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THERMAL DECOMPOSITION OF PYRIDINIUM ZIRCONYL AND HAFNYL OXALATES

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ABSTRACT

Thermal decomposition of pyridinium zirconyl/hafnyl oxalate have been investigated employing TG, DTA, IR and chemical analysis. The decomposition proceeds through three steps viz., dehydration, decomposition of anhydrous oxalate to an intermediate, $ZrO_2/HfO_2.x(C_5H_5N)$ and finally the decomposition of this intermediate to oxide. Reaction kinetics for the second step decomposition have also been evaluated.

INTRODUCTION

In the field of preparation of fine particles high purity oxide ceramic materials, considerable attention has been devoted to the decomposition of oxalate complexes. Thermal studies on a number of titanyl and zirconyl oxalates have been described (1). However, very little information is available on the corresponding hafnyl oxalates. In this communication thermal behaviour of pyridinium zirconyl and hafnyl oxalates is described.

EXPERIMENTAL

Both the compounds were prepared in a similar manner by adding an excess of pyridine to an aqueous solution of $ZrCl_4$ or $HfCl_4$ and oxalic acid as described for their titanyl analogue (2).

TG curves were recorded on a Stanton-Redcroft automatic thermorecording balance (model 770) while DTA was carried out on a Mettler TA 10 DTA unit (sample size ≃ 25 mg, heating rate 10K/min).

RESULTS AND DISCUSSION

The TG and DTA curves of pyridinium zirconyl and hafnyl oxalates are given in figure 1 and 2, respectively. From the

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thermograms it is evident that the decomposition of both the compounds proceeds through three steps viz., dehydration, decomposition of anhydrous oxalate to an intermediate pyridine adduct and finally the decomposition of this intermediate to oxide.

Dehydration

Both the hydrated oxalates dehydrated by a single step process. The expected endothermic behaviour associated with the dehydration process of these compounds has been observed from DTA curves in almost at same temperature ranges.

Decomposition of anhydrous oxalate

The oxalate decomposition is a complicated endothermic process. Infrared spectra of the compound for this decomposition step shows that the oxalate peaks disappear slowly while the peaks for the free pyridine become observable. This means that the part of the liberated pyridine stays strongly adsorbed by ZrO_2/HfO_2. No formation of carbonate could be detected but chemical analysis showed the presence of carbon which can be caused by the decomposition of pyridine.

Decomposition of intermediate pyridine adduct

Decomposition of intermediate pyridine adduct to oxide is also a single step process in both the complexes. No DTA curve corresponding to this decomposition is obtained due to the limited temperature range available in the instrument employed.

On the basis of above discussion the following general decomposition mechanism can be proposed for pyridinium zirconyl and hafnyl oxalates.

I. $(C_5H_5NH)_2MO(C_2O_4)_2.2H_2O \longrightarrow (C_5H_5NH)_2MO(C_2O_4)_2 + 2H_2O$

II. $(C_5H_5NH)_2MO(C_2O_4)_2 \longrightarrow MO_2.x(C_5H_5N) + H_2O + (2-x)C_5H_5N + 2CO_2 + 2CO$

$2CO + O_2 \longrightarrow 2CO_2$

III. $MO_2 \cdot xC_5H_5N \longrightarrow MO_2 + C +$ decomposition products of pyridine

$C + O_2 \longrightarrow CO_2$

(x = 1.29 when M = Zr, x = 1.24 when M = Hf)

Calculation of the apparent activation energy and order of reaction for the second step decomposition have also been performed using graphical method of Coats and Redfern (3). The plot of $-\log [-\log(1 - \alpha)/T^2]$ versus 1/T, for n = 1 (where n = apparent order of reaction) gives the straight line with the slope E/2.303R.

REFERENCES

1. A.K.Sharma and N.K.Kaushik, Thermochimica Acta (in Press) and references therein.
2. G.M.H.Van de Velde and P.J.D.Oranje, Thermal Analysis, Proc. Fourth ICTA, Budapest, 1 (1974) 851.
3. A.W.Coats and J.P.Redfern, Nature, 68 (1964) 201.

TABLE 1

Thermal stability data of the complexes

Decomposition steps	TG				DTA
	Decomp. temp. (K)	% weight loss obs.	% weight loss calc.	Activation energy	Peak temp. (K)
A. Decomposition of $(C_5H_5NH)_2ZrO(C_2O_4)_2.2H_2O$					
Dehydration	303-453	7.70	7.51		383
Decomposition of oxalate	453-603	45.50	45.49	13.41	543
Decomposition of intermediate	753-933	20.80	21.29		
B. Decomposition of $(C_5H_5NH)_2HfO(C_2O_4)_2.2H_2O$					
Dehydration	323-408	6.50	6.35		363
Decomposition of oxalate	453-613	39.00	39.15	12.45	563
Decomposition of carbonate	903-993	17.50	17.43		

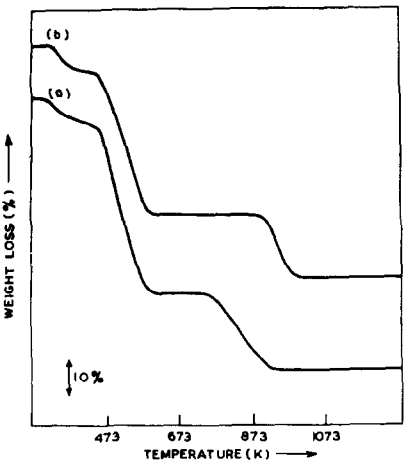

FIG 1 TG CURVES OF (a) $(C_5H_5NH)_2ZrO(C_2O_4)_2\ 2H_2O$ AND (b) $(C_5H_5NH)_2HfO(C_2O_4)_2\ 2H_2O$

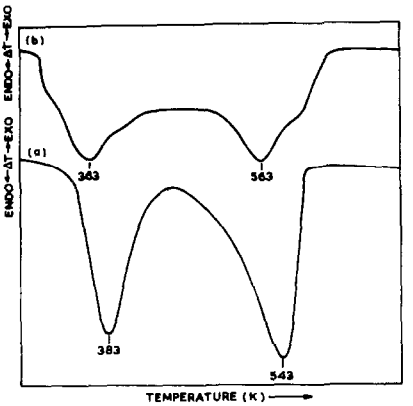

FIG 2 DTA CURVES OF (a) $(C_5H_5NH)_2ZrO(C_2O_4)_2\ 2H_2O$ AND (b) $(C_5H_5NH)_2HfO(C_2O_4)_2\ 2H_2O$

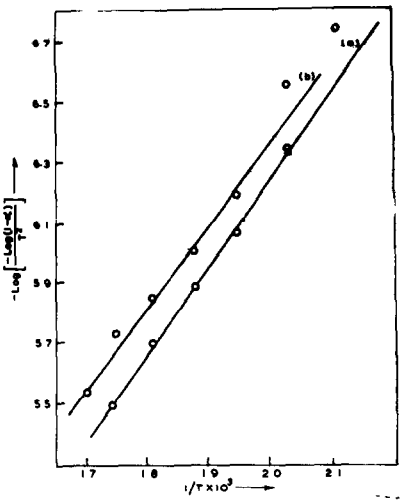

FIG 3 COATS AND REDFERNS LINEARISATION CURVES FOR THE SECOND STEP DECOMPOSITION REACTION OF
(a) $(C_5H_5NH)_2ZrO\ (C_2O_4)_2\ 2H_2O$
(b) $(C_5H_5NH)_2HfO(C_2O_4)_2\ 2H_2O$