xrightarrow{223°}$	$Ni_2U(SO_4)_2O_2$ 579.582 $dp_t = 20.79\%$ $dp_e = 20.89\%$	(b) $\xrightarrow[-SO_3]{639°}$	$Ni_2U(SO_4)O_3$ .... 499.516 $dp_t = 31.73\%$ $dp_e = 30.13\%$				
7. $V_2U(SO_4)_4(OH)_2 . 5\ H_2O$ 848.269	(a) $\xrightarrow[-5H_2O]{189°}$	$V_2U(SO_4)_4(OH)_2$ .... 758.194 $dp_t = 10.62\%$ $dp_e = 10.96\%$						
8. $Zn_4U(SO_4)_4(OH)_4 . 9\ H_2O$ 1113.941	(a) $\xrightarrow[-9H_2O]{212°}$	$[Zn_4U(SO_4)_4(OH)_4]$ 951.806 $dp_t = 14.56\%$ $dp_e = 15.18\%$	(b) $\xrightarrow[-2H_2O]{316°}$	$Zn_4U(SO_4)_4O_2$ 915.774 $dp_t = 17.79\%$ $dp_e = 19.94\%$	533° (c) $\xrightarrow[-SO_3]{582°}$	$Zn_4U(SO_4)_3O_3$ 680° .... 835.708 $dp_t = 24.98\%$ $dp_e = 25.79\%$		
9. $V_2U_2(SO_4)_6(OH)_2 \cdot 10\ H_2O$ 1368.506	$\frac{-10H_2O\ (a)\quad 210°}{-(H_2O + SO_3)} \rightarrow$	$V_2U_2(SO_4)_5O_2$ 1090.274 $dp_t = 20.33\%$ $dp_e = 20.75\%$	(b) $\xrightarrow[-4SO_3]{565°}$	$[V_2U_2(SO_4)O_6]$ .... 770.010 $dp_t = 43.73\%$ $dp_e = 45.14\%$				
10. $La_2U_2(SO_4)_6(OH)_2 \cdot 10\ H_2O$ 1544.442	(a) $\xrightarrow[-10\ H_2O]{204°}$	$[La_2U_2(SO_4)_6(OH)_2]$ 1364.292 $dp_t = 11.56\%$ $dp_e = 11.46\%$	$\swarrow -(H_2O + SO_3)$ (b) $\xrightarrow[-SO_3]{755°}$	$[La_2U_2(SO_4)_4O_3]$ 1186.144 $dp_t = 23.20\%$ $dp_e = 22.92\%$	(c) $\xrightarrow[-2SO_3]{849°}$	$[La_2U_2(SO_4)_2O_6]$ .... 1026.012 $dp_t = 33.57\%$ $dp_e = 33.85\%$		

Table 3

Endothermic effects
(characterized by the peak temperatures, °C)

Reaction no.	Steps			
	a	b	c	d
1	197	641	785–802–820–860	
2	(65)–104–(127) 185	580 603 615	708	
3	199		801	
4	111 131 142.5			
5	104 112 149		787	(870)
6	64 121 175–192		800 815	
7	(56) 112 170			
8	47 70 189	297	560	890
9	135 175	541 557	650–704 785 833	
10	(60) 154–172		(720) 805	

actions given in Table 2. The corresponding effects during the process (characterized by the temperatures of the minima) are summarized for each step in Table 3.

The difference between the experimental and theoretical weight changes should be due to overlapping between consecutive reactions of decomposition. Nevertheless, good horizontal sections in the weight-loss curves were obtained for the species $ZnU(SO_4)_2O$ (670–738°) $Li_2U(SO_4)_2O$ (605°–708°), $MgU(SO_4)_2O$ (668–717°), $Mn_3U_2(SO_4)_3O_4$ (609–650°) $Zn_4U(SO_4)_4O_2$ (316–533°) and $Zn_4U(SO_4)_3O_3$

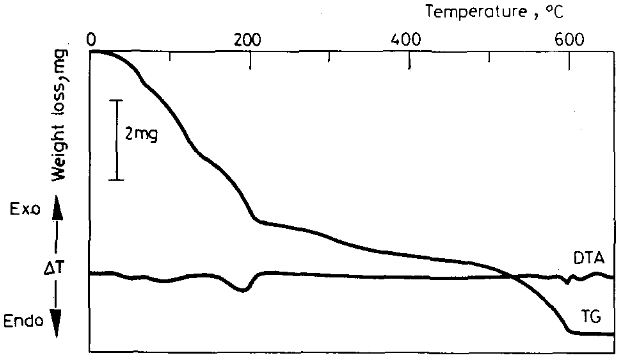

Fig. 2. TG and DTA curves of $Li_2U(SO_4)_3.7\ H_2O$

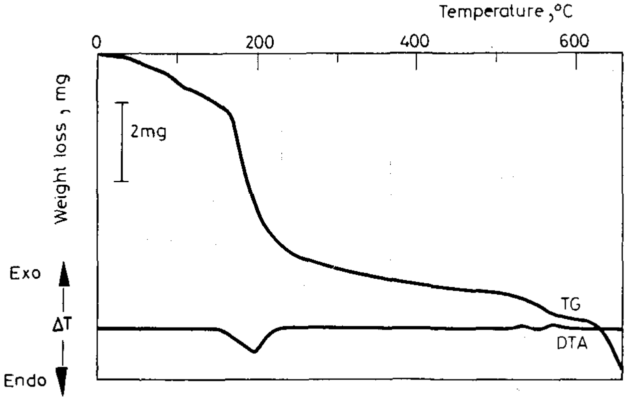

Fig. 3. TG and DTA curves of $MgU(SO_4)_3.9\ H_2O$

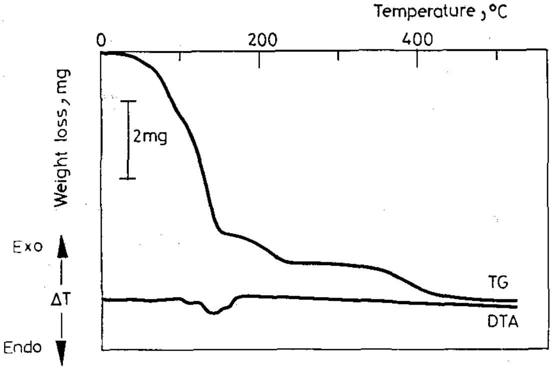

Fig. 4. TG and DTA curves of $Cd_5U(SO_4)_7.14\ H_2O$

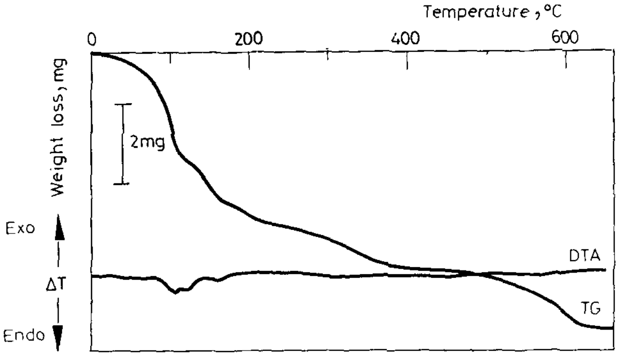

Fig. 5. TG and DTA curves of $Mn_3U_2(SO_4)_7.23\ H_2O$

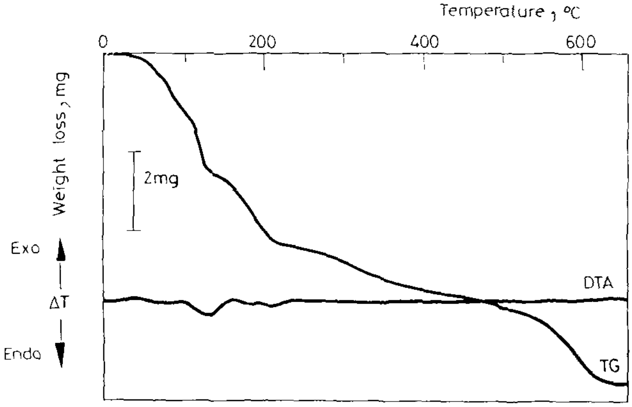

Fig. 6. TG and DTA curves of $Ni_2U(SO_4)_3(OH)_2.3\ H_2O$

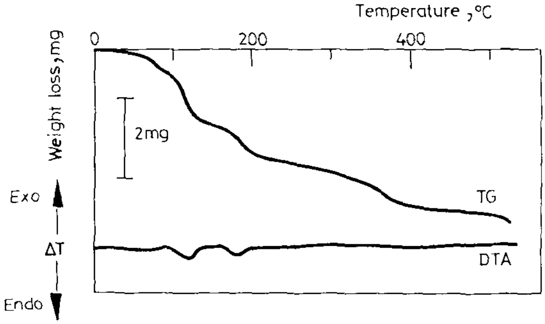

Fig. 7. TG and DTA curves of $V_2U(SO_4)_4(OH)_2.5\ H_2O$

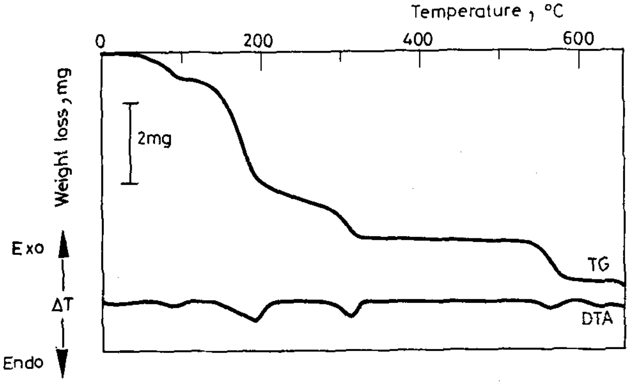

Fig. 8. TG and DTA Curves of $Zn_4U(SO_4)_4(OH)_4.9\ H_2O$

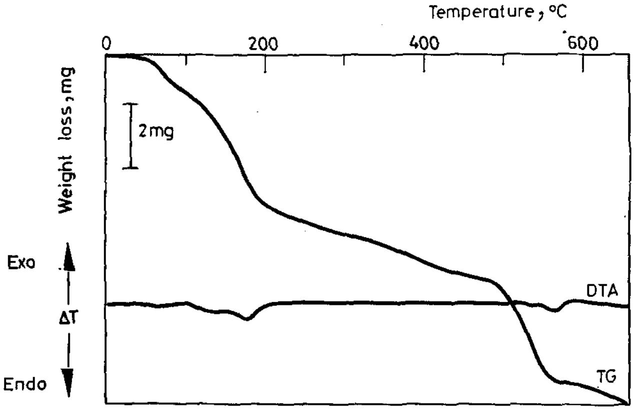

Fig. 9. TG and DTA curves of $V_2U_2(SO_4)_6(OH)_2.10\ H_2O$

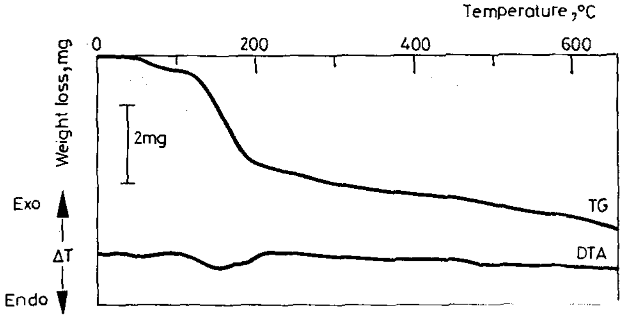

Fig. 10. TG and DTA curves of $La_2U_2(SO_4)_6(OH)_2.10\ H_2O$

(582 – 680°). The very unstable or poorly characterized species are given in square brackets.

Granted that non-horizontal sections in the TG curves after dehydration are due to instability of anhydrous compounds, we examined the corresponding effects in the differential thermal analysis curves. The end-temperatures of these endothermic effects correspond to the calculated loss of all water molecules in the neutral sulphates. In some hydroxy-sulphate complexes of uranium(IV) the dehydration is accompanied by the loss of SO_3, and as a result the earlier method was useless for accurately establishing the temperature at which water is lost.

After their dehydration the complexes decompose, involving progressive substitution of sulphur trioxide by oxygen, giving different oxy-sulphates before the end-products. Above 850° these should be oxy-compounds of types $M^{II}UO_3$ $M^{II}UO_4$, $M_2^{II}U_2O_7$ or $M_3^{III}U_2O_7$ (in the case of magnesium, the species identified at these temperatures is still an oxy-sulphate, $MgU(SO_4)O_2$). It is difficult to establish without ambiguity the nature of these residues. We attempted to characterize their approximate compositions by chemical analysis, and the results agree with those expected on the basis of the weight-losses. As regards contamination of the end-products by oxidation, we consider that this might occur, but the visible spectra of these residues are also typical of U^{IV}.

In conclusion, we deduce from the decomposition temperatures and the SO_4:O ratios of the products of thermal degradation that neutral uranium sulphate complexes of type $MU(SO_4)_3 \cdot xH_2O$ are more stable than the species of higher complexity, $M_5U(SO_4)_7 \cdot xH_2O$ or $M_3U_2(SO_4)_7 \cdot xH_2O$, granted that, on the other hand, the latter are more hydrated.

References

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Résumé — On a étudié la décomposition thermique des hydrates de 5 sulfates neutres complexes et de 5 hydroxysulfates complexes de l'uranium(IV). Les hydrates n'ont pas fourni de composés correspondants anhydres stables. Après leur déshydratation, les complexes se décomposent suivant des réactions endothermiques qui font intervenir substitution progressive de l'anhydride sulfurique (libéré) par de l'oxygène, donnant des oxy-sulfates et d'autres composés oxy.

Zusammenfassung — Die thermische Zersetzung der Hydrate von 5 neutralen Sulfatokomplexen und 5 Hydroxy-sulfatokomplexen des Uran(IV) wurde untersucht. Die Hydrate ergaben keine entsprechenden stabilen wasserfreien Verbindungen. Nach ihrer Dehydratisierung werden die Komplexe in endothermen Reaktionen durch fortschreitende Substituierung des (freigesetzten) Schwefeltrioxids durch Sauerstoff zersetzt, wobei Oxysulfate und andere Oxyverbindungen entstehen.

Резюме — Изучено термическое разложение 5 нейтральных сульфатных и 5 оксисульфатных комплексов урана(IV). Гидраты не давали соответствующих стабильных безводных соединений. После дегидратации комплексы разлагаются согласно эндотермических реакций, включая все увеличивающееся замещение трехокиси серы (которая выделялась) на кислород, давая оксисульфаты или другие оксисоединения.