

## **STUDIES OF DEHYDRATION PROCESS FOR ISOSTRUCTURAL SERIES OF LANTHANIDE(III) 2,6-DIHYDROXYBENZOATES**

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### **Abstract**

Dehydration kinetics of lanthanide 2,6-dihydroxybenzoates has been studied by thermogravimetry using the model-fitting method of calculation. Several kinetic models gave a good representation of the measured thermogravimetric (TG) curves but the calculation method allowed to propose the most probable dehydration mechanism. The activation energies of dehydration for isostructural 2,6-dihydroxybenzoates of lanthanides are similar for a given kinetic model. A change in the heating rate did not alter the dehydration mechanism. A linear correlation between the activation energy and the heating rate was observed for the systems studied.

**Keywords:** compensation effect, dehydration, lanthanide complexes, non-isothermal kinetics

### **Introduction**

Dehydration of solids is the subject of many kinetic studies. It helps to understand the following decomposition mechanism:  $A_{(s)} \rightarrow B_{(s)} + C_{(g)}$ . Dehydration is relatively easy to study because the reaction products are known, the reaction temperature is low and the loss of water molecules does not overlap with other decomposition reactions [1]. Therefore, there are many papers devoted to dehydration of inorganic salts as well as organic substances and metal complexes of organic ligands, e.g. [2–5].

The basic kinetic equation for decomposition of a solid is:  $d\alpha/dt = k(T)f(\alpha)$ , where  $\alpha$  is the extent of reaction,  $t$  is time,  $k(T)$  is the rate constant dependent on temperature,  $f(\alpha)$  is a function, usually empirical one, representing the reaction model [6]. In [6–8] one can find information on various reaction models used to study the kinetics of the solid decomposition. For most decomposition reactions, the Arrhenius equation is useful, although there are many obstacles associated with interpretation of experimental values of the activation energy,  $E$ , and the pre-exponential factor,  $A$ . Most often  $E$  is related to the enthalpy of activation and  $A$  – to the frequency of lattice vibrations [6].

Unfortunately, the use of non-isothermal experiments often gives inconsistent values of the Arrhenius parameters [9]. For any reaction model,  $E$  and  $A$  values show extensive variations for the same sample. The kinetics of solid state reactions is controlled by many factors, e.g. pressure, temperature, size of crystals, sample mass, gaseous atmosphere, heating rate, and therefore,  $E$  may vary with  $\alpha$  [10]. Because of this, it is impossible to know 'true' kinetic parameters for a single sample. However, the isothermal method has also the disadvantages. First of all, a sample requires some time to reach the experimental temperature. Moreover, each isothermal experiment needs the preparation of a new sample. The non-isothermal method resolves these problems [11]. Therefore, we decided to use the non-isothermal heating to study the dehydration process of metal complexes.

The present paper is a continuation of our studies on the dehydration process of metal complexes with various derivatives of benzoic acid and amino acids [12, 13]. The lanthanide compounds are often isostructural and the study of a single compound structure provides information about structure of other isostructural compounds. For the same measurement conditions, the dehydration process should depend mainly on the compound structure. If the isostructural series is investigated, the 'true' values of the activation energy are not the most important. In such a case, the kinetic parameters are used to compare the dehydration mechanism of complexes and to find the possible correlation between the way of water binding in a complex and the kinetics of its loss. In this paper we present the results of kinetic studies of dehydration for selected lanthanide(III) 2,6-dihydroxybenzoates and discuss the dependence of the dehydration mechanism on the heating rate when other measurements conditions are invariable.

## Experimental

### *Materials*

The complexes of La(III), Ce(III), Pr(III), Ho(III), Tm(III) and Lu(III) with 2,6-dihydroxybenzoic acid were prepared as reported by Brzyska *et al.* [14, 15]. The compounds were identified by means of elemental analysis and their structures were verified by X-ray diffraction method.

## Methods

### *Thermal analysis*

The TG and DTG curves of dehydration of the complexes studied were obtained with TA Instruments TG 2950 analyser at heating rates of 3, 6 and 10 K min<sup>-1</sup> in flowing nitrogen atmosphere ( $v=60$  cm<sup>3</sup> min<sup>-1</sup>). About 10 mg of powdered sample placed in an open platinum pan was used in each TG measurement.

### Kinetic treatment

The equation used for calculation of the  $E$  and  $A$  parameters is:

$$\ln(d\alpha/dT) - \ln(f(\alpha)) = \ln(A/\beta) - E/RT$$

where  $\alpha$  is the extent of reaction,  $T$  is temperature in K,  $f(\alpha)$  is the kinetic model [6–8],  $A$  is the pre-exponential factor in Arrhenius equation in  $\text{min}^{-1}$ ,  $\beta$  is the heating rate in  $\text{K min}^{-1}$ ,  $E$  is the activation energy in  $\text{kJ mol}^{-1}$  and  $R$  is the gas constant. According to the model-fitting method, when  $f(\alpha)$  is properly selected, the plot of the right-side of the aforementioned equation vs.  $1/T$  should be linear. The activation energy  $E$  can be calculated from the slope and the  $A$  factor – from the intercept. Over a dozen kinetic models were considered, that is Fn, Rn, Dn, An, Pn models. After the preliminary calculation it was necessary to reject some of the  $f(\alpha)$  functions. The majority of them have not given the linear dependence of  $\ln(d\alpha/dT) - \ln(f(\alpha))$  vs.  $1/T$  or in spite of linear plot the kinetic parameters were less than zero. Finally, only the following kinetic models were used to fit the dehydration TG curves: D2 – two-dimensional diffusion, D3 – three-dimensional diffusion, F1 – first order reaction, F2 – second order reaction, R2 – contracting cylinder, R3 – contracting sphere. Detailed descriptions of these models including analytical expressions for the corresponding  $f(\alpha)$  functions are given in [6, 8].

## Results and discussion

Complexes of lanthanides(III) with 2,6-dihydroxybenzoic acid have the empirical formula  $\text{Ln}(\text{C}_7\text{H}_5\text{O}_4)_3 \cdot n\text{H}_2\text{O}$  where  $n=4$  for La–Sm and  $n=6$  for Eu–Lu. The La, Ce and Pr complexes form the isostructural series having four water molecules bonded in the inner coordination sphere. The other isostructural series is formed by heavy lanthanides (Eu–Lu). In this case, four water molecules are in the inner sphere and two remaining molecules are in the outer coordination sphere [14–16]. In our work we examine in detail the dehydration process of the selected lanthanide 2,6-dihydroxybenzoates, i.e., those containing La(III), Ce(III) and Pr(III) as well as Ho(III), Tm(III) and Lu(III) as representatives of the light and heavy lanthanides, respectively. The TG curves of dehydration were measured from 20 to 160°C at three heating rates: 3, 6 and 10  $\text{K min}^{-1}$ . Under those conditions all compounds underwent complete dehydration. The composition of anhydrous complexes was verified by elemental analysis. All anhydrous compounds were roentgenographically amorphous.

The complexes of light lanthanides dehydrated during one step, whereas the dehydration of heavy lanthanide compounds was a several-step process as suggested by peaks on DTG curve. The two outer-sphere molecules were lost in the range of 40–80°C. The shape of the TG curves shows that those water molecules are loosely bound [14, 15]. The remaining four inner-sphere water molecules were lost in one stage in the range of 80–120°C. In the case of all lanthanide complexes studied, a change in the heating rate did not alter the shape of the TG curves and probably neither the mechanism of dehydration. An increase in the heating rate caused only an up

**Table 1** Kinetic parameters of dehydration of the La, Ce and Pr 2,6-dihydroxybenzoates for different heating rates calculated for  $\alpha \in (0.05; 0.90)$

Kinetic model	La 2,6-DHB			Ce 2,6-DHB			Pr 2,6-DHB		
	$E/\text{kJ mol}^{-1}$	$A/\text{min}^{-1}$	$r$	$E/\text{kJ mol}^{-1}$	$A/\text{min}^{-1}$	$r$	$E/\text{kJ mol}^{-1}$	$A/\text{min}^{-1}$	$r$
$\beta=3 \text{ K min}^{-1}$									
R2	77	$5.14 \cdot 10^9$	0.9972	77	$9.45 \cdot 10^9$	0.9942	70	$9.76 \cdot 10^8$	0.9672
R3	88	$1.19 \cdot 10^{11}$	0.9942	90	$4.55 \cdot 10^{11}$	0.9988	83	$5.41 \cdot 10^{10}$	0.9853
D2	154	$2.49 \cdot 10^{20}$	0.9993	156	$1.77 \cdot 10^{21}$	0.9905	–	–	–
D3	186	$2.71 \cdot 10^{23}$	0.9987	194	$1.86 \cdot 10^{26}$	0.9994	186	$1.36 \cdot 10^{25}$	0.9944
$\beta=6 \text{ K min}^{-1}$									
R2	74	$1.72 \cdot 10^9$	0.9985	77	$9.65 \cdot 10^9$	0.9943	71	$1.67 \cdot 10^9$	0.9554
R3	80	$1.10 \cdot 10^{10}$	0.9988	85	$1.01 \cdot 10^{11}$	0.9975	82	$5.02 \cdot 10^{10}$	0.9763
D2	148	$2.95 \cdot 10^{19}$	0.9966	151	$3.00 \cdot 10^{20}$	0.9950	–	–	–
D3	168	$5.15 \cdot 10^{21}$	0.9996	176	$2.91 \cdot 10^{23}$	0.9993	178	$8.06 \cdot 10^{23}$	0.9927
$\beta=10 \text{ K min}^{-1}$									
R2	61	$3.77 \cdot 10^7$	0.9953	64	$1.76 \cdot 10^8$	0.9961	56	$1.43 \cdot 10^7$	0.9632
R3	70	$4.43 \cdot 10^8$	0.9987	74	$2.96 \cdot 10^9$	0.9988	66	$2.70 \cdot 10^8$	0.9834
D2	127	$3.06 \cdot 10^{16}$	0.9932	129	$1.95 \cdot 10^{17}$	0.9926	–	–	–
D3	153	$4.29 \cdot 10^{19}$	0.9995	159	$9.28 \cdot 10^{20}$	0.9994	151	$8.87 \cdot 10^{19}$	0.9899

$r$  – correlation coefficient; codes of the kinetic models are explained in the experimental part

**Table 2** Kinetic parameters of dehydration of the Ho, Tm and Lu 2,6-dihydroxybenzoates for different heating rates calculated for  $\alpha \in (0.05; 0.90)$

Kinetic model	Ho 2,6-DHB			Tm 2,6-DHB			Lu 2,6-DHB		
	$E/\text{kJ mol}^{-1}$	$A/\text{min}^{-1}$	$r$	$E/\text{kJ mol}^{-1}$	$A/\text{min}^{-1}$	$r$	$E/\text{kJ mol}^{-1}$	$A/\text{min}^{-1}$	$r$
$\beta = 3 \text{ K min}^{-1}$									
F1	159	$1.80 \cdot 10^{22}$	0.9988	164	$4.86 \cdot 10^{22}$	0.9920	166	$7.42 \cdot 10^{22}$	0.9997
F2	282	$2.12 \cdot 10^{40}$	0.9898	262	$8.71 \cdot 10^{36}$	0.9905	266	$2.01 \cdot 10^{37}$	0.9908
R3	128	$5.70 \cdot 10^{20}$	0.9843	131	$2.88 \cdot 10^{17}$	0.9844	133	$3.81 \cdot 10^{17}$	0.9979
$\beta = 6 \text{ K min}^{-1}$									
F1	149	$3.65 \cdot 10^{20}$	0.9997	152	$6.23 \cdot 10^{20}$	0.9996	144	$1.15 \cdot 10^{20}$	0.9980
F2	263	$1.69 \cdot 10^{37}$	0.9899	247	$2.09 \cdot 10^{34}$	0.9899	246	$1.86 \cdot 10^{34}$	0.9921
R3	112	$1.58 \cdot 10^{14}$	0.9960	120	$6.45 \cdot 10^{15}$	0.9973	112	$3.08 \cdot 10^{14}$	0.9974
$\beta = 10 \text{ K min}^{-1}$									
F1	130	$2.60 \cdot 10^{17}$	0.9925	134	$1.40 \cdot 10^{18}$	0.9995	132	$1.08 \cdot 10^{18}$	0.9997
F2	243	$7.44 \cdot 10^{33}$	0.9940	221	$2.76 \cdot 10^{30}$	0.9898	227	$4.44 \cdot 10^{31}$	0.9917
R3	101	$7.11 \cdot 10^{12}$	0.9762	104	$3.72 \cdot 10^{13}$	0.9953	107	$1.03 \cdot 10^{14}$	0.9978

$r$  – correlation coefficient; codes of the kinetic models are explained in the experimental part

to 5°C rises in the initial temperature of dehydration and an up to 10°C rises in the final dehydration temperature. The kinetic parameters of dehydration for the La, Ce, Pr complexes and those related to the last step of dehydration for other lanthanide compounds were calculated using the model-fitting method. The results are presented in Tables 1 and 2. There are no kinetic parameters provided for the loss of outer water molecules in the case of the Ho, Tm, Lu complexes because the reaction occurs at least in two overlapping steps and it was impossible to separate them.

As can be seen from Tables 1 and 2 several kinetic models give a good representation of the dehydration process. This confirms our earlier statement that the calculation of the kinetic parameters for the dehydration process from thermogravimetric data is a very difficult task. Nevertheless, the model-fitting method allowed to select, from among of ten to twenty kinetic models, three or four the most probable ones and to propose the most probable dehydration mechanism. The analysis of the correlation coefficients in Tables 1 and 2 inclines to the choice of the D3 kinetic model in the case of the dehydration of light lanthanide complexes. However, one should not reject other models, i.e. D2, R2 and R3. It is possible that the rate of dehydration reaction is limited simultaneously by the nucleation process (R2 and R3 models) and by the diffusion of water molecules (D2 and D3 models). In the case of the heavy lanthanide complexes, the F1 model is the best fitting but also the use of the F2 and R3 functions gives a good agreement with the experimental TG curves. These models are not contradictory. Probably the rate of the dehydration process is limited by the reaction of loss of water molecules.

$E$  and  $A$  values generated by the selected models differ significantly. However, the parameters for isostructural compounds such as the activation energy of dehydration are similar for a given model and selected heating rate. For isostructural series of light lanthanide complexes,  $E$  values of dehydration obtained for R3 kinetic model vary from 66 to 88 kJ mol<sup>-1</sup>, according to the lanthanide atom and heating rate. The use of the same kinetic model (R3) for isostructural complexes of heavy lanthanides shows quite different values: 101–133 kJ mol<sup>-1</sup>. It suggests that the structure of a given complex controls the dehydration process. It is very probable that the  $E$  values of the last dehydration stage for all heavy lanthanide 2,6-dihydroxybenzoates resemble those for the Ho, Tm and Lu compounds.

A change in the heating rate does not alter the dehydration mechanism. In most cases the values of the activation energy decrease about 20% when the heating rate increases from 3 to 10 K min<sup>-1</sup>. The same effect was reported by Ingier-Stocka [17] for decomposition of the [Co(NH<sub>3</sub>)<sub>6</sub>]<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·4H<sub>2</sub>O complex. Similarly as in [17], the linear dependence of  $E=f(\beta)=m\beta+n$  was observed for the most systems studied. Coefficients  $m$  and  $n$  are given in Table 3. Their values for isostructural compounds are congruent for the same kinetic model. It confirms the importance of the complex structure in the decomposition process of solids. Also, the kinetic compensation effect  $\ln A=pE+q$  [18] was observed for the systems studied. The values of  $p$  and  $q$  are given in Table 4. The compensation effect associated with changes in the heating rate is rather common for thermal decomposition of solids with gaseous products [18–20].

**Table 3** Dependence of the activation energy on the heating rate  $E=m\beta+n$ , within the  $\beta$  range of 3–10 K min<sup>-1</sup>

Kinetic model	La			Ce			Pr		
	<i>m</i>	<i>n</i>	<i>r</i>	<i>m</i>	<i>n</i>	<i>r</i>	<i>m</i>	<i>n</i>	<i>r</i>
F1									
F2									
R2	-2.34	85.5	0.9653	-1.93	84.9	0.9042	*	*	*
R3	-2.57	95.6	0.9998	-2.31	97.6	0.9915	-2.51	92.9	0.9254
D2	-3.93	167.9	0.9741	-3.95	170.3	0.9647			
D3	-4.66	198.5	0.9910	-4.96	207.7	0.9951	-5.09	203.9	0.9756
Kinetic model	Ho			Tm			Lu		
	<i>m</i>	<i>n</i>	<i>r</i>	<i>m</i>	<i>n</i>	<i>r</i>	<i>m</i>	<i>n</i>	<i>r</i>
F1	-4.18	172.5	0.9955	-4.30	177.0	0.9994	-4.76	177.5	0.9688
F2	-5.54	297.8	0.9977	-5.89	280.6	0.9974	-5.53	281.3	0.9953
R2									
R3	-3.80	137.7	0.9822	-3.86	142.8	0.9997	-3.58	140.0	0.9116
D2									
D3									

\* linear dependence is not observed; *r* – correlation coefficient

**Table 4** Kinetic compensation effect  $\ln A = pE + q$

Kinetic model	La			Ce			Pr		
	<i>p</i>	<i>q</i>	<i>r</i>	<i>p</i>	<i>q</i>	<i>r</i>	<i>p</i>	<i>q</i>	<i>r</i>
F1									
F2									
R2	0.30	-1.05	0.9993	0.31	-0.65	0.9999	*	*	*
R3	0.31	-1.83	0.9997	0.32	-1.52	0.9999	0.32	-1.60	0.9991
D2	0.41	-14.92	0.9744	0.34	-3.61	0.9999			
D3	0.34	-6.17	0.9997	0.35	-7.16	0.9998	0.38	-11.37	0.9429

  

Kinetic model	Ho			Tm			Lu		
	<i>p</i>	<i>q</i>	<i>r</i>	<i>p</i>	<i>q</i>	<i>r</i>	<i>p</i>	<i>q</i>	<i>r</i>
F1	0.38	-9.81	0.9999	0.35	-4.88	0.9998	0.32	-0.86	0.9971
F2	0.38	-14.57	0.9999	0.36	-10.21	0.9991	0.33	-2.78	0.9996
R2									
R3	0.69	-42.15	0.9671	0.33	-3.19	0.9998	0.32	-2.48	0.9116
D2									
D3									

\* linear dependence is not observed; *r* – correlation coefficient



## Conclusions

One of the goals of the current work was to demonstrate the effect of the molecular structure on the dehydration mechanism. Therefore, all TG measurements were carried out at the same conditions, e.g., the sample preparation method, the size of crystals, the pan used and the atmosphere of furnace. The results present the same mechanism of dehydration within the isostructural series of the complexes and the similar values of the activation energy within the same kinetic model.

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