Kinetics of Multi-Step Processes of Thermal Degradation of Co(II) Complex With N-Benzyloxycarbonylglycinato Ligand. Deconvolution of DTG Curves

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Abstract:

Thermal decomposition of Co(II) complex with N-benzyloxycarbonylglycinato ligand, [Co(N-Boc-gly)$_2$(H$_2$O)$_4$]·2H$_2$O, in non-isothermal conditions occurs in three complex steps. In order to investigate detail kinetics of first two steps, dehydration and ligand degradation, DTG curves were deconvoluted using product of Gaussian and Lorentzian function. It was shown that process of complex dehydration consists of three, while process of ligand fragmentation consist of five elementary steps. For elementary steps the kinetic triplet (E$_a$, Z and f(α)) was determinated. Kinetic parameters were obtained by application of IKP method. On the basis of Màlek's criteria and Šesták-Berggren's method, Šesták-Berggren's model, f(α)=α^M(1-α)^N was suggested for all elementary steps, while Master plot method and Perez-Maqueda criteria confirmed suggested reaction models. The thermodynamic activation parameters were calculated for process of complex dehydration, and lifetime for first elementary step of the dehydration and ligand degradation processes was estimated.

Keywords: *Kinetics, Co-N-benzyloxycarbonylglycinato complex, Thermal degradation, DTG curves deconvolution.*

1. Introduction

This paper is a continuation of our previous study, which includes multidisciplinary researches of *d* metal complexes with *N*-benzyloxycarbonylglycinato ligand [1–5]. Co(II) complex with this type of ligand, [Co(*N*-Boc-gly)$_2$(H$_2$O)$_4$]·2H$_2$O, was synthesized and characterized by IR, NMR and EA spectroscopy. The structure was optimized by density functional theory calculations (DFT) [1]. The biological activity, the mechanism and kinetics of thermal decomposition were also investigated [1–3]. The specificity of this complex is presence of differently bonded water molecules. Four water molecules are in the inner and two water molecules are in the outer sphere. Complex has octahedral geometry with two monodentate ligands in the *tran*s position [1]. Thermal degradation of Co(II) complex occurs in three processes [2, 3] starting with loss of crystallization and coordinated water molecules followed by ligand fragmentation. The transformations in each process cause changes in the structure and chemical composition of investigated compound, affecting the course of further

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degradation. Individual degradation processes can be described using completely different reaction paths, affecting a profile of dependence of the Arrhenius parameters on conversion degree. These dependences showed that all three observed processes, of thermal degradation of the investigated compound are complex involving more than one individual process as can be expected for solid-state heterogeneous reactions. On the basis of these dependences we discussed the mechanism for each of the observed processes by using the Vyazovkin's algorithm [6]. In literature only few papers can be found in which the authors deal with the detailed kinetics of the complex compounds, including determination of kinetic triplet [7–10]. In order to deal with detail kinetics, to obtain the elementary steps of complex degradation processes and their kinetic triplets (E_a, Z and $f(\alpha)$), deconvolution of DTG curves of these processes was performed. The kinetic triplet is needed to provide mathematical description of the process [11]. If the kinetic triplet is determined correctly it can be used to reproduce the original kinetic data as well as to predict the process kinetics outside the experimental temperature region. For example, it may be used for predicting the time to reach any extent of conversion at any desired temperature [12].

2. Experimental

The investigated Co(II) complexes was prepared in a simple reaction between $CoCl_2 \cdot 6H2O$ and *N*-Boc-glyH (molar ratio 1:2, ethanol - water mixture at pH 5–6). Further details can be found in literature [1]. The TG data were collected on an SDT Q600 (TA Instruments) apparatus for simultaneous TG-DTA/DSC analysis. The instrument was calibrated by sapphire (for heat capacity), as well as by In and Zn (for temperature and DSC signals). TG/DSC experiments were performed from room temperature to 900 ºC with sample masses about 6 mg in a dry nitrogen atmosphere (flow rate 100 cm^3 min^{-1}). The alumina crucibles, with an empty crucible as a reference, were used. DTG curves at different heating rates (5 – 20 ºC min^{-1}) were obtained under similar conditions (mass of the samples: 5 mg) in Pt crucibles. A Pt crucible with a small amount of Al_2O_3 was used as a reference.

Deconvolution was performed by processing DTG peaks of these complexes to simple separated peaks, using the cross product of Gaussian and Lorentzian function:

$$y = \frac{a_0}{1 + a_3\left(\frac{T - a_1}{a_2}\right)^2 \exp\left[(1 - a_3)\frac{1}{2}\left(\frac{T - a_1}{a_2}\right)^2\right]},$$

where a_0 is peak amplitude, a_1 is peak center, a_2 is peak width, a_3 is peak shape and T is temperature. For deconvolution and determination of parameters values computer program Peak Fit 4.11 was used.

Methodological aspects of solid state kinetics in non-isothermal conditions

The reaction rate for solid state processes is function of two variables: temperature (T) and the conversion degree (α):

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where the reaction rate dependence of the temperature is presented with the rate constant, $k(T)$, and the dependence of the conversion degree is given with reaction model, $f(\alpha)$. In general $k(T)$ is described by an Arrhenius equation:

$$k(T) = Z\exp\left(\frac{-E_a}{RT}\right) \tag{2}$$

where Z and E_a are kinetic parameters, preexponential factor and the apparent activation

energy, R is the gas constant, and T is temperature (in K).

Combination of equations (1) and (2) leads to the equation that provides the basis for the differential kinetic methods:

$$\frac{d\alpha}{dt} = Z \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \tag{3}$$

In this form of equation (3) is applicable in isothermal, as well as in non-isothermal conditions, but also, with the introduction of $\beta = dT/dt$ equation (3) can be rearranged:

$$\beta \frac{d\alpha}{dT} = Z \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \tag{4}$$

Isoconversional methods also known as "model-free methods" require determination of the temperature T_α at which an equivalent stage of the reaction occurs for various heating rates [13]. Widely accepted procedure is Kissinger-Akahira-Sunose's (KAS) method [14, 15] in the form:

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = \ln\left(\frac{ZR}{E_{a,\alpha}} f(\alpha)\right) - \frac{E_{a,\alpha}}{RT_\alpha} \tag{5}$$

In this sense [14, 15], the linear isoconversional relationship of $\ln(\beta/T_\alpha^2)$ versus $1/T_\alpha$ can be used to determine the kinetic parameters: apparent activation energies $E_{a,\alpha}$ (from the slope) and $\ln[(ZRf(\alpha))/E_{a,\alpha}]$ intercepts for selected conversion degree according to equation (5), even without the knowledge of the true conversion function. If E_α does not depend on α, the investigated process can be treated as single-step process and should be described by a unique kinetic triplet. If E_α changes with α process is complex [16–19].

In order to obtain the appropriate conversion function for processes considered as single-step process, we can discriminate between the set of conversion functions [20] by applying the Màlek's method [21, 22], Šesták-Berggren's method [23], Master plot procedure [24], and Perez-Maqueda criteria [25].

Having determined apparent activation energy, Màlek's method [21] involves the introducing two new functions defined as

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right) \exp\left(\frac{E_a}{RT}\right) \text{ and } z(\alpha) \approx \left(\frac{d\alpha}{dt}\right) T^2 \tag{6}$$

These two functions can be easily obtained by a simple transformation of experimental data, $d\alpha/dt$, normalized within (0, 1) interval and by using values of E_a from KAS method. In non-isothermal conditions $y(\alpha)$ and $z(\alpha)$ plots are independent from heating rate and they exhibit maxima at α_y^* and α_z^* [21, 22]. These maxima have characteristic values for basic kinetic models [22].

In the case when the maximum α_y is in the range from 0 to α_z and α_z has no maximum at 0, empirical Šesták-Berggren's equation is applied in the form [23]:

$$f(\alpha) = \alpha^M (1-\alpha)^N \tag{7}$$

where M and N are kinetic parameters. In this case reaction rate is given as:

$$\frac{d\alpha}{dt} = Z \exp\left(-\frac{E_a}{RT}\right) \alpha^M (1-\alpha)^N \tag{8}$$

which can also be written in the following form:

$$\ln\left[\left(\frac{d\alpha}{dt}\right) \exp\left(\frac{E_a}{RT}\right)\right] = \ln Z + N \ln\left[\alpha^p (1-\alpha)\right] \tag{9}$$

where p is the ratio of the kinetic parameters, and can be calculated as follows:

$$p = \frac{M}{N} = \frac{\alpha_y^{max}}{(1-\alpha_y^{max})} \tag{10}$$

α_y^{max} is obtained from the function $y(\alpha)$, equation (6).

From the linear dependence $\ln[(d\alpha/dt)\exp(E_a/RT)] = f(\ln[\alpha^p(1-\alpha)])$ the parameter N, that represents the slope, is determined. Parameter M is determined from the ratio given by equation (10).

According to Master plot procedure [24], for a single-step process, the following equation is applied, taking $\alpha = 0.5$ as the reference value:

$$\frac{f(\alpha)}{f(0.5)} = \frac{d\alpha/dt}{(d\alpha/dt)_{0.5}}\frac{\exp(E_a/RT)}{\exp(E_a/RT_{0.5})} \tag{11}$$

where $(d\alpha/dt)_{0.5}$, $T_{0.5}$, and $f(0.5)$ are rate of the kinetic process, reaction temperature and conversion function at $\alpha = 0.5$. The left side of the equation is reduced theoretical curve characteristic for each kinetic model. Right side of the equation corresponds to a reduced rate of kinetic processes and can be obtained from experimental data if apparent activation energy, which has a constant value in the investigated temperature range, is known. Comparing the left and the right side of the equation (11) the reaction model that describes the experimental data of the process can be determined, i.e., for particular α experimentally determined value of reduced rate of kinetic processes $\dfrac{d\alpha/dt}{(d\alpha/dt)_{0.5}}\dfrac{\exp(E_a/RT)}{\exp(E_a/RT_{0.5})}$ and theoretically calculated values $\dfrac{f(\alpha)}{f(0.5)}$ are equal if appropriate reaction model is applied.

According to Perez-Maqueda criteria [25] correct reaction model corresponds to the independence of the activation parameters of the heating rate. If Coats-Redfern equation [26] is used

$$\ln\left(\frac{\beta g(\alpha)}{T_\alpha^2}\right) = \ln\left(\frac{Z_j}{E_{a,j}}\right) - \frac{E_a}{RT_\alpha} \tag{12}$$

where $g(\alpha)$ is integral form of reaction model, and j specifies the reaction model, then all the points (for all heating rates) of the dependence $\ln\left(\dfrac{\beta g(\alpha)}{T_\alpha^2}\right)$ *vs* $1/T$ should lie on a the same straight line if correct reaction model is used.

In accordance with IKP method based on the real compensation effect [24, 27] the straight lines of $\ln Z_j$ versus E_j dependences should be constructed using the apparent activation parameters obtained by Coats-Redfern method (for all heating rates). These straight lines should intersect in one point corresponding to the true values known as "invariant activation parameters", $\ln Z_{inv}$ and E_{inv} [28].

The invariant kinetic parameters $\ln Z_{inv}$ and E_{inv}, were evaluated by using the super-relation:

$$a_\beta = \ln Z_{inv} - b_\beta E_{inv} \tag{13}$$

The thermodynamic activation parameters, change of activation entropy ($\Delta S^{\#}$), activation enthalpy ($\Delta H^{\#}$) and Gibbs free energy of activation ($\Delta G^{\#}$), were calculated for the process of thermal degradation. From the Eyring theory of transition state [29–32] the change of activation entropy at the formation of the activated complex from the reagent may be calculated according to the formula [29–32]:

$$\Delta S^{\#} = R\ln\frac{Zh}{e\chi k_B T_p} \tag{14}$$

where h is the Planck constant, e is the Euler's number ($e = 2.7183$), χ is the transition factor (which is unity for mononuclear reactions), k_B is the Boltzmann constant and T_p is the peak temperature of DTG curve. Preexponential factor, Z, is calculated using equation (5) with appropriate reaction model.

Considering that

$$\Delta H^{\#} = E - RT_{\mathrm{p}} \quad\quad (15)$$

the changes of the enthalpy and Gibbs free energy for the activated complex formation can be calculated using thermodynamic equation:

$$\Delta G^{\#} = \Delta H^{\#} - T_{\mathrm{p}}\Delta S^{\#} \quad\quad (16)$$

Since lifetime estimations are very useful in development or selection of materials (e.g. polymers) for different applications we also used them in order to determine the application possibilities of the investigated complexes due to its biological activity. The estimated lifetime or the time accelerating aging (t_{f}) is defined as the time when the mass loss reaches five mass percent's, i.e., $\alpha = 0.05$ [33–36] and can be calculated by general equation:

$$t_f = \frac{g(0.05)}{Z}\exp\left(\frac{E_a}{RT}\right) \quad\quad (17)$$

3. Results and discussion

Thermal degradation of $[Co(N\text{-Boc-gly})_2(H_2O)_4]\cdot 2H_2O$ is a stepwise process involving one dehydration process and two processes of degradation of dehydrated complex [2, 3].

The dependence of Arrhenius parameters on conversion degree showed that all the observed processes of thermal degradation are complex, involving more than one single step [3]. KAS method for complex dehydration process shown that the activation energy increases from the value of 81.8 kJ mol^{-1}, reaching a maximum of 104.3 kJ mol^{-1}, and then decreases to the value of 74.5 kJ mol^{-1} [2]. The obtained profile indicates that dehydration process involves a series of competitive dehydration steps of differently bound water molecules [1] complicated by diffusion [37]. The obtained values of KAS method for complex ligand degradation process [2] shows that the activation energy increases from the value of 123.3 kJ mol^{-1}, and value of 156.6 kJ mol^{-1} reaches at the $\alpha = 0,6$, indicating complex mechanism involving parallel reactions [6].

In order to analyze each elementary step the DTG curves of first two complex processes, dehydration and decomposition of the ligand in the Co(II) complex, were deconvoluted into three, ie five elementary steps as presented in Fig 1. Further course of decomposition (third step) was not considered because of the great complexity of the process, as can be seen from α–T curves [3].
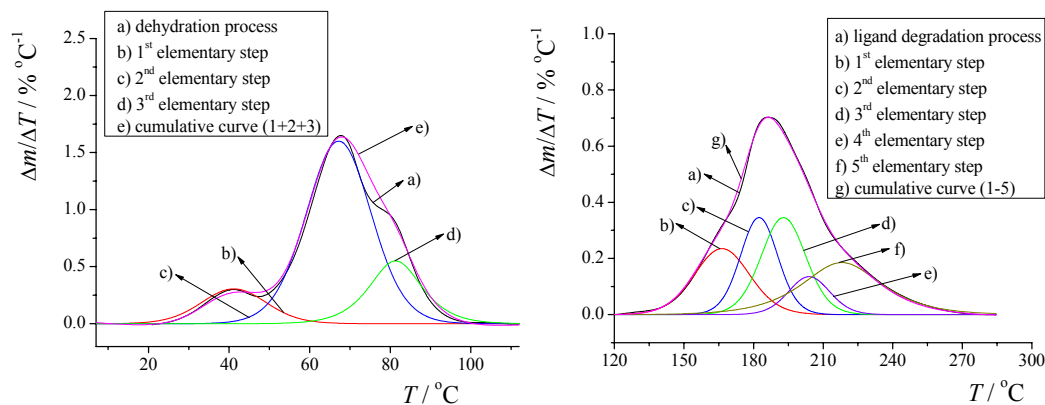

Fig. 1. Deconvolution of DTG curves for processes of dehydration and ligand degradation for the Co(II) complex, $\beta = 5$ °C min^{-1}.

Dehydration process

Deconvoluted curves were used to determine conversion degree. The constructed $\alpha-T$ curves were used for the application of KAS isoconversional method. The obtained dependence of activation energies on conversion degree are shown at Fig 2.
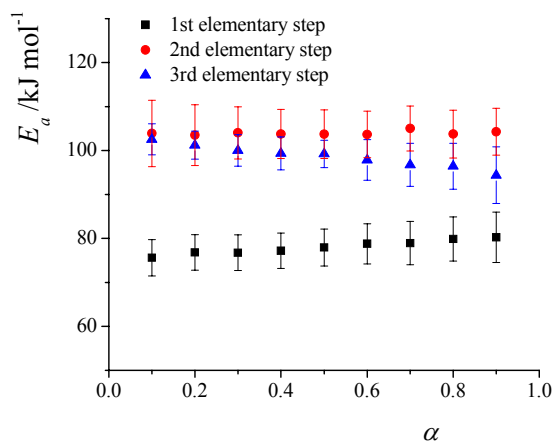

Fig. 2. The dependence of E_a *vs* α obtained by KAS isoconversional method for three elementary steps of dehydration process.

In the case of all three steps the activation energies, determined by KAS method show a slight change (1.5–8%) in the whole range of conversion degree, indicating single step processes with the average values of the activation energies of 78.0, 103.9 and 98.6 kJ mol^{-1}, respectively.

In order to determine isokinetic parameters, activation energy, E_a, and preexponential factor, Z, invariant kinetic parameters (IKP) method [24, 27] was applied. Values of invariant kinetic parameters are presented in Tab. I.

The aim of Màlek's method application was to find an appropriate reaction model for elementary steps [21, 22]. The results are shown in Fig 3.

In all three cases, the dependences $y(\alpha)-\alpha$, ie $z(\alpha)-\alpha$ have the same shape. Convex form and positions of maxima, $\alpha_{y\max} \approx 0.2$ and $\alpha_{z\max} \approx 0.5$, based on Màlek's criteria [22] suggest Šesták-Berggren's model [23]. Therefore Šesták-Berggren's method was applied in order to determine values of M and N parameters. Reaction models were established in the form as presented in Tab. I.

Tab. I Kinetic triplets for elementary steps of dehydration process.

	E_a /kJ mol^{-1}	Z /min^{-1}	$f(\alpha)$
1st elementary step	80.0±6.9	3.4·10^{12}	$\alpha^{0.31}(1-\alpha)^{1.24}$
2nd elementary step	103.5±8.2	1.3·10^{15}	$\alpha^{0.36}(1-\alpha)^{1.42}$
3rd elementary step	91.3±8.2	6.1·10^{12}	$\alpha^{0.64}(1-\alpha)^{1.49}$

The validation of determined kinetic triplets (Tab. I) was done by application of Master-plot method [24] and Perez-Maqueda criteria [25]. In Fig 4 comparison of experimental and theoretical curves for all three elementary steps were given, while in Fig 5 dependence of $\ln\left(\dfrac{\beta g(\alpha)}{T_\alpha^2}\right)$ *vs* $1/T$ using data at all four heating rates for obtained reaction models are shown.
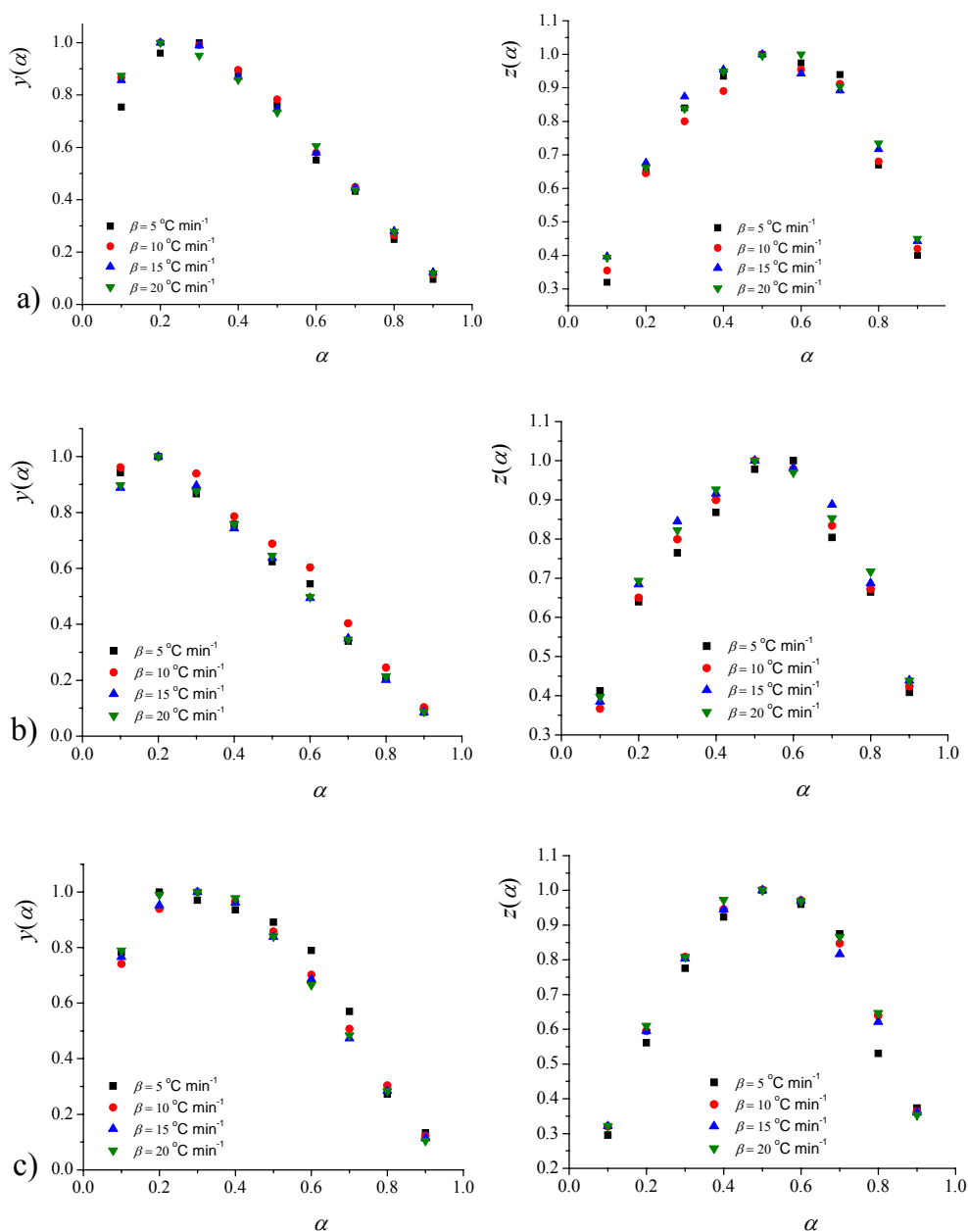
Fig. 3. Functions $y(\alpha)$ and $z(\alpha)$ for a) first, b) second c) third elementary step of dehydration process.

Matching of experimental and obtained curves shown at Fig 4, as well as linearity of dependences shown at Fig 5 confirmed validity of obtained kinetic triplets.

The values of the activation energy for individual elementary steps obtained by KAS (78.0, 103.9, 98.6 kJ mol^{-1}, respectively) and IKP method (Tab. I) are in very good agreement.
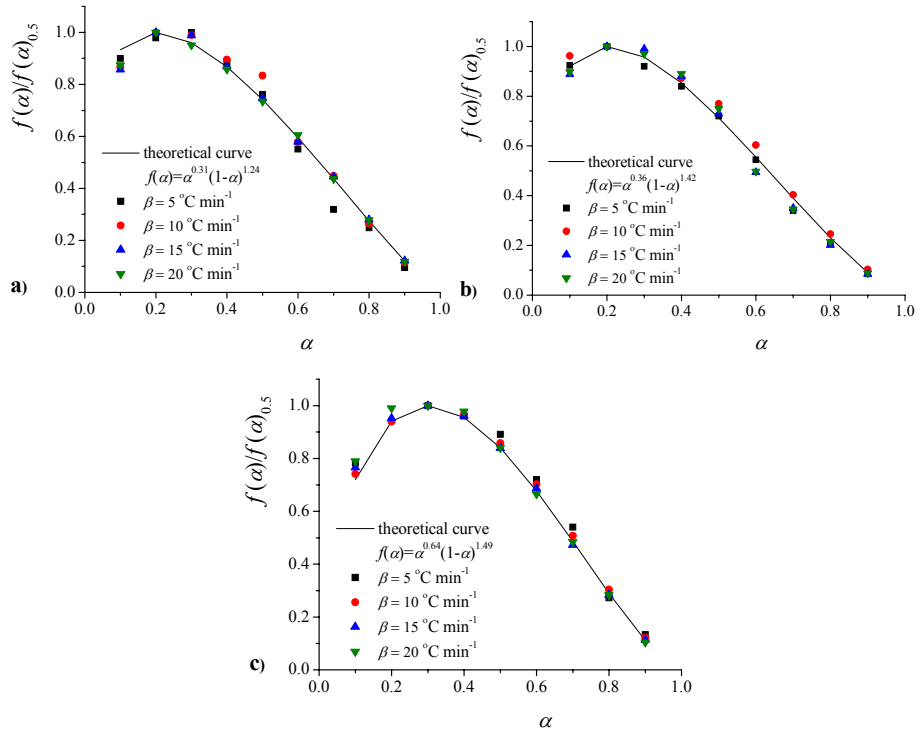
Fig. 4. Comparative review of the experimental and the curves obtained on the basis of certain models for a) first, b) second, c) third elementary step of dehydration process.
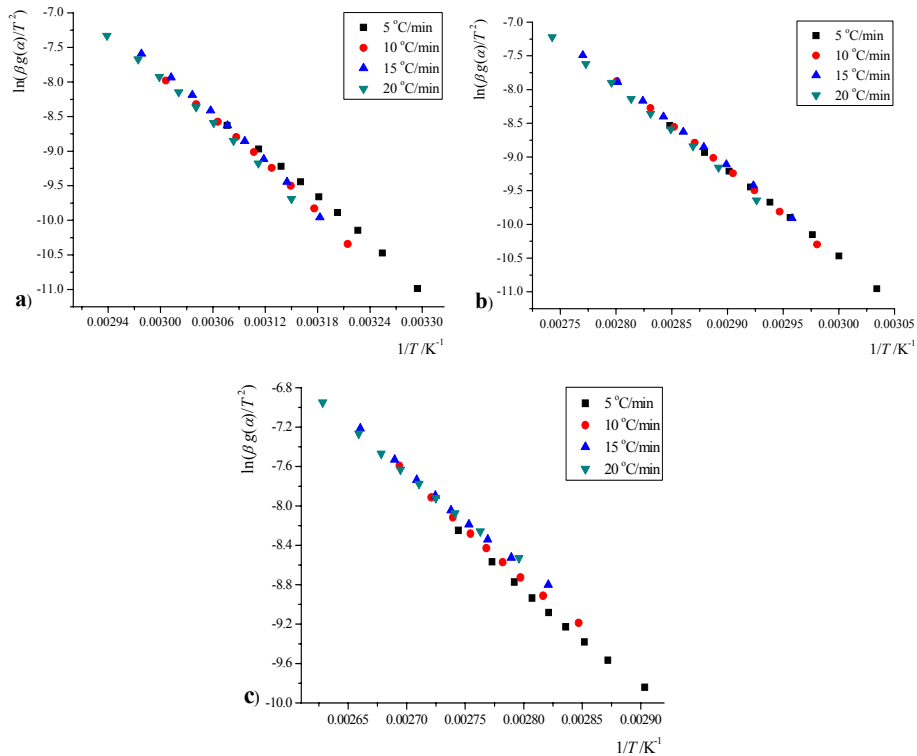

Fig. 5. Application of Perez-Maqueda criteria for determined kinetic models for a) first, b) second, c) third elementary step of dehydration process.

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Since activation energy changes during the thermal degradation process we examined changes of thermodynamic activation parameters during these processes. For this purpose we used equations (14)–(16) for calculation of the values of the change of entropy, $\Delta S^{\#}$, enthalpy, $\Delta H^{\#}$, and Gibbs free energy, $\Delta G^{\#}$, for the formation of the activated complex (Tab. II) for all three elementary steps. In order to obtain these parameters values of preexponential factor, Z, were calculated from intercepts $\ln[(ZRf(\alpha))/E_{a,\alpha}]$ for selected conversion degree according to equation (5), and values of $E_{a,\alpha}$ obtained by KAS method were used, as well as reaction models given in Tab. I.

As seen from Tab. II the difference in energy between the reagent and activated complex (change of activation enthalpy) is small for all three elementary steps (average values are 75.3, 101.1 and 95.6 kJ mol^{-1}, respectively) indicating that the formation of activated complex is favored because the potential energy barrier is low.

Tab. II Thermodynamic activation parameters for three elementary steps of dehydration process.

α	$\Delta S^{\#}$ /J mol^{-1} K^{-1}	$\Delta H^{\#}$ /kJ mol^{-1}	$\Delta G^{\#}$ / kJ mol^{-1}
First elementary step			
0.1	-3.8	72.9	74.1
0.2	-3.5	74.2	75.3
0.3	-5.7	74.1	75.9
0.4	-5.2	74.5	76.2
0.5	-3.2	75.3	76.3
0.6	-0.4	76.1	76.2
0.7	0.8	76.3	75.9
0.8	5.5	77.2	75.4
0.9	10.5	77.5	74.2
Second elementary step			
0.1	64.3	101.0	78.7
0.2	58.8	100.6	80.3
0.3	58.1	101.1	81.0
0.4	56.1	100.9	81.4
0.5	55.4	100.8	81.6
0.6	55.5	100.8	81.5
0.7	60.4	102.1	81.2
0.8	58.6	100.9	80.5
0.9	64.6	101.4	79.0
Third elementary step			
0.1	50.9	99.5	81.1
0.2	41.4	98.2	83.2
0.3	35.3	97.0	84.2
0.4	32.0	96.3	84.7
0.5	31.3	96.2	84.9
0.6	27.7	94.8	84.8
0.7	25.7	93.7	84.4
0.8	27.1	93.4	83.6
0.9	26.5	91.4	81.8

Low activation entropies in the first elementary step indicate that the complex has just passed through some kind of physical or chemical rearrangement of its initial structure, bringing it to a state close to its own thermodynamic equilibrium. Complex shows little reactivity, increasing the time necessary to form the activated complex. High activation

entropies obtained for the second and third elementary step point out that partially degraded complex is far from its thermodynamic equilibrium. The reactivity is higher and the system can react faster to produce the activated complex [38].

In all three elementary steps values of change of Gibbs free activation energy increase and then decrease during the process of degradation, with maximum at $\alpha = 0.5$. This trend reveals the total energy increase of the system at the approach of the reagents and the formation of the activated complex until the $\alpha = 0.5$.
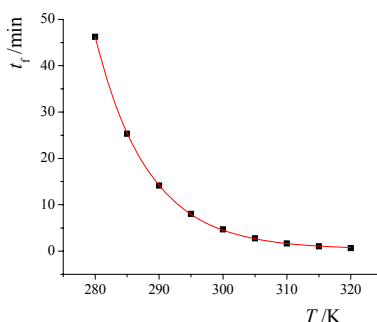
Fig. 6. Dependence of lifetime on the temperature at 5 % conversion for first elementary step of dehydration process.

Lifetime for Co(II) complex during the dehydration process was estimated for the first elementary step using equation (17), Fig 6. Values of activation energy and preexponential factor obtained by IKP method (Tab. I) were used, as well as, kinetic model presented in Tab. I. There was no sense to carry out lifetime predictions for remaining two steps since transition states were not determined.

Dependence of lifetime versus temperature is exponential function that can be presented with equation

$$y = A \cdot e^{(-x/B)} + C \qquad (18)$$

where values of parameters A, B and C are $1.9 \cdot 10^{16}$, 8.3 and 0.4, respectively.

From the results shown at Fig 6 we can conclude that the lifetime is a parameter strongly depending on the temperature and decreases with increase of the temperature.

Ligand degradation process

In the case of ligand degradation process only first three elementary steps were investigated, because of their importance. On the basis of data from sigmoid $\alpha-T$ curves values of activation energies on conversion degree by using KAS isoconversional method were obtained, Fig 7.
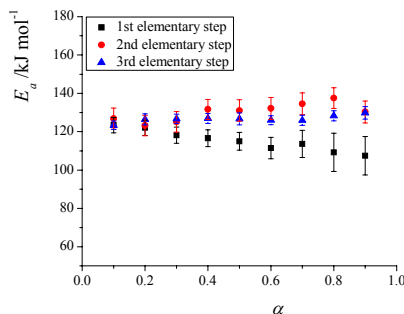

Fig. 7. The dependence of E_a *vs* α obtained by KAS isoconversional method for three elementary steps of ligand degradation process.

Small changes in the apparent activation energy with the degree of conversion (5–11%) indicate that examined steps are elementary. The average values of activation energies are 115.2, 130.3 and 126.7 kJ mol^{-1}, respectively.

The two members of kinetic triplet, activation energy, E_a, and preexponential factor, Z, were determined by IKP method [24, 27] and presented in Tab. III.

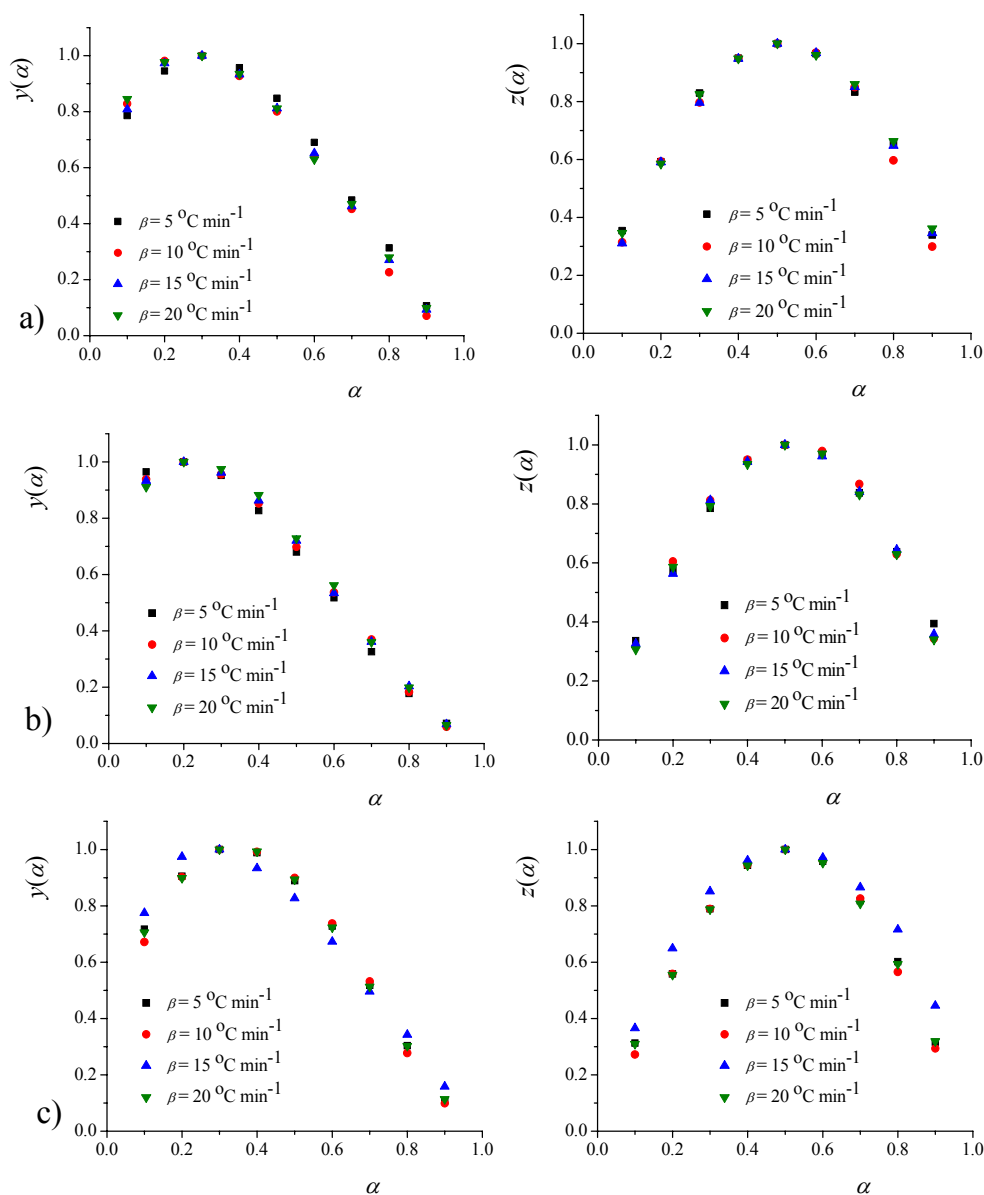To find a suiTab. reaction model for the elementary steps Màlek's method was applied [21, 22], Fig 8.

Fig. 8. Functions $y(\alpha)$ and $z(\alpha)$ for a) first, b) second c) third elementary step of ligand degradation processes.

In all three cases, the dependence $y(\alpha)$-α, ie $z(\alpha)$-α has the same shape and position of the maximum ($\alpha_{y\max} \approx 0.2$ and ($\alpha_{z\max} \approx 0.5$) as in the case of elementary steps of

dehydration process. The results for all three elementary steps, based on Màlek's criteria [22] suggest Šesták-Berggren's model [23] presented in Tab. III.

Tab. III Kinetic triplets for elementary steps of ligand degradation process.

	E_a /kJ mol^{-1}	Z /min^{-1}	$f(\alpha)$
1st elementary step	108.7±9.1	$1.0 \cdot 10^{12}$	$\alpha^{0.36}(1-\alpha)^{1.46}$
2nd elementary step	137.4±6.2	$1.1 \cdot 10^{15}$	$\alpha^{0.44}(1-\alpha)^{1.18}$
3rd elementary step	168.4±5.8	$1.0 \cdot 10^{18}$	$\alpha^{0.36}(1-\alpha)^{1.46}$

As in the case of elementary steps of dehydration process, verification of the kinetic triplets was performed by using Master-plot method [24] and Perez-Maqueda criteria [25]. Comparison of experimental and theoretical curves for the three elementary steps of ligand degradation is shown in Fig. 9.
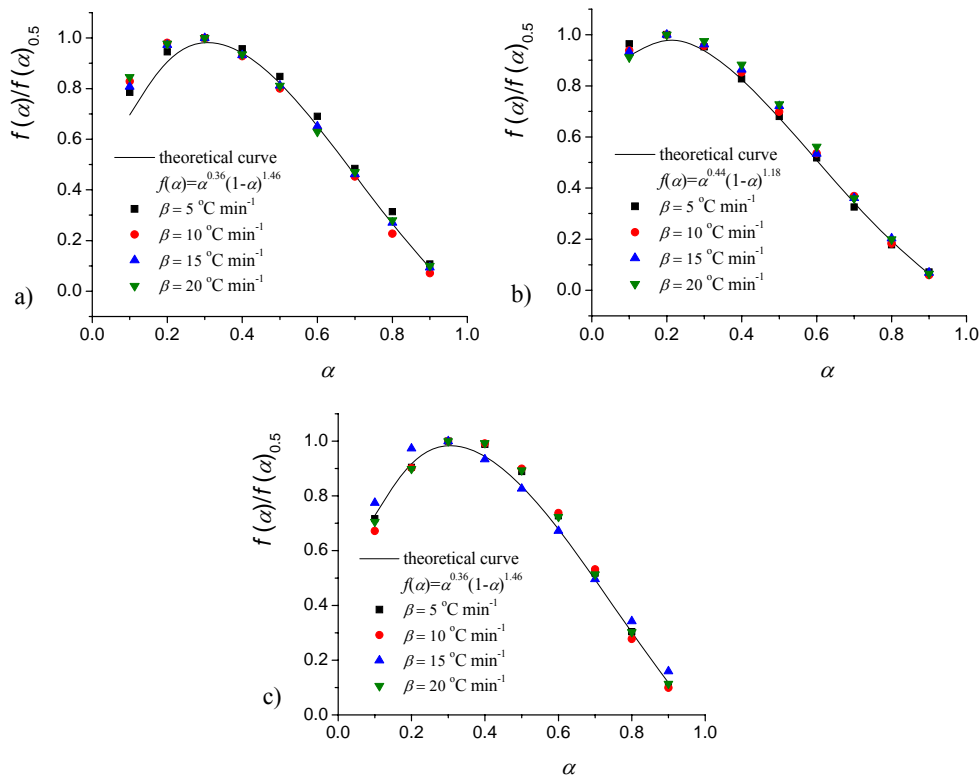

Fig. 9. Comparative review of the experimental and the curves obtained on the basis of certain models for a) first, b) second c) third elementary step of ligand degradation processes.

Results of Perez-Maqueda criteria application are shown at Fig 10. Results shown at Figs 10 and 11 confirmed accuracy of obtained kinetic models.

The activation energies obtained by KAS isoconversion method and the activation energy obtained by IKP method are in a good agreement (KAS method: 115.2, 130.3, 126.7 kJ mol^{-1}, respectively and IKP method is given in Tab. III).

As in the case of the dehydration process, estimation of lifetime for the first elementary step was carried out. Results are presented at Fig 11.
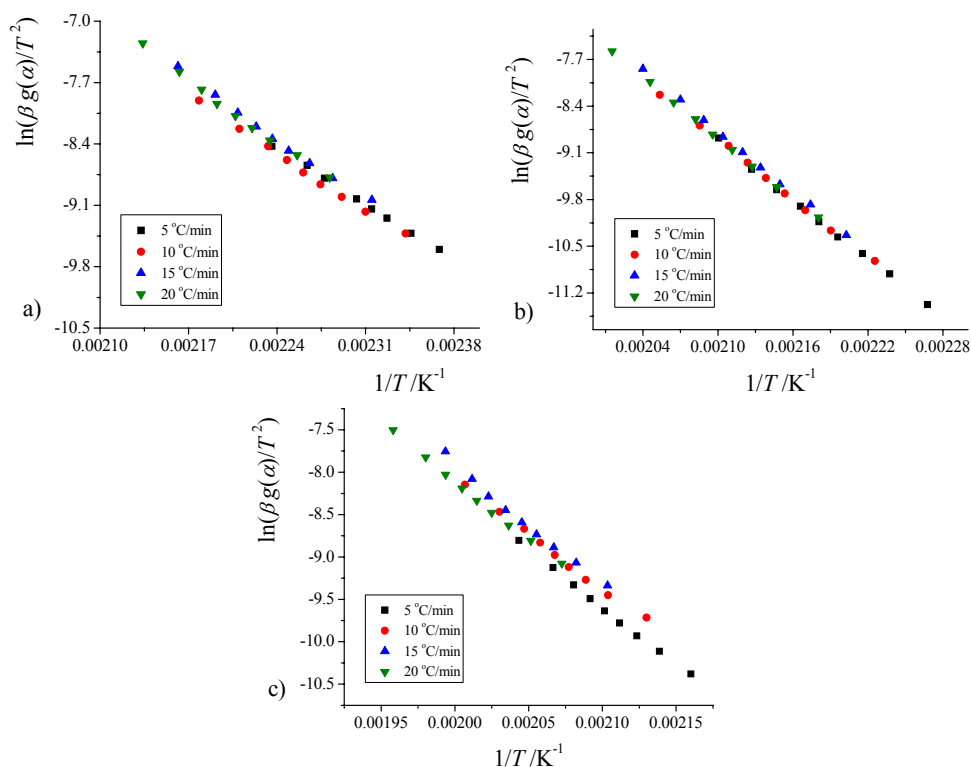
Fig. 10. Application of Perez-Maqueda criteria for determined kinetic models for a) first, b) second, c) third elementary step of ligand degradation processes.
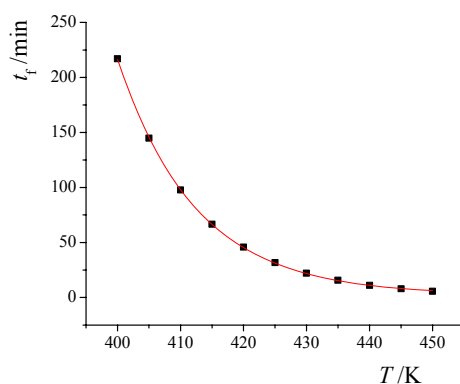

Fig. 11. Dependence of lifetime on the temperature at 5 % conversion for first elementary step of ligand degradation process.

     The same exponential function (equation (18)) describes the lifetime dependence of the temperature, for the dehydration process as well as the ligand degradation process. There are only the differences in values of A, B and C parameters, which are $2.1 \cdot 10^{16}$, 12.4 and 2.6, respectively. From Fig 11 it can be seen that dehydrated complex is quite sTab. at 127 °C (400 K), lifetime is more than 200 minutes.

     In order to verify accuracy of method used for separating individual peaks, as well as obtained kinetic triplets, equation (4) was used. On the basis of experimental data (β = 5 °C min^{-1}) the dependence $\beta d\alpha/dT$ = f(T) was formed, while on the basis of obtained kinetic triplets dependence $Z\exp(-E_a/RT)f(\alpha)$ = f(T) was formed. Both curves are normalized in (0, 1) area. Comparison of these two dependencies, the experimental and theoretical curves for

dehydration and ligand degradation processes for three elementary steps are shown in Figs 13 and 14, respectively.
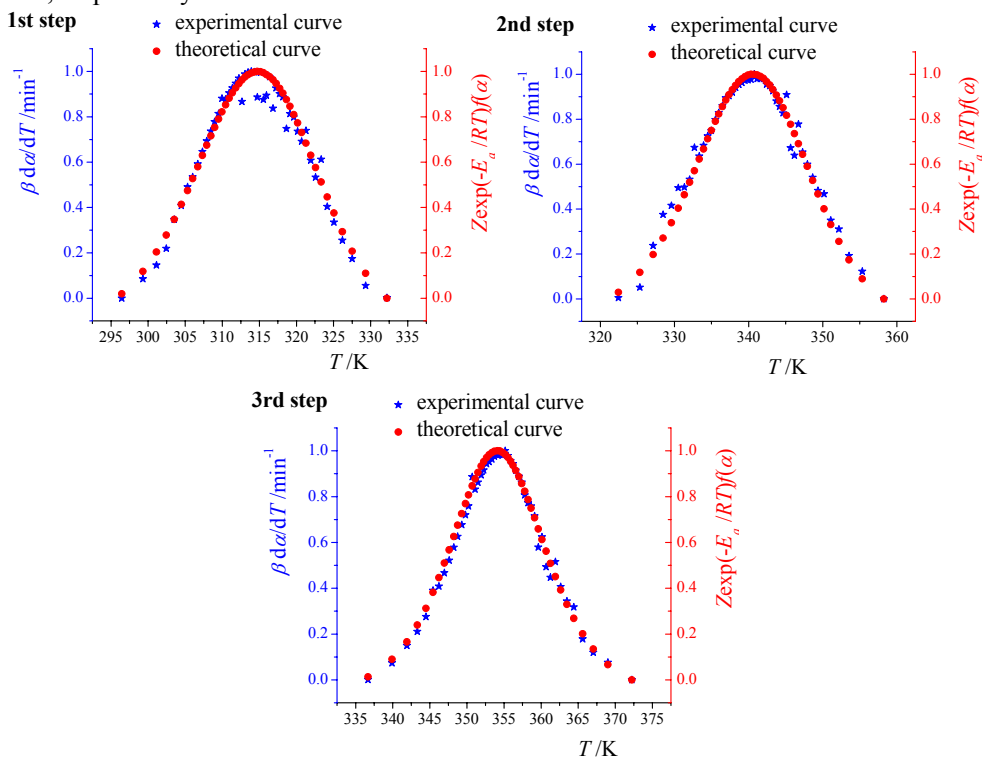

Fig. 12. Comparison of experimental and theoretical curves for the three elementary steps of dehydration process.
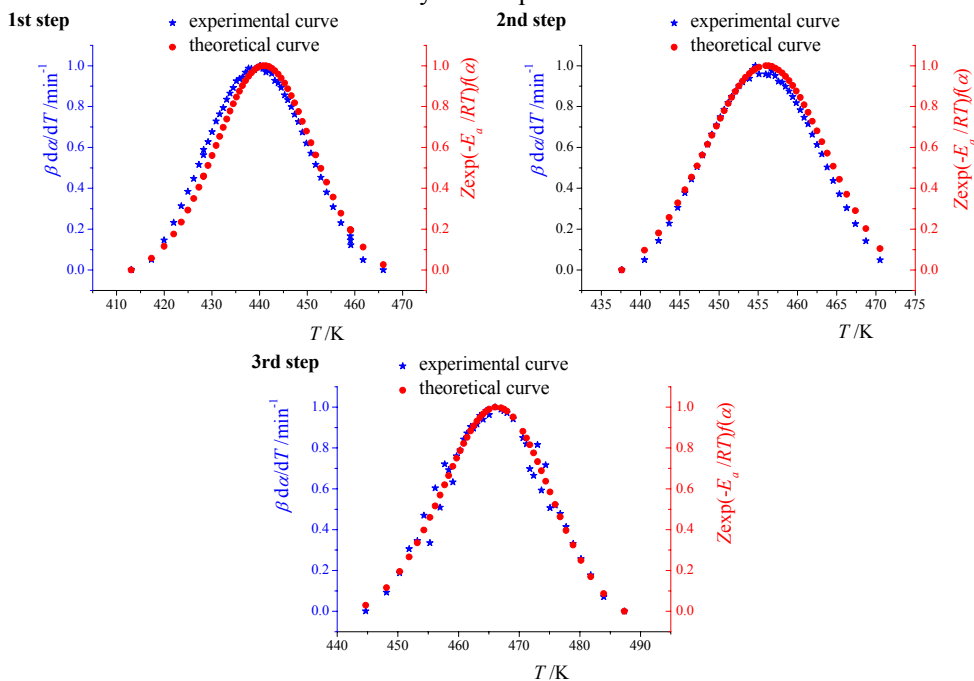

Fig. 13. Comparison of experimental and theoretical curves for the three elementary steps of ligand degradation process.

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Considering that the experimental and theoretical curves, in all cases, overlap, we have concluded that the DTG peaks are well deconvoluted, and that the obtained kinetic triplets are accurate.

4. Conclusion

Solid state reactions are in most cases complex processes involving several overlapping processes. In the case of investigated thermal decomposition of $[Co(N\text{-Boc-gly})_2(H_2O)_4]\cdot 2H_2O$ complex all three degradation steps are complex involving more then one elementary step. DTG curves of complex degradation processes were deconvoluted using product of Gaussian and Lorentzian function in order to obtain elementary steps, and to determinate the kinetic triplets (E_a, Z and $f(\alpha)$). DTG curves of dehydration process and of degradation ligand process were deconvoluted in three ie five individual steps. The trend of activation energy obtained by KAS method indicates that deconvoluted peaks correspond to the elementary processes. The values of the activation energy for the elementary steps obtained by KAS and IKP methods are in good agreement. Also, for all processes it was found that these values for the activation energies are in excellent agreement with values obtained by KAS method for complex processes [3]. Functions $y(\alpha)$ and $z(\alpha)$ for all elementary steps have the same shape and maxima in the same areas, and per Màlek's criteria indicates the Šesták-Berggren's model. The difference is in the parameters M and N, which were determinated by the Šesták-Berggren's method and therefore the kinetic models are different. The obtained reaction models are supported by the use of Master plot method, Perez-Maqueda criteria, as well as by comparison of the experimental and theoretical curves obtained by using equation (4). Estimation of lifetime for the dehydration process and ligand degradation process indicated that lifetime is more sensitive concerning the temperature for first elementary step of dehydration process, then for the first elementary step of ligand degradation process.

Acknowledgements

5. References

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Садржај: *Термичка разградња комплекса Co(II) са N-бензилоксикарбонилглицинатним лигандом, [Co(N-Boc-gly)₂(H₂O)₄]·2H₂O, у неизотермским условима одвија се у три сложена ступња. У циљу испитивања детаљне кинетике прва два ступња, дехидратације и деградације лиганда, DTG криве су раздвојене коришћењем векторског производа Гаусијан и Лоренцијан функције. Утврђено је да се сложени*

процес дехидратације састоји од три, док се процес фрагментације лиганда састоји од пет елементарних ступњева. За елементарне ступњеве одређени су кинетички триплети (E_a, Z и $f(\alpha)$). Кинетички параметри одређени су применом IKP методе. На основу Малековог критеријума и Шестак-Бергренове методе, Шестак-Бергренов модел $f(\alpha)=\alpha^M(1-\alpha)^N$ је предложен за све елементарне ступњеве, док су Мастер плот метода и Перез-Македа критеријум потврдили предложене реакционе моделе. Термодинамички активациони параметри израчунати су за процес дехидратације комплекса, а време живота је одређено за први елементарни ступањ дехидратације и деградације лиганда.

Кључне речи: *Кинетика, Со-N-бензилоксикарбонилглицинато комплекс, Термичка разградња, Раздвајање DTG кривих*