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A THERMOGRAVIMETRIC STUDY OF PRASEODYMIUM(III), NEODYMIUM, SAMARIUM, GADOLINIUM AND HOLMIUM ACETATES, BENZOATES AND ABIETATES

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The thermal decompositions of the acetates of Pr, Nd, Sm, Gd and Ho have been investigated using thermogravimetry and differential thermal analysis, together with infrared spectroscopy and X-ray diffraction. The thermal decompositions of the acetates of the rare earth elements exhibit several stages, depending upon both the number of crystal water molecules in the acetates and the rare earth element behaviour. Experiments with the benzoates and abietates of Pr, Nd, Sm, Gd and Ho indicate some correlations in the thermal decompositions of carboxylates of the rare earth elements.

The preparation of transition metal compounds and mixed oxides by solid-state reactions requires prior information on the compositions and the thermal dissociation behaviours of the individual reactants and precursors. The thermal decompositions of a number of oxysalts of the rare earth elements, *viz.* carbonates [1—3], formates [4, 5], oxalates [6—8], malonates [9], succinates [9], citrates [10], butyrates [11], terephthalates [12], benzoates [13], ortho-methoxybenzoates [14], diethylmalonates [15], adipates and sebacates [16], have been studied, but no such study appears to have been performed on the acetates of the rare earth elements. Witt and Onstott [17] studied some properties of the hydrated acetates of Pr, Nd and Sm, but they did not investigate the thermal decompositions of the compounds.

The present article reports a study of the thermal decompositions of the acetates $M(CH_3COO)_3 \cdot H_2O$ (M = Pr, Nd, Sm) and $M(CH_3COO)_3 \cdot 3\,H_2O$ (M = Gd, Ho), benzoates $M(C_6H_5COO)_3 \cdot 4\,H_2O$ (M = Pr, Nd, Sm, Gd, Ho) and abietates $M(C_{19}H_{29}COO)_3$ (M = Pr, Nd, Sm, Gd, Ho) in static air using thermogravimetry (TG), differential thermal analysis (DTA), IR spectroscopy and X-ray powder diffraction.

Experimental

The samples of rare earth element acetates used were $Pr(CH_3COO)_3 \cdot H_2O$, $Nd(CH_3COO)_3 \cdot H_2O$, $Sm(CH_3COO)_3 \cdot H_2O$, $Gd(CH_3COO)_3 \cdot 3\,H_2O$ and $Ho(CH_3COO)_3 \cdot 3\,H_2O$ of pure chemical grade (Rare Metal Plant, Novosibirsk). Rare earth benzoates were prepared by mixing aqueous solutions of lanthanide nitrates and ammonium benzoate. The precipitated lanthanide benzoates were filtered, washed with distilled water, recrystallized from hot distilled water and dried at room temperature. The compounds were white crystals with general formula $M(C_6H_5COO)_3 \cdot 4\ H_2O$. Lanthanide abietates were prepared from lanthanide nitrates and abietic acid in $CHCl_3 + Et_2O$ (1 : 1) mixtures. The compounds were voluminous amorphous precipitates with general formula $M(C_{19}H_{29}COO)_3$.

The TG and DTA analyses were performed with a MOM derivatograph, Model OD-102, and a platinum crucible (7 mm dia), with calcined alumina as the reference material in static air. In each case 30, 100 and 200 mg powdered samples with a particle size less than 35 microns were taken; the heating rates were 3, 7 and 10 deg/min for these quantities, respectively.

Infrared spectra were obtained using a UR-20 spectrophotometer (Karl Zeiss) in the region 4000 – 400 cm^{-1} (in KBr discs) and a Model 345 Hitachi in the region 800 – 200 cm^{-1} in CsI pellets. X-ray diffraction data were obtained with a Dron-I diffractometer with Fe-unfiltered radiation. The surfaces and the average sizes of the product particles were examined with a Jem-5Y (Jeol electron microscope).

Results and discussion

TG and DTA investigations on the lanthanide acetate hydrates indicate clearly that the thermal decompositions of the acetates, just as those of many other lanthanide carboxylates, involve a number of stages with separation of lanthanide oxycarbonates as intermediates. The total number of stages depends on the quantity of crystal water and the properties of the rare earth element; the heating rate is sometimes also a factor which may influence the number of decomposition stages, because some of the stages cannot be separated in the TG curves.

Praseodymium acetate, $Pr(CH_3COO)_3 \cdot H_2O$

Table 1

Thermogravimetric data and temperature intervals in the thermal decomposition of praseodymium acetate, $Pr(CH_3COO)_3 \cdot H_2O$

Decomp. stage	Temperature interval, °C	Mass loss, %	
		Theoretical	Observed
I	130–180	4.9	4.8
II	195–215	5.4	5.4
III	280–310	15.2	15.0
IV	320–370	33.0	33.2
V	380–445	43.8	44.2
VI	540–600	49.4	49.6
VII	940–960	50.9	51.0

The decomposition of praseodymium acetate may be represented as follows

$$Pr(CH_3COO)_3 \cdot H_2O \overset{\text{I}}{\text{——}} Pr(CH_3COO)_3 \cdot 0.1\ H_2O \overset{\text{II}}{\text{——}} Pr(CH_3COO)_3 \overset{\text{III}}{\text{——}}$$

$$Pr_2(CH_3COO)_4(CO_3) \overset{\text{IV}}{\text{——}} Pr_2O_2(CO_3) \overset{\text{V}}{\text{——}} Pr_2O_3 2\ C \overset{\text{VI}}{\text{——}} Pr_6O_{11} \overset{\text{VII}}{\text{——}} Pr_2O_3$$

The thermogravimetric data and temperature intervals are listed in Table 1. derivatogram of $Pr(CH_3COO)_3 \cdot H_2O$ is given in Fig. 1.

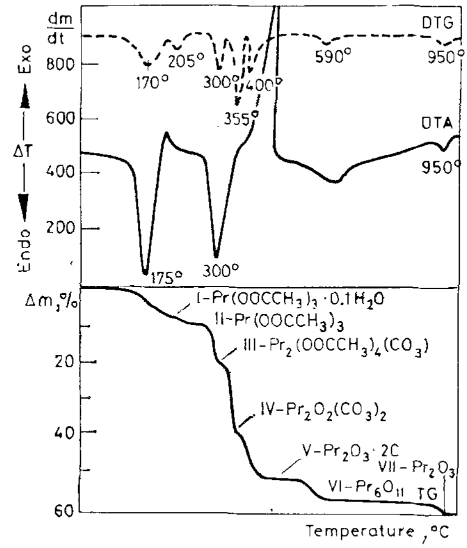

Fig. 1 Thermal curves of $Pr(CH_3COO)_3 \cdot H_2O$ (mass 100 mg, heating rate 7°/min)

We should like to emphasize that the thermal decomposition process involves an intermediate hydrate $Pr(CH_3COO)_3 \cdot 0.1\ H_2O$. The intermediate is always clearly revealed in the TG and DTG curves and infrared spectra of the product quenched from 150, 160 and 170° show a diffuse intense absorption band in the region 3500–3550 cm^{-1} ($\nu O-H$). It may be assumed that a small praseodymium(IV) content in the starting material is the reason for the intermediate hydrate formation.

Neodymium and samarium acetates, $Nd(CH_3COO)_3 \cdot H_2O$ and $Sm(CH_3COO)_3 \cdot H_2O$

The thermal decomposition behaviours of $Nd(CH_3COO)_3 \cdot H_2O$ and $Sm(CH_3COO)_3 \cdot H_2O$ are illustrated in Table 2 and Figs 2 and 3. The thermogravimetric analysis curves of the acetates show that they undergo decomposition in four stages. The molecule of crystal water is lost in one stage; all intermediates have analogous compositions in the two cases.

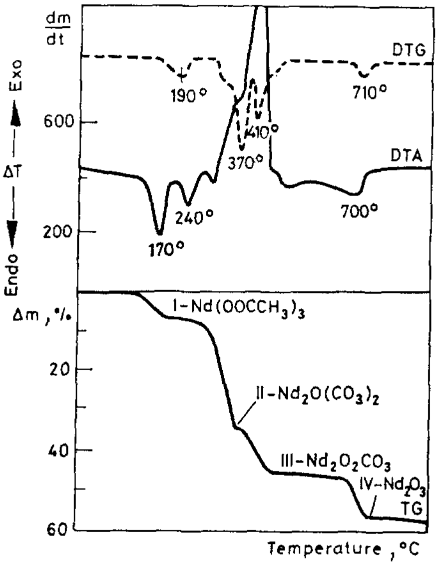

Fig. 2. Thermal curves of $Nd(CH_3COO)_3 \cdot H_2O$ (mass 30 mg, heating rate 3°/min)

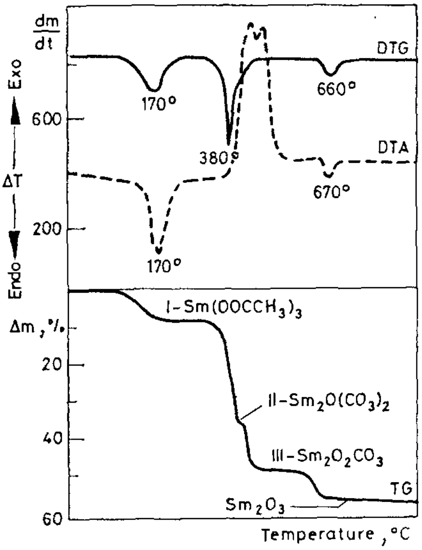

Fig. 3. Thermal curves of $Sm(CH_3COO)_3 \cdot H_2O$ (mass 30 mg, heating rate 3°/min)

Table 2

Temperatures of intermediate formation and mass losses for the termal decompositions of $Nd/CH_3COO)_3 \cdot H_2O$ and $Ho(CH_3COO)_3 \cdot H_2O$

Intermediate	M	Temperature of formation, °C	Mass loss, %	
			Theoretical	Observed
$M(CH_3COO)_3$	Nd	120–190	5.4	5.4
	Sm	100–170	5.2	5.1
$M_2O(CO_3)_2$	Nd	275–360	37.5	37.3
	Sm	305–380	35.8	36.3
$M_2O_2(CO_3)$	Nd	385–445	44.0	43.6
	Sm	400–455	42.1	42.0
M_2O_3	Nd	650–720	53.4	53.7
	Sm	620–680	50.8	50.5

Gadolinium acetate, $Gd(CH_3COO)_3 \cdot 3\,H_2O$

The thermal decomposition of $Gd(CH_3COO)_3 \cdot 3\,H_2O$ involves six steps and the following decomposition path is proposed:

$$Gd(CH_3COO)_3 \cdot 3\,H_2O \xrightarrow{\text{I}} Gd(CH_3COO)_3 \cdot H_2O \xrightarrow{\text{II}}$$

$$Gd(CH_3COO)_3 \cdot 0.5\,H_2O \xrightarrow{\text{III}} Gd(CH_3COO)_3 \xrightarrow{\text{IV}} Gd_2O(CO_3)_2 \xrightarrow{\text{V}}$$

$$Gd_2O_2(CO_3) \xrightarrow{\text{VI}} Gd_2O_3$$

The data on the thermal decomposition are given in Table 3 and Fig. 4.

Table 3

Data on the thermal decomposition of $Gd(CH_3COO)_3 \cdot 3\,H_2O$

Decomp. stage	Temperature interval, °C	Mass loss, %	
		Theoretical	Observed
I	50–100	9.3	9.3
II	105–130	11.6	11.8
III	150–170	13.9	14.0
IV	290–350	42.0	41.3
V	365–400	47.7	48.4
VI	560–600	53.3	53.5

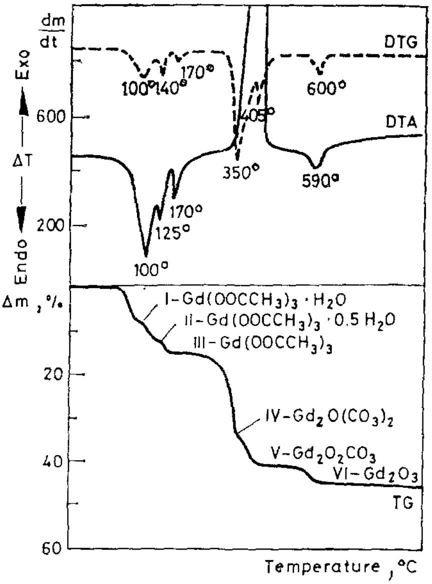

Fig. 4. Thermal curves of $Gd(CH_3COO)_3 \cdot 3\ H_2O$ (mass 100 mg, heating rate 7°/min)

Holmium acetate, $Ho(CH_3COO)_3 \cdot 3\ H_2O$

The thermal decomposition of holmium acetate trihydrate is a four-stage process, distinguished from the decomposition of gadolinium acetate trihydrate by the absence of an intermediate monooxycarbonate of formula $Ho_2O(CO_3)_2$. The thermogravimetric analysis data are given in Table 4 and the thermal curves of $Ho(CH_3COO)_3 \cdot 3\ H_2O$ in Fig. 5.

Table 4

Thermogravimetric data on the thermal decomposition of $Ho(CH_3COO)_3 \cdot 3\ H_2O$

Intermediate	Temperature interval of formation, °C	Mass loss, %	
		Theoretical	Observed
$Ho(CH_3COO)_3 \cdot 0.5\ H_2O$	56–120	11.4	11.0
$Ho(CH_3COO)_3$	130–160	13.7	13.9
$Ho_2O_2(CO)_3$	410–540	46.7	47.2
Ho_2O_3	650–740	52.3	52.0

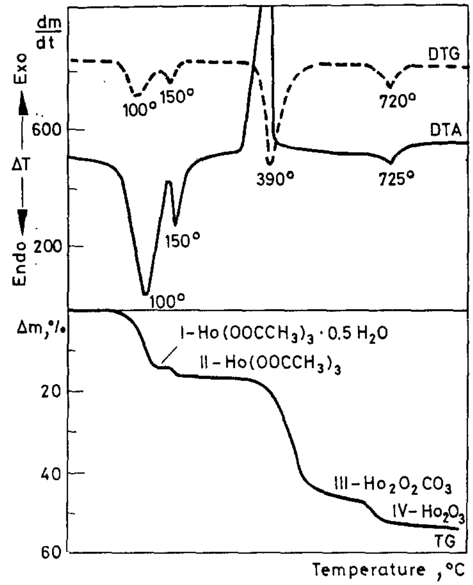

Fig. 5. Thermal curves of $Ho(CH_3COO)_3 \cdot 3\ H_2O$ (mass 100 mg, heating rate 7°/min)

The rare earth element benzoates and abietates

The results of the thermogravimetric investigations on praseodymium, neodymium, samarium, gadolinium and holmium benzoate tetrahydrates and the anhydrous abietates indicate that as the number of carbon atoms in the organic anion increases the thermal decomposition of the lanthanide carboxylates becomes simpler and the total number of decomposition stages decreases. In the thermal decompositions of the lanthanide benzoates, intermediate oxy-carbonates are not formed and the benzoates decompose into Nd, Sm, Gd, Ho sesquioxides (or into Pr_6O_{11} for the praseodymium compound); this is in accordance with the data in [13].

The thermogravimetric analysis curves of the lanthaide abietates, $M(C_{19}H_{29}COO)_3$, indicate the existence of intermediates of non-constant composition, with general formula $M_2O_2(CO_3)_x \cdot C$, where $0 < x \leq 1$, $1 < y < 3$. With elongation of the carbon chain *R* in the acid RCOOH, the temperature of formation of the lanthanide oxide decreases.

On the basis of the thermogravimetric analysis data on the benzoates and abietates, the following decomposition paths are proposed:

$M(C_6H_5COO)_3 \cdot 4\ H_2O \rightarrow M(C_6H_5COO)_3$ (in the interval 90–140°) – M_2O_3 (or Pr_6O_{11}) at 480–630°.

$M(C_{19}H_{29}COO)_3 \rightarrow M_2O_2(CO_3)_x \cdot yC$ (for $0 < x \leq 1$, $1 < y < 3$ in the temperature interval 160–500°) $\rightarrow M_2O_3$ (or Pr_6O_{11}) at 520–610°.

It should be noted that the DTA curves of the benzoates show an irreversible sharp endothermic peak (without mass loss in the TG curve) in the temperature region 245 – 270°, which must be associated with a phase transition of the benzoates, as found earlier [13].

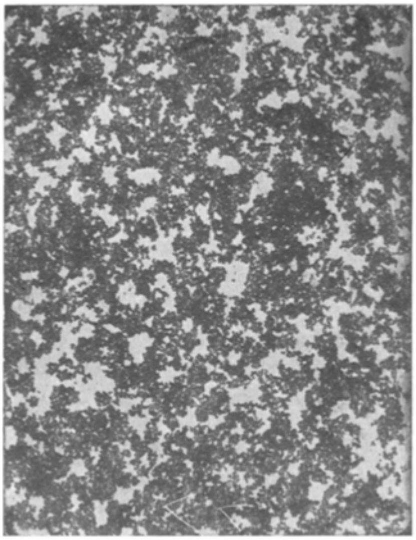

Fig. 6. Electron micrograph of Sm_2O_3 prepared by the thermal decomposition of $Sm(C_{19}H_{29}COO)_3$ at 650° (×24 000)

There is an important correlation between the particle size of the separating lanthanide sesquioxide and the number of carbon atoms in the carboxylate ion: the average particle size of the sesquioxide decreases as the number of carbon atoms in the carboxylate residue increases. For example, the average particle size of Sm_2O_3 as decomposition product in the thermal decompositions of samarium acetate, *n*-butyrate, benzoate and abietate was 6.0 ± 2.2; 4.8 ± 1.4; 2.1 ± 0.8 and 0.18 ± 0.06 microns, respectively (on the basis of electron micrographs). Samarium sesquioxide as the thermal decomposition product of samarium abietate $Sm(C_{19}H_{29}COO)_3$ is shown in Fig. 6.

From the data it may be concluded that the study of the thermal decompositions of Pr, Nd, Sm, Gd and Ho acetates, benzoates and abietates gives definite information about the compositions of the intermediates, the temperatures of stability of the compounds, and the formation conditions and particle sizes of the final products, used to prepare other rare earth compounds by solid-state reactions.

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Résumé — La décomposition thermique des acétates de Pr, Nd, Sm, Gd et Ho a été étudiée par thermogravimétrie et analyse thermique différentielle ainsi que par spectroscopie infrarouge et diffraction des rayons X. La décomposition thermique des acétates de terres rares se produit en plusieurs étapes qui dépendent à la fois du nombre de molécules d'eau de cristallisation de l'acétate et du comportement de l'élément des terres rares considéré. Des expériences effectuées avec les benzoates et abiétates de Pr, Nd, Sm, Gd et Ho montrent que la décomposition thermique des carboxylates dépend des éléments de terres rares considérés.

Zusammenfassung — Die thermische Zersetzung der Acetate von Pr, Nd, Sm, Gd und Ho wurde durch Thermogravimetrie und Differentialthermoanalyse in Verbindung mit der Infrarotspektroskopie und Röntgendiffraktionsmethode untersucht. Die thermische Zersetzung der Acetate der seltenen Erden verläuft in mehreren Stufen, welche sowohl von der Zahl der Kristallwassermoleküle in den Acetaten als auch von dem Verhalten der seltenen Erden abhängen. Experimente mit den Benzoaten und Abietaten von Pr, Nd, Sm, Gd und Ho zeigen gewisse Abhängigkeiten von der thermischen Zersetzung der Carboxylate der seltenen Erden.

Резюме — Исследовано термическое разложение ацетатов Pr, Nd, Sm, Gd и Ho, используя термогравиметрию и дифференциальный термический анализ, совместно с ИК-спектроскопией и рентгено-диффракционным методом. Термическое разложение ацетатов редкоземельных элементов имеет несколько стадий, зависящих как от числа кристаллизационной воды в ацетатах, так и от поведения редкоземельного элемента. Эксперименты с бензоатами и резинатами Pr, Nd, Sm, Gd и Ho указывают на некоторые зависимости термического разложения карбоксилатов редкоземельных элементов.