Journal of Thermal Analysis and Calorimetry, Vol. 93 (2008) 3, 805–809

‘MODEL-FREE’ APPROACH IN THE STUDY OF DECOMPOSITION KINETICS FOR CLUSTER COMPOUNDS AND COORDINATION COMPOUNDS

V. Logvinenko[*]

Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, Lavrentyev Ave. 3
Novosibirsk-90, 630090 Russia

‘Model-free’ approach was used for the study of decomposition kinetics: the dehydration of cluster compound $[\{Mg(H_2O)_5\}_2Re_6S_8(OH)_6]\cdot H_2O$ and the phase transformation under partial pyrolysis of bismuth oxohydroxolaurate $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6$.

The primary calculation of accurate activation energy values and the obvious discrimination of separate decomposition steps allow using further linear and non-linear regression methods for more accurate and full kinetic description.

Keywords: *cluster compounds, coordination compounds, dehydration processes, ‘model-free’ kinetics*

Introduction

‘Model-free’ approach is well known and widely distributed working method in the study of decomposition kinetics of solid substances. ‘Model-free’ approach in kinetics is connected with classical and important works of Kissinger [1], Anderson [2], Friedman [3, 4], Ozawa [5], Flynn and Wall [6] and Vyazovkin [7, 8].

This method of kinetic investigation is not the only one of its kind: there is Dispersive kinetics by Plonka *et al.* [9], Third-law methodology for kinetic parameters calculation (directly on the base of thermodynamic data) by L`vov [10], Meaningful kinetic constants in solid-phase reactions by Korobov [11, 12], Mechanistic interpretation of thermal processes in crystals by Galwey [13].

We prefer to use ‘model-free’ approach because of its possibility to calculate straight values of activation energies for the every point of experimental curves (TG, DSC, DTA).

Thermogravimetric curves are used for kinetic investigations usually, and accompanying DTG curves help to check steps of decomposition process. DSC data seldom are in use; in particular the additional problem is the baseline positioning, it can increase the calculation error.

In general the stages resolution of the multi-step decomposition can be quite different (or better, or worse) on TG or DSC curves. The steps contributions in the mass loss sum and in the heats sum are quite different because of the difference in molar mass of evolved gases and in reactions molar enthalpy.

The decomposition of studied cluster compounds and coordination compounds has important peculiarities.

Cluster compounds, being usually synthesized from water solutions, are hydrates, with coordinated and/or uncoordinated water molecules, so the decomposition beginning is dehydration process, without any destruction of stable cluster ions.

As for coordination compounds (e.g. with carboxylic acid anion as a ligand), we studied complicated reactions of full decomposition, affected the inner coordination spheres. In these multi-step complex reactions the ‘model-free’ approach was useful for the more distinct interpretation of individual steps, especially if we used different kinetic curves – TG, DSC – for processing.

Experimental

Used thermo-analytical methods are: thermogravimetry (with linear heating), differential scanning calorimetry. Used equipments: TG-209, DSC-204, (Netzsch), DSC-822e/700 (Mettler). Sample masses 7–35 mg, argon flow: 20–100 $cm^3 min^{-1}$.

TG and DSC data were processed using the computer program ‘Netzsch Thermokinetics’ (version 2001.9d); publications [4–6, 14–16] are the scientific base. Data processing can be done without

---

[*] val@che.nsk.su

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

the preliminary information about the kinetic topochemical equations.

Studied kinetic curves must be obtained under several different heating rates; the minimum set is two curves.

Results and discussion

Cluster compounds

For cluster compounds (synthesized from water solutions) the essential problems are the stability of the cluster ion itself and appropriate ligand selection, but also the obligatory insertion of water molecules for the formation of stable structures.

Coordination cluster compounds are usually synthesized in small-scale quantity, most of them are non-soluble in water; it is difficult to obtain their dissociation constants or reaction constants in solution (traditional quantitative characterization for coordination compounds). From this point of view the thermo-analytical investigation may give quite interesting quantitative data on kinetic and thermodynamic stability of these compounds in dehydration: reactions, deeply affected compound structure.

We studied rhenium cluster compounds. Coordination polymer compounds based on rhenium chalcohalide and chalcogenide clusters are known for a long time [17, 18]. Molecular octahedral rhenium cluster complexes have complex anions $[Re_6Q_8L_6]$ (where *Q*=S, Se, Te and *L*=appropriate terminal ligands) [19, 20].

$[\{Mg(H_2O)_5\}_2Re_6S_8(OH)_6]\cdot 6H_2O$ – this formula is for the known detailed structure of the monocrystal, but the compound easily dehydrates in the air, so we studied the cluster compound practically without uncoordinated water molecule (Fig. 1):

$$[\{Mg(H_2O)_5\}_2Re_6S_8(OH)_6]\cdot H_2O \rightarrow$$

$$[Mg_2Re_6S_8(OH)_6] + 11H_2O$$

$$(\Delta m(\text{calc.}) = 10.3\%)$$

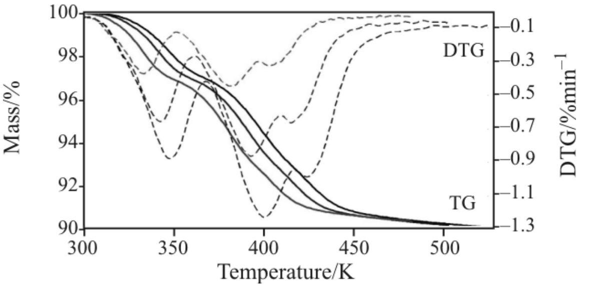

Fig. 1 TG and DTG curves for $[\{Mg(H_2O)_5\}_2Re_6S_8(OH)_6]\cdot H_2O$ dehydration; standard sample holder, heating rates 3.5, 7.1 and 10.7 K min^{-1}, argon flow 30 cm^3 min^{-1}

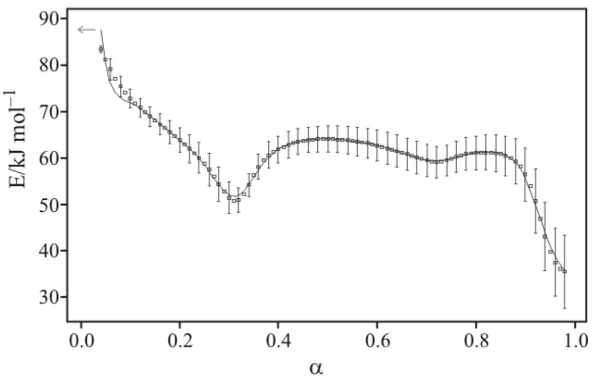

Fig. 2 Ozawa–Flynn–Wall analysis for $[\{Mg(H_2O)_5\}_2Re_6S_8(OH)_6]\cdot H_2O$ dehydration: the activation energies depending on the conversion degree. Perpendicular lines – standard deviation of calculation

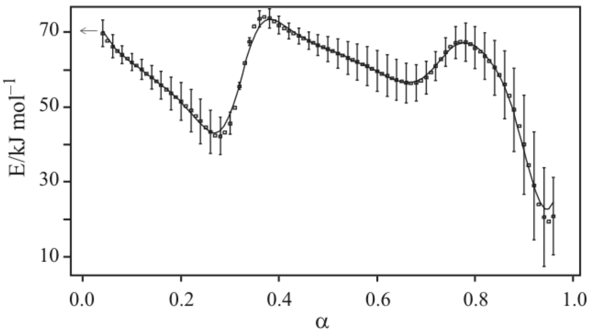

Fig. 3 Friedman analysis for $[\{Mg(H_2O)_5\}_2Re_6S_8(OH)_6]\cdot H_2O$ dehydration: the activation energies depending on the conversion degree. Perpendicular lines – standard

Table 1 Cluster compound $[\{Mg(H_2O)_5\}_2Re_2S_8(OH)_6]\cdot H_2O$. Data of F-test on fit quality (the search of the best kinetic description: α=0.05–99.95%)

No.	Eq.	F_{exp}	F_{crit} (0.95)	F_{act}	Corr. coeff.
1	D_3	1.00	1.15	585	0.996874
2	F_n	1.42	1.15	584	0.995708
3	CnB	1.42	1.15	583	0.995708
4	B_{na}	2.09	1.15	583	0.996021

It is clear that the dehydration process is stepwise (Figs 1–3).

We tried to find the best kinetic equations (Table 1). It is unusual that the best equation is the diffusion one (both for α=0.05–99.95%, and α=40.00–90.00%).

Activation parameters for diffusion step: *E*=56.1 kJ mol^{-1}, lg*A*=4.0 (α=0.05–99.95%) and *E*=59.5 kJ mol^{-1}, lgA=4.5 (α=40.00–90.00%).

So as the dehydration is three-step process (DTG curves, Fig. 1), we used the non-linear regression for kinetic parameter calculations and examined three-stepped process (F_n, F_n, D_3). Results of the calculation are:

$$1)\, f_1(\alpha) = (1-\alpha)^{1.8};\ E_1 = 67.7\pm0.6\ \text{kJ mol}^{-1},$$

$$\lg A_1 = 6.7\pm0.1;$$

$$2)\, f_2(\alpha) = (1-\alpha)^{2.1};\ E_2 = 78\pm3\ \text{kJ mol}^{-1},$$

$$\lg A_2 = 11\pm1;$$

$$3)\, f_3(\alpha) = (1-\alpha)^{1/3}/[(1-\alpha)^{-1/3}-1];$$

$$E_3 = 185\pm5\ \text{kJ mol}^{-1},\ \lg A_3 = 23.0\pm0.8.$$

The first two equations are n^{th} order equations with big reaction orders (and without simple topochemical content). We tried other equation combinations (D_3, D_3, D_3 and CnB, F_n, D_3), but the quoted variant is the best (59 calculation cycles, correlation coefficient 0.999935).

This non-linear regression can distort kinetic parameters for distant parts of curves. The above calculation results in big increase of activation energy for the third (diffusion) step.

We repeat this calculation, after fixing parameters E_3=59.5 kJ mol^{-1}, lgA_3=4.45 for the third step. Results of the recalculation are:

$$1)\, f_1(\alpha) = (1-\alpha)^{1.8};\ E_1 = 68.6\pm0.8\ \text{kJ mol}^{-1},$$

$$\lg A_1 = 6.8\pm0.1;$$

$$2)\, f_2(\alpha) = (1-\alpha)^{2.1};\ E_2 = 77\pm2\ \text{kJ mol}^{-1},$$

$$\lg A_2 = 11.5\pm0.5;$$

$$3)\, f_3(\alpha) = (1-\alpha)^{1/3}/[(1-\alpha)^{-1/3}-1];$$

$$E_3 = 59.5\ \text{kJ mol}^{-1},\ \lg A_3 = 4.45.$$

Correlation coefficient is 0.999931.

All activation energies are in the area, obtained by 'model-free' method (Fig. 4), and correlation coefficient is quite good.

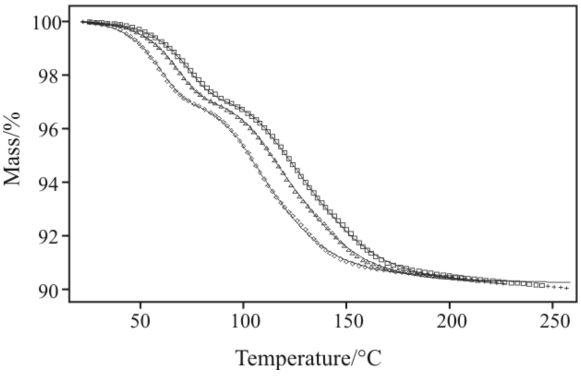

Fig. 4 Data processing for $[\{Mg(H_2O)_5\}_2Re_6S_8(OH)_6]\cdot H_2O$ dehydration. Curves fitting of non linear regression, simulated with F_n (the first step) and F_n (the second step), D_3 (the third step). Experimental points, calculated lines

So the better approach is to calculate preliminarily kinetic parameters for the farther step, and then use them fixed for all other calculations.

We do not think that the third step is water molecules diffusion through the product layer. It can be so called 'inner diffusion': the process of interchangeable sorption and desorption removing water molecules within the channels and cages, formed in the cluster structure during the dehydration process.

Coordination compound

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 [21].

The thermal decomposition of this coordination compound was studied earlier [22]. 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}.

There are three decomposition steps:

- The decomposition with small mass loss and endothermic effect (353–403 K);
- 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 this part of decomposition at 373–533 K (upon TG curves); 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 [21].

TG and DSC curves (Figs 5 and 6) 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

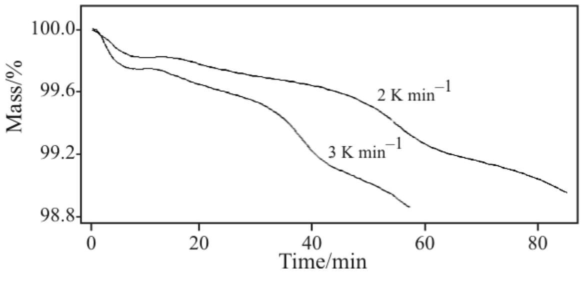

Fig. 5 TG curves for the decomposition of bismuth oxohydroxolaurate $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6$; standard aluminum sample holder for DSC measurement (the lid with holes), helium flow 30 cm^3 min^{-1}, heating rates 2 and 3 K min^{-1}

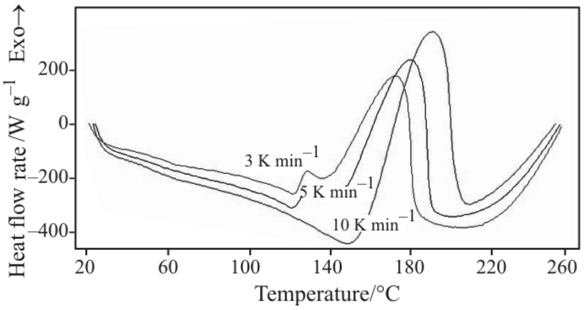

Fig. 6 DSC curves for the decomposition of bismuth oxohydroxolaurate $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6$; standard aluminum sample holder for DSC measurement (the lid with holes), helium flow 30 cm^3 min^{-1}, heating rates 3, 5 and 10 K min^{-1}

holes), helium flow 30 cm^3 min^{-1}. The temperature interval of this exothermic effect (403–463 K at 3 K min^{-1}) corresponds to the very beginning of the decomposition on TG curve (full $\Delta m \approx 1.2\%$ only, Fig. 5). We did not succeed in the calculation of kinetic parameters according to TG curves (2, 3, 5 and 10 K min^{-1}) because of the improper steps resolution.

In general the resolution of stages for the multi-step decomposition can be quite different (better or worse) on TG or DSC curves. The difference in molar mass of evolved gases and in molar enthalpy of reactions results in the difference in the step contributions in the mass loss sum and in the heats sum. 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.

Data of three DSC curves, obtained under linear heating (3, 5 and 10 K min^{-1}), were processed by Friedman analysis. The constancy of the activation energy exists in the extent of conversion interval 20–80%, E_a=103±1 kJ mol^{-1} (Fig. 7).

Kinetic parameters for this decomposition step were calculated by Borchardt–Daniels regression method (for the selected region of conversion: $0.20<\alpha<0.80$). The checking equations: F_n, CnB, B_{na}, R_2, D_3, A_3. The equations Fn (n=0.54±0.3), CnB and R_2 are indistinguishable by F-test (the autocatalysis contribution is small).

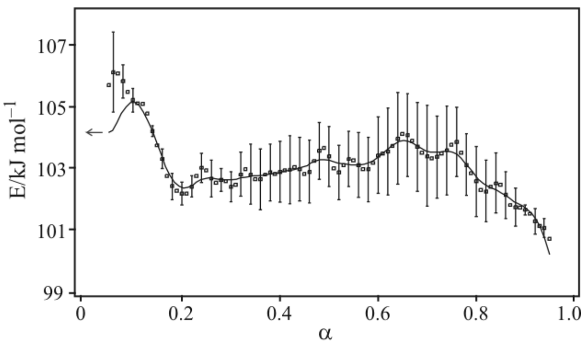

Fig. 7 Friedman analysis for the decomposition of bismuth oxohydroxolaurate $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6$: the activation energies depending on the conversion degree. Perpendicular lines – standard deviation of calculation

The equation of the contracting cylinder (R_2) is more probable: E_a=106±1 kJ mol^{-1}, log$A$=10.0±0.5. There is no diffusion hindrance in the process kinetics.

According to the mass spectrometric analysis, the beginning step of chemical transformations under heating proceeds inside polyatomic cation layers with lauric (dodecanic) acid elimination (403–483 K). This step has very small mass loss and noticeable exothermic effect (393–473 K); we believe that the studied process kinetics is connected in majority with the structure lattice reconstruction, but not with the remarkable decomposition process itself.

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 suitable difference in molar mass of evolved gases and in reactions molar enthalpy).

Conclusions

The method of calculation of kinetic parameters, well known as ‘model-free’ approach, is very useful in the study of decomposition processes in non-isothermal conditions.

For crystalline hydrates, where the decomposition process is simple: $A_{solid} \Leftrightarrow B_{solid}+C_{gas}$, it is possible to calculate the set of activation energies for the every decomposition point, single out steps (if they are present), and further, – using the regression methods (both of linear and non-linear regression) – to calculate kinetic parameters for reactions. For this aim the primary activation energies can be regarded as the ‘real’ ones (being not depending on the equation). During the calculation with regression methods you can compare these, newly calculated values (for certain topochemical equation), with those ‘real’ energies. The non-linear regression method often leads to topochemical equations, not clear from the physical-chemical point of view.

The complicated decomposition processes, – with intricate intramolecular reactions of oxidation or pyrolysis, – are not formally the processes for nonisothermal solid-state kinetics to deal with. But ‘model-free’ approach allows marking out the individual reaction step. For very complicated decomposition with pyrolysis we can change kinetic curves, from TG to DSC, and can calculate the separated individual step of complicated decomposition. But it will be the kinetic description of the structure transformation (which accompanied the decomposition process itself).

Quantitative data of non-isothermal kinetics have understandable physical-chemical meaning only for special series of compounds. Such series are: inclusion compounds with one and the same host matrix and different guests, inclusion compounds with different host matrix and one and the same guest, coordination compounds with one central atom and different ligands, coordination compound with different central atoms and identical ligand, etc. In this work we try to show that the 'model-free' approach gives the best fit for this; studied compounds are next specimens from such series, studied earlier [23–25]. It is the contribution to the solid-state chemistry of coordination compounds and cluster compounds nowadays.

Acknowledgements

The author is grateful to Netzsch firm for the possibility to work with new version of computer program 'Netzsch Thermokinetics'.

References

1 H. E. Kissinger, J. Res. Nat. Bur. Stds., 57 (1956) 217.
2 H. C. Anderson, J. Polym. Sci., Part C, (1963) 175.
3 H. L. Friedman, J. Polym. Sci., Part C, (1963) 183.
4 H. L. Friedman, J. Polym. Lett., 4 (1966) 323.
5 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
6 J. Flynn and L. A. Wall, Polym. Lett., 4 (1966) 232.
7 S. Vyazovkin and A. Lesnikovich, Russ. J. Phys. Chem., 62 (1988) 1535.
8 S. Vyazovkin, J. Therm. Anal. Cal., 83 (2006) 45.
9 J. Bednardek, A. Plonka, B. Pacewska and J. Pysiak, Thermochim. Acta, 282 (1996) 51.
10 B. V. L`vov, J. Therm. Anal. Cal., 84 (2006) 581.
11 A. Korobov, J. Chem. Inf. Comput. Sci., 36 (1996) 393.
12 A. Korobov, J. Thermal Anal., 44 (1995) 187.
13 A. K. Galwey, J. Therm. Anal. Cal., 87 (2007) 601.
14 J. Opfermann and E. Kaisersberger, Thermochim. Acta, 11 (1992) 167.
15 J. Opfermann, Rechentechnik/Datenverarbeitung, 22.3 (1985) 26.
16 H.-W. Jank and A. Meister, Kulturpflanze, 30 (1982) 26.
17 L. Leduc, A. Perrin and M. Sergent, Acta Crystallogr., Sect. C, 39 (1983) 1503.
18 M. Spangenberg and W. Bronger, Angew. Chem. Int. Ed. Engl., 17 (1978) 368.
19 S. S. Yarovoi, Yu. V. Mironov, D. Y. Naumov, Yu. V. Gatilov, S. G. Kozlova, D.-J. Kim and V. E. Fedorov, Eur. J. Inorg. Chem., (2005) 3945.
20 Yu. V. Mironov, V. E. Fedorov, H. Bang and S.-J. Kim, Eur. J. Inorg. Chem., (2006) 553.
21 K. Mikhailov 'Physical-chemical properties and thermal transformations of bismuth laurates', Ph.D. Thesis, 2005 (in Russian).
22 V. Logvinenko, K. Mikhailov and Yu. Yuchin, J. Therm. Anal. Cal., 81 (2005) 107.
23 V. Logvinenko, V. Fedorov, Yu. Mirinov and V. Drebushchak, J. Therm. Anal. Cal., 88 (2007) 687.
24 V. Logvinenko, Yu. Mikhailov, Yu. Yuchin and B. Bokhonov, J. Therm. Anal. Cal., 74 (2003) 407.
25 V. Logvinenko, K. Mikhailov and Yu. Yukhin, J. Therm. Anal. Cal., 88 (2007) 47.

DOI: 10.1007/s10973-008-9300-z