Journal of Thermal Analysis, Vol. 41 (1994) 889-897

STUDY OF THE THERMAL DECOMPOSITION KINETICS OF SOME RARE EARTH CARBONATES, FLUOROCARBONATES AND FLUOROOXALATES

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(Received September 12, 1993)

Abstract

The thermal transformations of Pr and La carbonates, La, Ce, Pr, Nd, Sm, Eu and Gd fluorocarbonates, and La, Nd, Dy and Ho fluorooxalates were investigated. A Derivatograph Q-1000 (MOM, Hungary) was used for thermal analysis. The kinetics of the processes was studied in a flow reactor. The activation energies and preexponential factors for dehydration and decarbonization were calculated. Samples of Pr fluorocarbonate, Ho fluorooxalate, and Pr and La carbonates were exposed to γ-irradiation (dose from $6.2 \cdot 10^6$ to $6.1 \cdot 10^7$ rad). The influence of the irradiation dose upon the kinetic parameters (E_a and A) of the processes was investigated.

Keywords: kinetics, rare earth carbonates, fluorocarbonates and fluorooxalates, thermal transformation

Introduction

The paper reports an investigation of the thermal transformation kinetics of Pr and La carbonates, La, Ce, Pr, Nd, Sm, Eu and Gd fluorocarbonates, and La, Nd, Dy and Ho fluorooxalates. Pr and La carbonates, Pr fluorocarbonate and Ho fluorooxalate were also exposed to γ-irradiation. The kinetic parameters of thermolysis of the rare earth carbonates were considered previously [1].

Experimental and discussion

The rare earth fluorocarbonates were obtained from the corresponding nitrate solutions by precipitating the carbonates with NH_4HCO_3, followed by

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fluorination with HF [2]. La fluorooxalate was prepared by mixing LaF_3 and a saturated solution of oxalic acid during a long period [3]. Nd fluorooxalate was synthesized by mixing an aqueous suspension of Nd fluorocarbonate and the calculated amount of $H_2C_2O_4 \cdot 2H_2O$ for 17 days [2].

Dy and Ho fluorooxalates were prepared by slowly pouring the corresponding nitrate solution into a stirred mixture of HF and $H_2C_2O_4$ solutions at 90°C. The concentration of the components in the initial solutions was 0.2 $mol \cdot dm^{-3}$, while the mole ratio of the components was $Ln^{3+}: F^-: C_2O_4^{2-} = 1:1:1$ [4, 5].

The compositions of the compounds obtained were determined by chemical analysis. The infrared spectra of the samples were recorded with a Brucker Infrared Furye-Spectrometer IFS-113 (in vaseline oil and KBr tablets).

The X-ray analysis was carried out with a DRON-2 diffractometer with filtered CuK_α radiation.

The sample irradiation was carried out with the j-plant MRX-j-20 in glass test-tubes closed with ground-glass stoppers and enveloped in aluminium foil. The γ-radiation was created by α ^{60}Co source. The dose rate in the side-chamber of the plant in which the samples were placed was 75 rad/sec, and the tempera-

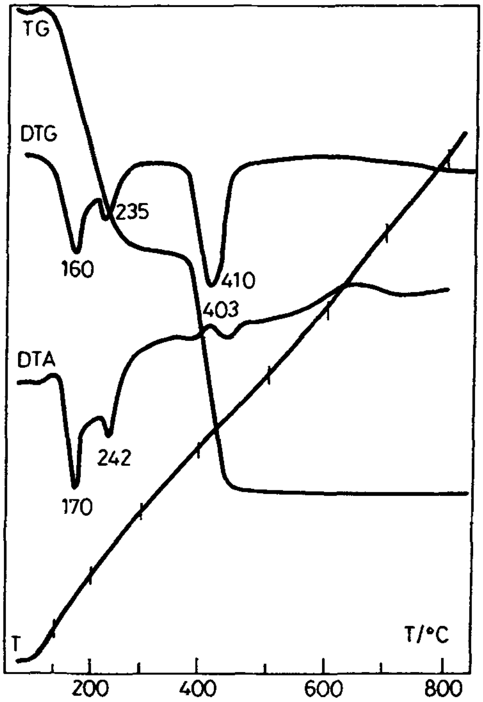

Fig. 1 Thermoanalytical curves of $HoFC_2O_4 \cdot 4H_2O$

ture was approximately 40°C. The test-tubes with the samples were exposed to γ-radiation during the calculated times equivalent to doses of $6.2\cdot10^6$ rad, $1.125\cdot10^7$ rad and $6.1\cdot10^7$ rad.

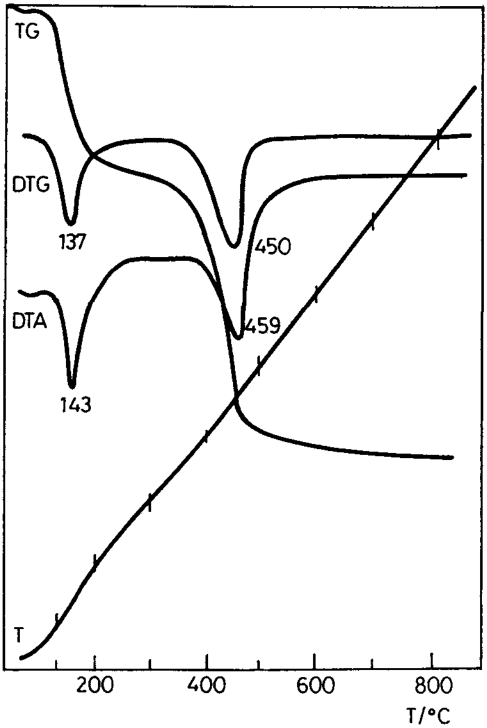

Fig. 2 Thermoanalytical curves of $PrFCO_3$

A Derivatograph Q-1000 (MOM, Hungary) was used for the thermal investigations. The samples mass was 200–300 mg, the heating rate was 10 deg·min^{-1}, and the atmosphere was air. Open quartz sample holders were used, with Al_2O_3 as reference material. The thermal curves obtained are presented in Figs 1 and 2. The kinetics of thermolysis of the compounds was studied under non-isothermal conditions of heating. A gas-flow reactor was used with a conductometric detector [6].

The sample had a mass of 10 mg, the heating rate was 5 deg·min^{-1}, and the helium flow rate was 60 cm^3/min. The kinetic analysis of the gas evolution curves was carried out by the integral method of Sestak and Satava with the computer program TA IB [6]. After tests of 13 kinetic equations (diffusion, nucleus formation, nucleus growth, and chemical reaction on the interphase

Table 1 Kinetic parameters of the first stage of dehydration of fluorooxalates $MFC_2O_4 \cdot nH_2O$

M	Equation	E_a / kJ·mol^{-1}	lg A / s^{-1}	T / °C
La	R3	106.8	11.7	70–134
Nd	R3	104.7	10.7	80–175
Dy	R3	107.2	12.4	53–119
Ho	R3	103.0	11.9	50–140

Table 2 Kinetic parameters of the second stage of dehydration of fluorooxalates $MFC_2O_4 \cdot nH_2O$

M	Equation	E_a / kJ·mol^{-1}	lg A / s^{-1}	T / °C
La	D5	257.9	30.6	99–165
Nd	–	–	–	–
Dy	R3	162.0	17.8	117–163
Ho	R3	173.8	16.3	160–240

boundary), we selected the equation best describing the process with linearity of the function lg $g(\alpha)$ *vs.* $1/T$.

La, Dy and Ho fluorooxalates undergo dehydration in two stages, whereas Nd fluorooxalate does so in one stage. The activation energy and preexponential factor data for the first step of the dehydration are given in Table 1. The equation best describing the process was the equation of a contracting sphere:

$$d\alpha/dt = k\,(1-\alpha)^{2/3} \text{ (mechanism R3)}$$

The values of the activation energy are close to one another for all compounds and lie in the range 103.0–107.2 kJ/mol. The values of the exponential factor (lg A) are 10.7 –12.4 / s^{-1}. The kinetic parameters for the second stage of fluorooxalate dehydration are listed in Table 2. For the Ho and Dy compounds, the equation best describing the process is again the equation of a contraction sphere (R3), while for La fluorooxalate it is the equation of three-dimensional diffusion:

$$d\alpha/dt = k[1-(1/(1-\alpha))^{1/3}]^{-1}\cdot(1-\alpha)^{4/3} \text{ (mechanism D5)}$$

The activation energies for the Ho and Dy salts are close to one another (173.8 and 162.0 kJ/mol, respectively, i.e. 1.5 times the activation energies for the first step of dehydration). The preexponential factors are 16.3 and 17.8 s^{-1}, respectively. The decomposition of the fluorooxalates investigated occurs in one stage and is described by the equation of a contracting sphere (R3) for the Nd, Dy and Ho compounds and by the equation of three-dimensional diffusion for the La compound.:

$$d\alpha/dt = k[(1+\alpha)^{1/3} - 1]^{-1}\cdot(1+\alpha)^{2/3} \text{ (mechanism D3)}$$

The activation energies are 443.4–551.0 kJ/mol, while the mean preexponential factors (lg *A*) are in the range 28.6–37.4 (Table 3). E_a and *A* decrease from Nd to Ho.

Table 3 Kinetic parameters of the decomposition reaction of fluorooxalates $MFC_2O_4\cdot nH_2O$

M	Equation	E_a / kJ·mol^{-1}	lg *A* / s^{-1}	*T* / °C
La	D3	528.0	35.4	372–489
Nd	R3	551.0	37.4	400–485
Dy	R3	525.9	34.9	406–510
Ho	R3	443.4	28.6	410–520

Thus, the dehydration of the fluorooxalates to the anhydrous fluorooxalates occurs in one in the temperature range 50–200°C. The kinetic parameters E_a and *A* change a little on variation of the metal. The decomposition proceeds in the range 370–520°C and is completed with the formation of oxyfluorides, LnOF. The formation of carbon according to the Buduar reaction is observed in all cases:

$$2CO \rightleftharpoons C + CO_2$$

The kinetic parameters decrease on replacement of Nd by Dy or Ho, while the temperature interval of the reaction is displaced to higher temperatures.

In contrast with the situation for the fluorooxalates and carbonates [1], the dehydration peaks in the gas evolution curves of the fluorocarbonates are weakly expressed, making their mathematical calculation impossible. We investigated only the decomposition process. Decarbonization of the fluorocarbonates proceeds in one stage and finishes with the formation of oxyfluorides (LnOF). The kinetic parameters of the process (E_a and *A*) are listed in Table 4. The sequence of kinetic stability of the fluorocarbonates according to the activation energy is as follows:

Table 4 Kinetic parameters of the decarbonization reaction of fluorocarbonates $MFCO_3$

M	Equation	E_a / kJ·mol^{-1}	lg *A* / s^{-1}	*T* / °C
La	R3	197.2	10.9	388–511
Ce	R3	233.6	13.3	388–520
Pr	R3	399.4	28.2	369–430
Nd	R3	92.9	4.6	252–417
Sm	R3	131.9	6.7	361–485
Eu	R3	176.3	9.8	386–492
Gd	D5	567.7	39.8	373–458
Ln	R3	168.7	11.3	282–387

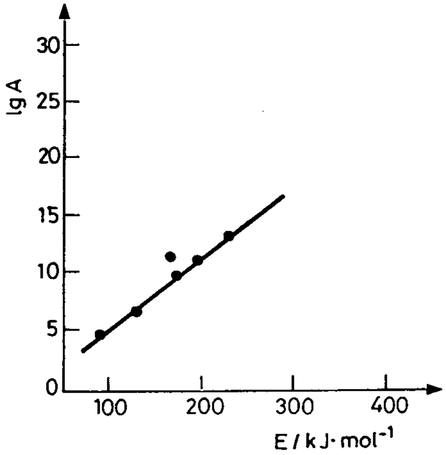

Fig. 3 The compensation dependence $\log A = aE + b$ of the decarbonization reaction of fluorocarbonates $MFCO_3$

Nd < Sm < Eu < La < Ce < Pr.

E_a and lg *A* for the decomposition of Nd fluorooxalate are larger than those for Nd fluorocarbonate: 551.0 kJ/mol and 92.9 kJ/mol, respectively. $NdFC_2O_4$ is kinetically more stable in the decomposition reaction than Nd fluorocarbonate, $NdFCO_3$. The compensation dependence is presented in Fig. 3.

As concerns the irradiated samples, we observed different regularities of the influence of the irradiation dose upon the kinetics of the processes investigated. For the dehydration of $Pr_2(CO_3)_3 \cdot 8H_2O$, it was noted that the type of kinetic equation R3 (chemical reaction on the interphase boundary), changed to D5 (three-dimensional diffusion). The temperature interval of the dehydration did not change. The data are given in Table 5.

Table 5 Kinetic parameters of the dehydration reaction of $Pr_2(CO_3)_3 \cdot nH_2O$

Irradiation dose / rad	Equation	E_a / kJ·mol^{-1}	lg A / s^{-1}	T / °C
initial	R3	46.9	2.7	67–204
$6.2 \cdot 10^6$	R3	52.8	3.3	86–223
$1.125 \cdot 10^7$	D5	151.6	15.4	79–215
$6.1 \cdot 10^7$	D5	129.0	12.8	65–221

Table 6 Kinetic parameters of the decarbonization reaction of $PrFCO_3$

Irradiation dose / rad	Equation	E_a / kJ·mol^{-1}	lg A / s^{-1}	T / °C
initial	R3	292.7	19.8	369–430
$6.2 \cdot 10^6$	R3	199.3	11.7	358–476
$1.125 \cdot 10^7$	R3	210.6	12.6	363–477
$6.1 \cdot 10^7$	R3	213.9	12.6	381–483

The irradiation influenced the kinetic parameters of decarbonization of $PrFCO_3$ (Table 6). The activation energy for the initial complex is 292.7 kJ/mol. This decreases to 199.3 kJ/mol following an irradiation dose of $6.2 \cdot 10^6$ rad, and subsequently remains almost constant. log A decreases from 19.8 to 11.7. The temperature interval of decarbonization is relatively constant. Irradiation of the sample does not influence the decarbonization of $La_2(CO_3)_3 \cdot 8H_2O$. The kinetic parameters are practically constant (Table 7).

Table 7 Kinetic parameters of the decarbonization reaction of $La_2(CO_3)_3 \cdot 8H_2O$

Irradiation dose / rad	Equation	E_a / kJ·mol^{-1}	lg A / s^{-1}	T / °C
initial	R3	316.1	18.4	422–545
$6.2 \cdot 10^6$	R3	324.5	18.9	440–543
$1.125 \cdot 10^7$	R3	344.2	20.0	442–553
$6.1 \cdot 10^7$	R3	304.0	17.3	436–551

$HoFC_2O_4 \cdot 4H_2O$ reveals three different kinds of influence of irradiation on the kinetics of dehydration and decomposition.

The values of E_a and lg A for the first stage of dehydration do not vary on irradiation and do not depend on the irradiation dose (Table 8). E_a is in the range 103.0–109.3 kJ/mol, and lg A in the range 11.9–12.8.

Table 8 Kinetic parameters of the first stage of dehydration of Ho fluorooxalates $HoFC_2O_4 \cdot 4H_2O$

Irradiation dose / rad	Equation	E_a / kJ·mol^{-1}	lg A / s^{-1}	T / °C
initial	R3	103.0	11.9	50–140
$6.2 \cdot 10^6$	R3	108.0	12.3	60–135
$1.125 \cdot 10^7$	R3	109.3	12.8	50–135
$6.1 \cdot 10^7$	R3	106.8	12.1	62–126

Table 9 Kinetic parameters of the second stage of dehydration of Ho fluorooxalates $HoFC_2O_4 \cdot 4H_2O$

Irradiation dose / rad	Equation	E_a / kJ·mol^{-1}	lg A / s^{-1}	T / °C
initial	R3	173.8	16.3	160–240
$6.2 \cdot 10^6$	R3	193.8	18.7	165–222
$1.125 \cdot 10^7$	R3	169.6	16.3	150–215
$6.1 \cdot 10^7$	R3	90.4	8.3	110–180

In the second stage of dehydration, E_a and lg A are practically unchanged on increase of the irradiation dose up to the maximum (Table 9), but in response to the maximum dose of $6.1 \cdot 10^7$ rad E_a falls sharply from 173.8 to 90.4 kJ/mol, i.e. it is nearly halved. The temperature interval moves to lower temperatures.

Table 10 Kinetic parameters of the decomposition reaction of Ho fluorooxalates $HoFC_2O_4 \cdot 4H_2O$

Irradiation dose / rad	Equation	E_a / kJ·mol^{-1}	lg A / s^{-1}	T / °C
initial	R3	443.4	28.6	410–515
$6.2 \cdot 10^6$	R3	369.7	23.3	405–518
$1.125 \cdot 10^7$	R3	368.4	23.2	410–525
$6.1 \cdot 10^7$	R3	587.0	37.9	438–525

Results on the decomposition of $HoFC_2O_4 \cdot 4H_2O$ are given in Table 10. E_a first decreases from 443.4 to 368.4 kJ/mol on increase of the irradiation dose and then rises to 587.0 kJ/mol following the maximum dose of irradiation. The value of log A changes analogously. The temperature interval of the reaction is displaced towards higher temperatures.

Thus, the irradiation dose exerts a complex effect upon the kinetic parameters (E_a and A) of the dehydration and decarbonization of the compounds studied.

Conclusions

The thermal transformations of some rare earth compounds have been investigated and kinetic data have been obtained. The sequence of kinetic stability of the fluorocarbonates as concerns decarbonization has been established. The influence of irradiation on the values of E_a and A has been studied.

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Zusammenfassung — Es wurden die thermischen Umwandlungen von Pr- und La-Karbonaten, von La-, Ce-, Pr-, Nd-, Sm-, Eu- und Gd-Fluorokarbonaten und von La-, Nd-, Dy- und Ho-Fluorooxalaten untersucht. Für die thermische Analyse wurde ein Derivatograph Q-1000 (MOM, Ungarn) verwendet. Die Kinetik des Prozesses wurde in einem Strömungsreaktor untersucht.Für Dehydratation und Dekarbonisierung wurden Aktivierungsenergie und präexponentieller Faktor ermittelt. Proben von Pr-Fluorokarbonat, Ho-Fluorooxalat sowie Pr- und La-Karbonat wurden einer *j*-Bestrahlung ausgesetzt (Dosis zwischen $6.2 \cdot 10^6$ und $6.1 \cdot 10^7$ rad). Der Einfluß der Strahlungsdosis auf die kinetischen Parameter (E_a und A) wurde untersucht.