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NON-ISOTHERMAL STUDIES ON MECHANISM AND KINETICS OF THERMAL DECOMPOSITION OF COBALT(II) OXALATE DIHYDRATE

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Abstract

Thermal decomposition of $CoC_2O_4·2H_2O$ was studied using DTA, TG, QMS and XRD techniques. It was shown that decomposition generally occurs in two steps: dehydration to anhydrous oxalate and next decomposition to Co and to CoO in two parallel reactions. Two parallel reactions were distinguished using mass spectra data of gaseous products of decomposition. Both reactions run according to Avrami–Erofeev equation. For reaction going to metallic cobalt parameter $n=2$ and activation energy is 97±14 kJ mol^{-1}. It was found that decomposition to CoO proceeds in two stages. First stage ($0.12<\alpha_{II}<0.41$) proceeds according to $n=2$, with activation energy 251±15 kJ mol^{-1} and second stage ($0.45<\alpha_{II}<0.85$) proceeds according to parameter $n=1$ and activation energy 203±21 kJ mol^{-1}.

Keywords: oxalates, oxy-salts of *d*-metals, thermal decomposition

Introduction

The dehydration and decomposition of *d*-electron metal oxalates is interesting because of application of those substances to metal oxides production for ceramics and electronic materials [1, 2]. The basic advantage of oxalates as precursors is low temperature of decomposition. Oxalates exist in the form of hydrated salts. Anhydrous salts are rarely observed. Decomposition of *d*-electron metal oxalates was studied previously [3, 4], but the detailed microscopic mechanism of this reaction and kinetic description related to this mechanism are not well known.

The route of oxalate decomposition is strongly affected by the surrounding environment as well as possible secondary reactions between products of the reaction. The mechanism of decomposition oxalates in oxidizing atmosphere is well tested but many controversies arise regarding the decomposition in inert atmosphere (helium, nitrogen).

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d-Metal oxalates are usually divided into two groups, depending on the kind of products formed during decomposition:

a) $MC_2O_4=M+2CO_2$
b) $MC_2O_4=MO+CO+CO_2$

The mechanism of decomposition depends on the strength of M–O and C–O bonds in an oxalate [5]. If M–O bonds are stronger than C–O bond, decomposition leads to the formation of carbon oxide at first and next metal oxide and carbon dioxide. If C–O bond is stronger, a metal and CO_2 is produced. It is generally accepted that in inert atmosphere cobalt oxalate decomposes according to Scheme a. However, some authors indicate that the solid product of decomposition is a mixture of metallic cobalt and different cobalt oxides [6, 7]. Lack of thermodynamic data for cobalt oxalate makes it impossible to predict the possible ways of reaction.

According to [3] the activation energy of CoC_2O_4 decomposition to Co is 47.4±0.7 kcal mol^{-1}. In [8] the kinetics of CoC_2O_4 decomposition in vacuum and isothermal conditions was studied. The final product of decomposition was metallic cobalt. It was found that the whole process proceeds in three stages and its kinetics depends on the temperature in which anhydrous oxalate was obtained. Induction period lasted approximately until decomposition degree $\alpha=0.5$ was reached and its activation energy varied between 48.7 and 53.7 kcal mol^{-1} for different samples. The main reaction lasted approximately to $\alpha=0.9$ and was described by Prout–Tompkins equation with activation energy 39.3 kcal mol^{-1}.

The goal of this paper is to find out the detailed mechanism of $CoC_2O_4{\cdot}2H_2O$ decomposition in inert atmosphere and the kinetics of this reaction. The results presented were obtained under a wide research program, which was undertaken to find out regularities in decomposition of *d*-metals oxy-salts.

Experimental

Cobalt oxalate dihydrate was prepared by precipitating from solution of appropriate cobalt(II) nitrate(V) and oxalic acid. The solution was acidified by HCl to pH~2.2 in order to prevent precipitation of cobalt(II) hydroxide or hydroxy-oxalate. The mixture was kept at 70°C for 6 h. The precipitate was filtered and washed in dilute oxalic acid, then in absolute alcohol. The obtained compound was dried at 50°C and exposed to air. The oxalate obtained was analyzed for oxalate ions by wet analysis and for cobalt ions by potentiometric titration. Analysis showed that the formula of samples was $CoC_2O_4{\cdot}2H_2O$ within 1% accuracy. XRD analysis showed that in obtained substances the only phase is cobalt(II) oxalate.

Measurements were carried out on SDT 2960 (TA Instruments) apparatus, which allowed simultaneous detection of sample mass changes (TG) and heat effect of reaction (DTA signal). The samples were heated in a standard platinum crucible. Gaseous products of reaction were analyzed by quadruple mass spectrometer (ThermoStar Balzers) connected on-line with TG-DTA apparatus.

Kinetic measurements of anhydrous metal oxalates decomposition were carried out in non-isothermal conditions at different heating rates, usually lower than 5 K min^{-1}. The mass of sample was 6.0 mg.

Substrate and solid product of decomposition were analyzed by X-ray diffraction using CuK_α radiation (Seifert XRD-7).

All experiments were performed in helium atmosphere (flow rate 0.1 $\text{dm}^3\ \text{min}^{-1}$).

Results and discussion

Mechanism of decomposition

As it was mentioned above, thermal decomposition of $CoC_2O_4{\cdot}2H_2O$ could be described by one of (or both) following reactions:

$$CoC_2O_4{\cdot}2H_2O=Co+2CO_2+2H_2O \tag{I}$$

$$CoC_2O_4{\cdot}2H_2O=CoO+CO+CO_2+2H_2O \tag{II}$$

Figure 1 shows DTA/TG/EGA results of thermal decomposition of $CoC_2O_4{\cdot}2H_2O$ obtained in helium atmosphere at non-isothermal conditions (heating rate β_h=2 K min^{-1}). EGA results are represented by ionic current corresponding to M/q ratio equal to 18 (H_2O), 28 (CO) and 44 (CO_2) (M – molar mass of ion, q – charge of ion expressed in units of electron charge) recorded by quadruple mass spectrometer (QMS) during sample heating. At first glance it seems that the discussed decomposi-

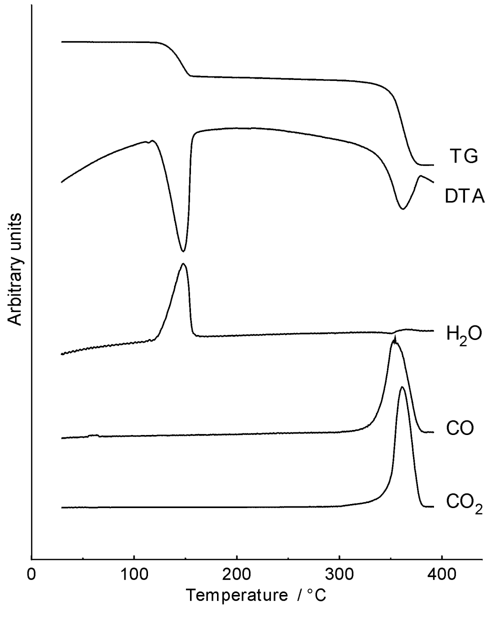

Fig. 1 TG, DTA and mass spectra curves of decomposition of $CoC_2O_4{\cdot}2H_2O$ in helium (heating rate 2 K min^{-1})

tion proceeds in two stages. The first could correspond to water removal, and the second seems to be related to $C_2O_4^{2-}$ anion degradation with CO and CO_2 evolution. It is necessary to emphasize that ionic current observed for M/q=28 (CO) may be not only a result of CO_2 fragmentation during ionization in QMS. As fragmentation is concerned, under conditions commonly used in QMS (energy of electron ionization equal to 70 eV), the ratio $I_{CO(fragm)}/I_{CO_2}=0.0658$ (where $I_{CO(fragm)}$ is an ionic current for M/q=28 resulting from the hypothetical process: $CO_2 \rightarrow CO^+ + O^-$ and I_{CO_2} is an ionic current for M/q=44). Figure 2 illustrates the comparison between $I_{CO(fragm)}$ and I_{CO} which is the actual observed ionic current for M/q=28 (CO). Looking at Fig. 2 it is obvious that CO has to form not only during fragmentation of CO_2 but additionally in reaction (II). This result is opposite to a fairly common opinion that thermal decomposition of $CoC_2O_4{\cdot}2H_2O$ leads to metal formation as it is described by reaction (I) with CO_2 as the only gaseous product.

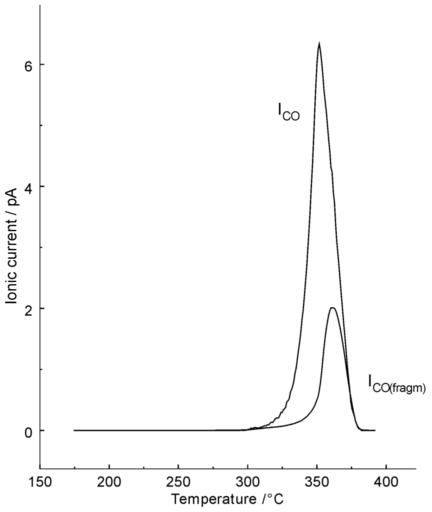

Fig. 2 Total ionic current of CO, I_{CO}, observed during decomposition of $CoC_2O_4{\cdot}2H_2O$ and ionic current of CO resulted from fragmentation of CO_2, $I_{CO(fragm)}$ ($I_{CO(fragm)}= 0.0658{\cdot}I_{CO_2}$)

As ionic currents, $I_{H_2O}, I_{CO}, I_{CO_2}$ corresponding to concentrations of H_2O, CO and CO_2 in atmosphere surrounding decomposing sample at temperature T are known, we can estimate the degree of decomposition $\alpha_{H_2O}(T), \alpha_{CO}(T)$ and $\alpha_{CO_2}(T)$ with regard to individual gaseous decomposition products according to the following dependencies:

$$\alpha_{H_2O}(T)=\frac{\int_0^T I_{H_2O}(\tau)d\tau}{\int_0^{T_k} I_{H_2O}(\tau)d\tau},\ \alpha_{CO}(T)=\frac{\int_0^T I_{CO}(\tau)d\tau}{\int_0^{T_k} I_{CO}(\tau)d\tau}\ \text{and}\ \alpha_{CO_2}(T)=\frac{\int_0^T I_{CO_2}(\tau)d\tau}{\int_0^{T_k} I_{CO_2}(\tau)d\tau} \quad (1)$$

where T_k represents temperature at which reaction is completed. In fact, in experimental conditions temperature T is a linear function of time ($T(t)=T_0+\beta_h t$, where β_h is the heating rate and T_0 is temperature for t=0). Thus, Eq. (1) express degree of conversion α as function of time. Graphs in Fig. 3 illustrate above dependencies as a function of temperature. Additionally, in Fig. 3 $\alpha_{TG}(T)$ is given. $\alpha_{TG}(T)$ is defined from TG measurements as:

$$\alpha_{TG}(T)=\frac{\Delta m(T)}{\Delta m_k} \tag{2}$$

where $\Delta m(T)$ represents loss of mass of decomposing sample in temperature T with respect to initial mass and Δm_k is total loss of mass (up to the end of reaction).

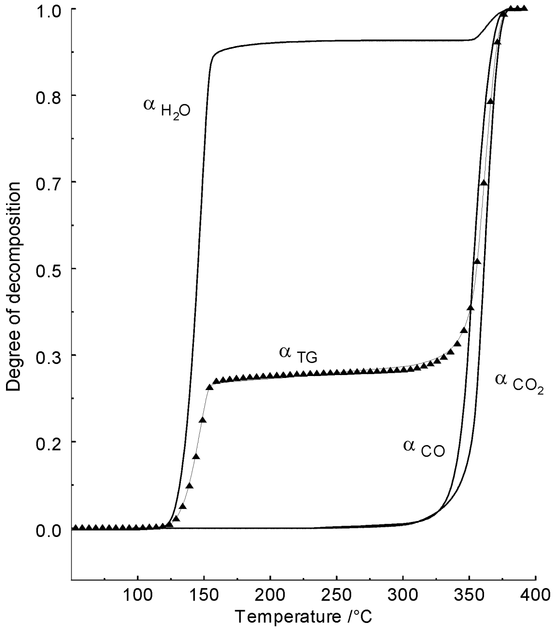

Fig. 3 Degree of decomposition of $CoC_2O_4 \cdot 2H_2O$ calculated for different gaseous products and total degree of decomposition α_{TG} *vs.* temperature (points – experimental data, line – fitted)

Analysis of results given in Figs 1 and 3 allows us to draw some important conclusions. It is easy to notice that water removing from $CoC_2O_4 \cdot 2H_2O$ during the first stage of the reaction (temperature <200°C) is not complete. Approximately 10% of water is removed above 340°C. A more important conclusion concerns CO and CO_2 evolution. We can see that when the temperature is higher than 320°C, the degree of CO evolution α_{CO} exceeds the degree of CO_2 evolution. This means that thermal decomposition of $CoC_2O_4 \cdot 2H_2O$ cannot be explained by taking into account only reaction (I). For reaction (II) the condition: $\alpha_{CO}(T)=\alpha_{CO_2}(T)$ should be fulfilled as a result of reaction stoichiometry. The observed result can be explained by assuming that independently of reaction (I), a parallel reaction (II) takes place, starting at a slightly higher temperature or running slightly slower. This is consistent with the observation that the total mass loss registered on TG curve does not correspond to either reaction (I) or reaction (II). Formation of metallic cobalt can be easily confirmed by changing gaseous atmosphere of reaction from helium to air at temperature higher than 380°C. If metallic cobalt was present in decomposition product, the sample mass should increase as a consequence of cobalt oxidation. This fact is actually observed – thus reaction (I) is one way of cobalt oxalate decomposition.

Parallel reactions (I) and (II) in thermal decomposition of $CoC_2O_4{\cdot}2H_2O$ were reported previously [6, 7], but there was no final proof of that. The origin of CoO as product of $CoC_2O_4{\cdot}2H_2O$ decomposition in inert atmosphere could be partial oxidation of metallic cobalt formed during reaction (I) by residual oxygen in purged gas (oxygen is an impurity of inert gas surrounding decomposing sample). Hence, the assumption that reaction (II) has actually occurred may not be necessary to explain CoO formation during thermal decomposition of $CoC_2O_4{\cdot}2H_2O$.

In the case of the presented measurements, formation of CoO is deduced from analysis of mass spectra of gaseous products. Possible oxidation of Co by residual oxygen cannot change values α_{CO} and α_{CO_2} estimated above. Therefore, our results show that reaction (II) does take place.

On the other hand, the presence of metallic cobalt in decomposition residue can result from the following secondary reaction:

$$CoO+CO=Co+CO_2 \tag{III}$$

between products of reaction (II). In this case reaction (III), instead of reaction (I), could be responsible for metallic cobalt formation. Such a mechanism was often indicated in earlier papers [9, 10].

Let us assume for a while that thermal decomposition of $CoC_2O_4{\cdot}2H_2O$ proceeds only according to reaction (II) and metallic cobalt in reaction products is formed only due to reaction (III). In this case recorded rate of CO evolution is the rate of producing CO in reaction (II) diminished by consumption of CO in reaction (III). Similarly, the recorded rate of CO_2 evolution is the CO production rate in reaction (II) increased by CO_2 production in reaction (III). Accordingly, the following dependencies can be written:

$$\left(\frac{d\alpha_{CO}}{dt}\right)_{obs}=\left(\frac{d\alpha_{CO}}{dt}\right)_0-v_{III}(t) \qquad \left(\frac{d\alpha_{CO_2}}{dt}\right)_{obs}=\left(\frac{d\alpha_{CO_2}}{dt}\right)_0+v_{III}(t)$$

where $\left(\frac{d\alpha_{CO}}{dt}\right)_0$, $\left(\frac{d\alpha_{CO_2}}{dt}\right)_0$ are actual rates of CO and CO_2 production in reaction (II) and $\left(\frac{d\alpha_{CO}}{dt}\right)_{obs}$, $\left(\frac{d\alpha_{CO_2}}{dt}\right)_{obs}$ are observed rates of CO and CO_2 production and $v_{III}(t)$ is rate of CoO reduction (reaction (III)). In reaction (II) $\left(\frac{d\alpha_{CO}}{dt}\right)_0$ and $\left(\frac{d\alpha_{CO_2}}{dt}\right)_0$ have to be the same, thus:

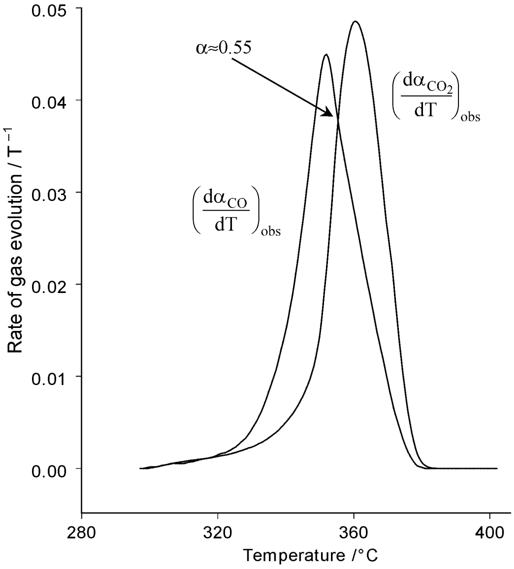

Fig. 4 Comparison between rates of CO and CO_2 evolution calculated from mass spectrum data

$$\Delta v_{obs}(t)=\left(\frac{d\alpha_{CO}}{dt}\right)_{obs}-\left(\frac{d\alpha_{CO_2}}{dt}\right)_{obs}=-2v_{III}(t)$$

Based on Fig. 4 it is easy to notice that in a wide range of decomposition degree ($<\approx0.5$–0.6) $\Delta v_{obs}(t)>0$. If reaction (III) takes place $v_{III}(t)>0$, the above equation cannot be fulfilled. In summary, we can say that our results can be explained only by taking the assumption that both reactions (I) and (II) take place simultaneously during decomposition of $CoC_2O_4{\cdot}2H_2O$.

As the values $\alpha_{H_2O}(T)$, $\alpha_{CO}(T)$, $\alpha_{CO_2}(T)$ and $\alpha_{TG}(T)$ are calculated from mass spectra data, we can find a relation between them assuming that $\beta=m_I/m_{II}$ represents the ratio of mass of the sample which decomposed according to reaction (I) (m_I) and to that of the sample decomposed according to reaction (II) (m_{II}):

$$\alpha_{TG}(T)=\frac{\alpha_{CO}(T)M_{CO}+(2\beta+1)\alpha_{CO_2}M_{CO_2}+v(\beta+1)\alpha_{H_2O}(T)M_{H_2O}}{M_{CO}+(2\beta+1)M_{CO_2}+v(\beta+1)M_{H_2O}} \tag{3}$$

where M_{CO}, $M_{\mathrm{CO_2}}$ and $M_{\mathrm{H_2O}}$ stand for molar mass of CO, CO_2 and H_2O, respectively and ν is number of water molecules per one molecule of CoC_2O_4 ($CoC_2O_4\cdot\nu H_2O$). In case of studied samples, ν=2±0.05. Using values $\alpha_{\mathrm{H_2O}}(T), \alpha_{\mathrm{CO}}(T), \alpha_{\mathrm{CO_2}}(T)$ and $\alpha_{\mathrm{TG}}(T)$ it is possible to find β by fitting right hand side of Eq. (3) to experimental line $\alpha_{\mathrm{TG}}(T)$. In Fig. 3 an example of pointed above procedure is given (points are experimental data and line α_{TG} is a result of fitting). It is easy to notice that the fitting quality is extremely good. Nevertheless, parameter β determined for many measurements, carried out at the same heating rate (2°C min^{-1}), varies in the range $0.7<\beta<1.2$. The value of β depends on conditions at which the reaction proceeds (rate of heating for instance), thus the particular value of this parameter has no important meaning and it is useful only as 'detector' that reactions (I) and (II) occur simultaneously. The values of parameter β fitted are collected in Table 1.

Table 1 Parameters fitted for measurements performed at heating rate 2 K min^{-1} (subscript I and II means reactions (I) and (II) respectively, subscript a and b means first and second stage of reaction (II), respectively)

Measurement	β	E_{I}	$\ln K_{\mathrm{I}}$	E_{IIa}	$\ln K_{\mathrm{IIa}}$	E_{IIb}	$\ln K_{\mathrm{IIb}}$
1	1.1	106	15	251	43	194	31
2	1.0	112	16	268	46	170	27
3	0.97	141	21	247	42	189	30
4	1.2	110	15	242	41	187	30
5	1.1	74	9	251	43	186	30
6	0.72	66	7	271	46	196	31
7	1.2	124	18	227	38	197	32
8	1.1	104	14	237	40	209	34
9	0.75	67	7	233	39	230	38
10	0.89	73	8	238	40	238	40
11	1.1	84	11	259	44	239	40
12	0.77	92	12	270	46	199	32
13	0.91	108	15	271	46	200	32

From Fig. 3 it is clearly seen that in the first step of the studied process almost complete dehydration occurs. This allowed us to separate data and to take for further considerations only data of decomposition of anhydrous CoC_2O_4.

Now let us define degrees of conversion α_{I} and α_{II} for reactions (I) and (II), respectively, as a functions of time:

$$\alpha_{\mathrm{I}}(t)=\frac{m^{\mathrm{I}}_{\mathrm{CO_2}}(t)}{m^{\mathrm{I}}_{\mathrm{CO_2}(\mathrm{k})}} \qquad \alpha_{\mathrm{II}}(t)=\frac{m^{\mathrm{II}}_{\mathrm{CO}}(t)+m^{\mathrm{II}}_{\mathrm{CO_2}}(t)}{m^{\mathrm{II}}_{\mathrm{CO(k)}}+m^{\mathrm{II}}_{\mathrm{CO_2}(\mathrm{k})}} \tag{4}$$

$m^{\mathrm{I}}_{\mathrm{CO_2}}(t), m^{\mathrm{II}}_{\mathrm{CO}}(t)$ and $m^{\mathrm{II}}_{\mathrm{CO_2}}$ are masses of CO and CO_2 evolved in reactions (I) and (II) till time *t*. $m^{\mathrm{I}}_{\mathrm{CO_2(k)}}, m^{\mathrm{II}}_{\mathrm{CO(k)}}$ and $m^{\mathrm{II}}_{\mathrm{CO_2(k)}}$ are total masses of CO and CO_2 evolved in reaction (I) and (II). Definitions (1) and (4) were used to derive the relationship between $\alpha_{\mathrm{H_2O}}(T(t)), \alpha_{\mathrm{CO}}(T(t)), \alpha_{\mathrm{CO_2}}(T(t))$ and $\alpha_{\mathrm{I}}(t)$, $\alpha_{\mathrm{II}}(t)$:

$$\alpha_{\mathrm{I}}(t)=\frac{(2\beta+1)\alpha_{\mathrm{CO_2}}(T(t))-\alpha_{\mathrm{CO}}(T(t))}{2\beta} \qquad \alpha_{\mathrm{II}}(t)=\alpha_{\mathrm{CO}}(T(t)) \tag{5}$$

In this way, it was possible to find kinetic information concerning reactions (I) and (II) and to carry out the kinetic analysis. In Fig. 5 reaction rates $\mathrm{d}\alpha_{\mathrm{I}}(t)/\mathrm{d}t$ and $\mathrm{d}\alpha_{\mathrm{II}}(t)/\mathrm{d}t$ as a function of temperature are shown. We can see that both reactions are relatively well separated, which is not evident from TG line. This can be considered as a proof that simultaneous quantitative TG/EGA analysis enables kinetic analysis of weakly separated parallel reactions.

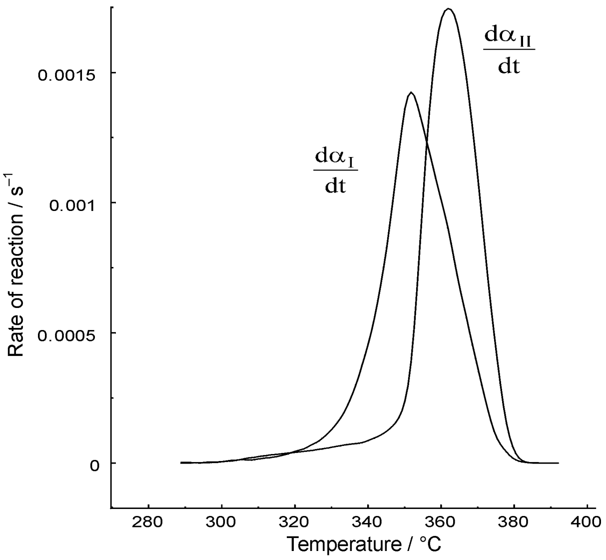

Fig. 5 Rate of reaction I and reaction II *vs.* temperature

Kinetic analysis

In general, the reaction rate $\mathrm{d}\alpha/\mathrm{d}t$ as a function of temperature *T* and degree of conversion α can be expressed by the following equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=K_0e^{-\mathrm{E_a/RT}}f(\alpha) \tag{6}$$

where K_0 is constant, E_a is activation energy and $f(\alpha)$ is a function of α that depends on a kinetic model (i.e. mechanism of reaction). It will be shown, that in case of our measurements Avrami–Erofeev model can be applied for kinetic description of both reactions (I) and (II) so function $f(\alpha)$ has the form:

$$f(\alpha)=(1-\alpha)\left[\ln\left(\frac{1}{1-\alpha}\right)\right]^{\left(1-\left(\frac{1}{n}\right)\right)} \tag{7}$$

Finally for non-isothermal conditions Eqs (6) and (7) can be transformed to:

$$\ln(\psi)=\ln(K_0)-\frac{E_a}{R(T_0+\beta_h t)}-\frac{1}{n}\ln\left[\ln\left(\frac{1}{1-\alpha}\right)\right] \tag{8}$$

where

$$\Psi=\frac{\frac{d\alpha}{dt}}{(1-\alpha)\left[\ln\left(\frac{1}{1-\alpha}\right)\right]}$$

The right hand side of Eq. (8) contains three kinetic parameters K_0, E_a and n that can be found by numerical fitting using following minimization condition:

$$\sum_{i=1}^{N}\left\{\ln(\Psi_i)-\ln K_0+\frac{E_a}{RT_i}+\frac{1}{n}\ln\left[\ln\left(\frac{1}{1-\alpha_i}\right)\right]\right\}^2\to\min$$

where N is number of points. Ψ_i can be calculated from experimental data because rates $d\alpha_I(t_i)/dt$, $d\alpha_{II}(t_i)/dt$ can be determined on the basis of Eq. (4) for every $\alpha_I(t_i)$ and $\alpha_{II}(t_i)$. T_i values corresponding to each $\alpha_I(t_i)$ and $\alpha_{II}(t_i)$ are known directly from the experiment.

Kinetic parameters of studied decomposition processes did not depend on the heating rate in the range 0.5 to 4 K min^{-1}. In the kinetic analysis measurements for heating rate equal to 2 K min^{-1} were used because separation of two reactions was in this case the best. Detailed analysis of all measurements made shows that the kinetics of reaction (I) can be described by Avrami–Erofeev equation with $n=2$ for range of decomposition degrees $0.2<\alpha_I<0.85$ with activation energy equal to 97±14 kJ mol^{-1} and $\ln K_0=13\pm3$ at level of confidence equal to 95%. As an example of fitting quality Fig. 6 shows plot of the following equation:

$$\ln[\Psi'(n)]=\ln\left\{\frac{\left(\frac{d\alpha}{dt}\right)_{\alpha=\alpha_i}}{(1-\alpha_i)\left[\ln\left(\frac{1}{1-\alpha_i}\right)\right]^{\left(1-\left(\frac{1}{n}\right)\right)}}\right\}=\ln K_0-\frac{E_a}{RT_i} \tag{9}$$

Points in this graph are experimental, the continuous line corresponds to parameters $n=2$, $\ln K_0=13$ and $E_a=98$ kJ mol^{-1}.

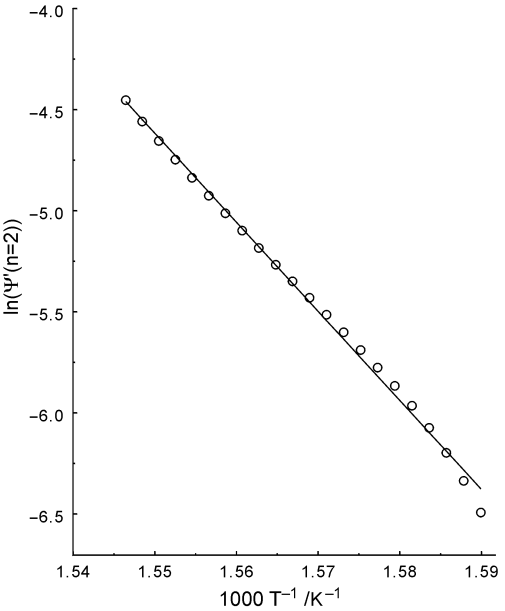

Fig. 6 Plot of Eq. (9) with parameters n=2, lnK_0=13 and E_a=98 kJ mol^{-1} (continuous line) and experimental data (points) for reaction (I)

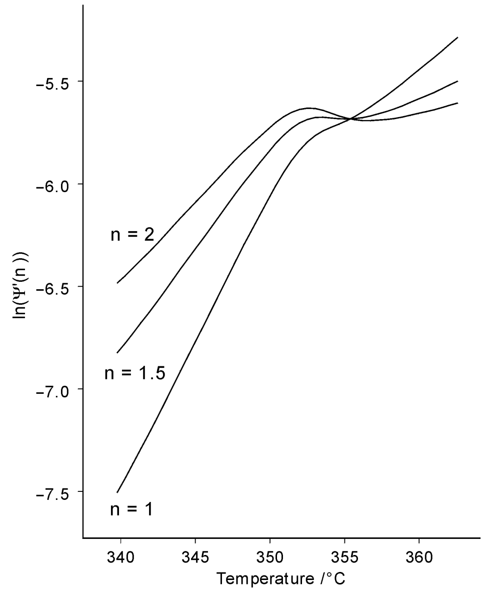

Fig. 7 Plot of Eq. (9) for reaction II with different parameter n

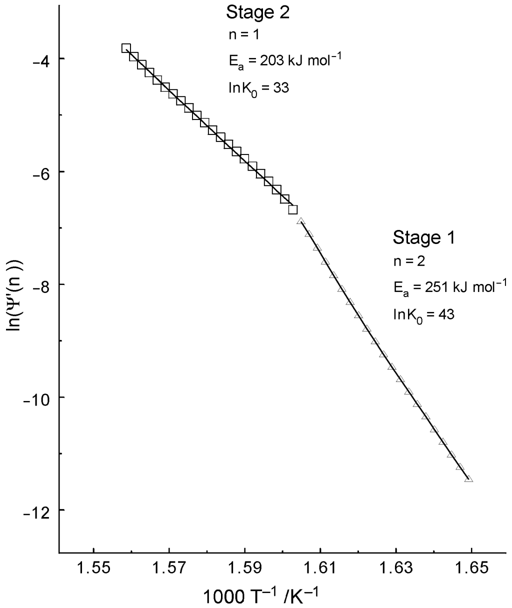

Fig. 8 Plot of Eq. (9) for two stages of reaction II

The course of reaction (II) is more complicated. As can be seen in Fig. 7 reaction (II) proceeds in two clearly separated stages, with different parameter *n* and different value of activation energy. Figure 8 shows plot of Eq. (9) for the whole reaction (II). Within the range $0.1<\alpha_{II}<0.4$ estimated parameter $n=2$ and $E_a=251\pm15$ kJ mol^{-1}, $\ln K_0=43\pm2$. Within the range ($0.45<\alpha_{II}<0.85$) estimated parameter $n=1$ and activation energy is equal to 203±21 kJ mol^{-1}, $\ln K_0=33\pm3$. The errors were calculated at level of confidence equal to 95%.

In our previous work on decomposition of CoC_2O_4 in isothermal conditions [11] metallic cobalt as the main product of reaction was found. Parameter *n* of Avrami equation was equal to 2 but exhibited slight dependence on temperature, which was possibly a manifestation of two parallel reactions stated in present studies, one of which additionally is a two-stage reaction. In isothermal measurements there was no possibility to analyze gaseous products of decomposition. Therefore, a small amount of CoO identified in a solid product was taken as a product of metallic cobalt oxidation (secondary reaction). Thus energy of activation equal to 227 kJ mol^{-1} determined for isothermal decomposition, being in fact a complex process, corresponds to the reaction with higher activation energy, that is reaction (II).

As the discussed reaction was successfully described by Avrami–Erofeev kinetic equation it means that rate-limiting step of the process is nucleation and growth of nuclei. Three-dimensional nuclei growth for parameter *n* in this equation lower or equal to 2 is of low probability. Change of parameter *n* values during the reaction is an evidence of changing mechanism of reaction. Change of reaction mechanism can be connected with the change of rate limiting step from surface reaction to diffusion or can be a result of change of nucleation rate from constant value to 0.

Conclusions

In summary, we can say that reaction of thermal decomposition of $CoC_2O_4{\cdot}2H_2O$ in helium at non-isothermal conditions proceeds as two parallel processes. The solid product of one reaction is Co and the solid product of the second reaction is CoO. The Co/CoO ratio in the solid product of decomposition depends on conditions of experiment, and primarily on the heating rate. Differences in the course of $CoC_2O_4{\cdot}2H_2O$ decomposition reported in previous papers become now understandable.

The detailed analysis (in a wide range of M/q ratios) of gaseous products observed when decomposition proceeds shows that the role of secondary processes between products of decomposition can be relatively easily minimized. In our opinion, detailed consideration of possible secondary reactions (sometimes encountered in published papers or discussions) has no meaning from the point of view of main mechanism of $CoC_2O_4{\cdot}2H_2O$ decomposition. The nature and significance of these processes depends on experimental conditions. Therefore, experiments should be performed in such a way as to avoid any disturbing effects. Otherwise we do not study thermal decomposition of $CoC_2O_4{\cdot}2H_2O$.

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