

Peculiarities of the Thermal Decomposition of Bismuth and Silver Carboxylates

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Abstract – Thermal decomposition of bismuth and silver carboxylates was studied (TG, DSC, mass-spectrometry, X-ray analysis, electron microscopy). Non-isothermal thermogravimetric data (obtained at two different rates of linear heating) were used for kinetic studies. All decomposition processes have multi-step character.

1. Introduction

Bismuth carboxylates are widely used in the synthesis of different bismuth oxide materials (such as superconductors, catalysts) and drugs. Silver carboxylates are used in photothermographic materials.

The thermal decomposition of metal salts of carboxylic acids is widely studied [1–3]. It is known, that such decomposition is the perspective way to product the nano-particles of metals. So, having this in view, we have synthesized and studied bismuth laureates, bismuth stearates and silver acetate of different composition.

2. Experimental

The salt AgCH_3COO was synthesized by the reaction of silver carbonate with glacial acetic acid at 45–60°C; the precipitate was filtered after cooling [4]. Five bismuth compounds were synthesized.

Two compounds (the bismuth oxohydroxolaurate and its solid solution with lauric acid): $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{11}\text{H}_{23}\text{COO})_6$ and $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{11}\text{H}_{23}\text{COO})_6 \cdot n\text{C}_{11}\text{H}_{23}\text{COOH}$, were synthesized by the precipitation from the water solutions.

The synthesis of the neutral salt $\text{Bi}(\text{C}_{11}\text{H}_{23}\text{COO})_3$ was carried out by the interaction of stoichiometric quantities of bismuth oxide and the molten lauric acid (the response time was 12 hours at 60°C).

Two compounds with different compositions, the bismuth oxohydroxostearate $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{17}\text{H}_{35}\text{COO})_6$ and its solid solution with stearic acid $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{17}\text{H}_{35}\text{COO})_6 \cdot n\text{C}_{17}\text{H}_{35}\text{COOH}$, were synthesized by the precipitation from the acidic solutions of the salts (pH = 1; $t^\circ = 80^\circ\text{C}$). The first one – with molar ratio sodium stearate/bismuth ion = 1/1, the second one – with molar ratio sodium stearate/bismuth ion = 3/1. $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{17}\text{H}_{35}\text{COO})_6 \cdot n\text{C}_{17}\text{H}_{35}\text{COOH}$ is the solid solution of the oxohydroxostearate with stearic acid.

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; the standard open crucible was used as the sample holder, sample mass was 100–110 mg, constant mass loss rate was 0,4 $\text{mg}\cdot\text{min}^{-1}$, atmosphere – helium (120 $\text{cm}^3\text{min}^{-1}$). Linear heating and plate-like sample holder were used for kinetic studies; sample mass was 20⁻¹⁰⁰ mg, heating rate 2.5, 5 and 10⁰ $^\circ\text{C}\text{min}^{-1}$, helium flow 60 – 120 $\text{cm}^3\text{min}^{-1}$.

Thermogravimetric data were processed using the computer program "NETZSCH Thermokinetics" (version 2001.9d) [5 – 11]. 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" (utilizing the dependence \lg of heating rate vs 1/T) and "FRIEDMAN Analysis" (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 multiple linear regression. F-test is used for the search of the best kinetic description. 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.

DSC curves were obtained on Mettler DSC-822e/700 ($m = 13.5\text{ mg}$, argon flow 25 $\text{cm}^3\text{min}^{-1}$).

For the study of the structural and morphological change in the silver acetate crystals, the sample ($m = 1\text{ g}$) was heated consecutively at $180 \pm 1^\circ\text{C}$, $210 \pm 1^\circ\text{C}$ and $350 \pm 1^\circ\text{C}$ (during 15 min, 25 min and 25 min, accordingly).

SEM and TEM studies of intermediate products and residue were made by means JEM-2000 FX II microscope (the resolution 200 Å), equipped by

ASID-20 gear, with the accelerating voltage 200 kV. The dimensions of product decomposition were evaluated by the examination of approximately 300 particles on TEM-images, formed by Sigma Scan Pro (version 3.0, Jandel Scientific Software, 1966).

Mass-spectrum were recorded by means of mass-spectrometer with high resolution ($R = 2000$) Funnigan MAT 8200; ionizing electrons energy 70 eV, accelerating voltage 3000 V. Gaseous products (from the special heating system) were injected into the ionic source through the leak (with molecular leaking regime), with ionic source temperature from 10 till 340 °C.

3. Results and discussion

The decomposition of the silver acetate AgCH_3COO (under the conditions of linear heating) proceeds at 170–280 °C, the mass loss (30%) corresponds to the formation of metallic silver.

The mass-spectrum of gaseous products points to the evolving of CO , CO_2 , H_2O , CH_3COOH and fragments with mass numbers 107, 216, 275.

DSC-curve confirms that the decomposition process itself is complex: the heat-evolution at 260–286 °C itself is multistep, the long flat exothermic peak at 286–331 °C is not connected with any mass-loss and can be refer to the fine particles enlargement (recrystallization).

The initial crystals of silver acetate are long needles: length is 70–100 micrometers, and thickness is 5–10 micrometers. The fine silver particles appearance is observed at the decomposition beginning (X-ray analysis detects the metal silver after 15 min heating at 180 °); the initial size of Ag-particles is 40–50 nanometers; they intergrow and form the porous structure at higher temperatures (Fig. 1). It is worth to note, that all consecutive temperatures of the long-term isothermal treatment of samples (for the study of the structural and morphological changes) are lower than appropriate transformation temperatures under linear heating, which is understandable.

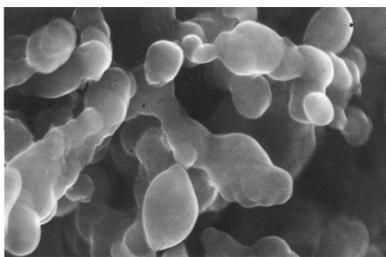


Fig. 1. The porous structure of silver composed of accreted particles (1–2 micrometers) at 350 °C (isothermal heating)

Kinetic parameters ($E_a = 358$ kJ/mol, $\lg A = 33$) are relatively constant only in the region of transformation $\alpha = 0.45 - 0.90$ (Fig. 2); the decomposition process is very complex (the mass-spectrum of the evolved gas consist CO , CO_2 , H_2O , CH_3COOH and

small quantity of radicals, included Ag). For the equations CnB or Bna (reactions with autocatalysis) $E_a = 358$ kJ mol⁻¹, $\log A = 33$. Both the high overheating (exothermic reaction,) and autocatalysis by the formed metal particles complicates the decomposition still more. So the calculated formal kinetic parameters are evaluative and conditional (which is well seen from the very high pre-exponential factor).

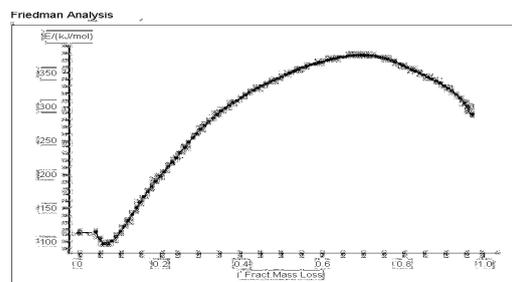


Fig. 2. The kinetic analysis by Friedman method of TG-curves (5 grad min⁻¹ and 10 grad min⁻¹)

The overall exothermic thermal effect of decomposition process (silver reduction at 270–286 °C with corresponding mass loss 30%) is 13 kJ mol⁻¹ (Fig. 3). The flat peak (290–330 °C, being not connected with mass loss, can be attributed to the particles enlargement. The thermal effect of this process is 33 kJ mol⁻¹. These values are evaluative ones (simple average from two measurements), but it is obvious that the formation of the silver nanoparticles (non-equilibrium and metastable) takes place at low temperatures, their enlargement occurs at 290–330 °C, and the heat of the enlargement is distinctly more than the heat of reduction reaction.

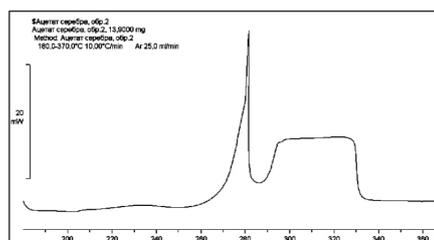
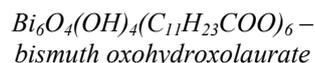


Fig. 3. DSC curve for the decomposition of AgCH_3COO ; $m = 13.9$ mg, standard aluminum-sample holder (the lid with holes), heating rate 10 K min⁻¹, argon flow (25 cm³ min⁻¹)



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

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, $E_a = 44 - 46 \text{ kJ mol}^{-1}$, $\log A = 1.2-2.0$. Correlation coefficients are neighbors too (0.9977, 0.9976 and 0.9975) (Fig. 4).

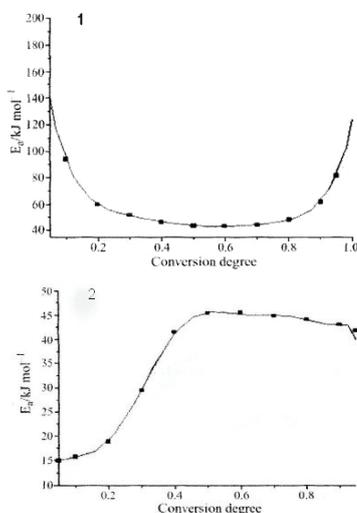


Fig. 4. Ozawa-Flynn-Wall Analysis for bismuth laurates thermal decomposition:

1. $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{11}\text{H}_{23}\text{COO})_6 \cdot n\text{C}_{11}\text{H}_{23}\text{COOH}$
– solid solution of bismuth oxohydroxolaurate and lauric acid
2. $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{11}\text{H}_{23}\text{COO})_6$
– bismuth oxohydroxolaurate

$\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{11}\text{H}_{23}\text{COO})_6 \cdot n\text{C}_{11}\text{H}_{23}\text{COOH}$ – solid solution of bismuth oxohydroxolaurate and lauric acid

This solid solution decomposes under quasi-isothermal conditions in three steps ($80-250^\circ\text{C}$, $250-320^\circ\text{C}$ and $320-420^\circ\text{C}$).

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 approximated by F-test, $E_a = 44 - 46 \text{ kJ mol}^{-1}$, $\log A = 1.2-2.0$.

$\text{Bi}(\text{C}_{11}\text{H}_{23}\text{COO})_3$ – bismuth laurate

The normal salt decomposes under quasi-isothermal conditions in two steps ($100-340^\circ\text{C}$ and $340-400^\circ\text{C}$). There is really no constancy of the calculated activation energy during the first decomposition step. This can point to the existence of several parallel-serial reactions or the additional phase transformation in this temperature region.

Bismuth stearate $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{17}\text{H}_{35}\text{COO})_6$

Data of two thermogravimetric curves, obtained under linear heating (5 and 10 grad/min), were processed by "FRIEDMAN Analysis", "OZAWA-FLYNN-WALL Analysis" and "ASTM E698". The checking equations: Fn, C1B, Bna, A3, R3, D4; the best one: C1B, the first-order equation with auto catalysis; $f(\alpha) = (1-\alpha) \cdot (1+3\alpha)$, $E_a = 93 \text{ kJ/mol}$, $\log A = 5.3$.

The "ASTM E698" Analysis gives $E_a = 100.3 \text{ kJ/mol}$, $\log A = 6.2$.

The nucleation equations without autocatalysis are not satisfactory as kinetic description.

Bismuth stearate



The kinetic parameters for the first decomposition step were calculated by Borchardt-Daniels method for the selected region of conversion ($0.20 < \alpha < 0.80$). The checking equations: Fn, C1B, CnB, R3, D3; the best one: Fn, the n-order equation, $n = 0.939$. $E_a = 72 \text{ kJ/mol}$, $\log A = 3.6$. It is really or the first-order equation of nucleation, or the decomposition reaction in the melt (Fig. 5).

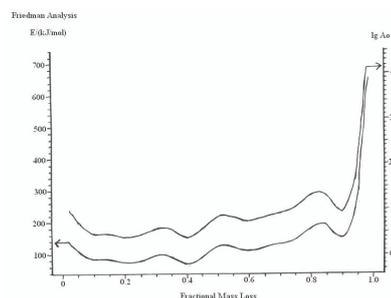


Fig. 5. Ozawa-Flynn-Wall Analysis for bismuth stearate $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{17}\text{H}_{35}\text{COO})_6 \cdot n\text{C}_{17}\text{H}_{35}\text{COOH}$ thermal decomposition

4. Conclusions

Thermal decomposition of silver acetate in the inert atmosphere is a favorable technique for the preparation of highly dispersed silver metal. Rather low temperature of this intramolecular reduction of metal (210°C under isothermal heating, $260-286^\circ\text{C}$ from DSC experiment) results in the formation of non-equilibrium and metastable nanoparticles of silver; this nanoparticle phase is kinetically hindered: the nanoparticles enlargement, occurring with the big exothermic effect (and the constant rate) at $290-330^\circ\text{C}$, confirms their non-equilibrium state in the moment of formation.

The thermal decomposition of salts and complex compounds of varied metals (lanthanides and transition metals, in general) with carboxylic and other organic ligands is widely studied nowadays. Most of decomposition processes were conducted in the air; really the studied process (terminologically) was not the substance "thermal decomposition" (intramolecular reduction of the metal by organic ligand), but the substance "thermooxidative degradation", i.e. oxidation by air oxygen under heating (intermolecular reaction); so the final residua were metal oxy-salts, oxides or sulfides (nanoparticles sometimes). Only the noble metals can be obtained directly during such thermal decomposition in air presence.

The silver nanoparticles formation (with the reduction of silver ions in aqueous solution by hydroquinone) was studied by the method of titration microcalorimetry. It is interesting to note that three consecutive steps of the formation of silver nanoparticles were discovered: 1) nucleation step (exothermic), 2) growth step (endothermic) and 3) aggregation step (exothermic).

Thermal decomposition of three synthesized bismuth laurates are complex, so the kinetics of the process (for the first step) can be studied (and calculated) only for bismuth oxohydroxo-derivatives: $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{11}\text{H}_{23}\text{COO})_6 \cdot n\text{C}_{11}\text{H}_{23}\text{COOH}$ and $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{11}\text{H}_{23}\text{COO})_6$.

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°C and 105–285°C, the calculated kinetic parameters are close to each other ($E_a = 43\text{--}46 \text{ kJ mol}^{-1}$, $\lg A = 1.2\text{--}2.0$). The possible explanation: initial redox decomposition reactions can be identical (progressing in $\text{Bi}_6\text{O}_4(\text{OH})_4\text{L}_6$ 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 $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{17}\text{H}_{35}\text{COO})_6 \cdot n\text{C}_{17}\text{H}_{35}\text{COOH}$ (solid solu-

tion, as well) and $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{17}\text{H}_{35}\text{COO})_6$ take place at 20–400°C, topochemical equations: nucleation and nucleation with autocatalysis, the activation parameters are distinctly higher and diverse ($E_a = 72 \text{ kJ mol}^{-1}$, $\log A_1 = 3.6$ and $E_a = 93 \text{ kJ mol}^{-1}$, $\log A_2 = 5.3$, accordingly). The principal difference in compounds composition lies only in the hydrocarbon chain length ($\text{C}_{11}\text{H}_{23}\text{COOH}$ and $\text{C}_{17}\text{H}_{35}\text{COOH}$).

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