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# THERMAL DECOMPOSITION OF HAFNYL OXALATE AND AMMONIUM/MAGNESIUM HAFNYL OXALATE

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## ABSTRACT

Conditions for the preparation of stoichiometric hafnyl oxalate, $HfOC_2O_4 \cdot 3.5H_2O$, ammonium hafnyl oxalate, $(NH_4)_2HfO(C_2O_4)_2 \cdot 3H_2O$ and magnesium hafnyl oxalate, $MgHfO(C_2O_4)_2 \cdot 7H_2O$ have been standardised. The thermal decomposition of these oxalates has been investigated employing thermogravimetric (TG), differential thermal analysis (DTA), infrared spectral and chemical analysis techniques. The decomposition proceeds through three major steps, viz. the dehydration of the hydrated oxalate, the decomposition of the anhydrous oxalate to the carbonate and, finally, the decomposition of the carbonate to the oxide. Pure hafnium oxide, $HfO_2$, is the end product in the thermal decomposition of simple hafnyl oxalate and ammonium hafnyl oxalate, while for magnesium hafnyl oxalate, $MgHfO_3$ is isolated as the final decomposition product.

## INTRODUCTION

Titanyl, zirconyl and hafnyl oxalates are technologically important materials as they can be used as a precursor for the preparation of synthetically pure oxides with desirable electrical properties. Thermal studies on a number of titanyl and zirconyl oxalates have been described and this work has been recently summarised by us in a review [1]. However, only little is known about the corresponding hafnyl derivatives. In order to compare the results of titanyl and zirconyl oxalates with their hafnyl analogues and to arrive at a composition that would give the most desirable product, the present investigation was made into simple and complex hafnyl oxalate.

## EXPERIMENTAL

All the reagents used for the preparation of these compounds were either BDH Analar or Merck Proanalysis grade.

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### *Preparation of hafnyl oxalate, $HfOC_2O_4 \cdot 3.5H_2O$*

Hafnium tetrachloride (5 g) was added slowly with continuous stirring to 50 ml ice-cold distilled water. To this was added, dropwise, a solution of 1.97 g oxalic acid in 50 ml water. It was shaken vigorously for 15 min. The white precipitate obtained was digested on a water bath and then filtered, washed with water, then with acetone and air dried. Chemical analysis of the air-dried product gave the following results: $C_2O_4$, 25.23; Hf, 51.81; $H_2O$, 18.40%; calculated for $HfOC_2O_4 \cdot 3.5H_2O$: $C_2O_4$, 25.17; Hf, 51.66; $H_2O$, 19.03%.

### *Preparation of ammonium hafnyl oxalate, $(NH_4)_2HfO(C_2O_4)_2 \cdot 3H_2O$*

$(NH_4)_2HfO(C_2O_4)_2 \cdot 3H_2O$ was prepared by a similar method as described for its titanium analogue $(NH_4)_2TiO(C_2O_4)_2 \cdot H_2O$ [2]. Crystals of the product were obtained from an aqueous concentrated solution of $HfCl_4$, oxalic acid and ammonia by carefully adding an excess of ethanol. These were filtered, washed with ethanol, then with acetone and air dried. Analysis of the crystalline product gave the following results: N, 6.10; $C_2O_4$, 37.92; Hf, 38.51; $H_2O$, 11.82%; calculated for $(NH_4)_2HfO(C_2O_4)_2 \cdot 3H_2O$: N, 6.05; $C_2O_4$, 38.05; Hf, 38.59; $H_2O$, 12.2%.

### *Preparation of magnesium hafnyl oxalate, $MgHfO(C_2O_4)_2 \cdot 7H_2O$*

Pure hafnium tetrachloride (5 g) was added in small proportions to 20 ml of ice-cold distilled water with vigorous stirring. To this, a solution of oxalic acid (4.3 g in 50 ml distilled water) was added. Magnesium carbonate (1.33 g) was taken in a beaker and the mixture of hafnium tetrachloride and oxalic acid was added to it with continuous stirring, with the temperature of the solution kept below 20°C. An excess of ethanol was added to this solution with stirring which resulted in the formation of a white precipitate. It was then filtered, washed with an acetone and ethanol mixture (1 : 1, v/v) and finally dried in air. Analytical results are: $C_2O_4$, 33.54; Mg, 4.72; Hf, 34.32; $H_2O$, 24.30%. Calculated for $MgHfO(C_2O_4)_2 \cdot 7H_2O$: $C_2O_4$, 33.89; Mg, 4.67; Hf, 34.20; $H_2O$, 24.19%.

### *Analysis*

Oxalate in the complexes and in the residue at different stages of thermal decomposition was determined by permanganate titration. For the estimation of the number of hydrated water molecules, the compound was dried in an oven at 120°C for several hours until it showed the absence of water molecules in its infrared spectra. Hafnium was determined gravimetrically as $HfO_2$ after its precipitation as hydroxide [3].

## PHYSICAL MEASUREMENT

Infrared spectra of these compounds were recorded in KBr pellets in the region 4000–200 $cm^{-1}$ with a Perkin-Elmer 621 spectrophotometer. The TG curves were obtained on a Stanton-Redcroft automatic thermorecording balance (Model TG 770) with a sample size of 18–25 mg and a heating rate of 10 K $min^{-1}$, in a self-produced air atmosphere. A silica crucible was used for these operations and the curve was recorded up to 1273 K. DTA of these compounds were carried out on a Mettler TA 10 DTA unit with a heating rate of 10 K $min^{-1}$, a sample size of 20–25 mg and powdered $\alpha$-alumina as a reference material. The curves were recorded upto 723 K.

## RESULTS AND DISCUSSION

The methods used for the preparation and isolation of these compounds yield materials of high purity as can be judged by the satisfactory elemental analyses, infrared spectra and thermoanalytical data. All the compounds were obtained in crystalline form. They are insoluble in water and common organic solvents.

### *Infrared spectral data*

The infrared spectra of these compounds have been discussed on the basis of the empirical bands assigned for the free oxalate anion [4]. In general, lattice water absorbs at 3550–3200 (antisymmetric and symmetric OH stretching) and 1632–1600 $cm^{-1}$ (HOH bending), although these compounds absorb clearly near 3300 $cm^{-1}$, which can be assigned to OH stretching vibrations. The HOH bending vibration, however, seems to be merged with asymmetric $C=O$ vibrations which appear in the range 1650–1750 $cm^{-1}$. Further, a series of coupled vibrations have been observed in these compounds around 1400, 1350, 910, 800, 525, 500 and 400 $cm^{-1}$ which can be assigned to $\nu(C{-}O)+\nu(C{-}C)$, $\nu(C{-}O)+\delta(O{-}C=O)$, $\nu(C{-}O)+\nu(Hf{-}O)+\delta(O{-}C=O)$, $\delta(O{-}C=O)+\nu(Hf{-}O)$, $\nu(C{-}C)+\nu(Hf{-}O)$, ring deformation $+\delta(O{-}C=O)$ and $\nu(Hf{-}O)+$ ring deformation, respectively, similar to their titanyl and zirconyl analogues [5–9].

## THERMAL STUDIES

Figures 1 and 2 present the TG and DTA curves, respectively, of hafnyl oxalate, ammonium hafnyl oxalate and magnesium hafnyl oxalate in a dynamic air atmosphere.

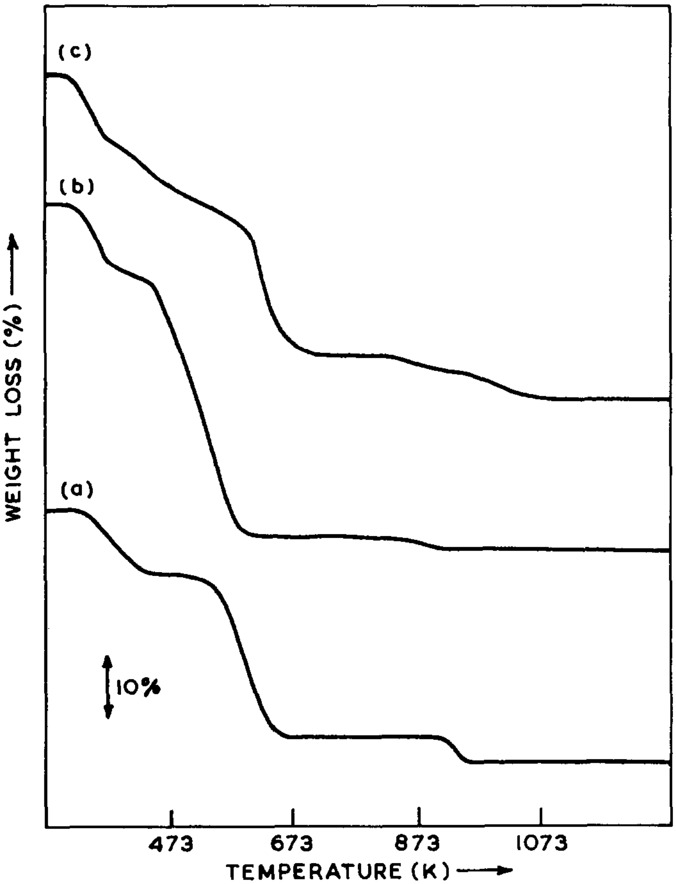

Fig. 1. TG curves of (a) $HfOC_2O_4 \cdot 3.5H_2O$, (b) $(NH_4)_2HfO(C_2O_4)_2 \cdot 3H_2O$, (c) $MgHfO(C_2O_4)_2 \cdot 7H_2O$.

It is evident from the TG and DTA curves that the thermal behaviour of all these compounds consists of three major changes, viz. the dehydration of the hydrated compounds, the decomposition of anhydrous oxalate to the respective carbonate and finally the decomposition of the carbonate to oxide.

## *Dehydration of the hydrated compounds*

All the three hydrated oxalates under investigation are dehydrated in two steps. Dehydration of hafnyl oxalate started at 323 K, and at 573 K a completely anhydrous oxalate was isolated. The two steps of hafnyl oxalate dehydration are separated by 30 K with the loss of 2.0 and 1.5 water molecules, respectively. The dehydration of ammonium hafnyl oxalate oc-

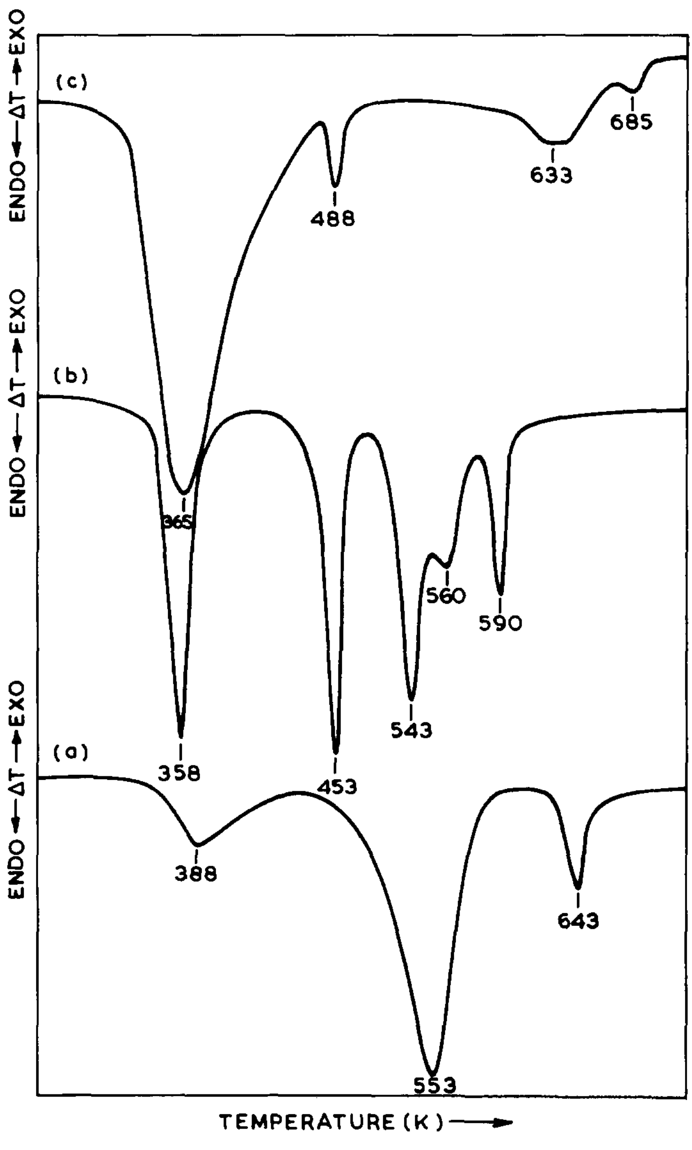

Fig. 2. DTA curves of (a) $HfOC_2O_4 \cdot 3.5H_2O$, (b) $(NH_4)_2HfO(C_2O_4)_2 \cdot 3H_2O$, (c) $MgHfO(C_2O_4)_2 \cdot 7H_2O$.

curs between 308–363 and 363–458 K, corresponding to the loss of 2.0 and 1.0 water molecules, respectively. Dehydration of magnesium hafnyl oxalate takes place between 303–373 and 373–578 K with the loss of 4.0 and 3.0 water molecules in these two steps, respectively. The expected endothermic behaviour for the dehydration processes associated with these compounds has also been observed from DTA curves in almost same temperature ranges.

## *Decomposition of dehydrated oxalate*

The decomposition of dehydrated oxalate to carbonate is the major event in the thermoanalytical studies. This stage of the oxalate decomposition involves simultaneous evolution of CO and $CO_2$ and is a complex set of reactions which includes the decomposition of oxalate, oxidation and/or disproportionation of carbon monoxide and oxidation of the carbon produced during the disproportionation of carbon monoxide. The true decomposition of the oxalate at this stage is an endothermic process. The comparatively low temperature necessary for the side reactions of carbon monoxide and the relatively high vapour pressure during this decomposition are the likely reasons why this reaction is endothermic in air.

The decompositions of the anhydrous hafnyl oxalate and ammonium hafnyl oxalate take place in a single step, resulting in the formation of a carbonate of the composition $HfO_{2-x}(CO_3)_x$ in both cases.

In the case of magnesium hafnyl oxalate the decomposition of anhydrous oxalate to carbonate, $Mg_2Hf_2O_5CO_3$, is observed in two consecutive steps through an intermediate carbonate with entrapped carbon dioxide, $Mg_2Hf_2O_5CO_3(CO_2)$. In addition to carbonate bonds, the IR spectra of this residue also show a strong band at 2350 $cm^{-1}$ which can only be assigned to the asymmetric stretching mode of free carbon dioxide.

## *Decomposition of the carbonate*

Decomposition of carbonate to oxide is a single-step process in all the three complexes under investigation. No DTA curves corresponding to this decomposition step were obtained, due to the limited temperature range available in the instrument employed.

On the basis of the above discussion, schemes I, II and III can be proposed for the thermal decomposition of hafnyl oxalate, ammonium hafnyl oxalate and magnesium hafnyl oxalate, respectively.

*Scheme I*

$$HfOC_2O_4 \cdot 3.5H_2O \xrightarrow{323\text{–}458\ \mathrm{K}} HfOC_2O_4 \cdot 1.5H_2O + 2H_2O$$

$$HfOC_2O_4 \cdot 1.5H_2O \xrightarrow{488\text{–}573\ \mathrm{K}} HfOC_2O_4 + 1.5H_2O$$

$$HfOC_2O_4 \xrightarrow{573\text{–}688\ \mathrm{K}} HfO_{2-x}(CO_3)_x + (2-x)CO$$

$$HfO_{2-x}(CO_3)_x \xrightarrow{923-948\ \mathrm{K}} HfO_2 + xCO_2$$

$(x = 0.25)$

*Scheme II*

$$(NH_4)_2HfO(C_2O_4)_2 \cdot 3H_2O \xrightarrow{308-363\text{ K}} (NH_4)_2HfO(C_2O_4) \cdot H_2O + 2H_2O$$

$$(NH_4)_2HfO(C_2O_4)_2 \cdot H_2O \xrightarrow{366-458\text{ K}} (NH_4)_2HfO(C_2O_4)_2 + H_2O$$

$$(NH_4)_2HfO(C_2O_4)_2 + O_2 \xrightarrow{458-673\text{ K}} HfO_{2-x}(CO_3)_x + 2NH_3 + 2CO + (2-x)CO_2 + H_2O$$

$$HfO_{2-x}(CO_3)_x \xrightarrow{773-933\text{ K}} HfO_2 + xCO_2$$

$(x = 0.25)$

TABLE 1

Thermal stability data of the complexes

| Decomposition steps | TG Temp. range (K) | % weight loss obs. | % weight loss calc. | DTA Peak temp. (K) |
|---|---|---|---|---|
| *Decomposition of $HfOC_2O_43 \cdot 5H_2O$* | | | | |
| Dehydration | 323–458 | 9.98 | 10.42 | 388 |
| | 488–573 | 8.50 | 7.81 | 553 |
| Decomposition of oxalate | 573–688 | 18.27 | 17.52 | 643 |
| Decomposition of carbonate | 923–948 | 3.47 | 3.32 | |
| Total % weight loss | | 40.22 | 39.07 | |
| *Decomposition of $(NH_4)_2HfO(C_2O_4)_2 \cdot 3H_2O$* | | | | |
| Dehydration | 308–363 | 8.00 | 7.78 | 358 |
| | 363–458 | 3.96 | 3.89 | 453 |
| Decomposition of oxalate | 458–673 | 40.04 | 40.44 | 543<br>560<br>590 |
| Decomposition of carbonate | 773–933 | 2.77 | 2.38 | |
| Total % weight loss | | 54.77 | 54.49 | |
| *Decomposition of $MgHfO(C_2O_4)_2 \cdot 7H_2O$* | | | | |
| Dehydration | 303–373 | 13.80 | 13.82 | 365 |
| | 373–578 | 10.20 | 10.37 | 488 |
| Decomposition of oxalate | 578–713 | 19.89 | 19.19 | 633 |
| Evolution of entrapped $CO_2$ | 813–938 | 3.49 | 4.22 | 685 |
| Decomposition of carbonate | 938–1083 | 4.61 | 4.24 | |
| Total % weight loss | | 51.99 | 51.84 | |

*Scheme III*

$$MgHfO(C_2O_4)_2 \cdot 7H_2O \xrightarrow{303-373\ K} MgHfO(C_2O_4)_2 \cdot 4H_2O + 3H_2O$$

$$MgHfO(C_2O_4)_2 \cdot 4H_2O \xrightarrow{373-578\ K} MgHfO(C_2O_4)_2 + 4H_2O$$

$$2MgHfO(C_2O_4)_2 \xrightarrow{578-713\ K} Mg_2Hf_2O_5CO_3(CO)_2 + 2CO_2 + 4CO$$

$$Mg_2Hf_2O_5CO_3(CO_2) \xrightarrow{813-938\ K} Mg_2Hf_2O_5CO_3 + CO_2$$

$$Mg_2Hf_2O_5CO_3 \xrightarrow{938-1083\ K} 2MgHfO_3 + CO_2$$

The thermal stability data and percentage weight loss for various decomposition reactions are presented in Table 1.

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