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THERMAL DECOMPOSITION OF BISMUTH LAURATES
Study of process kinetics

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Three bismuth compounds of lauric (dodecanic) acid: $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6$, $Bi_6O_4(OH)_4$ $(C_{11}H_{23}COO)_6\cdot nC_{11}H_{23}COOH$ and $Bi(C_{11}H_{23}COO)_3$ were synthesized. The thermogravimetry under quasi-isothermal conditions denotes the multi-step character of decomposition processes for compounds. Non-isothermal thermogravimetric data (obtained at two different rates of linear heating) were used for kinetic studies. Kinetic parameters were calculated only for chosen decomposition steps.

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

Introduction

Bismuth carboxylates are widely used in the synthesis of different bismuth oxide materials (such as superconductors, catalysts) and drugs (medication 'dermatol'– is bismuth hydroxogallate) [1].

The thermal decomposition of metal salts of carboxylic acids is widely studied [2–6]. It is known, that such decomposition is the perspective way to product the nano-particles of metals [7]. So, having this in view, we have synthesized and studied bismuth laurates of different composition.

Experimental

Two compounds (the bismuth oxohydroxolaurate and its solid solution with lauric acid): $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6$ and $Bi_6O_4(OH)_4$ $(C_{11}H_{23}COO)_6\cdot nC_{11}H_{23}COOH$, were synthesized by the precipitation from the water solutions. The water solution of bismuth perchlorate was added to the water suspension of the lauric acid (heated up to 60°C); the obtained mixture was mixed up during 1 h. The precipitate (after 1 h assertion) was filtered, washed by distilled water and aired. The bismuth oxohydroxolaurate was washed clean from the unreacted lauric acid by the ethanol and aired. The synthesis of the neutral salt $Bi(C_{11}H_{23}COO)_3$ was carried out by the interaction of stoichiometric quantities of bismuth oxide and the molten lauric acid (the response time was 12 h at 60°C).

The study of thermal decomposition was performed by means of Derivatograph Q-1500-D (MOM, Hungary). Quasi-isothermal heating was used for the checking of the step-by-step character of thermal decomposition processes [8]; the standard open crucible was used as the sample holder, sample mass was 100–110 mg, constant mass loss rate was 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°C min^{-1}; helium flow 120 cm^3 min^{-1}.

Thermogravimetric data were processed using the computer program 'Netzsch Thermokinetics' (version 2001.9d). So as the thermal decompositions are multi-step processes for all compounds, 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. Two different programs were used: 'Ozawa–Flynn–Wall Analysis' [9–11] (utilizing the dependence lg of heating rate *vs.* $1/T$) and 'Friedman Analysis' [12] (utilizing the dependence $\lg d\alpha/dt$ *vs.* $1/T$). They allow calculating the activation energies for the every experimental point of fractional conversion (in the interval $0.02<\alpha<0.98$, conjointly from several 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, Table 1). This calculation is made by the improved differential method of Borchardt–Daniels with

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Table 1 Bismuth laurate (solid solution) $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6.\ nC_{11}H_{23}COOH$. Data of F-test on fit–quality (for the search of the best kinetic description, α=0.30–0.80)

#	Code	Type	*F* act	*F* exp	*F* crit (0.95)
1	S	R3	23	1.00	2.02
2	S	C1B	22	1.57	2.04
3	S	Bna	21	3.15	2.06
4	S	D3	23	54.29	2.02
5	S	A3	23	342.01	2.02

Table 2 Bismuth laurate $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6.nC_{11}H_{23}COOH$. List of parameters and standard deviations (for the R3). Correlation coefficient is 0.998923

#	Parameter	Initial value	Optimal value	Sign	*T* standard dev.
1	$\log A/s^{-1}$	2.1988	1.2386		$6.7\cdot10^{-3}$
2	E_1 /kJ mol^{-1}	48.7603	44.0810	+	0.8151

multiple linear regression [13]. F-test is used for the search of the best kinetic description [14]. If the calculations result 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.

Results and discussion

The thermogravimetry under quasi-isothermal conditions denotes the multi–step character of decomposition processes for all compounds. These steps moved to higher temperatures under linear heating. So as the molar masses of the removing gases are different, reactions are apparently consecutive, we did not try to divide the steps and did not go beyond the study of the first step only. So as the processes are complex and multi-step, the calculated kinetic parameters are rank values. 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 for these irreversible reactions is about 5–7%.

$Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6{\cdot}nC_{11}H_{23}COOH$– solid solution of bismuth oxohydroxolaurate and lauric acid

This solid solution decomposes under quasi–isothermal conditions in three steps (80–250, 250–320 and 320–420°C).

Data of two thermogravimetric curves, obtained under linear heating (5 and 10°C min^{-1}), were processed by 'Friedman Analysis' and 'Ozawa–Flynn–Wall Analysis'. The comparative constancy of the activation energy exists in the conversion degree interval 30–80%, E_a=43–48 kJ mol^{-1} (Fig. 1).

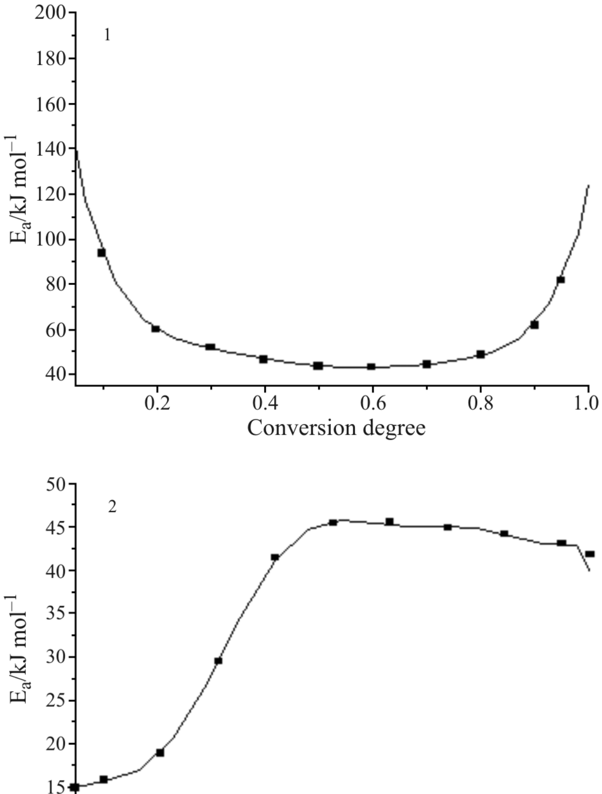

Fig. 1 Ozava–Flynn–Wall analysis for two bismuth laurates decomposition. 1 – solid solution $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6{\cdot}nC_{11}H_{23}COOH$, 2 – bismuth oxohydroxolaurate $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6$

Kinetic parameters for the first decomposition step were calculated by Borchardt–Daniels method for the selected region of conversion ($0.30<\alpha<0.80$). The checking equations: C1B, Bna, R3, Fn, D3, A3; equations R3, Fn (n=0.65) and C1B are closely ap-

Table 3 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=0.50–0.90)

#	Code	Type	*F* act	*F* exp	*F* crit. (0.95)
1	S	Fn	14	1.00	2.49
2	S	Bna	13	1.08	2.57
3	S	C1B	14	1.18	2.49
4	S	R3	15	4.21	2.43
5	S	D3	15	28.76	2.43
6	S	A3	15	263.34	2.43

Table 4 Compound $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6$. List of parameters and standard deviations (for the Bna, Prout–Tompkins equation, with autocatalysis). Correlation coefficient is 0.99759

#	Parameter	Initial value	Optimal value	Sign	*T* standard dev.
1	$\log A/s^{-1}$	2.0278	2.0128		0.2413
2	E_1 /kJ mol^{-1}	45.7306	44.0810	+	0.8767
3	Reaction order 1	0.5339	0.8348	+	0.3360
4	Exponenta1	0.3862	$7.6\cdot10^{-6}$	+	0.2815

proximated by F-test, E_a=44–46 kJ mol^{-1}, $\log A$=1.2–2.0 (Tables 1 and 2). Correlation coefficients are neighbors too (0.9989, 0.9983 and 0.9987).

$Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6$ – bismuth oxohydroxolaurate

This compound decomposes under quasi–isothermal conditions in two steps (100–260 and 260–400°C).

Data of two thermogravimetric curves, obtained under linear heating (2.5 and 10°C min^{-1}), were processed by 'Friedman Analysis' and 'Ozawa–Flynn–Wall Analysis'. The constancy of the activation energy exists in the fractional conversion interval 50–90%, E_a=42–45 kJ mol^{-1} (Fig. 1).

Kinetic parameters for the first decomposition step were calculated by Borchardt–Daniels method for the selected region of conversion ($0.50<\alpha<0.90$). The checking equations: Fn, Bna, C1B, R3, D3, A3; equations Fn (n=0.88), Bna and C1B are indistinguishable by F-test, E_a=44–46 kJ mol^{-1}, $\log A$=1.2–2.0 (Tables 3–4). Correlation coefficients are neighbors too (0.9977, 0.9976 and 0.9975).

$Bi(C_{11}H_{23}COO)_3$ – bismuth laurate

The normal salt decomposes under quasi-isothermal conditions in two steps (100–340 and 340–400°C).

Data of two thermogravimetric curves, obtained under linear heating (5 and 10°C min^{-1}), were processed by 'Friedman Analysis' and 'Ozawa–Flynn–Wall Analysis'. There is really no constancy of the calculated activation energy during the first decomposition step (Fig. 2). This can point to the existence of several parallel–serial reactions or the additional phase transformation in this temperature region.

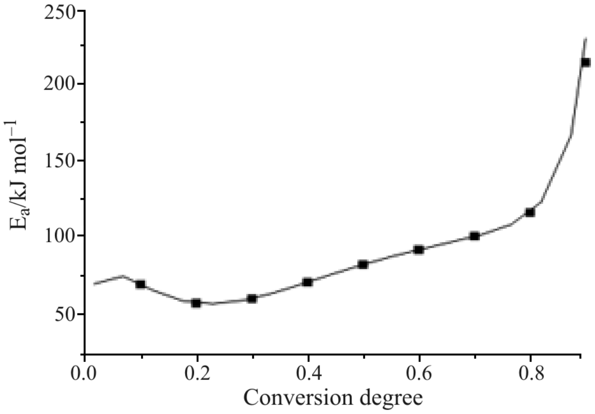

Fig. 2 Ozawa–Flynn–Wall analysis for bismuth laurate decomposition: normal salt $Bi(C_{11}H_{23}COO)_3$

Conclusions

Thermal decomposition of three synthesized bismuth laurates was studied. Decomposition processes are complex, so the kinetics of the process (for the first step) can be studied (and calculated) only for bismuth oxohydroxo-derivatives: $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6\cdot nC_{11}H_{23}COOH$ and $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6$.

Kinetic parameters, obtained from non–isothermal data, are conventional ones and cannot be interpreted in the terms of reaction mechanism. Nevertheless the changes of these parameters in specially formed series can open slightly the understanding of the decomposition processes. The first steps of the decomposition of the bismuth oxohydroxolaurate and its solid solution with lauric acid (under linear heating) are located in rather similar temperature intervals: 80–302 and 105–285°C, the calculated kinetic parameters are close to each other (E_a=43–46 kJ mol^{-1}, lg$A$=1.2–2.0). The possible explanation: initial redox decomposition reactions can be identical (progressing in $Bi_6O_4(OH)_4L_6$ coordination sphere), and free lauric acid in the solid solution does not participate in it directly, although the topochemical equations are different. Metallic bismuth, appearing in the first decomposition step, can catalyse the process (C1B equation).

It is worth to mention that the first decomposition step of similar bismuth oxohydroxostearates $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6 \cdot nC_{17}H_{35}COOH$ (solid solution, as well) and $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6$ take place at 20–400°C, topochemical equations: nucleation and nucleation with autocatalysis, the activation parameters are distinctly higher and diverse (E_a=72 kJ mol^{-1}, logA_1=3.6 and E_a=93 kJ mol^{-1}, logA_2=5.3, accordingly) [15]. The principal difference in compounds composition lies only in the hydrocarbon chain length ($C_{11}H_{23}COOH$ and $C_{17}H_{35}COOH$).

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