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Nonisothermal decomposition kinetics of $[CoC_2O_4{\cdot}2.5H_2O]_n$

Raluca Dumitru · Oana Carp · P. Budrugeac ·
M. Niculescu · E. Segal

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Abstract The authors present their results concerning the decomposition in air of the homopolynuclear coordination compound $[CoC_2O_4{\cdot}2.5H_2O]_n$. In the temperature range 20–300 °C, the heating curves TG, DTG and DTA allowed to evidence three decomposition steps. The kinetic analysis was performed on the second step which proved to be the only workable one. The application of nonlinear regression procedure shows that this is a complex process consisting in three successive steps. The checking of the mechanism and corresponding kinetic parameters for quasi-isothermal data ($T = 150$ °C) shows that the obtained results could be used for prediction of the thermal behaviour of the investigated compound in both isothermal and non-isothermal conditions.

Keywords Non-isothermal kinetics · Cobalt(II) oxalate · Thermal stability · 1,2-ethanediol · Nitrate

Introduction

In a recent previous article [1], a new synthesis method of the homopolynuclear coordination compound $[CoL{\cdot}2.5H_2O]_n$ $L = C_2O_4^{-2}$, based on the oxidation reaction of 1,2-ethanediol in an alcohol–water system by cobalt nitrate and nitric acid and the simultaneous isolation of the complex compound in the reaction system was presented. By applying some physico-chemical methods (chemical analysis, electronic and vibrational spectra, respectively, thermal analysis), it was pointed out that this compound is characterized by a (pseudo)octahedral configuration of the cobalt(II) ion and the oxalate anion functions as double-bridge ligand (tetradentate). From XRD pattern and IR spectrum of the product obtained after calcinations in air at 600 °C of the investigated compound show that in these condition the obtained compound is Co_3O_4 [1]. The present article is included in a series [1–10] devoted to the use of oxidation of diols (1,2-ethanediol, 1,2-propanediol or 1,3-propanediol) with metallic nitrates for obtaining some coordination compounds, which decompose at relatively low temperatures, forming simple or mixed oxides. It represents the completion of the characterization of $[CoC_2O_4{\cdot}2.5H_2O]_n$ performed in our previous study [1] with the kinetic analysis of thermal decomposition of this coordinative compound.

Experimental

The method of synthesis of $[CoC_2O_4{\cdot}2.5H_2O]_n$ as well as their characterization by some physical–chemical methods was given in our previous article [1].

The simultaneous recording of thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal

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R. Dumitru (✉) · M. Niculescu
Faculty for Industrial Chemistry and Environmental Engineering, University ‘Politehnica’ of Timisoara, Piata Victoriei 2, 30006 Timisoara, Romania
e-mail: raluca.dumitru@chim.upt.ro

O. Carp
Institute of Physical Chemistry ‘I. G. Murgulescu’ of the Romanian Academy, Splaiul Independentei 202, 060021 Bucharest, Romania

P. Budrugeac
National Institute for Research and Development in Electrical Engineering ICPE-CA, Splaiul Unirii 111, 030138 Bucharest, Romania

E. Segal
Department of Physical Chemistry, University of Bucharest, 70606 Bd. Elisabeta 4-12, Bucharest, Romania

analysis (DTA) curves were obtained using a STA-PC Luxx equipment provided by NETZSCH GERATEBAU GMBH-Germany in the following conditions:

- Temperature range: 25–500 °C;
- Heating rates: 2.5, 5, 7.5 and 10 K min^{-1};
- Platinum crucible with pierced lid;
- Sample mass in the range: 9.50–10.89 mg;
- Synthetic air flow under purity of 99.999% and flow rate 30 mL min^{-1}.

The thermal analysis of $[\text{CoC}_2\text{O}_4{\cdot}2.5\text{H}_2\text{O}]_n$ was also performed in synthetic air flow (30 mL min^{-1}; purity of synthetic air: 99.999%) and the following imposed quasi-isothermal temperature program ($T = 150$ °C): $25\,^\circ\text{C} \xrightarrow{2.5\ \text{K min}^{-1}} 150\,^\circ\text{C} \xrightarrow{200\,\text{min}} 150\,^\circ\text{C}$. The thermal inertness of STA apparatus oven determines the increase of temperature to 155.6 °C, which is followed by its decrease to constant 150 °C in about 49 min. The real temperature program determined by using experimental T vs. t curve is the following:

$$25\,^\circ\text{C} \xrightarrow{2.5\ \text{K min}^{-1}} 136.4\,^\circ\text{C} \xrightarrow{2.26\ \text{K min}^{-1}} 155.6\,^\circ\text{C} \xrightarrow{-0.15\ \text{K min}^{-1}}$$
$$151.5\,^\circ\text{C} \xrightarrow{-0.07\ \text{K min}^{-1}} 150\,^\circ\text{C} \xrightarrow{151\,\text{min}} 150\,^\circ\text{C}$$

Applied methods for kinetic analysis

"Netzsch Thermokinetics: A Software Module for the Kinetic Analysis of Thermal Measurements" [11] was used for processing the non-isothermal data and comparing the calculated and experimental curve corresponding to quasi-isothermal experiment. This program allows assessing the dependence of activation energy (E) on conversion degree (α) by means of Friedman (FR) [12] and Ozawa–Flynn–Wall (OFW) [13, 14] model-free methods, the determination the kinetic triplet (E, pre-exponential factor (A), conversion function ($f(\alpha)$) for the single-step, and the determination of the complex mechanism of the investigated reactions and the corresponding kinetic parameters. Recently [15–25] this program was used for kinetic analysis of some non-isothermal data.

Results and discussion

Figures 1a–c show the TG, DTG and DTA curves for the nonisothermal heating of the compound $[\text{CoC}_2\text{O}_4{\cdot}2.5\text{H}_2\text{O}]_n$ recorded at 7.5 K min^{-1}; similar results were obtained for the other used heating rates.

As one can see the progressive heating of the sample in the temperature range 20–300 °C, determines a thermal decomposition in three steps, two endothermic ones (steps I and II) and one exothermic (step III). The characteristic parameters of these steps are given in Table 1.

The mass losses put in evidence in TG curves and the results obtained by IR spectroscopy [1] suggest the following sequence for thermal decomposition in air flow:

$$\left[\text{CoC}_2\text{O}_4(\text{OH}_2)_2{\cdot}0.5\text{H}_2\text{O}\right]_{n(\text{s})} \rightarrow 0.5n\ \text{H}_2\text{O}_{(\text{g})} + \left[\text{CoC}_2\text{O}_4(\text{OH}_2)_2\right]_{n(\text{s})} \tag{I}$$

$$\left[\text{CoC}_2\text{O}_4(\text{OH}_2)_2\right]_{n(\text{s})} \rightarrow 2n\ \text{H}_2\text{O}_{(\text{g})} + n\ \text{CoC}_2\text{O}_{4(\text{s})} \tag{II}$$

$$n\,\text{CoC}_2\text{O}_{4(\text{s})} + \frac{(4+x)n}{6}\text{O}_2 \rightarrow 2n\,\text{CO}_{2(\text{g})} + n/3\,\text{Co}_3\text{O}_{4+x(\text{s})} \tag{III}$$

In the first stage of kinetic analysis of nonisothermal data we consider the following normed form for the degree of conversion:

$$\alpha_t = \frac{\%\Delta m}{\%\Delta m_\text{t}} \tag{1}$$

where $\%\Delta m_\text{t}$ is the total percentage of the mass loss in the entire decomposition (steps I + II + III (53.58 ± 1.03)).

Figure 2 shows the dependencies of Friedman activation energy (E_FR) and of the corresponding pre-exponential factor evaluated assuming the first order model on the degree of conversion for the steps I + II + III. Figure 3

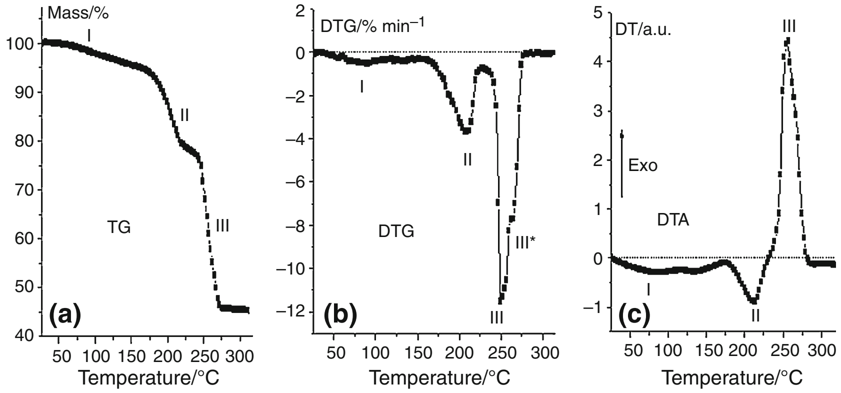

Fig. 1 TG (**a**), DTG (**b**) and DTA (**c**) curves for decomposition of $[\text{CoC}_2\text{O}_4{\cdot}2.5\text{H}_2\text{O}]_n$, recorded at 7.5 K min^{-1}

Table 1 Characteristic parameters of the decomposition steps

	Step I			Step II			Step III			
β/K/min	$\%\Delta m/\%$	$T_{\mathrm{min}}^{\mathrm{DTG}}/°\mathrm{C}$	$T_{\mathrm{min}}^{\mathrm{DTA}}/°\mathrm{C}$	$\%\Delta m/\%$	$T_{\mathrm{min}}^{\mathrm{DTG}}/°\mathrm{C}$	$T_{\mathrm{min}}^{\mathrm{DTA}}/°\mathrm{C}$	$\%\Delta m/\%$	$T_{\mathrm{min}}^{\mathrm{DTG}}/°\mathrm{C}$	$T_{\mathrm{min}}^{\mathrm{DTA}}/°\mathrm{C}$	$\%\Delta m_t/\%$
2.5	4.06	60.4	≈60	18.92*	189.4	191.5	29.40	246.1	234.1 246.8	52.38
5	4.06	≈60	≈67	18.96*	202.2	202.7	31.16	240.4 255.7	242.6 255.7	54.18
7.5	409	≈89	≈89	18.94*	208.2	212.8	31.63	249.9 263.3	257.0	54.66
10	4.09	≈81	≈97	18.95*	214.0	218.7	30.07	255.2 272.9	269.3	53.11

β is the heating rate; $\%\Delta m$ is the mass loss; $T_{\mathrm{min}}^{\mathrm{DTG}}$ is the temperature corresponding to the minimum of DTG curve; $T_{\mathrm{min}}^{\mathrm{DTA}}$ is the temperature corresponding to the minimum of DTA curve; $T_{\mathrm{max}}^{\mathrm{DTA}}$ is the temperature corresponding to the maximum of DTA curve; $\%\Delta m_{\mathrm{t}}$ is the total mass loss; * the value was obtained by extrapolation of the TG curve

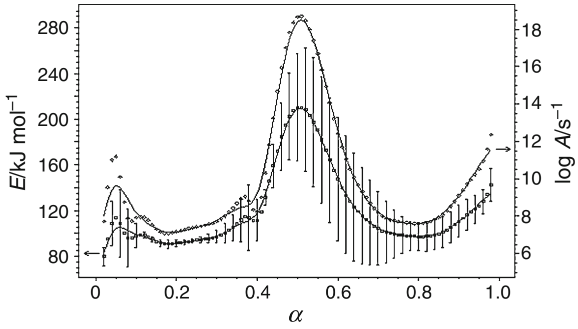

Fig. 2 The curves E_{FR} vs. α_t and log A vs. α_t for entire decomposition (steps I + II + III) of $[CoC_2O_4(OH_2)_2{\cdot}0.5H_2O]_n$ in air flow

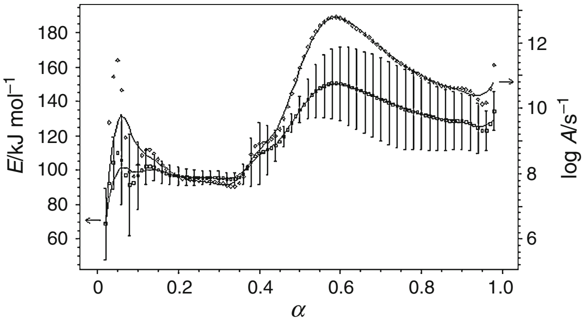

Fig. 3 The curves E_{OFW} vs. α_t and log A vs. α_t for entire decomposition (steps I + II + III) of $[CoC_2O_4(OH_2)_2{\cdot}0.5H_2O]_n$ in air flow

was similarly recorded for the Ozawa–Flynn–Wall activation parameters.

In these two figures the values of the degree of conversion α_t corresponding to the end of steps I, II and III are, respectively, 0.08, 0.35 and 1. The analysis of the presented data shows that:

a. the curves $E_{\mathrm{FR}}(\alpha_t)$ and $E_{\mathrm{OFW}}(\alpha_t)$ exhibit the same shape but for a given value of the degree of conversion $E_{\mathrm{FR}} \neq E_{\mathrm{OFW}}$;
b. for the first step the activation energy increases with conversion but its values exhibit quite high percentage standard deviations (>10%);
c. in the range $0.08 < \alpha_t < 0.33$, step II exhibits a practically constant value of the activation energy with percentage standard deviations lower than 10%;
d. in the range $0.33 < \alpha_t < 0.35$, the activation energy of step II increases with the conversion;
e. for step III the curves $E_{\mathrm{FR}}(\alpha_t)$ and $E_{\mathrm{FWO}}(\alpha_t)$ exhibit a maximum, and the standard deviations of these quantities are relatively high.

The differences between the values E_{FR} and E_{OFW} could be explained by considering the relations which ground the isoconversional methods [26–28]. If E depends on the degree of conversion it is recommended to apply the Friedman method which uses punctual values of the reaction rate and does not include through integration the history of the system in the range 0–α. This is the reason for which the results obtained by means of this method were used in order to find the complex mechanism of heterogeneous reactions [22–25].

For step II the following relation for calculating the degree of conversion was considered:

$$\alpha = \frac{\%\Delta m}{18.94} \quad (2)$$

where 18.94 is the total percentage mass loss in this step.

Figures 4 and 5 show the obtained results by using the isoconversional methods of Friedman and Flynn–Wall–Ozawa. As expected both the values E_{FR} and E_{FWO} are in rather good agreement with those from Figs. 2 and 3 for

$0.08 < \alpha < 0.35$. In both cases log A was calculated considering the first order model.

From Fig. 4 it turns out that:

- for $0 < \alpha < 0.08$, E_{FR} increases from 65 to 105 kJ mol^{-1};
- for $0.08 < \alpha < 0.25$, E_{FR} decreases from 105 to 90 kJ mol^{-1};
- for $0.25 < \alpha < 0.81$, E_{FR} increases from 90 to 99 kJ mol^{-1};
- for $0.81 < \alpha < 0.91$, E_{FR} increases from 99 to 126 kJ mol^{-1};
- the percentage standard deviation of E_{FR} is lower than 10% only for $0.05 < \alpha < 0.82$.

All these facts support the idea that step II is a complex one, which consists probably in a sequence of successive and/or parallel reactions. In order to find the mechanism of the investigated step and the corresponding kinetic parameters, we used the "Netzsch Thermokinetics" program—"Multivariate non-linear regression" based on the assumption that the kinetic parameters are identical for measurements at all heating rates [11]. The procedure was performed to obtain the formal kinetic model to be used in predictions. This aim corresponds to the "technical aspect" of non-linear regression analysis, according to which the kinetic analysis is examined as a tool for data reduction [11].

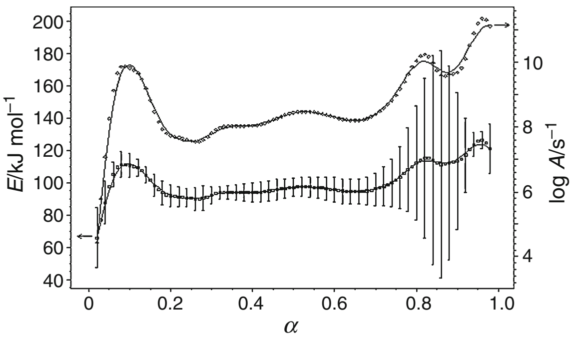

Fig. 4 The curves E_{FR} vs. α and log A vs. α for step II of decomposition of $[CoC_2O_4(OH_2)_2{\cdot}0.5H_2O]_n$ in air flow

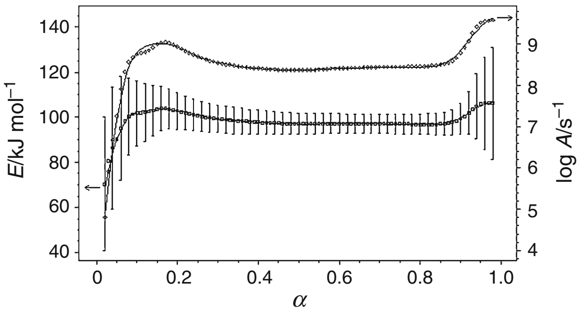

Fig. 5 The curves E_{OFW} vs. α and log A vs. α for step II of decomposition of $[CoC_2O_4(OH_2)_2{\cdot}0.5H_2O]_n$ in air flow

The trials were performed considering the following kinetic models:

- The model of the reaction order, Fn, with $f(\alpha) = (1-\alpha)^n$ where n is the reaction order;
- The Avrami–Erofeev model, An, with $f(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{(1-1/n)}$;
- The Prout and Tompkins model, Bn, with $f(\alpha) = (1-\alpha)^n \alpha^a$.

Some reaction schemes given in the "Netzsch Thermokinetics" program and consisting in consecutive, parallel and/or reversible reactions were taken into account. The values of E vs. α obtained by FR isoconversional method were used as starting parameters for non-linear regression model-fitting procedure. By nonlinear regression, after running the TG experimental data recorded at the above mentioned four heating rates and many reaction schemes, the decomposition of $[CoC_2O_4(OH_2)_2{\cdot}0.5H_2O]_n$ in air flow was found to be satisfactorily described by the scheme: t:f,f: $A \xrightarrow{1} B \xrightarrow{2} C \xrightarrow{3} D$; with the kinetic models Bn–Bn–Bn (the codifications are those used in "Netzsch Thermokinetics" program; A, B, C and D are solid compounds; 1, 2 and 3 denote the mechanistic steps). The kinetic parameters corresponding to this sequence are listed in Table 2.

Table 2 Non-isothermal kinetic parameters after non-linear regression through the t:f,f mechanism of decomposition of $[CoC_2O_4(H_2O)_2{\cdot}0.5H_2O]_n$—step II

Parameter	Value
log A_1/s^{-1}	10.018
E_1/kJ mol^{-1}	110.0
n_1	0.858
Exponent a_1	0.113
log A_2/s^{-1}	8.512
E_2/kJ mol^{-1}	95.0
n_2	0.220
Exponent a_2	0.618
log A_3/s^{-1}	10.792
E_3/kJ mol^{-1}	115.0
n_3	2.32
Exponent a_3	0.230
FollReact 1[a]	0.75
FollReact 2[b]	0.10

Statistical parameters

Correlation coefficient	Durbin–Watson factor	t-critic (0.95; 159)
0.995934	3.411	1.966

[a] Share of reaction step 1 (A → B) in the total process

[b] Share of reaction step 2 (B → C) in the total process

The share of step 3 (C → D) is given by $1 - \sum$(FollReact)

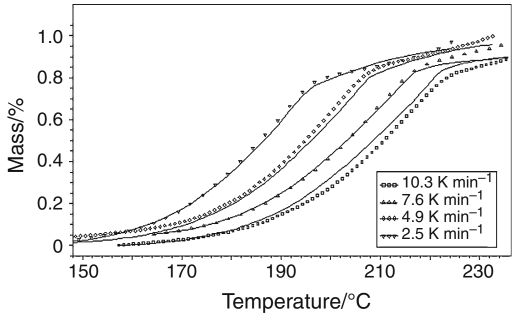

Fig. 6 Checking the validity of t:f,f mechanism of decomposition of $[CoC_2O_4(H_2O)_2 \cdot 0.5H_2O]_n$—step II and parameters given in Table 2. *Filled square* TG experimental values; *continuous lines* TG calculated curve

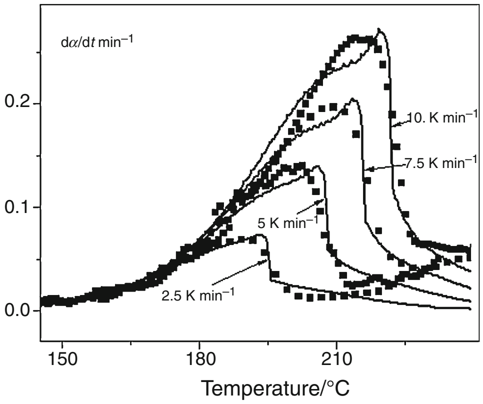

Fig. 7 Checking the validity of t:f,f mechanism of decomposition of $[CoC_2O_4(H_2O)_2 \cdot 0.5H_2O]_n$—step II and parameters given in Table 2. *Filled square* DTG experimental values; *continuous lines* DTG calculated curve

Figures 6 and 7 show, for comparison, the experimental and calculated (using the parameters from Table 2) TG and DTG curves.

For $0.05 < \alpha < 0.90$ one has to notice a satisfactory agreement between experimental and calculated curves which was obtained by heating the samples with 2.5, 5 and 7.55 K min^{-1}. The relative higher differences for $\beta = 10$ K min^{-1} show a possible change of the reaction mechanism when the heating rate is higher than 10 K min^{-1}.

The “Netzsch Thermokinetics” program allows calculation $\alpha(t)$ curve for any temperature program by using the kinetic parameters determined by the nonlinear regression. The kinetic parameters from Table 2 were used in order to calculate the $\alpha(t)$ curve corresponding to the temperature program of the real quasi-isothermal experiment ($T = 150$ °C). The obtained results are shown comparatively with the experimental ones in Fig. 8a. In Fig. 8b the relative errors of t evaluation, $e = \frac{t_{calc} - t_{exp}}{t_{exp}} \times 100$ (t_{exp} is the time necessary to reach the degree of conversion α experimentally determined, t_{calc} is the time to reach the degree of conversion α calculated using the kinetic parameters from Table 2), are shown.

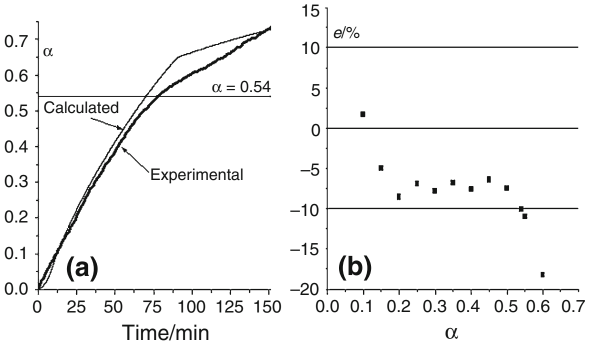

Fig. 8 **a** TG curves experimental and calculated for the quasi-isothermal data; **b** the relative errors of t evaluation for the quasi-isothermal data

We obtained $e < 10\%$ for $\alpha < 0.54$. It means that for $\alpha > 0.54$ either the mechanism of the investigated process is more complex involving a reaction scheme with much more steps, or the dehydration process is overlapped with the subsequent decomposition of the anhydrous compound (step III).

Conclusions

1. The heating curves (TG, DTG and DTA) of the compound $[CoC_2O_4(H_2O)_2 \cdot 0.5H_2O]_n$ in the temperature range 20–300 °C evidence three main decomposition steps.
2. The kinetic analysis of the second step (step II), the only workable kinetically, was performed using the NETZSCH-Thermokinetics program.
3. The isoconversional methods due to Friedman and Flynn–Wall–Ozawa as well as linear and nonlinear regression methods were applied.
4. The applied program, which uses the test F, allowed finding the models which realize the best fitting between the calculated and experimental TG curves.
5. The best fitting was realized for the sequence $A \xrightarrow{1} B \xrightarrow{2} C \xrightarrow{3} D$ with the kinetic models Bn–Bn–Bn.
6. One has to notice a satisfactory agreement between the calculated and experimental TG and DTG curves.
7. The validity of the mechanism scheme obtained by processing of non-isothermal data was also confirmed by the good agreement between $t = t(\alpha)$ calculated and experimental curves for quasi-isothermal data ($T = 150$ °C).

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