Journal of Thermal Analysis and Calorimetry, Vol. 74 (2003) 407–411

THERMAL DECOMPOSITION OF BISMUTH STEARATES
Study of process kinetics

V. Logvinenko[*1], *A. Minina*[2], *Yu. Mikhaylov*[2], *Yu. Yukhin*[2] *and*
B. Bokhonov[2]

[1]Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences,
Ac. Lavrentyev Ave. 3, Novosibirsk-90, 630090, Russia
[2]Siberian University of Consumer's Cooperation, K. Marx Ave. 26, Novosibirsk, 630087, Russia

Abstract

Two bismuth salts, $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6$ and $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6{\cdot}nC_{17}H_{35}COOH$, were synthesized. The thermogravimetry under quasi-isothermal conditions denotes the multi-step character of decomposition processes for both compounds. The thermogravimetry under linear heating was used for kinetic studies. Thermogravimetric data (obtained at different rates of linear heating) were processed with 'Netzsch Thermokinetics' computer program. Kinetic parameters were calculated only for the first decomposition step for both salts, the process is described by different nucleation equations (with and without autocatalysis).

Keywords: 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.

The thermal decomposition of metal salts of carboxylic acids is widely studied [1–4]. It is known, that such decomposition is the perspective way to product the nano-particles of metals [5]. So, having this in view, we have synthesized and studied bismuth stearates of different composition.

Experimental

Two compounds with different compositions, $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6$ and $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6{\cdot}nC_{17}H_{35}COOH$, were synthesized by the precipitation from the acidic solutions of the salts (pH=1; t^0=80°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. $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6{\cdot}nC_{17}H_{35}COOH$ is the solid solution of the oxohydroxostearate with stearic acid.

---

[*] Author for correspondence: E-mail: val@che.nsk.su

1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

The study of thermal decomposition was performed by means of Derivatograph Q-1500-D (MOM, Hungary). Quasi-isothermal heating was used both for the investigation of the step-by-step character of thermal dissociation processes, for the attempt to check the possible stable intermediate phases [6] and for kinetic study [7]. Two sample holders (plate-like and standard open crucible) were used, sample mass was 200 mg, constant mass loss rates were 0.2 and 0.53 mg min^{-1}, atmosphere – helium (60 cm^3 min^{-1}). Linear heating was used for kinetic studies; sample mass was 50–60 mg, heating rate 2, 5 and 10°C min^{-1}, helium flow 120 cm^3 min^{-1}.

Thermoanalytical studies indicated that decomposition processes are accompanied by melting; the final products were both the bismuth oxide, and the dispersed metal (the endothermic effect at 271°C can be attributed to the melting of bismuth, the exothermic effects above 500°C can be connected with bismuth oxidation).

Thermogravimetric data were processed using the computer program 'Netzsch Thermokinetics'(version 2001.9d). So as the thermal decompositions are multi-step processes 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' [8] enables to calculate the averaged values of activation energy and preexponential factor according to maximum rate temperatures. Program 'Friedman Analysis' [9] allows calculating both the activation energies, and preexponential factors (assuming a first-order reaction) for the every experimental point of fractional conversion, program 'Ozawa–Flynn–Wall Analysis' [10–12] 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, Table 1)). This calculation is made by the improved differential method of Borchardt–Daniels with multiple linear regression [13]. *F*-test is used for the search of the best kinetic description [14]. 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.

Results and discussion

The thermogravimetry under quasi-isothermal conditions denotes the multi-step character of decomposition processes for all compounds. 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.

Bismuth stearate $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6{\cdot}nC_{17}H_{35}COOH$

Data of two termogravimetric curves, obtained under linear heating (5 and 10°C min^{-1}), were processed by 'Friedman Analysis', 'Ozawa–Flynn–Wall Analysis' (Fig. 1) and

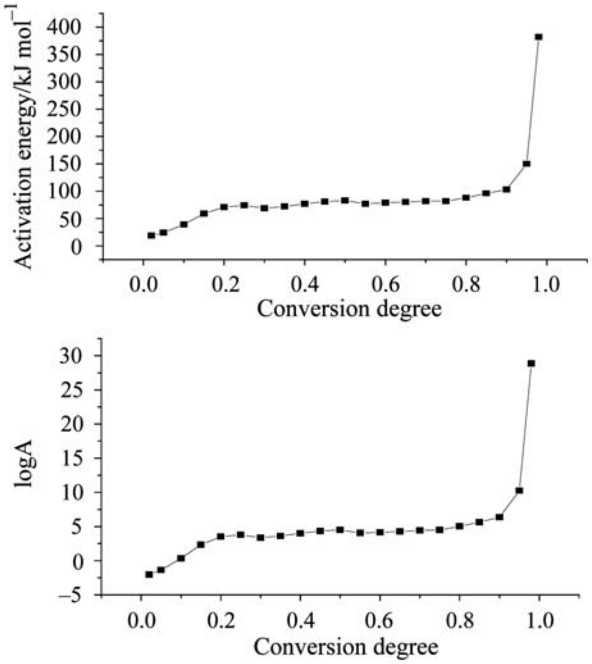

Fig. 1 Ozawa–Flynn–Wall Analysis for bismuth stearate (solid solution) $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6\cdot nC_{17}H_{35}COOH$ decomposition

'ASTM E698'. 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, $n=0.939$. $E_a=72$ kJ mol^{-1}, log$A$=3.6. It is really or the first-order equation of nucleation, or the decomposition reaction in the melt.

We used the quasi-isothermal experiments for the kinetic parameters estimation. Two thermogravimetric curves ($q_1=0.21$ and $q_2=0.53$ mg min^{-1}) were recorded. It is possible to calculate the activation energy for the any pair of points (with one and the same conversion level) according to equation:

$$\ln(q_1/q_2)=E/R(1/T_2-1/T_1)$$

$E_a=58\pm6$ kJ mol^{-1} (in the interval $7\leq\alpha\leq28\%$), the value is near to the value, obtained with analysis by 'ASTM E698'($E_a=66$ kJ mol^{-1}, log$A$=3.1).

Bismuth stearate $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6$

Data of two thermogravimetric curves, obtained under linear heating with 5 and 10°C min^{-1}, were processed by 'Friedman Analysis', 'Ozawa–Flynn–Wall Analysis' and 'ASTM E698'. Kinetic parameters for the first decomposition step were calculated by Borchardt–Daniels method for the selected region of conversion ($0.10<\alpha<0.80$). The checking equations: Fn, C1B, Bna, A3, R3, D4; the best one:

C1B, the first-order equation with autocatalysis; $f(\alpha)=(1-\alpha)(1+3\alpha)$, $E_a=93$ kJ mol^{-1}, log$A$=5.3 (Tables 1 and 2).

Table 1 Bismuth stearate $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6$. Data of *F*-test on fit-quality (for the search of the best kinetic description, $\alpha=0.10-0.80$)

#	Code	Type	*F* act	*F* exp	*F* crit (0.95)
1	S	CIB	46	1.00	1.63
2	S	Bna	45	1.16	1.64
3	S	R3	47	7.56	1.63
4	S	D4	47	56.51	1.63

Table 2 Bismuth stearate $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6$. List of parameters and standard deviations (for the C1B, the first-order equation with autocatalysis). Correlation coefficient is 0.999162

#	Parameter	Initial value	Optimal value	Sign	*t* standard dev.
1	log$A$/s^{-1}	6.5840	5.2584		0.1710
2	E_1/kJ mol^{-1}	107.9319	92.8634	+	1.7761
3	log$K$ cat	0.4500	0.4794		$4.17\cdot 10^{-2}$
4	Mass diff. 1%	242.2854	2424.2854		constant
5	Mass diff. 2%	3205.4011	3205.4011		constant

The 'ASTM E698' Analysis gives $E_a=100.3$ kJ mol^{-1}, log$A$=6.2.

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

Conclusions

Thermal decomposition of two synthesized bismuth stearates was studied. The kinetics of the process (for the first step) is described by different nucleation equation. The products contain both metal bismuth, and Bi_2O_3. The possible explanation for the difference in the nucleation equations: the appearance of the metallic bismuth (as the possible catalyst) during the first decomposition step of the stearate $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6$.

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.

For example, the kinetics for the first decomposition steps for solid solutions of Co–Ni, Fe–Ni and Zn–Ni bimaleates was studied [15]. The kinetic parameters are:

Co–Ni bimaleates (1:1) solid solution. $E_a=120$ kJ mol^{-1}, log$A$=7.6.
Fe–Ni bimaleates (1:1) solid solution. $E_a=274$ kJ mol^{-1}, log$A$=21.
Zn–Ni bimaleates (1:1) solid solution. $E_a=111$ kJ mol^{-1}, log$A$=6.5.

The decomposition of transition metals salts with unsaturated carboxylic acid leads to metal–polymer composites. It is probable, that this rather high values level of kinetic parameters (as compared with bismuth stearates) is connected with the low rate of polymerization processes. More simple thermal decomposition of bismuth stearate salts (without polymerization) is connected with low values of kinetic parameters.

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 differ from data, received by 'Friedman Analysis' and 'Ozawa–Flynn–Wall Analysis'

* * *

The authors are grateful to Prof. J. Opfermann and Dr. V. Drebushchak for the possibility to work with computer program 'Netzsch Thermokinetics' (version 2001.9d).

References

1 M. Pajtásová, E. Jona and P. Šimon J. Therm. Anal. Cal., 67 (2002) 129.
2 W. Wolodkievicz, J. Therm. Anal. Cal., 68 (2002) 141.
3 A. I. El-Saidasmaa, J. Therm. Anal. Cal., 68 (2002) 917.
4 S. A. Abdel-Latif and H. B. Hassib, J. Therm. Anal. Cal., 68 (2002) 983.
5 V. A. Logvinenko, N. F. Yudanov, G. N. Chekhova, Yu. G. Kriger, L. I. Yudanova and N. N. Rudina, Chem. Sus. Dev., 8 (2000) 171.
6 V. A. Logvinenko, F. Paulik and J. Paulik, Quasi-equilibrium Thermogravimetry in the Up-to-date Inorganic Chemistry. Novosibirsk, Nauka 1989 (in Russian).
7 J. M. Criado, A. Ortega and F. Gotor, Thermochim. Acta, 157 (1990) 171.
8 H. E. Kissinger, J. Res. Nat. Bur. Stds., 57 (1956) 217.
9 H. L. Friedman, J. Polym. Lett., 4 (1966) 323.
10 T. Ozawa, Bull. Chem. Soc. Japan, 38 (1965) 1881.
11 J. Flynn and L. A. Wall, Polymer Lett., 4 (1966) 232.
12 J. Opfermann and E. Kaisersberger, Thermochim. Acta, 11 (1992) 167.
13 J. Opfermann, Rechentechnik/Datenverarbeitung, 22 (1985) 26.
14 H.-W. Jank and A. Meister, Kulturpflanze, 30 (1982) 26.
15 V. Logvinenko, L. Yudanova, N. Yudanov and G. Chekhova, J. Therm. Anal. Cal., 74 (2003) 395