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STUDIES ON THE THERMAL BEHAVIOUR AND DECOMPOSITION MECHANISM OF COMPLEXES OF RARE EARTH(III) NITRATES) WITH BENZO-15-CROWN-5

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Thermal dissociation reactions and mechanism of complexes of rare earth(iii) nitrates with the crown ether benzo-15-crown-5 were investigated by means of TG–DTG, DSC, DTA and IR technique. The results have shown that the dissociation processes of the complexes consist of several steps, one of which is a fast decomposition reaction. The fast decomposition peak temperatures (DSC) of all the complexes of the lanthanides (except Pm and Tm) decrease regularly with increasing atomic number. Moreover, values of the enthalpy change of desolvation, fast and the fourth step of decomposition and the apparent activation energies of fast and the fourth step of decomposition were obtained.

There has been considerable interest in the rare earth(III) complexes of crown ethers during the past several years. Their thermal behaviour has been studied in some papers [1–4], while the decomposition mechanism has been reported in few papers, especially for the complexes of the rare earth nitrates with benzo-15-crown-5. In this paper, we performed detailed investigations on the solid-state thermal behaviour of fifteen complexes of rare earth(III) nitrates (except Pm) with benzo-15-crown-5 (B15C5) by means of TG–DTG, DSC and DTA and presented their dissociation steps and conceivable mechanism with IR as an assistant method.

Experimental

Preparation of the complexes

The rare earth nitrate complexes with the ligand B15C5 were prepared as previously reported [5]. The stoichiometries of the complexes are

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$RE(NO_3)_3 \cdot B15C5 \cdot 2H_2O$ (RE = La, Ce, Pr and Nd), $RE(NO_3)_3 \cdot \cdot B15C5 \cdot 3H_2O \cdot 0.65CH_3COCH_3$ (RE = *Sm*–Yb, and Y) and $Lu(NO_3)_3 \cdot \cdot B15C5 \cdot 3H_2O$.

Apparatus and conditions of experiments

TG and DTG data were simultaneously obtained by the use of a Perkin–Elmer Model TGS–2, and DSC data were obtained by using a DSC–2C. DTA data were obtained by using a Model LCT–1 Differential Thermal-Balance Instrument made in Beijing Optical Instrument Plant. All TG–DTG and DSC tests were carried out in dynamic atmosphere of dry nitrogen (40 ml·min^{-1}) at a heating rate of 10 deg min^{-1}. Sample masses were about 1 mg for DSC and TG–DTG tests and aluminium crucible was used for DSC. DTA tests were carried out in static air and with about 4 mg of sample in Al_2O_3 crucible.

The IR spectra of the complexes and intermediates formed as the complexes were heated, were obtained by the use of Perkin–Elmer Model 580B Infrared Spectrophotometer.

Results and discussion

Thermal decomposition mechanism of the complexes

Three examples of thermoanalytical curves obtained for rare earth(III) complexes of benzo-15-crown-5 are given in Figs 1 and 2, in which Ho complex is regarded as an example of the type $RE(NO_3)_3 \cdot B15C5 \cdot 3H_2O \cdot 0.65CH_3COCH_3$.

The thermal decomposition mechanism of these complexes determined on the basis of the TG curves is as follows:

$$La(NO_3)_3 \cdot B15C5 \cdot 2H_2O \xrightarrow{I} La(NO_3)_3 \cdot B15C5 \xrightarrow{II} 10La(NO_3)_3 \cdot 9B15C5$$

$$\xrightarrow[*]{III} 5La(NO_3)_3 \cdot B15C5 \xrightarrow{IV} La(NO_3)_3 \xrightarrow{V} La_2O_3$$

$$Ce(NO_3)_3 \cdot B15C5 \cdot 2H_2O \xrightarrow{I} Ce(NO_3)_3 \cdot B15C5 \xrightarrow{II} 10Ce(NO_3)_3 \cdot 9B15C5$$

$$\xrightarrow[*]{V} CeO_2$$

$$Pr(NO_3)_3 \cdot B15C5 \cdot 2H_2O \xrightarrow{I} Pr(NO_3)_3 \cdot B15C5 \xrightarrow{II} 10Pr(NO_3)_3 \cdot 7B15C5$$

$$\xrightarrow[*]{\text{III}} 5Pr(NO_3)_3 \cdot B15C5 \xrightarrow{\text{IV}} Pr(NO_3)_3 \xrightarrow{\text{V}} Pr_2O_3$$

$$Nd(NO_3)_3 \cdot B15C5 \cdot 2H_2O \xrightarrow{\text{I}} Nd(NO_3)_3 \cdot B15C5 \xrightarrow{\text{II}} 5Nd(NO_3)_3 \cdot 3B15C5$$

$$\xrightarrow[*]{\text{III}} NdONO_3 \cdot Nd(NO_3)_3 \xrightarrow{\text{V}} Nd_2O_3$$

$$RE(NO_3)_3 \cdot B15C5 \cdot 3H_2O \cdot 0.65CH_3COCH_3 \xrightarrow{\text{I}} RE(NO_3)_3 \cdot B15C5 \xrightarrow[*]{\text{II}}$$

$$5RE(NO_3)_3 \cdot 3B15C5 \xrightarrow{\text{III}} 5RE(NO_3)_3 \cdot B15C5 \xrightarrow{\text{IV}} REONO_3 \cdot RE(NO_3)_3$$

$$\xrightarrow{\text{V}} RE_2O_3 \qquad (RE = Sm\text{–}Lu \text{ and } Y)$$

The TG data of the rare earth nitrate complexes with B15C5 are reported in Table 1.

Table 1 TG data of the rare earth nitrate complexes with B15C5

RE	Decomposition steps									
	I		II		III		IV		V	
	weight loss, %		weight loss, %		weight loss, %		weight loss, %		weight loss, %	
	calc.	found	calc.	found	calc.	found	calc.	found	calc.	found
La*	5.7	5.1	10.0	9.6	39.8	40.6	48.4	50.3	—	—
Ce	5.7	6.4	10.0	9.0	—	—	—	—	73.3	72.7
Pr*	5.7	5.4	18.5	17.7	39.7	38.8	48.2	48.0	—	—
Nd	5.7	5.5	22.6	22.2	56.5	57.4	—	—	73.5	73.6
Sm	13.2	12.5	—	—	44.0	44.0	59.5	58.2	75.0	74.0
Eu	13.1	13.2	—	—	43.9	44.1	59.3	58.2	74.8	76.0
Gd	13.1	13.6	35.9	35.5	43.6	42.6	58.9	57.9	74.2	73.3
Tb	13.0	12.0	28.2	28.0	43.5	42.8	58.7	58.2	74.1	72.0
Dy	13.0	12.3	28.0	28.7	43.3	43.7	58.0	58.4	73.7	71.9
Ho	12.9	12.3	28.0	27.2	43.1	43.0	58.2	60.4	73.4	72.1
Er	12.9	12.3	27.9	25.0	43.0	42.0	58.1	57.0	73.2	71.0
Tm	12.8	12.0	—	—	42.9	42.6	57.9	57.3	73.0	72.0
Yb	12.8	12.5	27.7	27.2	42.8	42.4	57.6	58.2	72.7	72.2
Lu**	7.9	7.9	23.6	23.2	39.4	41.5	55.2	58.6	71.0	70.0
Y	14.5	14.2	31.4	32.8	48.3	49.0	65.2	65.5	82.3	79.7

* For La and Pr complexes the test processes did not come up to the temperature at which they completely decomposed to form La_2O_3 and Pr_2O_3.

** The stoichiometry of the Lu complex is $Lu(NO_3)_3 \cdot B15C5 \cdot 3H_2O$.

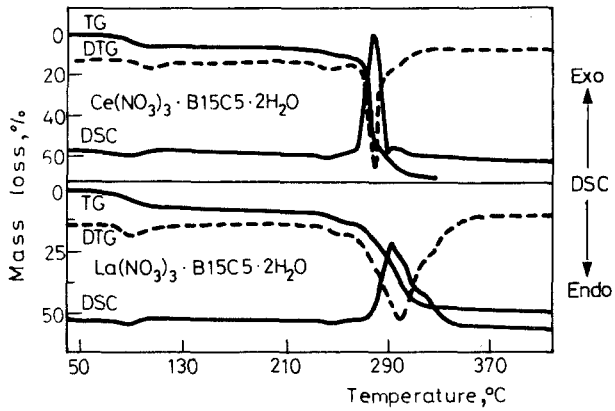

Fig. 1 DSC and TG–DTG curves of $RE(NO_3)_3 \cdot B15C5 \cdot 2H_2O$ (RE = La and Ce)

As can be seen, all these complexes (except Ce, Nd, Sm, Eu and Tm) decompose by a five-step process. The steps with star are fast decomposition reactions. $5RE(NO_3)_3 \cdot 2B15C5$ is formed in step II of Gd. Step II is absent for Sm, Eu and Tm and their fast decomposition reaction is step III. It should be pointed out that a part of the ligand was released undecomposed during the thermal decomposition of the complexes. A white sublimate, which was collected during the thermal decomposition of the complex, was identified by measuring the melting point and IR spectrum to be B15C5. In order to examine the decomposition mechanism mentioned above, we have identified the intermediates (corresponding to

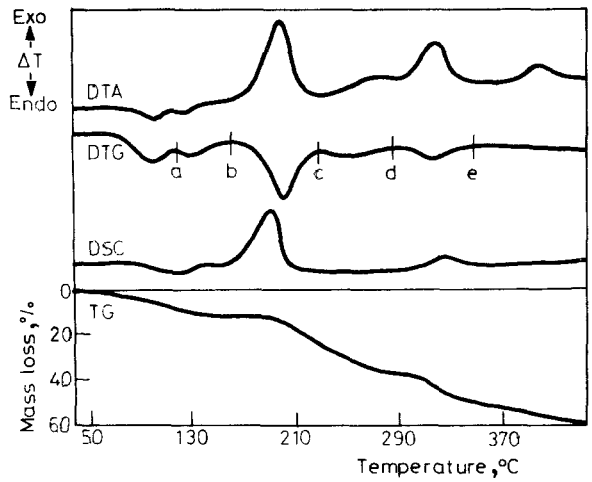

Fig. 2 TG–DTG, DTA and DSC curves of $Ho(NO_3)_3 \cdot B15C5 \cdot 3H_2O \cdot 0.65CH_3COCH_3$. The a–e positions are the points at which the sample was cooled and IR analysis was carried out

compounds formed at points, a, b, c, d and e of the TG curve in Fig. 2) during the thermal decomposition of the Ho complex by IR spectra. The IR spectra (Fig. 3) showed that the complex completely lost the solvent molecule after step I and decomposed after step IV to a mixture of $HoONO_3$ and $Ho(NO_3)_3$ at a 1 : 1 mole ratio. The Ho complex finally decomposed to form Ho_2O_3 (step V).

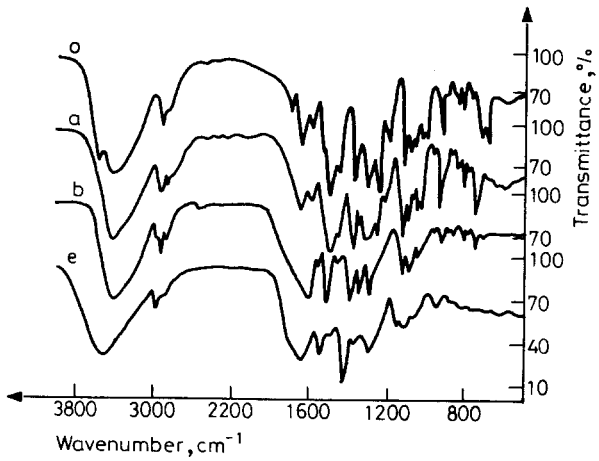

Fig. 3 IR spectra of $Ho(NO_3)_3 \cdot B15C5 \cdot 3H_2O \cdot 0.65CH_3COCH_3$ and its residue after the thermal decomposition process. ° – untreated sample; a, b and e – the samples corresponding to the positions in Fig. 2

Enthalpies of the desolvation and decomposition reaction and activation energies for the complexes

The complexes of lighter lanthanides (La–Nd) have only one endothermic process with a weight loss corresponding to the loss of two water molecules, while that of heavier lanthanides (Sm–Yb) and yttrium have two endothermic processes corresponding to the release of 0.65 acetone and three water molecules in succession. Steps II, III, IV and V are exothermic for all these complexes. It could be found from Table 2 that the fast decomposition peak temperatures, T_p (DSC), of all the rare earth complexes of B15C5 (except Pm) are above 175° and their values, except for Tm, decrease regularly with increasing atomic number.

As can be seen in Fig. 4, the T_p values of La–Sm complexes rapidly decrease with increasing atomic number of the lanthanide, while those of Sm–Lu (except Tm) complexes more slowly. The two straight lines having different slopes are obtained for light and heavy rare earth ions, respectively, and they intersect at Sm. The two

Table 2 Data obtained from thermal analysis for the complexes

RE	Desolvation		Fast decomposition			Step IV		
	T_p, °C	ΔH_{ds}, kJ/mol	E_a, kJ/mol	T_p, °C	ΔH_{fd}, kJ/mol	E_{IV}, kJ/mol	T_{IV}, °C	ΔH_{IV}, kJ/mol
La	97.0			295.4				
Ce	97.5			283.2				
Pr	126.2			254.6				
Nd	123.5	75.6		245.7	459.6			
Sm	131.0	88.9	267.4	213.7	483.2	157.6	304.9	95.7
Eu	122.6	82.9	187.4	206.9	396.6	177.7	290.6	167.0
Gd	125.0	112.7	147.3	202.2	388.7	184.4	309.0	157.4
Tb	124.0	93.8	120.4	197.2	421.5	169.3	304.0	159.0
Dy	124.0	121.5	121.1	191.8	331.2	174.1	308.9	154.2
Ho	146.2	117.8	126.1	191.5	376.9	166.2	307.7	124.6
Er	126.0	157.0	117.0	188.6	368.9	171.6	306.3	148.9
Tm	142.0	99.0	151.9	211.8	321.9	178.0	294.4	158.6
Yb	145.0	130.6	151.6	179.4	321.7	165.4	304.3	167.3
Lu	155.0	253.7	135.4	175.6	312.9	154.3	303.5	172.6
Y	128.2	162.6	94.5	196.5	279.0	161.9	312.1	147.7

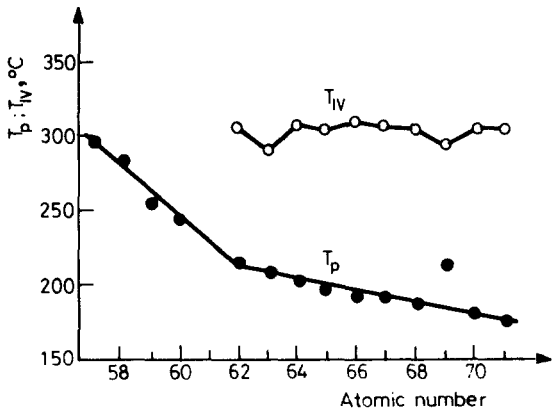

Fig. 4 T_p of the fast decomposition and T_{IV} of step IV as a function of atomic numbers for lanthanide elements

linear functions could be described by using two expressions as follows:

$$T_p = 1241.4 - 16.6 \cdot n$$

where n = 57–60 and 62, the correlation coefficient is 0.9906, and

$$T_p = 457.9 - 4.0 \cdot n$$

where n = 62–71 (except 69), the correlation coefficient is 0.9900.

Moreover, it is also shown in Fig. 4 that the decomposition peak temperatures, T_{IV} of step IV are independent of the atomic number and nearly constant. These values do not display any obvious periodicity between the lighter and the heavier rare earth cations.

In order to obtain the enthalpies of desolvation and (or) dehydration, ΔH_{ds}, the fast decomposition reaction, ΔH_{fd}, and decomposition step IV, ΔH_{IV}, DSC tests were carefully carried out using a sample size of 1 mg and a heating rate of 10 deg/min. On the basis of DSC peak temperatures T_p at various heating rates θ (2.5, 5, 10, 20 and 40 deg/min), the apparent activation energies of the fast decomposition, E_a, and step IV, E_{IV}, were obtained by means of Kissinger's method [6]. The results are shown in Table 2.

The enthalpies of desolvation, ΔH_{ds}, show a rising trend with the atomic number of lanthanide, though not in a regular manner. If the fast decomposition ΔH_{fd} and E_a are plotted against the ionic radius of rare earth cations, the curves show the so called "tetrad effect" (see Fig. 5). Similarly, the ΔH_{IV} and E_{IV} for step IV are plotted against the ionic radius of rare earth cations, the curves also show a "tetrad effect" (see Fig. 6).

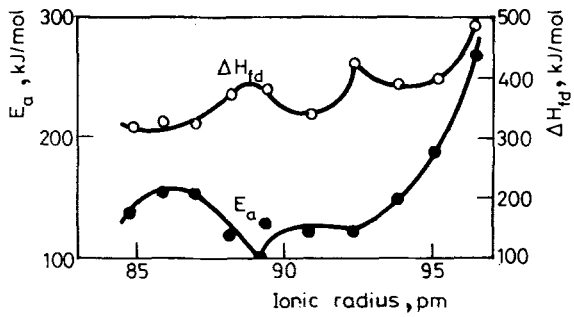

Fig. 5 Plot of E_a and ΔH_{fd} values *vs.* ionic radius of rare earth cations (RE = Sm–Lu, Y)

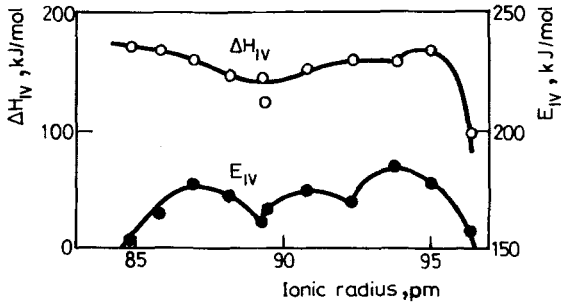

Fig. 6 Plot of E_{IV} and ΔH_{IV} values *vs.* ionic radius of rare earth cations (RE = Sm–Lu, Y)

It is worth noting that the observed regularities show that a certain amount of covalency is present between the rare earth cation and crown ether B15C5.

Influence of the test conditions on the results of the thermal analysis for the complexes

The thermal decomposition reaction can be strongly influenced by the experimental conditions like the sample size and heating rate. The increase in sample size, e.g. of the Ho complex. The higher the heating rate, the higher is the temperature and a decrease of the peak temperature of the fast decomposition. Additionally, steps III and V disappear in the DSC curve probably due to the small sample size, e.g. fo the Ho complex. The higher the heating rate, the higher is the decomposition peak temperature for the general materials including heavier lanthanides Sm–Lu and yttrium, on the contrary, the temperatures for the complexes of some lanthanides as La, Ce, Pr and Nd are nearly constant or decrease with increasing heating rate.

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Zusammenfassung — Mittels TG–DTG-, DSC-, DTA- und IR-Techniken wurden einschließlich Mechanismus die thermischen Dissoziationsreaktionen von Komplexen der Seltenerden(III)nitrate mit dem Titelkronenether untersucht. Die Ergebnisse zeigen, daß die Dissoziationsvorgänge der Komplexe aus mehreren Schritten bestehen, von denen einer eine schnelle Zerfallsreaktion ist. Die Peaktemperaturen für die schnellen Zersetzungen (DSC) aller Lanthanidenkomplexe (ausgenommen Pm und Tm) sinken mit ansteigender Ordnungszahl der Lanthaniden ständig im Wert. Außerdem wurden Werte für die Enthalpieänderungen bei der Desolvatation, für den schnellen und den vierten Zersetzungsschritt und für die Aktivierungsenergien des schnellen und vierten Zersetzungsschrittes erhalten.

Резюме — Методами ТГ–ДТГ, ДТА, ДСК и ИК спектроскопии изучены реакции и механизм термической диссоциации комплексов нитратов редкоземельных элементов с краун-эфиром бензо-15-краун-5. Результаты показали, что процессы диссоциации комплексов протекают в несколько стадий, одной из которых является реакция быстрого разложения. Температурный пик реакции быстрого разложения для всех комплексов лантаноидов (за исключением прометия и тулия) уменьшается с увеличением атомного веса элементов. Кроме того, были получены значения изменения энтальпии процесса десольватации, реакций быстрого и четвертой стадии разложения, а также энергии активации этих двух процессов.