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KINETICS OF DEHYDRATION OF LANTHANIDE(III) 2-AMINO-4-CHLOROBENZOATES

M. Sikorska

Department of Inorganic and General Chemistry, Faculty of Chemistry, Marie Curie Skłodowska University, 20–031 Lublin, Poland

Abstract

The 2-amino-4-chlorobenzoates of Y(III), La(III), Pr(III), Sm(III), Gd(III), Dy(III), Tm(III) and Lu(III) were prepared. Their general formula is $Ln(C_6H_3NH_2ClCOO)_3 \cdot H_2O$. X-ray analysis demonstrated that all the prepared complexes are isostructural. This indicates the same mode of coordination of water and organic ligands throughout the whole series of lanthanide(III) 2-amino-4-chlorobenzoates. The dehydrations of the complexes were studied under non-isothermal conditions in air. From the thermogravimetric data on the dehydrations, the kinetic models best fitting the experimental TG curves were selected. These models suggest that the dehydration is governed by diffusion processes. Kinetic parameters such as the activation energy and pre-exponential factor were calculated by means of the differential and integral methods.

Keywords: dehydration, kinetics, lanthanide complexes

Introduction

The dehydration reactions of crystal solids have been the subject of many kinetic studies [1–4]. The interdependence between the course of the thermal dehydration and the structure of the investigated compound is obvious. However, it is impossible to predict the course of the thermal decomposition reaction on the basis of the crystal structure.

Previous papers [5, 6] reported studies on some properties of lanthanide compounds with 2-amino-4-chlorobenzoic acid. The compounds are isostructural, with the general formula $Ln(C_6H_3NH_2ClCOO)_3 \cdot H_2O$. Analysis of the complexes indicated the same mode of coordination throughout the whole series of 2-amino-4-chlorobenzoates of the lanthanides(III) and it has been suggested that the crystallization water molecule is bonded directly to the metal ion. The similar structures and properties of the investigated compounds suggested similar thermal behaviour. In the present paper, the thermal dehydrations of yttrium(III) and some lanthanide(III) 2-amino-4-chlorobenzoates have been investigated. For all

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the investigated compounds, the same conditions of thermal decomposition were applied as concerns sample mass, crystal grain size, heating rate, crucible size, etc. In this way, an attempt was made to eliminate the influence of the experimental conditions on the thermal reactions. The differences in thermal behaviour observed between the individual lanthanide complexes are then caused primarily by differences in compound properties. The results of non-isothermal kinetic analyses of the thermal dehydrations of the complexes are also reported.

Experimental

Materials

The preparation and properties of the 2-amino-4-chlorobenzoates of Y(III), La(III), Pr(III), Gd(III), Dy(III), Tm(III) and Lu(III) were described in a previous paper [5].

Methods

The thermal dehydrations of the complexes were studied by means of simultaneous TG-DTG-DTA techniques under non-isothermal conditions. The measurements were made with a Paulik-Paulik-Erdey Q-1500D Derivatograph at 293–573 K, with a linear heating rate of 10 deg $\min^{-1}$ in static air. The sample mass was 100 mg and the sieve mesh was ≤ 0.05 mm. The DTA reference material was α-Al_2O_3. Ceramic crucibles (Ø9 mm) were used both for the samples and for the reference material.

Results and discussion

During heating above 400 K, the 2-amino-4-chlorobenzoates of Y(III) and lanthanides(III) lose the crystallization water molecule, with a sharp endothermic effect at about 470 K in the DTA curve. The dehydration is completed at

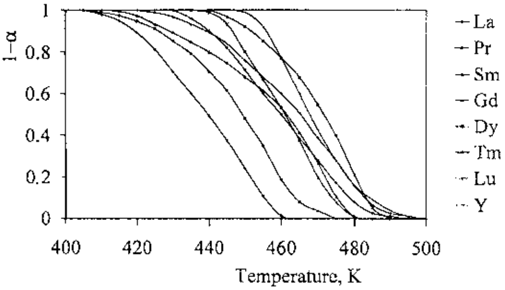

Fig. 1 Complementary extent of reaction (1–α) as a function of temperature T for the dehydration reactions of yttrium(III) and lanthanide(III) 2-amino-4-chlorobenzoates

about 490 K. The anhydrous products were identified by elemental analysis and IR spectroscopy. Powder diffraction analysis revealed that all the anhydrous complexes are amorphous. Data on the dehydration process are presented in Table 1 and the shape of the TG curves is illustrated in Fig. 1.

Table 1 Thermoanalytical results on dehydration of $LnL_3{\cdot}H_2O$ (L=$C_6H_3NH_2ClCOO^-$)

Complex	Temp. range of dehydration/K	Temp. of DTG peak/K	Temp. of DTA peak/K	Mass loss/%	
				found	calcd.
$YL_3{\cdot}H_2O$	448–496	483	483	3.00	2.91
$LaL_3{\cdot}H_2O$	407–465	453	455	2.80	2.70
$PrL_3{\cdot}H_2O$	408–475	464	468	2.77	2.68
$SmL_3{\cdot}H_2O$	414–485	473	473	2.75	2.65
$GdL_3{\cdot}H_2O$	440–482	468	473	2.54	2.60
$DyL_3{\cdot}H_2O$	440–490	478	483	2.72	2.60
$TmL_3{\cdot}H_2O$	430–490	468	473	2.60	2.57
$LuL_3{\cdot}H_2O$	422–497	480	483	2.50	2.55

Kinetic analysis of the experimental TG curves obtained under non-isothermal conditions was performed by means of the differential method [7] (Eq. (1)) and the modified Coats-Redfern integral method [7, 8] (Eq. (2))

$$\ln\left(\frac{d\alpha}{dT}\right)-\ln[f(\alpha)]=\ln\left(\frac{A}{\beta}\right)-\frac{E}{RT} \qquad (1)$$

$$\ln\left[\frac{g(\alpha)}{T^2}\right]=\ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT} \qquad (2)$$

where α is the degree of conversion, A is the pre-exponential factor, E is the activation energy, R is the gas constant, β is the heating rate, and T is the temperature. The α values were obtained from the ratio of the mass loss at any instant to the total loss in mass in the plateau region at about 500 K in the TG curves. The algebraic expressions of the functions $f(\alpha)$ and $g(\alpha)$ for the investigated kinetic models are presented in Table 2.

If the left side of Eqs (1) or (2) is plotted against $1/T$, the activation energy can be obtained from the slope, and A from the intercept. Estimated values of E and A and the linear regression coefficient r are listed in Table 3. The values presented were obtained from the tested equations which best fitted the experimental TG curves.

From Table 3, it can be seen that the kinetic models selected as best fitting the dehydrations of the complexes, were the same with the two tested methods. The

Table 2 Kinetic equations examined

Equation type	$f(\alpha)$	$g(\alpha)$
Based on order of reaction		
F1 first-order	$(1-\alpha)$	$-\ln(1-\alpha)$
F2 second-order	$(1-\alpha)^2$	$1/(1-\alpha)$
F3 third-order	$0.5(1-\alpha)^3$	$[1/(1-\alpha)]^2$
Based on diffusion mechanism		
D1 one-dimensional	$1/2\alpha$	α^2
D2 two-dimensional	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
D3 three-dimensional	$1.5(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
D4 Ginstling-Brounshtein	$1.5[(1-\alpha)^{1/3}-1]^{-1}$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$
Based on geometrical models		
R2 contracting area	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
R3 contracting volume	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$

activation energy values calculated for a particular model with the differential and the integral methods are not the same, but they are close to one another. The activation energies calculated for a particular complex with the different kinetic models differ, in some cases significantly. For example, the activation energy obtained for the Pr(III) complex with the D3 model is twice as high as that obtained with the R2 model (Table 3). However, the E values obtained with the diffusion models D2, D3 and D4 for a particular complex are in good agreement. The difference does not exceed 15%.

The diffusion processes (D3, D4 or D2) seem to be the most appropriate as the rate-controlling step. This is to be expected because the dehydrations of lanthanide 2-amino-4-chlorobenzoates proceed at temperatures above 400 K. At temperatures higher than the boiling point of water, the rate of evaporation of water from solid compounds is very rapid and the diffusion of water molecules through the product layer controls the rate of reaction [9]. The shapes of the $(1-\alpha)$ *vs.* T curves (Fig. 1) are in good agreement with the theoretical curves presented by Elder [10] for diffusion kinetic models, with E=220 kJ mol^{-1} and log$A$= 15.10 min^{-1}. Only the shapes of the curves obtained for the Y(III), Gd(III) and Tm(III) complexes are a little different, and this finds expression in the kinetic results (Table 3). However, in these cases the diffusion model D3 is suitable, too.

The activation energy values calculated on the basis of the diffusion equations are high (140–280 kJ mol^{-1}). This fact, the high temperatures of dehydration and the shapes of the DTA curves (the sharp endothermic effect in the dehydration temperature range) (Table 1) confirm the assumption that the water molecule in

Table 3 Values of kinetic parameters calculated by using differential and integral methods

Lanthanide	Kinetic model	Range of α	Differential method			Integral method		
			E/kJ mol^{-1}	log$A$/min^{-1}	r	E/kJ mol^{-1}	log$A$/min^{-1}	r
Y	D3	0.12–0.85	272.0	19.20	0.98931	247.9	17.43	0.99311
	F3		229.4	25.93	0.99962	222.6	23.28	0.98838
	F2		155.1	17.38	0.99863	137.4	17.08	0.98774
La	D3	0.20–0.87	163.7	18.12	0.99961	185.0	21.94	0.99963
	D4		142.9	15.72	0.99912	165.5	19.61	0.99907
	D2		142.8	10.95	0.99892	155.9	9.12	0.99838
	D1		95.6	10.67	0.99397	127.2	8.29	0.98987
Pr	D3	0.20–0.75	220.4	24.32	0.99969	209.1	24.20	0.99943
	D4		201.1	22.16	0.99952	194.6	22.47	0.99991
	D2		188.7	21.14	0.99978	187.4	22.26	0.99997
	R3		112.8	12.22	0.99911	100.9	12.63	0.99939
	R2		102.4	11.15	0.99911	95.5	12.18	0.99981
Sm	D3	0.30–0.88	238.7	25.69	0.99929	–	–	–
	D4		217.3	23.33	0.99972	191.3	20.42	0.99704
	D2		209.3	22.84	0.99941	189.9	19.78	0.99813
	D1		159.9	17.40	0.99815	143.5	17.07	0.99961

Table 3 Continued

Lanthanide	Kinetic model	Range of α	Differential method			Integral method		
			E/kJ mol^{-1}	log$A$/min^{-1}	r	E/kJ mol^{-1}	log$A$/min^{-1}	r
Gd	D3	0.10–0.75	252.1	27.37	0.99961	260.1	22.58	0.99730
	F1		143.6	13.82	0.98366	158.5	15.17	0.99873
	R3		119.9	9.75	0.98753	121.2	6.73	0.99714
Dy	D3	0.13–0.88	275.9	23.34	0.99949	287.3	21.53	0.99956
	D4		249.9	22.53	0.99961	267.5	19.29	0.99911
	D2		237.0	20.52	0.99937	257.7	18.84	0.99847
	D1		194.4	20.94	0.99421	203.7	16.42	0.99583
	R3		–	–	–	139.8	16.20	0.99956
	R2		116.5	12.21	0.99848	132.5	15.57	0.99928
Tm	D3	0.22–0.87	176.9	16.46	0.99870	185.4	15.96	0.99717
	D4		160.5	13.52	0.99927	168.1	18.96	0.99476
	F1		93.9	12.22	0.98321	102.8	13.08	0.99877
Lu	D3	0.13–0.84	178.9	18.73	0.99965	196.9	21.99	0.99862
	D4		163.3	17.05	0.99942	182.8	20.36	0.99722
	D2		151.0	16.07	0.99937	175.8	20.21	0.99613
	D1		120.5	12.79	0.99424	148.5	18.51	0.99239
	F1		–	–	–	105.9	13.28	0.99916

the complexes is strongly bonded in the inner coordination sphere, in a hydrogen-bonding system.

The kinetic parameters of the dehydrations depend on many structural factors, e.g. the lengths of the metal–oxygen bonds, that undergo splitting the system of intra- and intermolecular hydrogen-bonds, the lattice energy, etc. [11, 12]. In general, the differences between the reactant and the product of the dehydration have the most important effect on the activation parameter value. In conclusion, the similar structures of the studied complexes are reflected by the similar mechanisms of dehydration. However, the activation energy values for the individual compounds differ significantly. This confirms earlier observations that it is impossible to estimate the values of kinetic parameters on the basis of the structure of the complex.

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