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The thermal decomposition of solid state complexes of some rare earths (lanthanons) with bis-(2-ethylhexyl) phosphoric acid

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Abstract

The thermal decomposition of LnA_3 (Ln is Ce, Pr, Nd, Er; A is $[CH_3CH(CH_2CH_3)$-$(CH_2)_4O]_2PO_2^-)_2$ has been studied. It is established that heating to 443–453 K leads to recrystallization of the LnA_3 complexes accompanied by a partial annealing of the crystal defects. Their decompositions start above these temperatures and are complete at 583–608 K, producing $Ln(PO_3)_3$. The decomposition process proceeds in a number of stages, namely the step-wise release of 6 mol of CH_3, 6 mol of C_3H_6 and 3 mol of $C_8H_{16}O$, followed by a crystallization of the metaphosphates formed. Their activation energy depends on the nature of the lanthanon and (mainly for the first decomposition stages) on the heating atmosphere. Although a strong dependence is not apparent, it is clear that these factors are of prime importance for the determination of the rate-controlling processes.

Keywords: Activation energy; Atmosphere; Boundary; Crystallization; Decomposition; DTA; DTG; Interface; Lanthanon compound; TG; XRD

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1. Introduction

Solid state complexes of lanthanons (rare earth, RE) with bis-(2-ethylhexyl) phosphoric acid (HA) were obtained a long time ago in the course of the liquid–liquid extraction of RE [1]. Meanwhile, complexes with a composition LnA_3

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(Ln is RE, A is $[CH_3CH(CH_2CH_3)(CH_2)_4O]_2PO_2^-$) have been prepared for all the rare earths, excluding Pm [2–7]. Some of them have been used as catalysts in the production of *cis*-1,4-polyisoprene and *cis*-1,4-polyisobutadiene. Some data on their IR spectra [2,6], X-ray powder diffractograms [8], and solubility in specific solvents [7,9] have been published. Investigations of their crystal structure are still in progress. A model of the structure of NdA_3 and EuA_3 has been proposed [10,11] suggesting that they are anhydrous coordinative polymers in which the Ln^{3+} ions are bonded through acylphosphate bridges. According to ref. 10, the large acyl radicals inhibit the formation of a three-dimensional set. Instead, a layer structure is formed. The layers (consisting of NdO_6 octahedra) are bonded by Van der Waals interactions between hydrocarbon fragments. However, a more recent investigation [11] has demonstrated the formation of axial structures and polymeric chains parallel to the *c*-axis of the hexagonal crystal cell.

The thermochemical properties of the LnA_3 complexes are described in ref. 5. It is established that they decompose without melting at about 573 K with $\Delta H = 250$–$318\ \mathrm{kJ\ mol^{-1}}$. Complexes of Ce were not studied in ref. 5.

The aim of the present work is to investigate the processes taking place during the heating of the Ce, Pr, Nd and Er complexes with bis-(2-ethylhexyl) phosphoric acid. The results could provide a better understanding of the nature of the complexes and of the role of Ln in their action as specific catalysts in processes involving hydrocarbon compounds.

2. Experimental

The studied complexes were prepared by interaction of $Ln(NO_3)_3$ in acetone solution with HA sodium salt (NaA). Commercially available bis-(2-ethylhexyl) phosphoric acid (Fluka) was purified from mono-(2-ethylhexyl) phosphoric acid by the method proposed in ref. 12. For the preparation of the complexes, sufficient 0.5 M NaOH was added to a weighed amount of pure diester for complete neutralization. After prolonged agitation of NaA thus prepared, $Ln(NO_3)_3$ acetone solution ($100\ \mathrm{g\ cm^{-3}}$) was added in the mol ratio $NaA:Ln^{3+} = 3:1$, and stirred for 1 h. Addition of a volume of water equal to that of acetone present, produced a solid phase. This was filtered after 24 h, washed with water and acetone, and dried in a desiccator above conc. H_2SO_4 for not less than 48 h. The elemental analysis and IR spectra confirm the complex composition, i.e. LnA_3 (Table 1).

The thermal decomposition was studied using a MOM derivatograph (Paulik–Paulik–Erdey), by heating approx. 0.25 g samples in synthetic corundum crucibles in air or N_2 atmosphere ($5\ \mathrm{K\ min^{-1}}$) up to 723 K. Samples of NdA_3 were also heated to 1173 K ($10\ \mathrm{K\ min^{-1}}$). Al_2O_3 was used as a standard. The calibration for TG and DTA was made with $CaC_2O_4 \cdot 2H_2O$. The investigation of the thermal behaviour of the complexes in air was performed mainly with respect to their eventual catalytic application. The final product and some of the intermediate ones were characterized by IR spectroscopy (FT spectrometer, Bomem, Michelson 100) and X-ray powder diffraction (Siemens URD-6 diffractometer). The activation energies of the stages of the processes were calculated by the method proposed in ref. 13.

Table 1
Elemental composition of the LnA_3 complexes investigated

Complex	H/%		C/%		P/%		Ln/%	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
CeA_3	9.07	9.31	52.41	52.20	8.29	8.42	12.43	12.70
PrA_3	9.40	9.30	51.44	52.17	8.12	8.41	13.20	12.75
NdA_3	9.17	9.28	51.52	51.96	8.20	8.39	13.40	13.07
ErA_3	9.09	9.28	51.09	50.95	7.96	8.22	14.19	14.78

3. Results and discussion

DTA, DTG and TG curves of the studied samples are shown in Figs. 1–3.

The thermal decomposition of the Pr, Nd and Er complexes starts at approx. 458 K but the stability of CeA_3 is rather lower, with its decomposition starting at 413 K. The decomposition takes place without melting. This fact can be explained with reference to the strong bonding of the alcylphosphate bridges [11].

The elemental analysis, X-ray diffractometry and the weight lost after heating to 773 K (Table 2) confirm that the final products of the decomposition are $Ln(PO_3)_3$, as established in ref. 5. The X-ray diffractometry of $Nd(PO_3)_3$ shows that up to 673 K, the product is amorphous. After heating to 1173 K, the crystal structure is clear (Fig. 4). The elemental analysis and IR spectroscopy confirm that the heating atmosphere (air or N_2) does not influence the chemical nature of the final product (Table 2).

As can be seen in Figs. 1–3, the thermal decomposition of the complexes proceeds in a step-wise manner but with significant overlapping of the stages. This is most apparent in the 483–593 K interval in the absence of O_2 (Fig. 1). It is accompanied by similar activation energies (Table 2). An attempt was made to describe the observed decrease in mass with some of the known kinetic equations of the process $A(s) \rightarrow B(s) + C(g)$. The close values of the determined and calculated activation energies, as well as the correlation coefficients, were taken as criteria for the adequacy of the model. The results obtained for PrA_3 are shown in Table 3. A fully satisfactory description of the process was not achieved for the other complexes. The overlapping stages make it difficult to identify the nature of the thermal processes. Nevertheless, a hypothesis can be suggested that is in corroboration with the structural model proposed in ref. 11. (In the text below the temperature intervals for PrA_3 heated in air are shown.)

It seems most probable that a recrystallization takes place up to 453 K, and that the organic fragments are already arranged adjacent to each other, such that the attraction between them increases. A weak exo effect accompanies this process in some cases. The partial annealing of the crystal defects and the increased regularity of the crystal lattice is confirmed by the decreasing peak widths of the X-ray diffractogram. The interlayer distances are slightly (2%) shifted to lower values, demonstrating some decrease in the unit cell volume.

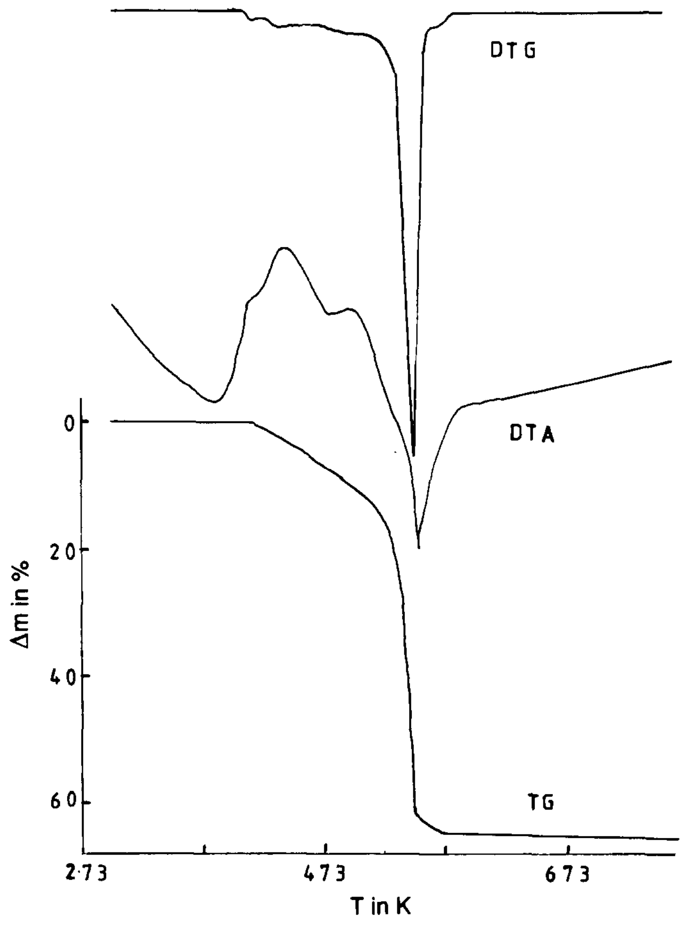

Fig. 1. TG, DTG and DTA curves of CeA_3 heated in air. Sensitivity: TG, 200 mg; DTA, 1/5.

The decrease in mass between 453 and 508 K strongly suggests a release of 2 mol of CH_3 (most probably connected with a tertiary C atom) from each ligand. The significant difference between the activation energies on heating in air and in N_2 confirms that the oxidation of the released product contributes to the effects observed. The kinetic analysis of the results for air-heated PrA_3 shows that the rate-controlling stage is one-dimensional diffusion. This could be taken as confirmation of the proposed [11] axial crystal structure. The limited number of investigated rare-earth complexes makes it difficult to make any final conclusions on the role of the nature of the lanthanon. Nevertheless, a trend of decreasing activation energy with increasing atomic number of the lanthanon and a respective decreasing of its ionic radius can be observed.

In the subsequent temperature interval (508–543 K), 2 mol of C_3H_6 are released from each ligand. In the case of PrA_3 heated in air, the interface boundary motion is the rate-controlling stage. The behaviour of CeA_3 is, however, quite different. The

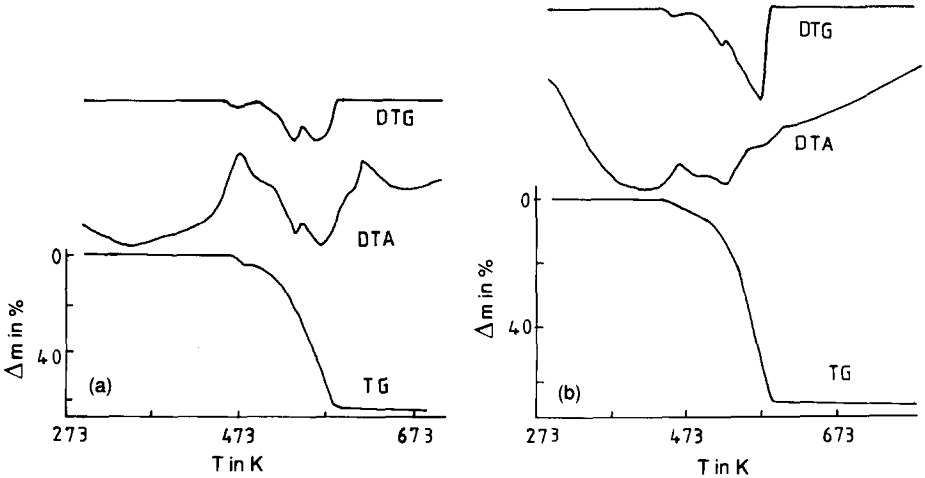

Fig. 2. TG, DTG and DTA curves of PrA_3 heated (a) in air and (b) in N_2. Sensitivity: TG, 500 mg (a), 200 mg (b); DTA, 1/5 (a), 1/10 (b).

release of CH_3 and C_3H_6 from NdA_3 proceeds practically simultaneously and the kinetic analysis of the results indicates the role of both one-dimensional diffusion and interface boundary motion.

According to the activation energy values, the changes between 543 and 563 K are less sensitive to the nature of the lanthanon and the heating atmosphere. The kinetic equations for PrA_3 heated in N_2 and for air-heated NdA_3 for this stage, are different from those in Table 3, but lead to the same mechanism for the

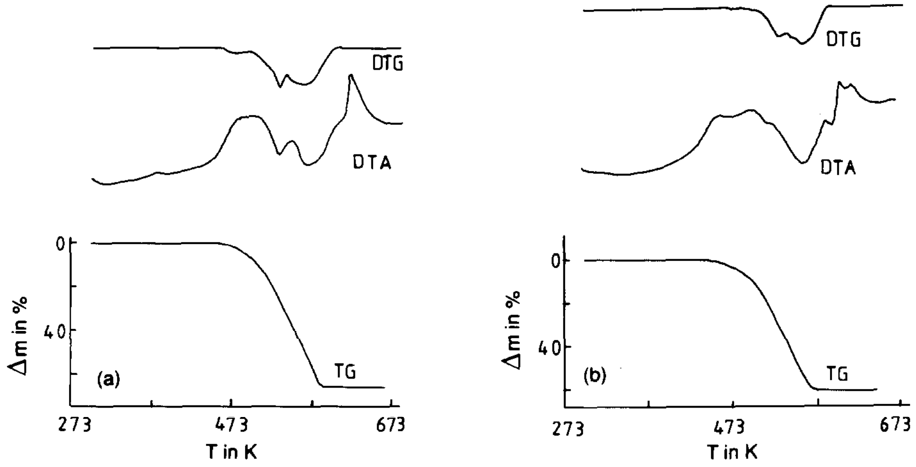

Fig. 3. TG, DTG and DTA curves of (a) NdA_3 and (b) ErA_3. Sensitivity: TG, 500 mg; DTA, 1/5.

Table 2

Thermochemical changes of the complexes of Ce, Pr, Nd, Er with bis-(2-ethylhexyl) phosphoric acid

Ln	Temperature interval according to DTA curve in K	Probable process	Mass loss in % relative to initial mass		Temp. of DTG peaks in K	Activation energy in kJ mol^{-1}
			Found	Calc.		
Ce	<468	Release of 6 mol CH_3	6.6	8.2	423	169
	468–528	Release of 6 mol C_3H_6	23.5	22.9	525	38
	528–583	Release of 3 mol $C_8H_{16}O$	32.9	31.9	549	312
	583–723	Crystallization starts				
		Total [a]	63.0	63.0		
Pr	<508	Release of 6 mol CH_3	8.1	8.2	473	148
	508–543	Release of 6 mol C_3H_6	22.3	22.8	541	163
	543–563	Release of	11.8	34.8	573	271
	563–603	3 mol $C_8H_{16}O$	22.8			
	603–693	Crystallization starts	1.1	0		
		Total [a]	66.1	65.8		
Pr [b]	<508	Release of 6 mol CH_3	7.5	8.2	461	70
	508–553	Release of 6 mol C_3H_6	23.7	22.8	526	220
	553–603	Release of 3 mol $C_8H_{16}O$	32.5	34.8	573	225
	603–753	Crystallization starts	1.9	0		
		Total [a]	65.9	65.8		
Nd	298–538		26.5		538	152
	538–568		16.1		568	169
	568–613		21.0			
	613–833		0.4			
		Total [a]	64.0	65.5		
Er	298–493		5.0		468	74
	493–543		28.2		528	167
	543–618		31.1		558	257
	618–633					
	633–773		1.5			
		Total [a]	65.8	64.2		

[a] $LnA_3 \rightarrow Ln(PO_3)_3$. [b] Heated in N_2 atmosphere.

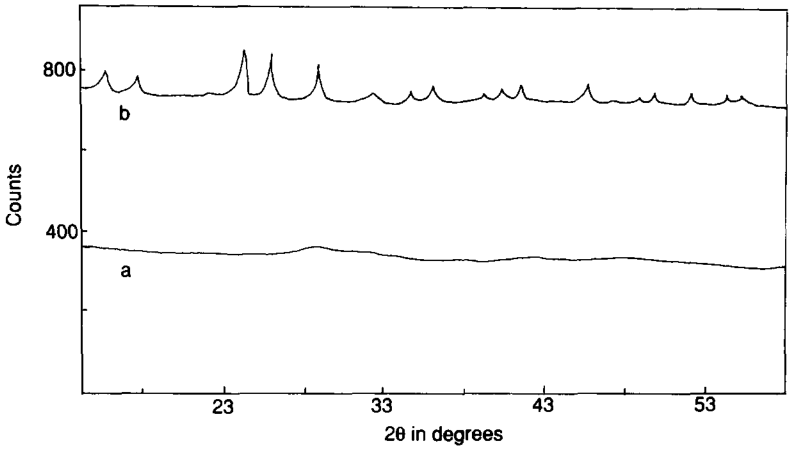

Fig. 4. X-ray diffractogram of $Nd(PO_3)_3$ obtained after heating up to 673 K (a) and 1173 K (b).

Table 3
Kinetic model of the PrA_3 decomposition (heated in air)

Temperature interval in K	Kinetic equation proposed[a] $d\alpha/dt$ =	Activation energy in kJ mol^{-1}		Process mechanism
		Found	Calc.	
453–508	$k\alpha^{-1}$	148	146	One-dimensional diffusion with constant diffusion coefficient
	$k[-\ln(1-\alpha)]^{-1}$		186	Three-dimensional diffusion with spherical symmetry
508–543	$k(1-\alpha)^{2/3}$	163	155	Interface boundary motion with spherical symmetry
543–563	$k(1-\alpha)^{2/3}\{1-(1-\alpha)^{1/3}\}^{-1}$		142	Three-dimensional diffusion
563–603	$k[-\ln(1-\alpha)]^{-1}$	271	246	Three-dimensional diffusion with spherical symmetry
	$k[(1-\alpha)^{-1/3}-1]^{-1}$		282	

[a] According to ref. 14; α = mole fraction or amount of reactant.

rate-controlling processes, i.e. a spherically symmetric diffusion. At this stage, the axial structure is probably already sufficiently disturbed. As can be seen from the DTA curve in Fig. 2a this stage itself is complex. This is to be expected if it is borne in mind that two types of bonds (C–O and P–O) are disrupted in this interval.

4. Conclusions

The reported study reveals a number of significant features of some RE complexes with bis-(2-ethylhexyl) phosphoric acid. Heating LnA_3 (Ln is Pr, Nd, Er) up to 433 K leads to their recrystallization, accompanied by a partial annealing of the crystal defects. The thermal decomposition of the complexes proceeds through a number of stages, the characteristics of which (temperature interval and activation energy) depend on the nature of lanthanons, and, to some extent, on the heating atmosphere. The final products obtained at 573 K from all the studied complexes are linear metaphosphates.

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