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THERMAL DECOMPOSITION OF TETRAKISOXALATOURANATES(IV) OF MIXED METALS: CHARACTERISATION OF A NEW POTASSIUM URANATE PHASE

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ABSTRACT

The thermal decomposition of $K_2CaU(C_2O_4)_4 \cdot 8H_2O$ and $K_2CdU(C_2O_4)_4 \cdot 8H_2O$ have been studied in air. Both compounds lead to the formation of a new potassium uranate phase at 900 °C. The new uranate is shown to be a cubic K_2UO_4 phase stabilised by either Ca or Cd ions. The X-ray powder data of the tetraoxalates and potassium uranate are indexed.

INTRODUCTION

Potassium uranium(IV) tetraoxalate has been prepared as a pentahydrate [1,2] and as a tetrahydrate [3] in the solid state. The X-ray crystal structures of the two crystalline modifications of the tetrahydrate have been published recently. The corresponding calcium and cadmium uranium(IV) tetraoxalates, $M_2U(C_2O_4)_4 \cdot nH_2O$ (Ca, $n = 4$; Cd, $n = 6$) have been prepared by reacting solutions of the potassium salt with hot aqueous solutions of the chloride or sulphate of calcium and cadmium [4]. The thermal decomposition of these oxalates leads to the formation of the respective metal uranates. The uranates formed are K_2UO_4 from the potassium compound, $CdUO_4$ from the cadmium and a mixture of $CaUO_4$ and Ca_3UO_6 for the calcium compound. When the potassium ions in $K_4U(C_2O_4)_4 \cdot 5H_2O$ are only partially replaced by either calcium or cadmium ions, we can expect the oxalates to decompose to form either mixtures of metal uranates or quarternary mixed metal uranates. In order to study the nature of the uranates formed under these conditions, we have prepared the oxalate compounds $K_2CaU(C_2O_4)_4 \cdot 8H_2O$ and $K_2CdU(C_2O_4)_4 \cdot 8H_2O$ and studied their thermal decomposition in air. Although the preparation of the calcium compound has been reported earlier [5], its thermal decomposition has not been studied.

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EXPERIMENTAL

$K_4U(C_2O_4)_4 \cdot 5H_2O$ was prepared by the method described earlier [2]. Dilute solutions of calcium chloride (L.R.) and cadmium sulphate (A.R.) were mixed with 5% aqueous solutions of $K_4U(C_2O_4)_4 \cdot 5H_2O$ at room temperature in stoichiometric ratio sufficient to replace half of the potassium ions. The solids precipitated were washed with alcohol and dried in air. Chemical analysis for uranium was done by potentiometric method [6], oxalate by titrating against $KMnO_4$, potassium and cadmium by atomic emission spectroscopic methods and calcium by EDTA titrations. The water molecules were determined by thermogravimetry by heating upto 200°C. The results of analysis agree with the compositions as shown below where the values within parentheses are the values expected.

$K_2CaU(C_2O_4)_4 \cdot 8H_2O$: %U = 25.8(27.9); %K = 8.4(9.2); %Ca = 4.7(4.7); $\%C_2O_4$ = 40.4(41.3); $\%H_2O$ = 17.2(16.9).

$K_2CdU(C_2O_4)_4 \cdot 8H_2O$: %U = 25.9(25.7); %K = 7.7(8.5); %Cd = 10.9(12.2); $\%C_2O_4$ = 37.1(38.1); $\%H_2O$ = 15.9(15.6).

The X-ray diffraction patterns were recorded on a diffractometer using copper K_α raditaion. Simultaneous TG and DTA were done on a Mettler TA1 thermoanalyser in a flowing stream of dry air. Preheated alumina was used as the reference material. The infrared spectra were recorded on a Perkin-Elmer Model 180 spectrophotometer with the samples mixed with KBr and pressed as pellets. The UV/visible spectra were recorded on samples dissolved in 0.2 M H_2SO_4 in a Beckman Spectrophotometer Model DU7.

RESULTS AND DISCUSSION

The X-ray powder patterns of the two compounds, namely $K_2CaU(C_2O_4)_4 \cdot 8H_2O$ and $K_2CdU(C_2O_4)_4 \cdot 8H_2O$ were quite similar but different from those of the component oxalates. The data could be indexed on the basis of orthorhombic cells. While the powder lines are listed in Table 1, the crystal parameters derived are compared with those of orthorhombic $K_4U(C_2O_4)_4 \cdot 4H_2O$ in Table 2. The IR spectra were almost identical indicating that the two compounds have similar structures. The spectrum obtained for $K_2CdU(C_2O_4)_4 \cdot 8H_2O$ is shown in Fig. 1.

The thermograms are reproduced in Figs. 2 and 3. Both compounds lose all the water molecules on heating upto 200°C forming anhydrous compounds. This dehydration is accompanied by two endothermic peaks in the DTA. The anhydrous compounds decompose at 325°C. This decomposition is characterised by sharp exothermic DTA peaks due to the oxidation of the liberated CO. The decomposition of the cadmium compound gives a second sharp exothermic peak at 345°C, while that of the calcium compound has

TABLE 1

X-ray powder patterns of the tetraoxalates

$K_2CaU(C_2O_4)_4 \cdot 8H_2O$		$K_2CdU(C_2O_4)_4 \cdot 8H_2O$	
Intensity	*d* (obs)	Intensity	*d* (obs)
10	8.75	100	7.03
8	7.62	5	6.79
100	6.99	30	5.72
8	6.70	5	4.86
20	5.75	10	4.63
6	4.91	5	4.48
15	4.65	5	4.32
20	4.48	5	4.17
5	4.30	35	3.978
5	4.17	25	3.870
25	3.985	25	3.509
15	3.857	30	2.882
35	3.532	5	2.850
5	3.295	15	2.757
5	3.191	15	2.698
5	3.136	5	2.616
40	2.893	5	2.583
10	2.762	5	2.493
8	2.717	10	2.431
10	2.501	40	2.348
10	2.445	30	2.239
40	2.355	5	2.158
8	2.323	20	2.088
30	2.243	10	2.035
5	2.168	10	1.992
20	2.089	5	1.932
10	2.049	5	1.887
8	1.997	5	1.851
10	1.935	20	1.764
5	1.904	5	1.724
5	1.860	5	1.652
5	1.832	5	1.622
5	1.799	5	1.574
8	1.769		
5	1.726		
5	1.624		
5	1.586		

($\lambda = 1.54178$ Å).

two broad exothermic DTA peaks at 380 and 485 °C. These DTA peaks could have resulted from the decomposition of the carbonates formed and are accompanied by slow loss in the weight of the sample. The weight changes observed in the thermograms have been interpreted in terms of the reaction products shown in Table 3. Thus the anhydrous compounds decom-

TABLE 2

Cell parameters on orthorhombic tetraoxalatouranates(IV)

	$K_2CaU(C_2O_4)_4 \cdot 8H_2O$	$K_2CdU(C_2O_4)_4 \cdot 8H_2O$	$K_4U(C_2O_4)_4 \cdot 4H_2O$
a	17.491(12) Å	17.169(11) Å	30.09(2) Å
b	13.403(7) Å	13.584(9) Å	22.18(1) Å
c	9.316(7) Å	9.248(6) Å	12.747(6) Å
ρ(meas)	2.65 g ml^{-1}	2.73 g ml^{-1}	2.55 g ml^{-1}
ρ(calc)	2.59 g ml^{-1}	2.84 g ml^{-1}	2.56 g ml^{-1}
z	4	4	16

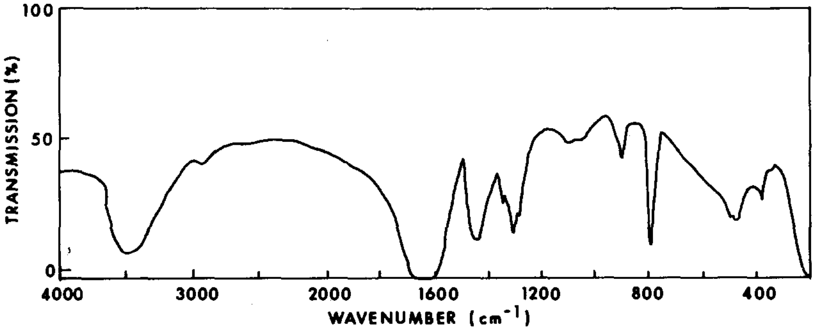

Fig. 1. IR Spectrum of $K_2CdU(C_2O_4)_4 \cdot 8H_2O$.

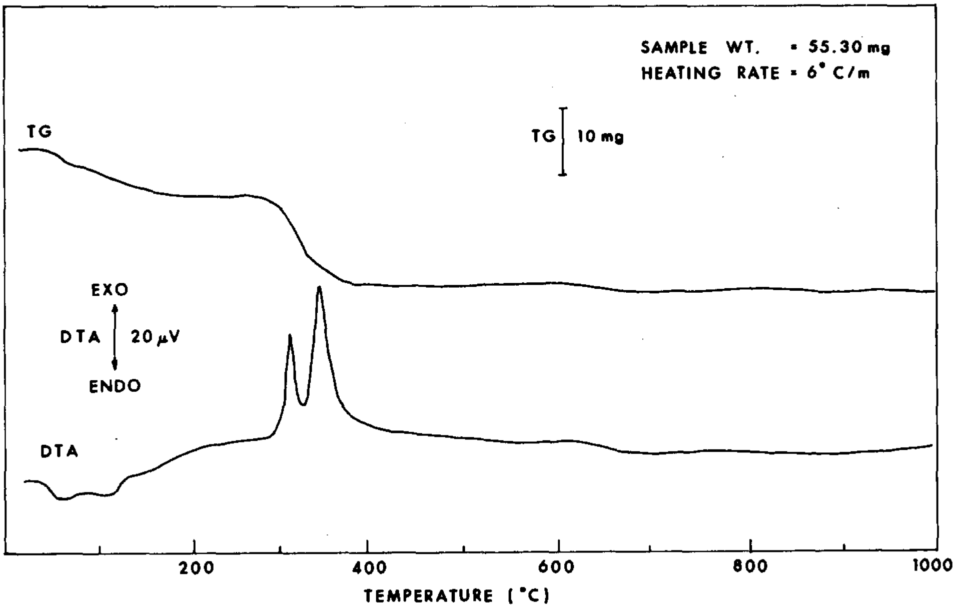

Fig. 2. TG and DTA curves for $K_2CdU(C_2O_4)_4 \cdot 8H_2O$.

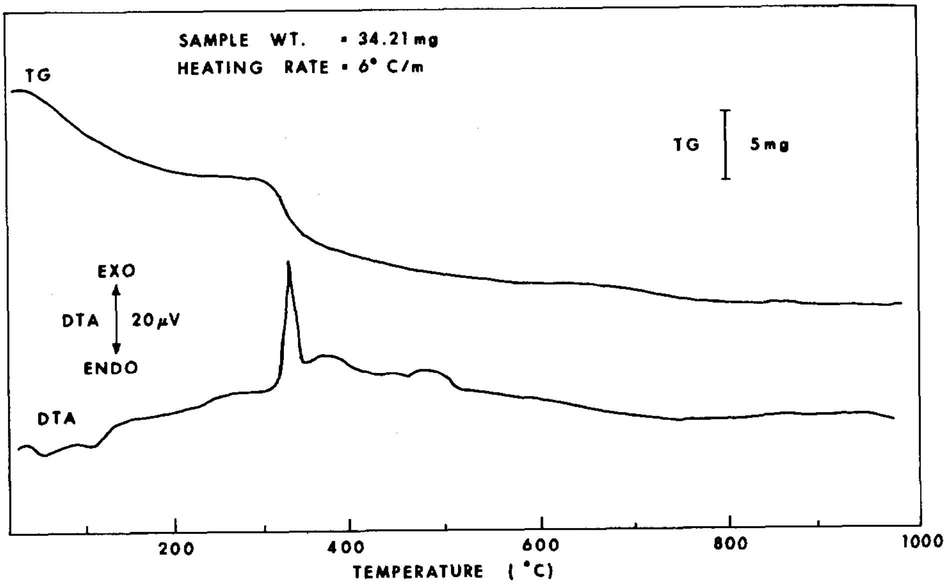

Fig. 3. TG and DTA curves for $K_2CaU(C_2O_4)_4 \cdot 8H_2O$.

pose to form first U_3O_8 and metal carbonates which on further heating forms uranates. Although only CdO and $CaCO_3$ lines were detected in the X-ray diffraction patterns of the products obtained by heating, respectively, the cadmium and calcium compounds upto the intermediate temperatures, the formation of U_3O_8 and metal carbonate is assumed as in the decomposition of $K_4U(C_2O_4)_4$, $Cd_2U(C_2O_4)_4$ and $Ca_2U(C_2O_4)_4$. However, all the products formed at 900°C gave good X-ray diffraction patterns. The decomposition product of $K_2CdU(C_2O_4)_4$ was identified to be a mixture of CdO and a new phase. The X-ray pattern of the new phase is listed in Table 4. Since cadmium has been identified and accounted qualitatively to be present as CdO it is reasonably assumed that the additional lines observed

TABLE 3

Thermogravimetric data on tetraoxalatouranates(IV)

Compound	Temp. (°C)	% Weight loss		Reaction products
		Observed	Calculated	
$K_2CaU(C_2O_4)_4 \cdot 8H_2O$	200	17.25	16.90	$K_2CaU(C_2O_4)_4$
	460	40.01	39.12	$K_2CO_3 + CaCO_3 + U_3O_8$
	900	48.2	–	(K, Ca)Uranate + K_2UO_4 [a]
$K_2CdU(C_2O_4)_4 \cdot 8H_2O$	210	15.91	15.58	$K_2CdU(C_2O_4)_4$
	600	41.95	40.80	$K_2CO_3 + CdO + U_3O_8$
	900	45.30	45.00	$CdO + K_2UO_4$ [a]

[a] New cubic phase.

TABLE 4

X-ray pattern for the new potassium uranate phase

I/I_0	d(obs)	h	k	l	d(calc)	I/I_0	d(obs)	h	k	l	d(calc)
15	6.10	1	1	0	6.07	18	1.358	6	2	0	1.357
65	4.29	2	0	0	4.29	3	1.326	5	4	1	1.325
12	3.513	2	1	1	3.505	7	1.296	6	2	2	1.294
100	3.038	2	2	0	3.035	3	1.268	6	3	1	1.266
8	2.718	3	1	0	2.715	7	1.240	4	4	4	1.239
10	2.481	2	2	2	2.478			7	1	0	1.214
10	2.295	3	2	1	2.295	3	1.215	5	5	0	1.214
35	2.149	4	0	0	2.146			5	4	3	1.214
7	2.025	4	1	1	2.024	8	1.191	6	4	0	1.191
		3	3	0	2.024			7	2	1	1.168
32	1.920	4	2	0	1.920	2	1.169	6	3	3	1.168
4	1.833	3	3	2	1.830			5	5	2	1.168
40	1.752	4	2	2	1.753	15	1.148	6	4	2	1.147
7	1.685	5	1	0	1.684	4	1.073 [a]	8	0	0	1.073
		4	3	1	1.684	8	1.041 [a]	8	2	0	1.041
6	1.569	5	2	1	1.567			6	4	4	1.041
20	1.519	4	4	0	1.518	10	1.011 [a]	8	2	2	1.012
3	1.473	5	3	0	1.472			6	6	0	1.012
		4	3	3	1.472	3	0.9842 [a]	6	6	2	0.9848
15	1.431	6	0	0	1.431	5	0.9595 [a]	8	4	0	0.9599
		4	4	2	1.431	5	0.9366 [a]	8	4	2	0.9367
5	1.392	6	1	1	1.393	5	0.9151 [a]	6	6	4	0.9152
		5	3	2	1.393	5	0.8761 [a]	8	4	4	0.8762

[a] Lines for $K_{\alpha_1} = 1.54056$ Å ($\lambda = 1.54178$ Å).

for the new phase could be that of a potassium uranate. The strong lines in this pattern were indexed on the basis of a cubic cell with $a = 4.29$ Å, while a doubled cubic cell of 8.58 Å is required to satisfy other weak lines present.

The K–U–O systems have been investigated repeatedly by various groups. The available data show three potassium uranates to have all their strong X-ray lines satisfying cubic or pseudocubic cells around 4.3 Å. These are KUO_3 [7,8], K_4UO_5 [9] and β-K_2UO_4 [10]. The formation of KUO_3 containing pentavalent uranium by reacting UO_2 with tetragonal K_2UO_4 at about 800°C in inert atmosphere described by Rudorff et al. [7] has been confirmed by Van Egmond and Cordfunke [11]. The existence of the other two potassium uranates both containing U(VI) have been questioned by latter workers. Efremova et al. [9] reported the preparation of K_4UO_5 by heating a mixture of K_2CO_3 and UO_3 in the ratio of 2 : 1 at 1000°C. Kovba et al. [10] found that the continuous calcination of the well characterised tetragonal K_2UO_4 at 900°C resulted in the formation of β-K_2UO_4. Although the strong lines in the X-ray patterns of both K_4UO_5 and β-K_2UO_4 indicated a cubic subcell of $a = 4.29$ Å, the superstructure lines were different. It was therefore postulated that both have disordered dense potassium and oxygen packing. Hoekstra and Siegel [12] and Van Egmond and Cordfunke [11] could not confirm the preparation of K_4UO_5 although the procedure described by Efremova et al. was duplicated. Similarly, for β-K_2UO_4 Hoekstra [13] found that long continued heating of K_2UO_4 at 900°C or above resulted in a gradual loss of potassium resulting in $K_2U_2O_7$, while Van Egmond and Cordfunke [11] failed to observe any phase transition in their high temperature X-ray work. The latter authors suggested the formation of KUO_3 under conditions employed by Kovba et al. The superstructure lines in the X-ray pattern of the new phase is different from such lines reported for both K_4UO_5 and β-K_2UO_4 but the strong lines correspond to those from KUO_3. That the new phase is not KUO_3 was verified from the absorption spectra of the new phase measured on a solution in 0.2 M sulphuric acid which showed that all the uranium is present as U(VI). KUO_3 on the other hand, under identical conditions gives absorption bands corresponding to U(IV) and U(VI), both being formed by the disproportionation of U(V).

The decomposition product from $K_2CaU(C_2O_4)_4$ gave the X-ray pattern listed in Table 5. On the basis of additional experiments described below, this pattern could be interpreted as a mixture of the same potassium uranate(VI) phase obtained from the cadmium compound and possibly a new calcium potassium uranate phase. The lines ascribed to the latter phase do not correspond to any known uranate phase of either calcium or potassium.

Since $K_4U(C_2O_4)_4$ decomposes to give tetragonal K_2UO_4 and the partial replacement of potassium ions by calcium and cadmium ion leads to the formation of the new cubic phase, it appears reasonable to assume that both calcium and cadmium are responsible for this conversion. In order to

TABLE 5

X-ray pattern of the decomposition products of $K_2CaU(C_2O_4)_4 \cdot 8H_2O$

Intensity	*d*(obs)	Intensity	*d*(obs)
12	6.11	8	2.295
60	4.83 [a]	65	2.149
60	4.71 [a]	65	2.118 [a]
45	4.29	6	2.025
10	3.513	42	1.920
85	3.382 [a]	80	1.821 [a]
85	3.038	45	1.799 [a]
100	2.766 [a]	30	1.768 [a]
20	2.718	45	1.752
15	2.481	30	1.685
20	2.417 [a]	20	1.589 [a]
20	2.353 [a]	30	1.569

[a] Lines ascribed to the unknown (Ca, K) uranate phase (λ = 1.54178 Å).

confirm this, $K_4U(C_2O_4)_4 \cdot 5H_2O$ was mixed with calcium oxalate in different ratios and heated at about 800°C. When the percentage of calcium is very low (around 10 mol%) the product formed was only the new potassium uranate(VI) phase to the complete exclusion of the tetragonal phase. With increasing amounts of calcium, the additional lines listed in Table 5 started appearing and at 100 mol% of calcium, the product obtained gave a pattern identical to that obtained from the decomposition product of $K_2CaU(C_2O_4)_4$. Identical results were also obtained even when tetragonal K_2UO_4 was used in place of $K_4U(C_2O_4)_4 \cdot 5H_2O$ thereby confirming that the new phase is actually K_2UO_4 stabilised by ions like Ca and Cd. It is possible that the formation of the new phase requires the presence of some ions like Ca or Cd at least as impurity.

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