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THERMAL STUDIES ON BERYLLIUM, MAGNESIUM AND CALCIUM HAFNYL OXALATES

O.P. PANDEY, S.K. SENGUPTA * and S.C. TRIPATHI

Department of Chemistry, University of Gorakhpur, Gorakhpur 273001 (India)

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ABSTRACT

Beryllium hafnyl oxalate tetrahydrate, magnesium hafnyl oxalate tetrahydrate and calcium hafnyl oxalate tetrahydrate abbreviated as BHO, MHO and CHO, respectively, have been prepared in an aqueous medium and characterized by elemental analysis, magnetic susceptibility measurements and infrared spectral data. The thermal behaviour of these compounds in non-isothermal conditions have been investigated by employing TG, DTG and DSC techniques. The intermediates obtained at the end of various thermal decomposition steps were identified on the basis of elemental analysis and infrared spectral studies. The graphical method of Coats and Redfern has been employed to evaluate the kinetic parameters such as apparent activation energy and order of reaction. Heat of reaction for different decomposition steps have been calculated from the DSC curves.

INTRODUCTION

Mixed metal oxides have considerable technological applications in ceramic technology, in production of refractory materials, porcelain and earthenwares, ceramic colours, special electrical engineering and other materials [1]. The technological importance and special properties of ABO_3-type mixed oxides prompted the development of chemical methods for preparing them as high purity materials. Mixed metal oxalates are particularly useful as a synthetic intermediates in the preparation of mixed metal oxides [2–13]. In the present paper, we report the thermal decompositions of beryllium, magnesium and calcium hafnyl oxalate tetrahydrates in nitrogen and oxygen atmospheres which give a pure form of the corresponding hafnates at higher temperature.

All reagents used for the preparation of these compounds were either BDH AnalaR or E. Merck "Proanalysi" grade.

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* Author to whom correspondence should be addressed.

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PREPARATION OF COMPOUNDS

Beryllium, magnesium and calcium hafnyl oxalate tetrahydrates have been prepared by mixing an aqueous solution of hafnium tetrachloride (0.50 mol) and beryllium, magnesium or calcium chloride (0.54 mol) with stirring. This mixture was then added to a hot solution of oxalic acid (1.15 mol) with constant stirring. Excess of acetone was added to this mixture until turbidity appears. The resulting solution was kept for 3–4 days to obtain a crystalline product. The product was filtered, washed with acetone and finally with petroleum ether. It was dried in vacuum over P_2O_5 at room temperature.

Analyses

The carbon and hydrogen contents in the compounds were estimated at the Central Drug Research Institute, Lucknow. To determine beryllium, magnesium, calcium, and hafnium, the compounds were first ignited to give their oxides and the residues so obtained were digested in dilute hydrochloric acid to give a solution of pH ~ 4.0. Excess of EDTA solution was added and from this solution, beryllium, magnesium or calcium were precipitated as their respective oxides and hafnium was determined by its precipitation with cupferron in strongly acidic medium [14].

Physical measurements

Infrared spectra of the compounds were recorded in the 4000–200 cm^{-1} region with a Perkin-Elmer 621 grating spectrophotometer and Acculab-9 spectrophotometer. Magnetic susceptibility measurements were carried out on a Gouy's balance at room temperature using mercury tetrathiocyanatocobaltate(II) ($\chi_g = 16.44 \times 10^{-6}$ e.g.s. unit) as calibrant.

TG and DTG curves were recorded simultaneously on a "SETARAM G-70" thermoanalyser, Lyon, France, with sample size 26–36 mg, heating rate 8 K min^{-1}, and flow rate of gas 10 ml min^{-1}. The DSC curves were recorded on a Perkin-Elmer differential scanning calorimeter model DSC-1 over a temperature range of 273–773 K in nitrogen atmosphere only using about 10 mg sample mass. The intermediate compounds obtained at various steps during the thermal decomposition have been identified with the help of elemental analyses and infrared spectral studies.

RESULTS AND DISCUSSION

The method used for the preparation and isolation of these compounds yields materials of high purity as can be judged by satisfactory elemental analyses (Table 1) and infrared spectral studies. The elemental analyses

TABLE 1

Analytical data of BHO, MHO, CHO and their intermediate products from various thermal decomposition steps

Compound	Found (Calcd.) (%)			
	C	H	Hf	Be/Mg/Ca
$BeHfO(C_2O_4)_2 \cdot 4H_2O$	10.5	1.8	39.4	2.0
	(10.6)	(1.8)	(39.5)	(2.0)
$BeHfO(C_2O_4)_2$	12.5	–	47.0	2.2
	(12.6)		(47.0)	(2.4)
$Be_2Hf_2O_5CO_3$	2.1		69.1	3.5
	(2.3)	–	(69.3)	(3.5)
$BeHfO_3$			75.6	3.6
	–	–	(75.8)	(3.8)
$MgHfO(C_2O_4)_2 \cdot 4H_2O$	10.1	1.6	38.0	5.2
	(10.3)	(1.7)	(38.2)	(5.2)
$MgHfO(C_2O_4)_2$	12.0		45.1	6.0
	(12.2)	–	(45.2)	(6.2)
$Mg_2Hf_2O_5CO_3$	2.0		65.2	8.8
	(2.2)	–	(65.4)	(8.9)
$MgHfO_3$			71.0	9.5
	–	–	(71.2)	(9.7)
$CaHfO(C_2O_4)_2 \cdot 4H_2O$	9.7	1.4	37.0	8.1
	(9.9)	(1.6)	(37.0)	(8.3)
$CaHfO(C_2O_4)_2$	11.4		43.4	9.6
	(11.7)		(43.5)	(9.7)
$Ca_2Hf_2O_5CO_3$	1.8		61.7	13.9
	(2.0)	–	(61.9)	(13.9)
$CaHfO_3$			66.8	14.9
	–	–	(67.0)	(15.0)

correspond to the formula $[MHfO(C_2O_4)_2 \cdot 4H_2O]$ (M = Be, Mg or Ca). These complexes are soluble only in dimethylformamide and dimethylsulfoxide. They are stable in air. Magnetic susceptibility measurements indicate their diamagnetic nature.

Infrared spectral studies

The infrared spectra of these oxalates have been discussed on the basis of empirical band assignments for the free oxalato anion [15,16].

In general lattice water absorbs at 3550–3200 cm^{-1} (antisymmetric and symmetric OH stretching). These compounds absorb clearly near 3300 cm^{-1} which can be assigned to O–H stretching vibrations. However H–O–H bending vibrations seem to be merged with the asymmetric C=O vibrations appearing in the range 1650–1700 cm^{-1}. Further a series of coupled vibrations has been observed in these compounds at ~ 1400 cm^{-1}, ~ 1350 cm^{-1},

~ 900 cm^{-1}, ~ 800 cm^{-1}, ~ 500 cm^{-1} and ~ 400 cm^{-1}, which can be assigned to $\nu(C-O) + \nu(C-C)$, $\nu(C-O) + \nu(M-O) + \delta(O-C=O)$, $\nu(C=O) + \delta(O-C=O)$, $\delta(O-C=O) + \nu(M-O)$ ring deformation + $\delta(O-C=O)$, $\nu(M-O)$ + ring deformation (M = hafnium).

Thermal analysis

The TG and DTG curves for the compounds indicate that the thermal decomposition of BHO, MHO and CHO in inert as well as in oxidising atmospheres involves three major steps i.e. dehydration of the hydrated compounds, decomposition of the dehydrated oxalates to the respective carbonates and finally the conversion of these carbonates to the mixed oxides. There is a qualitative 1 : 1 correspondence between DSC and DTG curves for BHO, MHO and CHO (except the last exothermic peak of BHO) indicating that every thermal effect is accompanied by the appropriate mass loss.

The temperature ranges for the different stages of decomposition of BHO, MHO and CHO are given in Table 2.

Dehydration of the hydrates

From TG curves, it is evident that the dehydration of these compounds occurs in a single step. The weight loss observed after first step decomposition of BHO, MHO and CHO corresponds to the loss of four water molecules of crystallisation. As could be expected the dehydration of these compounds is endothermic and takes place at lower furnace temperatures.

Decomposition of dehydrated oxalates

The decomposition of anhydrous BHO, MHO or CHO is endothermic and completes in one step. This decomposition results in the formation of carbonates having the general formula $M_2Hf_2O_5CO_3$ (M = Be, Mg or Ca). The nature of the carbonate group is ionic as suggested by its infrared spectral bands at ca. 1445–1430 cm^{-1} (νasym.), 1030–1020 cm^{-1} (νsym.), 850–840 cm^{-1} and 690–680 cm^{-1} (deformations) [15]. This is further supported by its subsequent decomposition.

Decomposition of the carbonates

The decomposition of the carbonates to the respective mixed oxides takes place at higher temperatures (Table 2) and is endothermic in nature. In the case of BHO an extra exothermic peak is observed beyond 630 K. This exothermic peak is probably due to the transition of beryllium hafnate, formed after decomposition of the carbonate, from one crystalline state to another.

TABLE 2

Temperature range, weight loss, activation energy and heat of reaction for different decomposition steps of BHO, MHO and CHO

Decomposition	Temperature range (K) in N_2 (in O_2)	% weight loss		Heat of reaction (Kcal mol^{-1})	Activation energy (Kcal mol^{-1})	Order of reaction
		Calc.	Found in N_2 (in O_2)			
Decomposition of $BeHfO(C_2O_4)_2 \cdot 4H_2O$						
1. Dehydration	330–460 (340–455)	15.9	16.2 (15.9)	11.4	–	–
2. Decomposition of oxalate	470–530 (465–540)	32.1	31.8 (32.0)	75.4	30.2	Ist
3. Decomposition of carbonate	530–625 (545–630)	8.5	8.3 (8.2)	50.6	18.5	Ist
4. Transition of oxide	630–670	0	0	45.2	–	–
Decomposition of $MgHfO(C_2O_4)_2 \cdot 4H_2O$						
1. Dehydration	338–473 (348–460)	15.4	15.0 (15.1)	19.2	–	–
2. Decomposition of Oxalate	482–525 (480–530)	30.9	29.5 (30.7)	20.8	18.5	Ist
3. Decomposition of carbonate	540–655 (570–670)	8.0	7.8 (7.9)	58.5	32.2	Ist
Decomposition of $CaHfO(C_2O_4)_2 \cdot 4H_2O$						
1. Dehydration	345–473 (350–465)	14.9	14.1 (14.3)	20.8	–	–
2. Decomposition of Oxalate	490–538 (485–545)	29.7	29.0 (29.3)	48.2	28.5	Ist
3. Decomposition of carbonate	580–675 (590–690)	7.6	7.4	62.5	15.2	Ist

On the basis of this discussion, the following scheme may be proposed for the decomposition of BHO, MHO and CHO.

$MHfO(C_2O_4)_2 \cdot 4H_2O \rightarrow MHfO(C_2O_4)_2 + 4H_2O$

$2MHfO(C_2O_4)_2 \rightarrow M_2Hf_2O_5CO_3 + 4CO + 3CO_2$

$M_2Hf_2O_5CO_3 \rightarrow 2MHfO_3 + CO_2$

(M = Be, Mg or Ca)

The calculation of apparent activation energy and order of reaction has been performed from measurements taken in nitrogen atmosphere employing the graphical method of Coats and Redfern [17]. The plot of $-\log[-\log(1-\alpha)/T^2]$ against $1/T \times 10^3$ for $n = 1$ (where n = apparent order of reaction) results in a straight line with a slope of $-E/2.303R$ for the second and last step decomposition steps.

The calculation of heat of reaction has been performed with the help of DSC curves by using the simple expression $\Delta Hm = KA$. The apparent activation energy, order of reaction and heat of reaction are given in Table 2.

CONCLUSION

These results show that the thermal decomposition of all the compounds i.e. BHO, MHO and CHO proceeds through three major steps. The first step is dehydration, the second step involves the decomposition of the oxalate to give an intermediate carbonate and in the last step the carbonate decomposes to a mixed oxide. However, in case of BHO, the formation of a mixed oxide is again followed by an exothermic peak. This may be due to the transition of beryllium hafnate from one crystalline state to another. The beryllium compound, BHO, is less stable than the magnesium compound, MHO, which in turn is less stable than the calcium compound, CHO.

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