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THERMOCHEMICAL BEHAVIOUR OF LANTHANUM COMPLEXES OF 2-ETHYLHEXYL PHOSPHORIC ACID

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Abstract

The thermochemical behaviour of solid-state complexes of lanthanum with mono-(2-ethylhexyl) phosphoric acid (H_2B) ($La(HB)_3 \cdot 1.5H_2O$ and $La_2B_3 \cdot 3H_2O$) was studied. The thermal decomposition of these complexes proceeds without melting to yield $La(PO_3)_3$ and a mixture of $La(PO_3)_3$ and $LaPO_4$, respectively. $La(HB)_3 \cdot 1.5H_2O$ decomposes via dehydration (323–383 K), condensation of the OH-groups with formation of a diphosphate structure (383–458 K) and a stepwise degradation of the hydrocarbon chains (443–565 K). The dehydration of $La_2B_3 \cdot 3H_2O$ (333–433 K) is followed by decomposition of the hydrocarbon group. From a combination of the present results with previous data [1], it was concluded that the temperatures and mechanisms of the decomposition of the hydrocarbon part of the lanthanide complexes of (2-ethylhexyl) phosphoric acids depend on the nature of the lanthanide, the atmosphere, and the structure of the complexes.

Keywords: activation energy, complexes, IR, lanthanides, TG-DTG-DTA

Introduction

Solid-state complexes of the rare earth metals (*Ln*) with bis-(2-ethylhexyl) phosphoric acid ($HA, A = /CH_3(CH_2)_3CH(CH_2CH_3)CH_2O/_2PO_2^-$) of the type LnA_3 have been prepared for all of the rare earths, except Pm [1]. The corresponding IR spectra [2, 3] and X-ray powder diffractograms [4] have been published. Investigation of the relevant crystal structures is still in progress [5, 6]. The thermochemical properties of these complexes have also been reported [1, 7]. It was established [7] that they decompose without melting to metaphosphates with ΔH=250–318 kJ mol^{-1} at about 573 K. Several decomposition stages have been identified [1], commencing at 443–453 K with recrystallization of the complexes accompanied by a partial annealing of the crystal defects. Subsequently, a stepwise release of 6 moles of CH_3, 6 moles of C_3H_6 and 3 moles of $C_8H_{16}O$ takes place, followed by crystallization of the metaphosphates formed.

However, similar studies of rare earth metal complexes of mono-(2-ethylhexyl)phosphoric acid (($H_2B, B = CH_3(CH_2)_3CH(CH_2CH_3)CH_2OPO_3^{2-}$) have not

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been reported, except the communication about their existence in the organic phase of a liquid–liquid extraction of *Ln* [8]. Recently, complexes of the type $Ln(HB)_3 \cdot nH_2O$ and $Ln_2B_3 \cdot nH_2O$ have been prepared in the solid state [9]. The corresponding IR spectra were discussed relative to the spectra of the parent acids and of the LnA_3-type complexes [10]. The presence of an OH-group (substituting one of the hydrocarbon fragments) in $Ln(HB)_3 \cdot nH_2O$ causes a significant change in the structure and solubility in comparison to LnA_3. It was found out also that in solution $La(HB)_3 \cdot nH_2O$ was more stable in the presence of HNO_3 than LaA_3. This property, together with the difference in the solubility of the two types of complexes have been used for the separation of La from other rare earths [11]. The *Ln*-complexes of H_2B have a potential application as specific catalysts in organic synthesis.

The aim of the present work was to study the thermal decomposition of H_2B-lanthanide complexes and to correlate such data with the supposed structure of these complexes. The reported results could also be useful in assessing the possibilities of employing these complexes as catalysts and in lanthanide separation processes.

Experimental

The investigated complexes $La(HB)_3 \cdot 1.5H_2O$ and $La_2B_3 \cdot 3H_2O$ were prepared as follows:

– $La(HB)_3 \cdot 1.5H_2O$: A known mass (10 g) of H_2B was mixed with 0.5 mol l^{-1} NaOH in a molar ratio $H_2B/NaOH=1$. After prolonged stirring, $La(NO_3)_3$ in acetone (100 g dm^{-3}) was added (molar ratio $NaHB/La^{3+}>3$) and stirred for 1 h. H_2O was then added as a desalting agent. The solid product was separated after 24 h, washed with acetone and water and dried for 48 h in a desiccator above conc. H_2SO_4.

– $La_2B_3 \cdot 3H_2O$: 0.5 mol l^{-1} NaOH was added to H_2B in an amount necessary for complete neutralization of the acid. After prolonged agitation, the solution of $La(NO_3)_3$ in acetone was added in a molar ratio $Na_2B/La^{3+}=1.5$ and then the procedure previously described was followed.

$La(NO_3)_3$ was obtained by dissolving La_2O_3 with an assay of 99.9% in a stoichiometric amount of HNO_3. H_2B was separated from commercially available bis-(2-ethylhexyl) phosphoric acid (Fluka) (the latter represents a mixture of 62% HA and 37% H_2B) by the method proposed in [12]. Potentiometric data showed that the H_2B was obtained with an assay >99%.

The results of elemental analysis (Table 1) confirm the proposed formula of the complexes. C and H were determined by Körbl's method whereas P and La – by ICP-atomic emission method.

Simultaneous TG/DTG/DTA analysis was performed using a MOM derivatograph (Paulik–Paulik–Erdey) by heating (5 K min^{-1}) samples of approx. 0.2 g

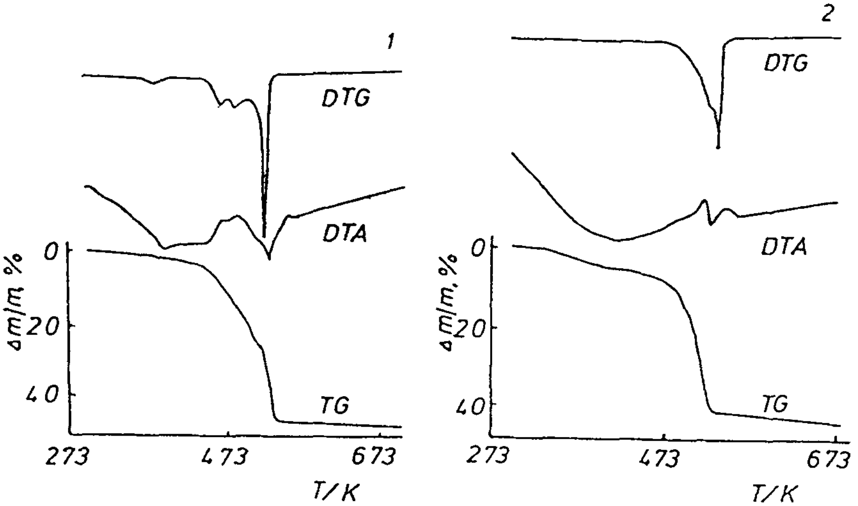


Fig. 1 TG, DTG and DTA curves of $La(HB)_3{\cdot}1.5H_2O$ (1) $La_2B_3{\cdot}3H_2O$ (2)

mass to 723 K in synthetic corundum crucibles in static air. Al_2O_3 was used as reference. Calibration was made with $CaC_2O_4{\cdot}H_2O$.

FT-IR spectra (400–4000 cm^{-1}) were recorded as nujol mulls with a Bomem, Michelson 100 Spectrometer. The resolved spectra were obtained as averages of 50 scans. Strongly overlapping bands were subjected to a deconvolution prior to the resolving.

Results and discussion

TG, DTG and DTA curves of the investigated complexes are shown in Fig. 1. Some quantitative characteristics of the decomposition processes are given in Table 2. The activation energies are calculated by the method proposed in [13].

1. $La(HB)_3{\cdot}1.5H_2O$. A detailed interpretation of the IR spectrum of this complex has been reported [10]. The complexes are coordinative polymers. La forms La–O–P bonds mainly of the bridging type but, probably, some chelation also takes place (bands at 1167, 1114, 1081 and 1046 cm^{-1}, Fig. 2). However, in contrast to LnA_3, the structure of $La(HB)_3{\cdot}1.5H_2O$ includes also P–O–H...O(H)–P hydrogen bonds due to the OH-groups present (band at 1144 cm^{-1}, Fig. 2). The elemental analysis and IR-data (bands at 3425 and 1645 cm^{-1}) confirm also the presence of hydrated water which is missing in LnA_3-type complexes.

The TG curve shows that no mass change occurs up to 323 K. Within the interval 323–383 K, dehydration takes place (Table 2), which is confirmed by the disappearance of the bands at 3425 and 1645 cm^{-1} in the corresponding IR

Table 1 Elemental composition of the investigated Ln-complexes of H_2B and of the final decomposition products

Compound	H-%		C-%		P-%		La-%	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$La(HB)_3 \cdot 1.5H_2O$	7.32	7.44	36.92	37.71	11.9	12.0	17.7	18.0
$La_2B_3 \cdot 3H_2O$	6.18	6.01	30.87	30.14	9.3	9.7	28.9	29.0
$La(PO_3)_3$*	–	–	–	–	24.6	24.7	36.8	37.0
$1.5LaPO_4 + 0.5La(PO_3)_3$**	–	–	–	–	17.0	17.2	51.3	51.6

* Final product of $La(HB)_3 \cdot 1.5H_2O$ heated to 1023 K.

** Final product of $La_2B_3 \cdot 3H_2O$ heated to 1023 K.

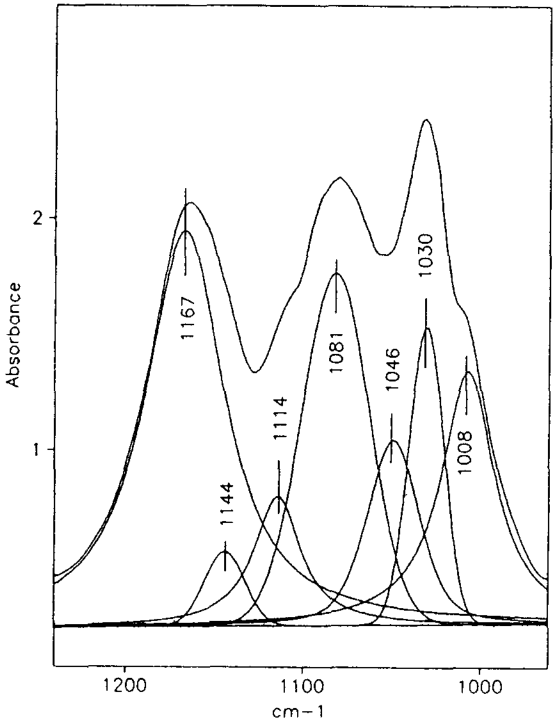


Fig. 2 IR spectrum (1300–900 cm^{-1}) of La(HB)$_3$·1.5H$_2$O

spectrum. The kinetic analysis /performed according to [14] on the basis of the process A(s)→B(s)+C(g)/ and the corresponding mass loss data show that the rate-determining stage of this process is three-dimensional diffusion. By contrast, the rate-determining stage of the first decomposition step of LnA$_3$ is one-dimensional diffusion [1]. This difference in kinetic behaviour suggests that the crystal structures of LnA$_3$ and La(HB)$_3$·1.5H$_2$O are different and the latter does not form an axial structure characteristic of LnA$_3$ [6]. This supposition is supported by our X-ray powder diffraction data: La(HB)$_3$·1.5H$_2$O has an amorphous structure in contrast to the well-defined hexagonal [6] or monoclinic [5] structure of LnA$_3$.

The IR spectrum of the product obtained after heating to 458 K is different from that of the initial material: the bands at 3250 and 1144 cm^{-1} practically disappear and the intensity of the absorption around 1030 cm^{-1} decreases (Fig. 3). As was shown in [10], the band at 3250 cm^{-1} corresponds to (OH) – bridged in P–OH..O(H)–P– associates and the bands at 1144 and ~1030 cm^{-1}, characteristic of the P–OH group of La(HB)$_3$, are due to ν(P–OH) (1030 cm^{-1}) and γ(P–O–H) (1144 cm^{-1}), respectively. Obviously, heating to 458 K causes the disappearance of the OH-groups existing in La(HB)$_3$. The presence of resid-

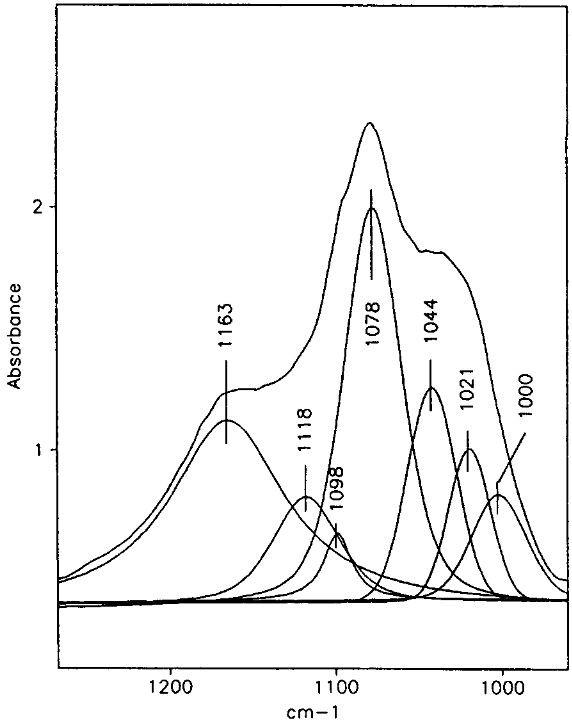


Fig. 3 IR spectrum (1300–900 cm^{-1}) of $La(HB)_3 \cdot 1.5H_2O$ after heating to 458 K

ual absorption in the region around 1030 cm^{-1} is not surprising – it is well known [15] that the P–O–alkyl stretching vibration has a strong band in that frequency interval (and at ~1000 cm^{-1}). As can be seen from Table 2, the mass loss between 383 and 443 K is related to the release of ~1 mol of H_2O/mol/$La(HB)_3$. The latter process continues above 443 K and reaches 1.5 mol H_2O/mol (Table 2). Both IR and TG data encouraged us to suggest that a condensation process takes place in the temperature range 380–450 K; the OH-groups and the associated hydrogen bonds disappear with the formation of P–O–P bridges. The obtained intermediate (which could be taken already as a complex of (2-ethylhexyl) diphosphoric acid) has a more regular structure. As a result, the spectral curve in the region 620–450 cm^{-1} ($\nu_4(F_2)$–PO_4-vibration) has a more symmetrical form (Fig. 4).

Above 443 K degradation of the hydrocarbon groups begins. The process is essentially analogous to the observed for PrA_3 and other LnA_3 compounds [1, 7]. The decomposition proceeds without melting, consistent with the strength of the alkylphosphate moiety and of the newly formed P–O–P bridges. The product of heating is $La(PO_3)_3$. For the complexes studied, the latter was verified by the total mass loss after heating (Table 2), X-ray powder diffrac-

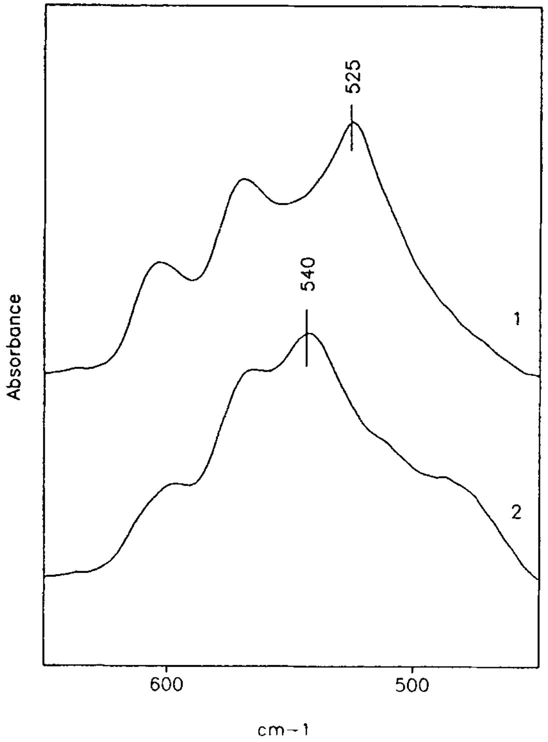


Fig. 4 IR spectrum (650–450 cm^{-1}) of La(HB)$_3$·1.5H$_2$O (1) and of the product obtained after heating to 458 K (2)

tometry and elemental analysis data (Table 1). The exact nature of the released products was not identified, but, from the corresponding mass loss (Table 2), it is assumed that the process takes place in three partially overlapping stages with the release of 3 moles of CH$_3$, 3 moles of C$_3$H$_6$ and 3 moles of C$_4$H$_8$O$_{0.5}$ per mol La(HB)$_3$.

The rate-controlling reactions are three-dimensional diffusion for the CH$_3$-release and spherically symmetric diffusion for the release of the last part (C$_4$H$_8$O$_{0.5}$) of the hydrocarbon chains. A fully satisfactory description of the C$_3$H$_6$-release was not achieved. Comparison of the results reported above with those for LnA$_3$ [1] suggests that the mechanism and some quantitative parameters of the degradation of hydrocarbon fragments depend on the nature of the *Ln*, the complex structure and the atmosphere. The temperatures of the decomposition stages of the hydrocarbon part (Table 2) are 15–45 K lower for La(HB)$_3$·1.5H$_2$O than for LnA$_3$ complexes. The axial structure of the LnA$_3$ conditions the one-dimensional diffusion as a rate-controlling stage of the CH$_3$-release [1]. Three-dimensional diffusion kinetics observed in the present study for the same step, is consistent with the expected three-dimensional poly-

Table 2 Thermal decomposition of $La(HB)_3{\cdot}1.5H_2O$ and $La_2B_3{\cdot}3H_2O$

Compound	T/K	Mass loss/%		Suggested process	DTG-peak/K	E_a/kJ mol^{-1}
		found	calcd.			
$La(HB)_3{\cdot}1.5H_2O$	323–383	3.7	3.4	Loss of 1.5 mol H_2O	373	36
	383–443	2.1	3.4	Condensation		
	443–473	6.8	5.7	Loss of 3 mol CH_3, continuing the condensation proc.	459	146
	473–513	16.0	15.9	Loss of 3 mol C_3H_6	479	47
	513–565	21.0	23.2	Loss of 3 mol $C_4H_8O_{0.5}$	528	216
	>565	2.1	–	Crystallization		
	Total[1]	51.7	51.6			
$La_2B_3{\cdot}3H_2O$	333–433	5.8	5.7	Loss of 3 mol H_2O		
	433–498	4.9	4.7	Loss of 3 mol CH_3		
	498–543	26.7	26.4	Loss of 3 mol C_6H_{12}	528	63
	543–570	5.9	6.9	Loss of 3 mol $CH_2O_{0.5}$	548	200
	>570	1.0	–	Crystallization		
	Total[2]	44.3	43.7			

1 $La(HB)_3{\cdot}1.5H_2O \rightarrow La(PO_3)_3$

2 $La_2B_3{\cdot}3H_2O \rightarrow 1.5LaPO_4 + 0.5La(PO_3)_3$

meric intermediate diphosphate structure, obtained from $La(HB)_3$ after condensation.

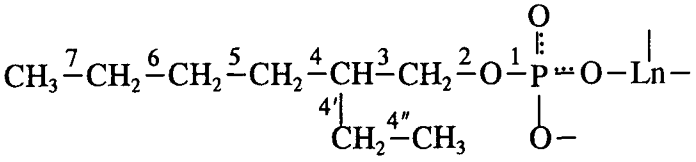
The C_3H_6-release seems to be the most sensitive to the nature of the compound and the atmosphere. The activation energies for this process are rather different: 163 and 220 kJ mol^{-1} for PrA_3 heated in air and N_2, respectively, 38 kJ mol^{-1} for CeA_3 [1] and 47 kJ mol^{-1} for $La(HB)_3$ (Table 2). Interface boundary motion was established to be the rate-controlling process for PrA_3 heated in air [1], but kinetic equations were not derived for the same compound heated in N_2, nor for CeA_3 and $La(HB)_3$. C_3H_6 is released from NdA_3 practically simultaneously with the release of CH_3 and a kinetic analysis of the results indicates the role of both one-dimensional diffusion and interface boundary motion [1].

The activation energies for the release of the last part of the hydrocarbon chains are: 312 kJ mol^{-1} for CeA_3, 271 and 225 kJ mol^{-1} for PrA_3 heated in air and in N_2, 169 kJ mol^{-1} for NdA_3, 257 kJ mol^{-1} for ErA_3 [1] and 216 kJ mol^{-1} for $La(HB)_3$ (Table 2). The kinetic equations derived lead to the same mechanism for the rate-controlling processes, namely, a spherically symmetric diffusion. At this stage, the structure of the initial compound is already sufficiently disturbed and it could not be an important factor in determining the decomposition mechanism. However, a difference in the thermal decomposition behaviour between the two types of complexes is apparent in this stage also. The degradation of $C_4H_8O_{0.5}$ from LaA_3 (*Ln*=Pr, Nd, Er) proceeds in two partially overlapping but distinguishable steps during which (according to the mass loss data) 6 moles of C_2H_5 (538–568 K) and 6 moles of $C_2H_3O_{0.5}$ (568–613 K) per mol LaA_3 are released [1]. However, 3 moles of $C_4H_8O_{0.5}$/mol $La(HB)_3$ are released in one step at 513–565 K (Table 2, Fig. 1.1).

2. $La_2B_3 \cdot 3\,H_2O$. The stoichiometric composition of the complex presumes a 'mixed-type' bidentate coordination of La-bridging and chelating. This structure is reflected by the 1200–1000 cm^{-1} IR spectral region [10].

The decomposition of the complex proceeds without melting and follows generally the same pattern as for $La(HB)_3 \cdot 1.5\,H_2O$. Again, some differences between the two types of complex are apparent. Naturally, the condensation stage is missing. The dehydration and the CH_3-release are completed at 20–50 K higher temperatures in comparison with the analogous steps for $La(HB)_3 \cdot 1.5H_2O$ (Table 2). In contrast with the LnA_3 and $La(HB)_3$ types of complexes, the release of C_6H_{12} instead of C_3H_6 is observed in the following stage. It is seen that in all of the studied complexes, the C–C bond at the tertiary C-atom is disrupted but on different 'sides' of this atom. The process for La_2B_3 is complete at approximately the same temperature at which the C_3H_6 is released from PrA_3 and ErA_3. Subsequently, at 543–570 K the rest of the hydrocarbon is released from La_2B_3 as a result of the disruption of C–O and P–O bonds. It may be mentioned that a pattern analogous to that found for La_2B_3 was found for CeA_3, obtained as an intermediate formed from CeA_3NO_3 on heating [16]. The corresponding DTG peaks of the last two degradation stages are at 528 and 548 K for La_2B_3 and at 538 and 551 K for the specifically prepared CeA_3.

From a combination of the results reported in [1] and in the present work it may be concluded that, depending on the nature of the complex, its hydrocarbon chain



$$CH_3\overset{7}{-}CH_2\overset{6}{-}CH_2\overset{5}{-}CH_2\overset{4}{-}\underset{\overset{4'|}{CH_2\overset{4''}{-}CH_3}}{CH}\overset{3}{-}CH_2\overset{2}{-}O\overset{1}{-}\underset{\underset{|}{O-}}{\overset{\overset{O}{\vdots}}{P}}\cdots O-\overset{|}{Ln}-$$

can be thermally disrupted at the following positions: PrA_3, ErA_3: 7, 4, 4′, 2 or 1; NdA_3: 4, 4′, 2 or 1; $La(HB)_3 \cdot 1.5\,H_2O$: 7, 4, 2 or 1; $La_2B_3 \cdot 3H_2O$: 7, 3, 2 or 1.

The final product of heating of $La_2B_3 \cdot 3H_2O$ consists of a mixture of $LaPO_4$ and $La(PO_3)_3$ in a molar ratio of 1.5/0.5. This is confirmed by elemental analysis data (Table 1), total mass loss (Table 2) and X-ray powder diffractometry and is consistent with the stoichiometry proposed.

Conclusion

The thermochemical behaviour of La-complexes of mono-(2-ethylhexyl) phosphoric acid supports the overall composition and structure of the complexes as proposed in [10], namely: the presence of hydrated H_2O and of OH-groups, associated through hydrogen bonds and taking part in a condensation process (380–450 K). It appears that the heating of $La(HB)_3 \cdot 1.5H_2O$ to a defined temperature might be used as method for preparation of Ln-complexes of alkyldiphosphoric acids.

The results reported here together with those available for LnA_3 [1] suggest that the temperatures and mechanisms of the decomposition of hydrocarbon fragments depend on the particular lanthanide element, the atmosphere and the solid state structure.

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