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THERMAL DECOMPOSITION PROCESSES OF LANTHANIDE TRIFLUOROACETATES TRIHYDRATES

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Abstract

The thermal decomposition of several lanthanide salts $Ln(CF_3COO)_3\cdot 3H_2O$ (*Ln*=La, Gd, Tb) was studied under quasi-equilibrium conditions and under linear heating. According to mass spectral data, H_2O is the single product of thermal decomposition up to 120–140°C. Thermogravimetric data were processed with 'Netzsch Thermokinetics' computer program. Kinetics parameters of the first decomposition step (as the simple dehydration process, not complicated by the water hydrolysis with the liberation or the decomposition of the organic ligand) were calculated.

Keywords: coordination compounds, 'model free' kinetics, quasi-equilibrium thermogravimetry

Introduction

The detailed structures of these compounds are known: the La-complex has two-dimensional polymeric structure, CF_3COO^- anions are coordinated (by oxygen atoms) as a bridge ligands, two water molecules are coordinated, the third one occupies a lattice site, so the lanthanum coordination number is eight [1, 2]. The Gd- and Tb-complexes are binuclear: four CF_3COO^- anions are bidentate bridge ligands, two are monodentate ones, all water molecules are coordinated, so the lanthanide coordination number is eight [3].

It has been established that compounds of Tb and Gd have luminescent properties, connected with the energy transfer from the ligand to the lanthanide cation [4–6]. The intensity of the luminescence depends on the partial dehydration of the salts. So it is important to understand, are any dehydration steps accompanied with possible partial hydrolysis:

$$[Ln_2(CF_3COO)_6(H_2O)_n]\leftrightarrow[Ln_2(CF_3COO)_5(CF_3COOH)(H_2O)_{n-1}(OH)]$$

The dehydration of these compounds was studied earlier, but under linear heating only [7].

The thermoanalytical investigation of metal complexes with carboxylic acids is the traditional subject of their characterization (e.g., recent works, [8–11]), but the study under quasi-equilibrium conditions are rare events.

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Experimental

Compounds $Ln(CF_3COO)_3 \cdot 3H_2O$ (*Ln*=La, Gd, Tb) were synthesized according to the known methods: compounds Tb and Gd have been prepared from chloride lanthanides through the precipitation stage with ammonia, obtained lanthanides hydroxides were filtered and dissolved in trifluoroacetic acid (TFA) [7]. It is known that Gd and Tb salts have absorption line of 1715–1720 cm^{-1} in IR-spectra [7], this can confirm the –COOH presence in the salts. La-salt was obtained by direct reaction between the lanthanum oxide and TFA acid [4].

Thermal decomposition was studied by means of Derivatograph Q-1500-D (MOM, Hungary). Quasi-equilibrium thermogravimetry was used for the investigation of step-by-step character of the thermal dissociation processes and for the attempt to check the stable intermediate phases [12]. Different sample holders were used, sample mass was 200 mg, constant mass loss rate was 0.4 mg min^{-1}, atmosphere – static air.

Kinetics studies were carried out under different conditions: sample mass was 140 mg, a sample holder was plate-like crucible; heating rates were 2,5; 5 and 10°C min^{-1}, helium flow rate was 120 cm^3 min^{-1}.

Thermogravimetric data were processed with the computer program 'Netzsch Thermokinetics' (version 2001.9d). So as the decomposition follows the dehydration step for all salts, we select the convenient variant of calculation. Special program module 'Model free' allows processing several thermogravimetric curves, obtained with different heating rates, without the information about the kinetic topochemical equations. Program 'ASTM E698' [13] enables to calculate the averaged values of activation energy and preexponential factor according to temperatures of maximum rate. Program 'Friedman analysis'[14] allows calculating both the activation energies, and preexponential factors (assuming a first-order reaction) for every experimental point of fractional conversion, program 'Ozawa–Flynn–Wall analysis'[15–17] allows calculating only activation energies for every experimental point (in the interval $0.02<\alpha<0.98$). The same set of experimental data is used further for searching the topochemical equation (the selection from 16 equations (chemical reaction on the interface, nucleation, and diffusion). This calculation is made by the improved differential method of Borchardt–Daniels, with multiple linear regression method [18]. It is very important, that the interval of conversion degree (α) for this calculation can be chosen on the relative constancy of the calculated kinetic parameters from 'Friedman analysis' or 'Ozawa–Flynn–Wall' analysis. *F*-test is used for the search of the best kinetic description. If the calculation results in two or three kinetics equations with near values of correlation coefficients (or *F*-test), but with noticeably different values of kinetics parameters, it is rationally to choose the equation with parameters values near to data of 'Model free' module programs.

The mass spectra were recorded on an MI-1201 mass spectrometer with a modified design of the molecular beam source [19].

Results and discussion

According to mass spectral data, H_2O is the single product of thermal decomposition of $La(CF_3COO)_3 \cdot 3H_2O$ up to 140°C, of $Gd(CF_3COO)_3 \cdot 3H_2O$ up to 120°C and of $Tb(CF_3COO)_3 \cdot 3H_2O$ up to 140°C. So we can calculate kinetic parameters of the first decomposition step as for the simple dehydration process, not complicated by the water hydrolysis with the liberation (or the decomposition) of the organic ligand.

$[La(CF_3COO)_3(H_2O)_2] \cdot H_2O$

Under quasi-equilibrium conditions (in plate-like sample holder) the decomposition is multi-step process with one noticeable stable phase: $La(CF_3COO)_3 \cdot 0.5H_2O$. The decomposition of this phase started at 125°C.

Thermogravimetric curves, obtained with different rates of linear heating, were processed by ‘Friedman analysis’ and ‘ASTM E698’ programs. The kinetic parameters of the first decomposition step were calculated by Borchardt–Daniels method, the region of conversion ($0.25<\alpha<0.65$) was selected from the ‘Model free’ data (on the kinetic parameters constancy). The checking equations: A2, R3, D3; the best one: R3, the contracted sphere equation, $f(\alpha)=(1-\alpha)^{0.67}$, $E_a=61$ kJ mol^{-1}, $\log A=6.8$.

The ‘ASTM E698’ gives $E_a=82.9$ kJ mol^{-1}, $\log A=10.9$.

$[Tb_2(CF_3COO)_6(H_2O)_6]$

Under quasi-equilibrium conditions (in plate-like sample holder) the first step of dehydration (60–100°C) is the loss of four water molecules, the loss of mass of the next step (120–140°C) of decomposition corresponds quantitatively more than two water molecules, so the second dehydration step is accompanied by the organic ligand involvement in the decomposition (not unlikely with partial water hydrolysis). It is interesting that the formed ‘anhydrous’ phase is practically stable up to 225°C (Fig. 1).

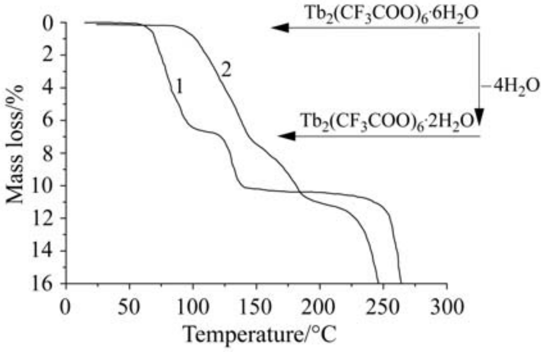

Fig. 1 TG curves of $[Tb_2(CF_3COO)_6(H_2O)_6]$. 1 – heating under quasi-equilibrium conditions (plate-like sample holder, sample mass 200 mg, $q=0.4$ mg min^{-1}, atmosphere: static air). 2 – linear heating (plate-like sample holder, sample mass 140 mg, 5°C min^{-1}, He flow: 120 cm^3 min^{-1})

It is clearly seen, that it is impossible to say something certain about the intermediate phases composition, if the heating is linear.

Thermogravimetric data, being obtained under linear heating (5 and 10°C min^{-1}), were processed by 'Friedman analysis' and 'ASTM E698' programs. The kinetic parameters for the first decomposition step were calculated by Borchardt–Daniels method, the region of conversion ($0.20<\alpha<0.80$) was selected from the 'Model free' data (on the kinetic parameters constancy). The checking equations: F1, Fn, An, CnB, R3, D3; the best one: F1, $f(\alpha)=(1-\alpha)$, nucleation equation of the first reaction order, E=73 kJ mol^{-1}, log$A$=8.3.

The 'ASTM E698' gives E_a=91.9 kJ mol^{-1}, log$A$=11.1.

[$Gd_2(CF_3COO)_6(H_2O)_6$]

Under quasi-equilibrium conditions (in plate-like sample holder) the first step of dehydration (60–90°C) is the lost of three water molecules, the next one (90–110°C) – the lost of one water molecule; they are poorly divided. $Gd_2(CF_3COO)_6{\cdot}2H_2O$ is stable up to 125°C, it is evident that organic ligand takes part in the subsequent decomposition process (Fig. 2).

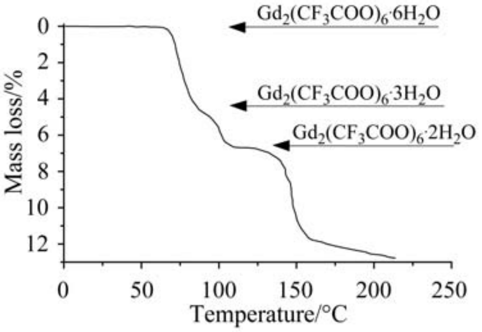

Fig. 2 TG curves of [$Gd_2(CF_3COO)_6(H_2O)_6$] under quasi-equilibrium conditions (plate-like sample holder, sample mass 200 mg, q=0.4 mg min^{-1}, atmosphere: static air)

Thermogravimetric data (being obtained under linear heating with 5°C min^{-1}) was processed. The kinetics parameters for the first decomposition step were calculated for the selected region of conversion ($0.3<\alpha<0.8$). The checking equations: A1, A2, R3, D3; the best one: R3, the contracted sphere equation, $f(\alpha)=(1-\alpha)^{0.67}$, E_a=67 kJ mol^{-1}, log$A$=6.1.

We have studied single samples of compounds and so we did not calculate random errors; the estimated error of E_a and log$A$ values is about 5–7%.

Conclusions

Thermal decomposition of lanthanide compounds $Ln(CF_3COO)_3{\cdot}3H_2O$ (*Ln*=La, Gd, Tb) was studied. The first step is not accompanied by the ligand decomposition or free acid liberation. The kinetics of the first step of dehydration was studied. Kinetics of the dehydration process is described by different equations: contracted sphere, nucleation (n=1). It can be connected with different activation mechanism.

It is worth to note, that programs ‘Friedman analysis’ and ‘Ozawa–Flynn–Wall analysis’ (in program module ‘Model free’) were better for our goals for the region of conversion selection. The end of the first step and the beginning of the second step are divided not enough, so the maximum rate of the first step is distinctly displaced. The program ‘ASTM E698’ calculates the averaged values of activation energy and preexponential factor according to temperatures of maximum decomposition rate. So the calculated activation energy values are noticeably overstated.

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