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X-ray, thermal and infrared spectroscopic studies on lithium and sodium oxalate hydrates

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Abstract

Lithium uranyl oxalate hydrate, $Li_2UO_2(C_2O_4)_2{\cdot}5H_2O$ and sodium uranyl oxalate hydrate, $Na_2UO_2(C_2O_4){\cdot}4H_2O$ have been prepared and characterized by chemical and thermal analyses as well as X-ray diffraction and infrared spectroscopy. X-ray powder data show that the compounds belong to a monoclinic system. Thermal decomposition and infrared studies show that the compounds decompose to monouranates through the formation of alkali metal carbonates and UO_2 as intermediates. © 1997 Elsevier Science B.V.

Keywords: Decomposition; DTA; Lithium\Sodium uranyl oxalate; X-ray diffraction

1. Introduction

Alkali metal and ammonium uranyl oxalates with UO_2^{2+} to $C_2O_4^{2-}$ ration of 1 : 2 are known [1]. X-ray structural analysis on $(NH_4)_2UO_2(C_2O_4)_2$ [2] and $K_2UO_2(C_2O_4)_2{\cdot}3H_2O$ [3] have been reported. It has been shown that in both compounds the linear uranyl ion has five oxygen atoms forming a plane perpendicular to the O–U–O axis. The ammonium salt has the polymeric anion$[UO_2(C_2O_4)_2]_n^{2n-}$ in which all the five oxygen atoms are from three oxalate groups, none of which are planar. However, in the potassium salt the five oxygen atoms from two planar oxalate groups and a water molecule are present. Hence monomeric $[UO_2(C_2O_4)_2{\cdot}H_2O]$ units are present in the structure. The non-planarity of the oxalate groups and the polymeric structures of the former can be traced to the formation of hydrogen bonds of the hydrogen atoms on the ammonium ion. A structural study of the ions of lighter alkali metals such as Li^+ and Na^+ have been taken up to understand to which of the above two structures these will belong. In the present paper, the results of the thermal analysis studies on $Li_2UO_2(C_2O_4)_2{\cdot}5H_2O$ and $Na_2UO_2(C_2O_4)_2{\cdot}4H_2O$ are described.

2. Experimental

Saturated solutions of lithium or sodium oxalate and uranyl oxalate were mixed in equilmolar proportions, heated to boiling and allowed to cool slowly. The yellow crystals separated were washed with ice cold water, alcohol and then dried in air. The method employed for the preparation of these compounds has been described earlier [1]. The X-ray diffraction

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(XRD) patterns were recorded on a Siemen's diffractometer using CuK_α radiation and graphite monochromater. The infrared absorption spectra(IR) were recorded on a Perkin-Elmer 180 spectrophotometer with the samples dispersed in KBr discs. Simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) were carried out on ULVAC Thermal Analyzer in a flowing stream of dry air or argon gas using preheated alumina as reference material for DTA.

3. Analysis

The compounds were analyzed for their uranium oxalate, carbon, hydrogen and water contents. Uranium was estimated potentiometrically using the Davis and Gray method [4] and oxalate by volumetric titration with $KMnO_4$. The carbon and hydrogen analysis were carried out on a Carlo Erba elemental analyzer. Water content was determined from the thermogravimetric curves. The results of the analyses are shown in Table 1. The analysis result confirmed the compounds to be $Li_2UO_2(C_2O_4)_2{\cdot}5H_2O$ and $Na_2UO_2(C_2O_4)_2{\cdot}4H_2O$.

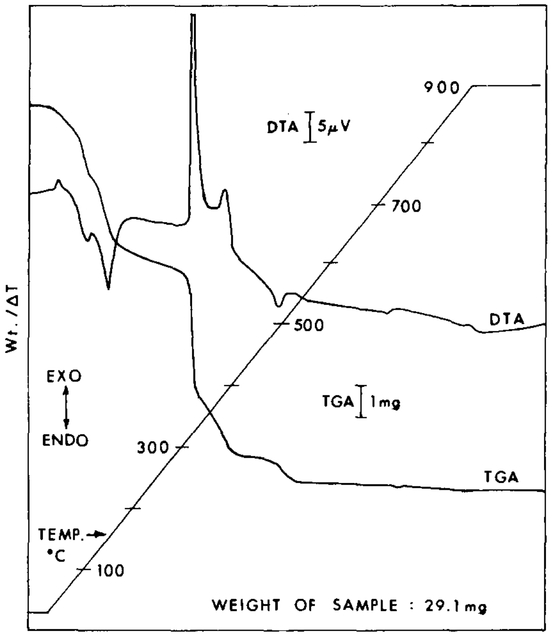

Fig. 1. TG and DTA of $Li_2UO_2(C_2O_4)_2{\cdot}5H_2O$ in air.

4. Results and discussion

The TG and DTA curves recorded for the thermal decomposition of $Li_2UO_2(C_2O_4)_2{\cdot}5H_2O$ in flowing atmosphere of dry air and argon gas shown respectively in Figs. 1 and 2. In both cases, the five water molecules were lost in two steps, each of which were accompanied by endothermic DTA peaks centered around 110° and 155°C. The analysis of the TG curves indicated that the number of water molecules lost at 110°C and 155°C were respectively two and three. In the absence of a clear plateau even after dehydration, the exact weight loss was determined by heating the sample at ~100°C and 150°C for few hours. The loss in weight observed corresponded to the loss of all the five water molecules both under argon and air. The anhydrous compound thus obtained gave diffuse XRD pattern. The TG curve for anhydrous compound in air showed three more distant weight loss steps; these were also accompanied by three DTA peaks; two exotherms at 330° and 390° and an endotherm at 500°C. As in the dehydration step no definite plateau is observed except after 530°C. The final product of decomposition after heating upto 900°C was identified as Li_2UO_4. In an argon atmosphere for the anhydrous compound the first two weight loss steps occurred

Table 1
Chemical Analysis in weight %

Compound	$Li_2UO_2\ (C_2O_4)_2{\cdot}5H_2O$		$Na_2UO_2\ (C_2O_4)_2{\cdot}4H_2O$	
	Found	Cal.	Found	Cal.
Uranium	43.30	43.27	42.40	42.20
Oxalate	32.12	32.00	31.37	31.21
Carbon	8.66	8.73	8.54	8.51
Hydrogen	1.75	1.82	1.43	1.42

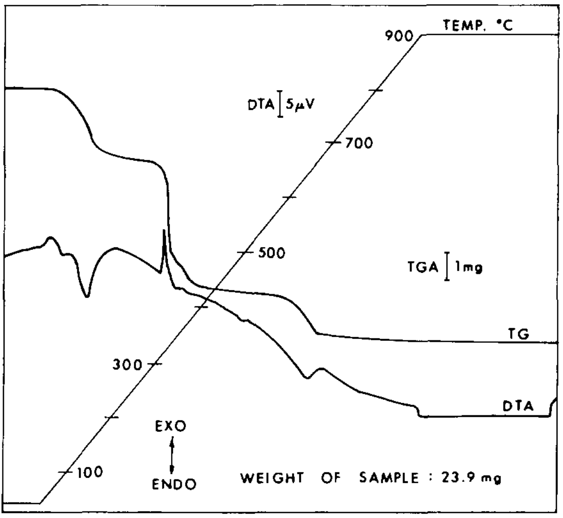

Fig. 2. TG and DTA of $Li_2UO_2(C_2O_4)_2{\cdot}5H_2O$ in argon.

below 400°C. From 400°C to 500°C there was no weight loss. Above 500°C a third weight loss occurred accompanied by an endothermic peak at 650°C. The product obtained after heating up to 900°C was as before Li_2UO_4. The observed weight loss of 42.5% is in agreement with that calculated for conversion to Li_2UO_4 (42.56%). In order to identify the intermediate products formed in the thermal decomposition the samples were heated in air or argon at 350°C for few hours. The product obtained in argon gave the XRD pattern of UO_2. The IR spectra of the product showed bands due to carbonate. The weight loss was in agreement with the formation of Li_2CO_3 and UO_2 as intermediate which reacted at 650°C to form Li_2UO_4. Heating in air, however, did not show the presence of UO_2 probably because in air it reacted immediately with Li_2CO_3.

The TG and DTA curves recorded for the thermal decomposition of $Na_2UO_2(C_2O_4){\cdot}4H_2O$ in flowing atmospheres of air and argon are shown in Figs. 3 and 4 respectively. The compound lost four water molecules below 150°C in a single step which was accompanied by endothermic DTA peaks under air and argon. The anhydrous compound remained stable up to 300°C above which weight losses continued up to 770°C. The product obtained at 800°C was identified from its XRD pattern to be α-Na_2UO_4. Although the nature of weight losses in both atmospheres were almost identical the DTA curves were different. While the reaction between 300°C and 450°C in air was accompanied by two exothermic peaks at 340° and 400°C and in argon had an exothermic peak at 330°C and two endothermic peaks at 345° and 420°C. Above

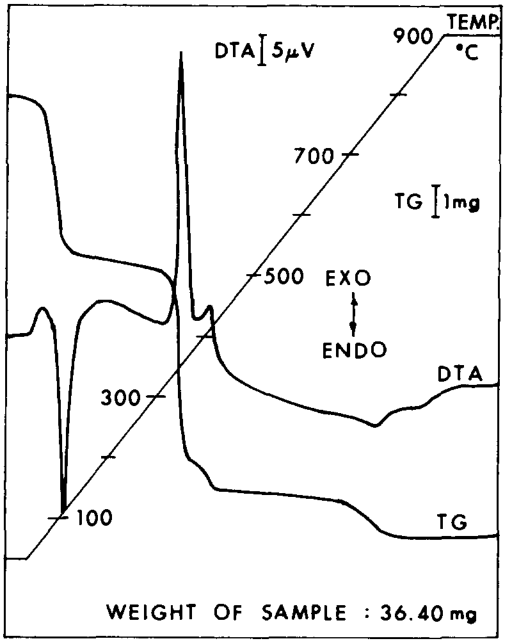

Fig. 3. TG and DTA of $Na_2UO_2(C_2O_4)_2{\cdot}4H_2O$ in air.

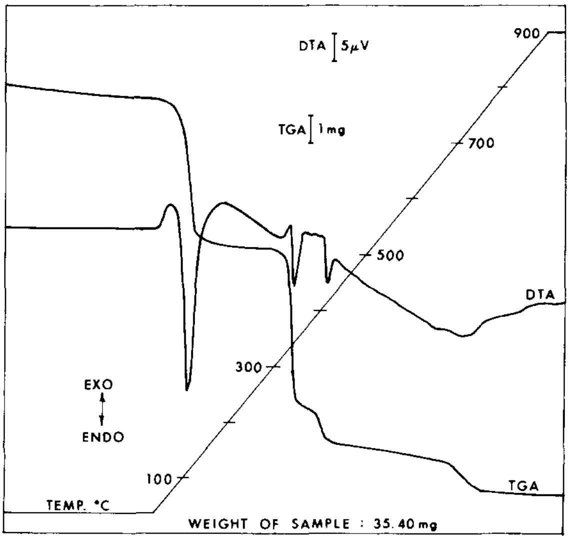

Fig. 4. TG and DTA of $Na_2UO_2(C_2O_4)_2{\cdot}4H_2O$ in argon

450°C there was a weak endothermic peak around 770°C under argon and air.

In the absence of any plateau in the TG curve where DTA indicated a reaction , identification of the intermediate reaction products were tried by heating the sample at 350°C for long duration. The product obtained in argon at 350°C gave the XRD pattern of UO_2 whereas in air, diffuse pattern was obtained. The weight losses were in agreement with the formation of Na_2CO_3 and UO_2. (Found 33.01%; calculated 33.3%). It therefore follows that the thermal decomposition can be represented as:

$$M_2UO_2(C_2O_4)_2 \cdot nH_2O \xrightarrow{100\,\text{to}\,160C} M_2UO_2(C_2O_4)_2 \xrightarrow{\sim 300C}$$

$$UO_2 + M_2C_2O_4 \xrightarrow{300\,\text{to}\,400C} UO_2 + M_2CO_3$$

$$\xrightarrow{700\,\text{to}\,800C} M_2UO_4$$

$$(M = Na/Li)$$

The formation of M_2UO_4 even under low oxygen potential conditions as in the case of Cs_2UO_4 [5] is a measure of the stability of this structure.

The X-ray diffraction patterns of $Li_2UO_2(C_2O_4)_2 \cdot 5H_2O$ and $Na_2UO_2(C_2O_4)_2 \cdot 4H_2O$ are indexed as a monoclinic unit cells of dimensions a=10.123(3) A°, b=11.948(2) A°, c=12.789(3) A° and β=107.81°(2), and a=15.179(2) A°, b=6.701(1) A°, c=14.012(3) A° and β= 93.61°(2) respectively. The density of the compounds were determined by pycnometric method using dry toluene. The measured and calculated densities are in good agreement and the number of formula units per cell is 4.

The infrared spectra of the two oxalates were similar. Both have absorption bands from the water molecules and coordinated oxalate groups. The infrared spectrum of $K_2UO_2(C_2O_4)_2 \cdot 3H_2O$ has been discussed in terms of a simple penta coordinated arrangement involving two bidentate oxalate groups and a water molecule [3,6]. As a result of this compound loses water molecules in two steps, two water molecules are lost below 75°C accompanied by a DTA peak at 50°C, the remaining water molecule is lost between 75 to 190°C accompanied by a weak endotherm at 140°C. The similarity of the IR bands with those of the potassium salt indicate similarity in structure.

The thermal decomposition scheme discussed above is further confirmed by the IR spectra of these compounds heated to about 350°C in argon atmosphere. Spectral bands due to carbonate appear in the range 1100–1080 cm^{-1} and uranyl bands in the range 945–927cm^{-1} disappear as expected. In argon atmosphere the reactions are comparatively slow and formation of UO_2 could be observed. When heated in air formation of intermediate compound UO_2 is not observed.

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