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THERMAL DECOMPOSITION OF URANYL PROPIONATE DIHYDRATE

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The thermal behaviour of uranyl propionate dihydrate was investigated by differential thermal analysis, thermogravimetry and X-ray diffraction analysis. Differential thermal analysis showed that anhydrous uranyl propionate, which is stable at lower temperatures, transforms into an enantiotropic form at higher temperatures.

The crystallographic characteristics of uranyl propionate dihydrate and its structural relationship with uranyl acetate dihydrate have been studied by Ferrari and co-workers using X-ray diffraction technique [1]. In an earlier paper we have already reported the results of infrared spectroscopic studies on both anhydrous and hydrated uranyl propionates, demonstrating their complex character; the uranyl ion exhibits co-ordination numbers $n = 4$ and $n = 6$, respectively [2].

In this paper thermal decomposition studies of uranyl propionate dihydrate are dealt with, using differential thermal analysis (DTA), thermogravimetry (TG) and X-ray diffraction techniques.

The existence is shown of two enantiotropic forms of anhydrous uranyl propionate.

Experimental

The synthesis of uranyl propionate dihydrate was carried out according to Courtois and Ferrari, from propionic acid and uranium trioxide; and anhydrous uranyl propionate was prepared by dissolving uranyl propionate dihydrate in propionic acid [1, 3].

The air-dried products were analysed for carbon, hydrogen and uranium. The analyses and empirical formulae of the compounds are given below:

Calculated for $(UO_2(C_2H_5COO)_2 \cdot 2H_2O)$

% Carbon 15.93; % Hydrogen 3.12; % U_3O_8 62.07

Experimental

% Carbon 15.4; % Hydrogen 3.3; % U_3O_8 62.13

Calculated for $(UO_2(C_2H_5COO)_2)$

% Carbon 17.31; % Hydrogen 2.42; % U_3O_8 67.44

Experimental

% Carbon 17.02; % Hydrogen 2.54; % U_3O_8 67.49

Apparatus

Differential thermal analysis and thermogravimetric data were obtained with the aid of a Deltatherm Model D-2000 apparatus manufactured by Technical Equipment Corporation; a static air atmosphere was employed. The heating rate for TG and DTA experiments was 5°/min. The sample was about 200 mg.

X-ray powder patterns were obtained with a Philips Model 1310/00 and a 114.83 mm Debye–Scherrer camera. Cu Kα radiation, Ni-filtered, was used.

Results and discussion

The following conclusion can be drawn from the DTA and TG curves for uranyl propionate dihydrate (Fig. 1).

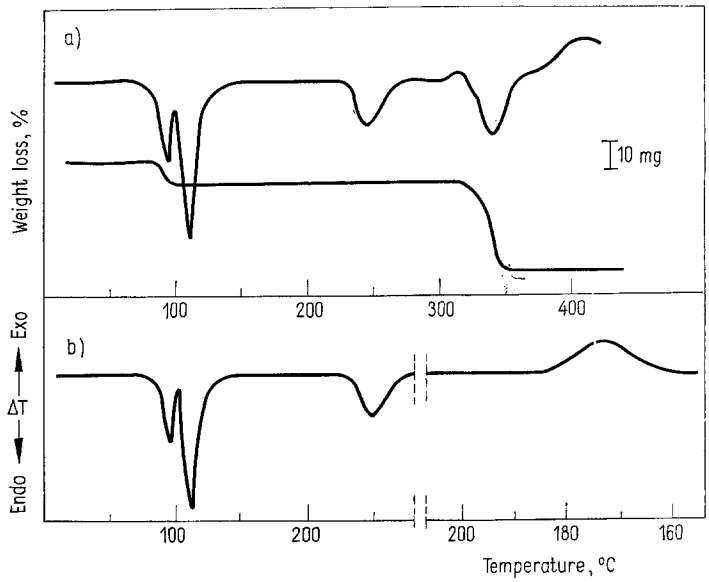

Fig. 1. a) DTA and TG curves of $(UO_2(C_2H_5COO)_2 \cdot 2\ H_2O)$; 1. b) Heating and cooling DTA curves of $(UO_2(C_2H_5COO)_2 \cdot 2\ H_2O)$

In the range 73 to 125° two very close endothermic peaks appear on the DTA curve at peak temperatures of 97° and 115°, respectively. The TG curve shows a first weight loss in the range 70 to 105°. This weight loss corresponds to the first endothermic effect and is ascribed to the evolution of water. The theoretical and experimental weight losses for this transformation are 7.96% and 7.99%, respectively. The second endothermic peak is ascribed to a structural regrouping (structural reorganization) in the anhydrous compound to a crystalline phase stable in the temperature range 130 to 240°.

In Table 1 are given the interplanar spacings, d (Å), and relative intensities, I, for the X-ray powder pattern of this anhydrous form, and for hydrated uranyl

Table 1

Interplanar spacings, d, and relative intensities, I, for the X-ray powder patterns of hydrated and anhydrous uranyl propionate

d Å	I	d Å	I
7.31	5	7.43	60
6.97	100	7.02	100
5.64	40	6.60	50
5.47	40	4.17	60
5.21	40	3.93	60
4.21	40	3.69	50
3.73	100	3.54	80
3.56	30	3.00	40
3.30	30	2.97	40
3.15	30	2.76	40
3.07	30	2.67	15
2.96	10	2.63	15
2.83	20	2.55	15
2.77	20	2.38	10
2.65	25	2.29	10
2.63	25	2.17	10
2.59	90	2.12	8
2.50	30	2.05	8
2.41	40		
2.38	45		
2.35	30		
2.30	30		
2.19	40		
2.16	30		
2.11	30		
2.06	40		
2.04	30		
2.02	50		
1.95	60		
1.91	40		
1.87	50		

propionate. The *d* values for the anhydrous salt have been calculated from a sample obtained by heating the hydrated salt at 125 to 130°. The X-ray powder photograph of this sample is the same as that of the anhydrous compound obtained by direct synthesis.

The endothermic effect observed at 230 to 255° does not correspond to a weight loss in the TG curve; it was checked previously that the compound does not melt. Furthermore, the X-ray powder pattern for anhydrous uranyl propionate after heating at 250° is identical with the powder diagram obtained after heating at 130°.

These results show that the last endothermic effect is due to an enantiotropic transformation in the anhydrous uranyl propionate, the transition temperature being about 245°. In order to confirm this, the cooling curve was obtained by heating the uranyl propionate to 260°, switching off the furnace current when this temperature was reached, and allowing the product to cool. The cooling curve (Fig. 1b) shows an exothermic effect nearly symmetrical to the endothermic one on the heating curve. This demonstrates decisively the existence of a reversible phase transformation at 245° in anhydrous uranyl propionate.

The endothermic and exothermic effects observed at 300 to 400° in the DTA curve correspond to the pyrolysis of the compound. The weight loss in the TG curve is equivalent to the stoichiometric removal of the organic matter to produce uranium oxide U_3O_8.

References

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3. G. COURTOIS, Compt. Rend., 158 (1914) 1511.

RÉSUMÉ — On a étudié le comportement thermique du propionate d'uranyle dihydraté par thermogravimétrie, analyse thermique différentielle et diffraction de rayons X. L'examen par ATD a montré que le propionate d'uranyle anhydre, stable aux basses températures, se transforme en une forme énantiotropique aux températures élevées.

ZUSAMMENFASSUNG — Das thermische Verhalten von Uranylpropionatdihydrat wurde durch Differentialthermoanalyse, Thermogravimetrie und Röntgendiffraktionsanalyse geprüft. Durch die erste Methode wurde bewiesen, daß das bei niedriger Temperatur stabile Anhydro-Uranylpropionat, bei höheren Temperaturen in eine enanthiotrope Form übergeht.

Резюме — Термическое поведение двухводного уранилпропионата исследовано методами термогравиметрии, дифференциального термического анализа и диффракции рентгеновских лучей. По результатам дифференциального термического анализа установлено, что безводный уранил пропионата, стабильный при низких температурах, переходит при высоких температурах в энантиотропную форму.