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THE KINETICS OF THERMAL DECOMPOSITION OF BISMUTH OXOHYDROXOLAURATE

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The bismuth salt of lauric (dodecanic) acid $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6$ was studied earlier. This salt has layer structure (the interlaminar distance=37.50 Å), under heating this liquid-crystalline state has the mesomorphic transformation, turns to the amorphous state, decomposes stepwise with the formation of well-ordered layers of bismuth nanoparticles. DSC-curves were used for the study of the decomposition kinetics in the area of decomposition with small mass loss and exothermic effect (423–483 K).

Keywords: *bismuth, coordination compounds, 'model free' kinetics*

Introduction

The hydroxo-salt of lauric (dodecanic) acid: $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6$ was studied earlier [1].

Bismuth oxohydroxolaurate $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6$ has layer structure, the interlaminar distance=37.50 Å, under heating this liquid-crystalline state has the mesomorphic transformation, turns to the amorphous state, decomposes stepwise with the formation of well-ordered layers of bismuth nanoparticles [2].

The beginning step of chemical transformations under heating proceeds inside polyatomic cation layers with lauric (dodecanic) acid elimination (403–483 K), lauryl ketone evolves later.

This compound decomposes (with mass loss ≈40%) under quasi-isothermal conditions in two steps: $\Delta m_1\approx14\%$ (373–533 K) and $\Delta m_2\approx26\%$ (533–673 K). Experimental conditions: the standard open crucible, sample mass 100 mg, constant mass loss rate 0.4 mg min^{-1}, atmosphere – helium (120 cm^3 min^{-1}).

Linear heating and plate-like sample holder were used for kinetic studies; sample mass was 20 mg, heating rate 2.5, 5 and 10 K min^{-1}; helium flow 120 cm^3 min^{-1}. The mentioned temperature intervals change (so as the kinetic stability of intermediates governs the process), and the first temperature interval (14% of mass loss) becomes multi-step one.

There are three decomposition steps:

- The decomposition with small mass loss and endothermic effect (353–403 K, if *m*=10 mg);
- The decomposition with small mass loss and exothermic effect (423–483 K);
- The decomposition with noticeable mass loss and inessential heat effect (473–553 K); we studied the kinetics of the decomposition at 373–533 K; the constancy of the activation energy was observed at 50–90% of decomposition degree (that is 473–553 K interval). The final results: E=44–46 kJ mol^{-1}; lg$A$=1.2–2.0 [1].

In general the stages resolution of the multi–step decomposition can be quite different (better or worse) on TG or DSC curves. The steps contributions in the mass loss sum and in the heats sum are different because of the difference in molar mass of evolved gases and in reactions molar enthalpy. So we tried to obtain the kinetic parameters of the very initial stage of decomposition (353–483 K), by processing the DSC data of this reaction.

Experimental

The synthesis of the salt was described earlier [1].

DSC curves and TG curves (Figs 1, 2) were obtained by means of thermoanalyzer Netzsch STA 449C; experimental conditions: sample mass was about 10 mg (DSC) or 60 mg (TG), standard aluminum sample holder for DSC measurement (the lid with holes), helium flow 30 cm^3 min^{-1}. We used for the calculation only the big DSC peak.

The temperature interval of this exo effect (403–463 K at 3 K min^{-1}) corresponds to the very beginning of the decomposition on TG curve (full $\Delta m\approx1.2\%$ only, Fig. 1). We did not succeed in the calculation of kinetic parameters according to TG curves

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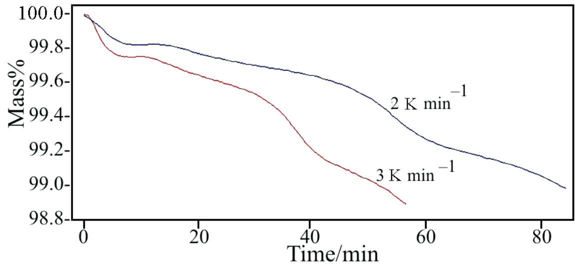

Fig. 1 TG curves of $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6$; sample mass 60.29 mg, helium flow 30 cm^3 min^{-1}, heating rates 2 and 3 K min^{-1}

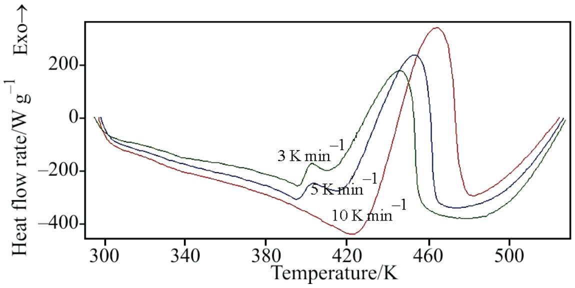

Fig. 2 DSC curves of the $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6$; sample mass 10.0 mg, standard aluminum sample holder (the lid with holes), helium flow 30 cm^3 min^{-1}, heating rates 3, 5 and 10 K min^{-1}

(2, 3, 5 and 10 K min^{-1}) because of the improper steps resolution, so we tried to use DSC curves.

We used 'Model free' approach for the kinetic study. It is worth to remind that the 'Model free' approach in kinetics is connected with classical and important works of Kissinger, Ozawa, Friedman, Anderson, Flynn and Wall [3–7]. The following active penetration of the iso-conversion method into the daily job of thermo-analysts is connected with works of Vyazovkin. His early works [8, 9] already included the computer program for such calculations.

DSC data were processed using the computer program 'Netzsch Thermokinetics' (version 2001.9d). Special program module 'Model free' allows processing several DSC curves, obtained with different heating rates, without the information about the kinetic topochemical equations. Programs 'Ozawa–Flynn–Wall Analysis' and 'Friedman Analysis' allow calculating activation energies for the every experimental point of fractional conversion (in the interval $0.02<\alpha<0.98$, conjointly from three curves). The same set of experimental data was 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 linear regression. F-test is used for the search of the best kinetic description [10, 11].

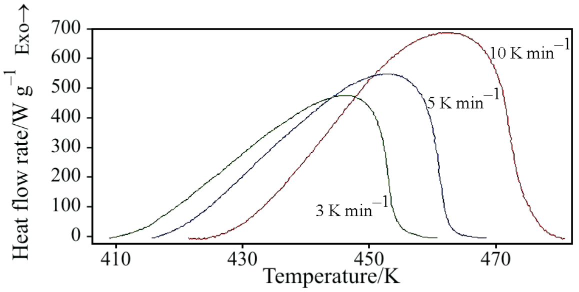

Fig. 3 DSC curves of the $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6$, used for the kinetic calculations, heating rates 3, 5 and 10 K min^{-1}

Results and discussion

Data of three DSC curves (Fig. 3), obtained under linear heating (3, 5 and 10 grad min^{-1}), were processed both by Friedman Analysis, and Ozawa–Flynn–Wall Analysis. The constancy of the activation energy exists in the fractional conversion interval 20–80%, E_a=103±1 kJ mol^{-1} (Fig. 4).

Kinetic parameters for the first decomposition step were calculated by Borchardt–Daniels regression method (for the selected region of conversion: $0.20<\alpha<0.80$). The checking equations: Fn, CnB, Bna, R2, D3, A3. The equations Fn (n=0.54±0.3), CnB and

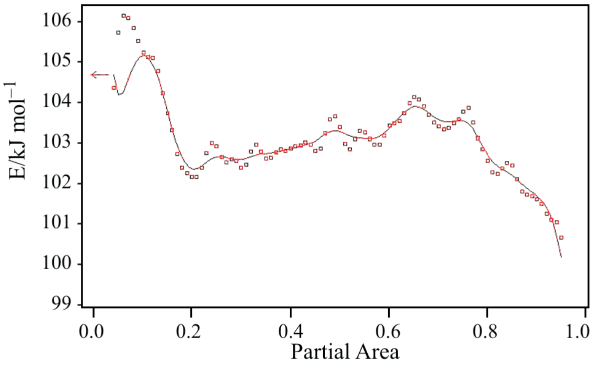

Fig. 4 Friedman analysis for bismuth oxohydroxolaurate $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6$ decomposition. Activation energy depending on the degree of conversion

Table 1 Compound $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6$. Data of F-test on fit-quality (for the search of the best kinetic description, α=0.20–0.80)

#	Code	Type	F_{act}	F_{exp}	F_{crit} (0.95)	Corr. coeff.
1	S	Fn	332	1.00	1.20	0.98960
2	S	CnB	331	1.00	1.20	0.98960
3	S	R2	333	1.10	1.20	0.98847
4	S	Bna	331	1.29	1.20	0.09896
5	S	D3	333	30.69	1.20	
6	S	A3	333	164.50	1.20	

Table 2 Compound $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6$. List of parameters and standard deviations for the Fn equation

#	Parameter	Inital value	Optimal value	Standard dev.
1	$\log A/s^{-1}$	8.942	9.9735	0.0378
2	E_1/kJ mol^{-1}	98.6349	105.5470	0.4127
3	Reaction order	0.6245	0.5443	0.0302

R2 are indistinguishable by F-test (the autocatalysis contribution is small), E_a=106±1 kJ mol^{-1}, log$A$=10.0±0.5 (Tables 1, 2). Correlation coefficients are neighbors too (0.9885–0.9896). The equation of the contracting cylinder is more probable. There is no diffusion hindrance in the process kinetics.

Conclusions

The exothermic effect (393–473 K) corresponds to very small mass loss, so the studied process kinetics is connected in majority with the structure lattice reconstruction but not with the noticeable decomposition process (the redox reaction) itself.

This step of chemical transformations under heating proceeds inside polyatomic cation layers with lauric (dodecanic) acid elimination (403–483 K) [2].

The equation of the contracting cylinder can be connected with the compound structure: arrangements of long chains $-CH_2-$ in its crystal structure.

It is turned out that the stages resolution for this studied multi-step reaction is better in DSC curves (because of the difference in molar mass of evolved gases and in reactions molar enthalpy). Just therefore it is worth to draw attention to the enlargement of experimental data set for kinetic calculations. TG curves are now traditional for such studies [12–14]. The importance of the DSC (and DMA) curves for kinetic studies is confirmed by recently published works [15–19].

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