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Mechanism and kinetics of thermal decomposition of zinc oxalate

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Abstract

Thermal decomposition of ZnC_2O_4 in helium atmosphere in isothermal and non-isothermal conditions was studied. Decomposition of ZnC_2O_4 is a single-stage reaction with ZnO as final product. The kinetics of reaction is described in terms of the Avrami–Erofeev equation with $n \approx 2$ both for non-isothermal and isothermal measurements. The activation energy of ZnC_2O_4 decomposition is 181.4–186.5 and 190.8 kJ mol^{-1} for non-isothermal and isothermal conditions, respectively.

Keywords: Zinc oxalate; Thermal decomposition; Kinetics

1. Introduction

Zinc oxalate exists in two polymorphic forms [1]. Crystallographic structure of β-ZnC_2O_4 belongs to space group $P2_1/n$. β-ZnC_2O_4 consists of cation–anion chains, –C_2O_4–Zn–C_2O_4–Zn, connected by Zn–O bonds. The coordination of Zn is octahedral. Oxygen atoms are connected with zinc by different number of bonds so that the length of C–O bonds in $C_2O_4^{2-}$ ion is not the same (1.40 and 1.15 Å). β-ZnC_2O_4 is isotypic with other d-metal oxalates like FeC_2O_4, CoC_2O_4 and NiC_2O_4. α-ZnC_2O_4 is a disordered phase and crystallises in the space group *Pnnm*. Structure of α-ZnC_2O_4 corresponds to α-CuC_2O_4, in which interlace two orderly phases consisting of endless cation–anion chains.

Few papers are concerned with the thermal decomposition of ZnC_2O_4 [2–6]. ZnC_2O_4 is obtained by dehydration of dihydrate. Decomposition of zinc oxalate in inert atmosphere is a simple, one stage reaction leading to ZnO as solid and CO and CO_2 as gaseous products. According to [3] decomposition of ZnC_2O_4 in nitrogen atmosphere is a first order reaction with activation energy of 435 kJ mol^{-1}. Kinetics of isothermal decomposition of ZnC_2O_4 in an atmosphere of CO, CO_2 and H_2O was performed by Kornienko [7] and the results were described by the Avrami–Erofeev equation with $n = 2$ and an activation energy of 183 kJ mol^{-1}. Since these significant discrepancies between kinetic data of the decomposition of ZnC_2O_4 in the present work a systematic study of the process was performed in isothermal as well as in non-isothermal conditions. The present work is a part of the wide research program, which was undertaken to find out regularities in decomposition of d-metals oxy-salts.

2. Experimental

In all experiments zinc oxalate dihydrate was used. $ZnC_2O_4{\cdot}2H_2O$ was prepared by precipitation from a mixture of zinc nitrate and oxalic acid solutions. pH of the solution was brought to 4 by addition of ammonia and HCl. The solution was kept at 340 K for 5 h. The precipitate was filtered and washed first with dilute oxalic acid and then with absolute alcohol and afterwards dried at 330 K. The oxalate was analysed for oxalate ions and for zinc ions by wet analysis. Analysis showed that the formula $ZnC_2O_4{\cdot}2H_2O$ was correct within 0.5%.

Thermal decomposition was performed with an apparatus that enabled simultaneous recording of TGA and DTA signals (SDT 2960 TA INSTRUMENTS). This apparatus was connected on-line with a quadruple mass spectrometer (QMD 300 THERMOSTAR BALZERS) so parallel analysis of gaseous products of reaction was carried out by evolved gas analysis, EGA. The samples (mass app. 6 mg) were heated in a standard platinum sample pan. All experiments were carried out in helium with a flow rate of

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$0.1\,dm^3\,min^{-1}$. Non-isothermal measurements were performed with the heating rates of 2, 4, 7 and $10\,K\,min^{-1}$. Ten experiments were done at each heating rate. Isothermal experiments were carried out at temperatures in the range of 613–625 K. At each chosen temperature five experiments were done. A special heating program was applied for isothermal measurements: the sample was isothermally heated at 395 K for 20 min to complete dehydration of $ZnC_2O_4{\cdot}2H_2O$, then the temperature was increased (with a heating rate of $50\,K\,min^{-1}$) to the value at which the experiment was performed. The experiment was continued until the rate of mass changes was smaller than $10^{-6}\,g\,min^{-1}$ (balance sensitivity). The substrates and solid products of decomposition were analysed by X-ray powder diffraction on a Seifert XRD-7 apparatus with Cu Kα radiation.

3. Results and discussion

Fig. 1 shows the experimental TG, DTA and EGA curves obtained during heating of $ZnC_2O_4{\cdot}2H_2O$ with constant rate. TG curves show two weight losses. The first weight loss accompanied by an endothermic effect on the DTA curve corresponds to dehydration. The calculated weight loss agrees with the evolution of 1.88 mol H_2O (confidence interval 1.85–1.91) per mole of oxalate. This means that dehydration was not completed and some water remained in occlusions in the oxalate structure. X-ray diffraction pattern of the sample after dehydration showed the presence of α-ZnC_2O_4. The dehydration stage is clearly separated from the decomposition stage, which starts about 600 K. The shape of the endothermic DTA signal indicates that decomposition is a single-stage process. EGA signals show that CO and CO_2 evolve simultaneously during decomposition with the same rate. The molar ratio CO:CO_2, calculated from EGA signals, is 1. The only solid product of decomposition found by XRD analysis is ZnO.

3.1. Kinetics of reaction in non-isothermal conditions

The degree of decomposition, α, was determined in two ways: first α was calculated as fraction $\alpha = \Delta m_t/\Delta m$, where Δm_t represents the loss of mass after time t with respect to initial mass and Δm the total loss of mass when the decomposition is complete. Another set of α values was obtained from intensities of CO^+ and $CO_2{}^+$ ionic currents by a procedure described in [8]. Non-isothermal α versus time curves for the decomposition of ZnC_2O_4 were sigmoid shaped. Plots for typical experiments are shown in Fig. 2.

The determination of the kinetic parameters of a reaction proceeding in non-isothermal conditions is possible by using the differential form of the kinetic equation:

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

where $f(\alpha)$ is a function of α depending on a kinetic model (i.e. on a mechanism of reaction):

$$\kappa(T) = \kappa_0\,e^{-E_a/RT} \tag{2}$$

where E_a is the activation energy and κ_0 the pre-exponential factor. Arrhenius parameters can be determined only if $\kappa(T)$ and $f(\alpha)$ are separated.

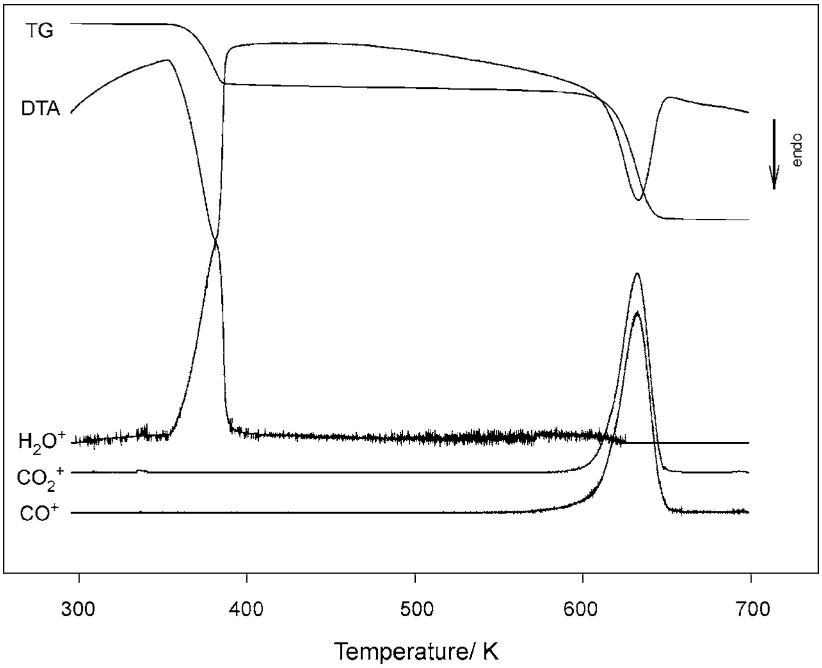

Fig. 1. TG and DTA curves for thermal decomposition of $ZnC_2O_4{\cdot}2H_2O$ in helium ($q = 2\,K\,min^{-1}$) and normalised intensities of ion current of gaseous decomposition products.

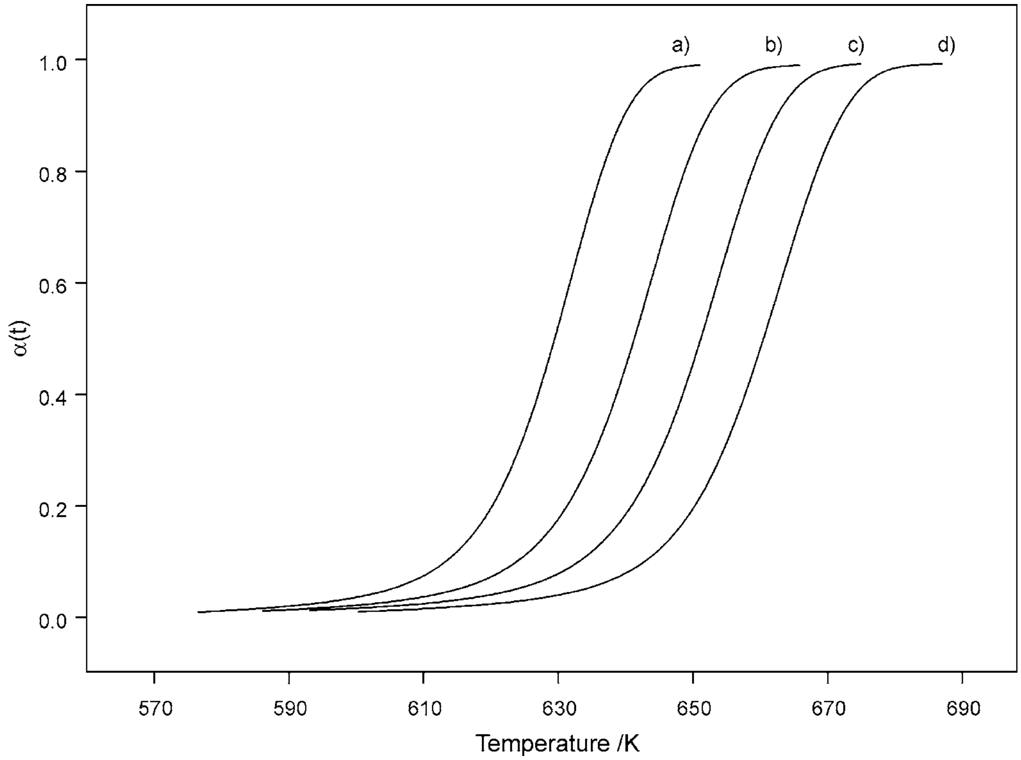

Fig. 2. $\alpha(t)$ plots for non-isothermal decomposition of ZnC_2O_4 with different heating rates: (a) 2 K min^{-1}, (b) 4 K min^{-1}, (c) 7 K min^{-1} and (d) 10 K min^{-1}.

The sigmoid shaped kinetic curves suggest existence of an induction period connected with nucleation of new phase. Therefore several kinetic equations based on the models with induction period were tested for a description of experimental data. In case of our results the Avrami–Erofeev equation gave the best fit to the experimental data:

$$f(\alpha) = (1-\alpha)\left[\ln\left(\frac{1}{1-\alpha}\right)\right]^{(1-1/n)} \tag{3}$$

where n is a parameter connected with the mechanism of reaction. Finally the following expression was used to find kinetic parameters of the reaction [8]:

$$\ln(\Psi) = \ln(\kappa_0) - \frac{E_a}{R\,(T_0+qt)} + \left(1-\frac{1}{n}\right)\ln\left[\ln\left(\frac{1}{1-\alpha}\right)\right] \tag{4}$$

where $\Psi = (\mathrm{d}\alpha/\mathrm{d}t)/(1-\alpha)$, T_0 is the initial temperature and q the heating rate.

The parameters κ_0, E_a and n were calculated by the numerical fitting the experimental data in the range of decomposition degrees $0.2 < \alpha < 0.85$ with Eq. (4) using least square fitting procedure implemented in the computer program MATHCAD 2001.

Table 1 contains the calculated parameters for the heating rates 2, 4 and 7 K min^{-1} with their confidence intervals (level of confidence 0.95). Estimation of parameters for the heating rate 10 K min^{-1} failed. Parameters obtained did not depend on the way of determination of α. In case of heating rates 2 and 4 K min^{-1} the assumption that $n = 2$ was confirmed at a level of confidence 0.95. For heating rate 7 K min^{-1} a test of significance showed that n differs from 2. The parameter n and the activation energy seem to increase with heating rate however all values are within the limit of error.

As example of fitting quality Fig. 3 shows the experimental values of Ψ and a plot of the right hand side of Eq. (4) with obtained parameters as a function of temperature.

3.2. Kinetics of reaction in isothermal conditions

All the measurements were performed in the temperature range of 613–625 K. The Avrami–Erofeev equation in the integral form was used to calculate kinetic parameters of the reaction:

$$\alpha = 1 - \exp(-kt^n) \tag{5}$$

where k is a constant connected with the reaction rate constant κ by the dependence:

$$\kappa = nk^{1/n} \tag{6}$$

Eq. (5) was fitted to the experimental data in the α range $\alpha = 0.2$–0.85 using a non-linear regression procedure implemented in the computer program MATHCAD 2001. The estimated values of n and k are given in Table 2. Mean value of n is 2.09 (confidence interval 2.04–2.16) at a level of confidence 95%. The parameter n does not depend on temperature which means that the whole temperature dependence of the reaction constant is hidden in parameter k. Fig. 4 shows the experimental data of the isothermal zinc

Table 1
Estimated parameters of Eq. (4) for non-isothermal experiments

q (K min^{-1})	E_{akt} (kJ mol^{-1})	Confidence interval for E_{akt} (kJ mol^{-1})	n	Confidence interval for n	$\ln \kappa_0$	Confidence interval for $\ln \kappa_0$
2	181.4	178.1–184.8	2.05	1.99–2.10	29.00	28.34–29.60
4	185.8	179.4–189.6	2.08	1.97–2.16	29.68	28.92–30.27
7	186.5	178.7–193.8	2.14	2.02–2.24	29.94	29.23–30.56

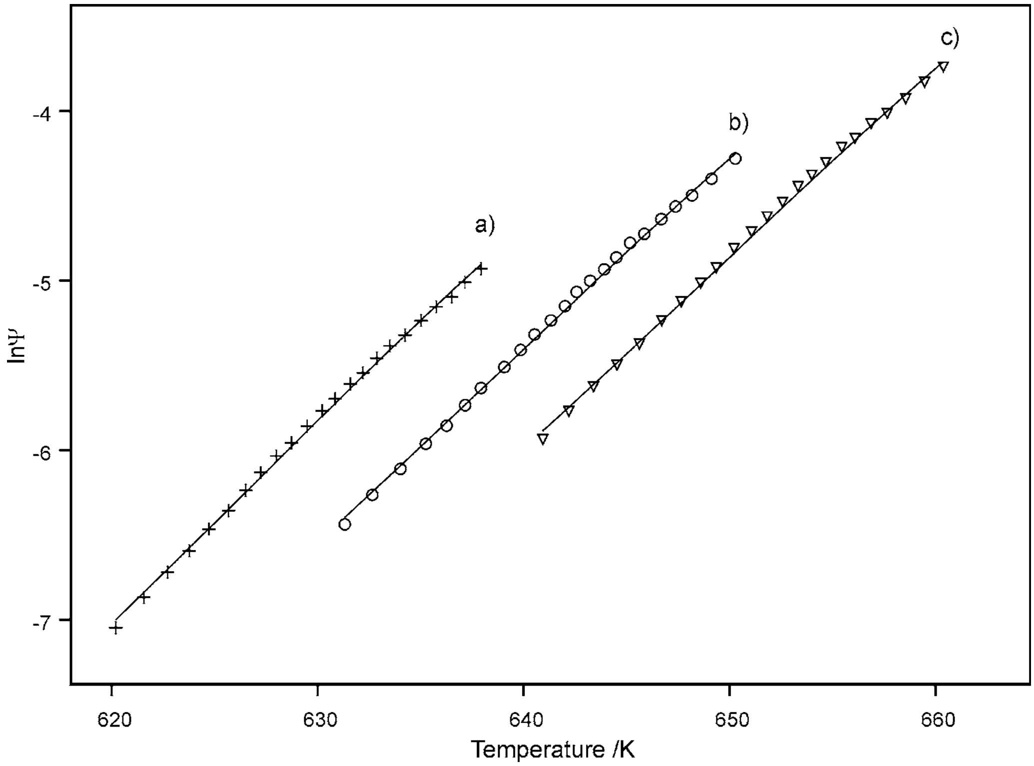

Fig. 3. Experimental values of Ψ (points) and plot of Eq. (4) with estimated parameters (lines): (a) $q = 2\,\mathrm{K\,min^{-1}}$, $n = 2.06$, $E_a = 183.5$, $\ln \kappa_0 = 29.55$; (b) $q = 4\,\mathrm{K\,min^{-1}}$, $n = 2.10$, $E_a = 185.1$, $\ln \kappa_0 = 29.68$; (c) $q = 7\,\mathrm{K\,min^{-1}}$, $n = 2.14$, $E_a = 188.8$, $\ln \kappa_0 = 30.35$.

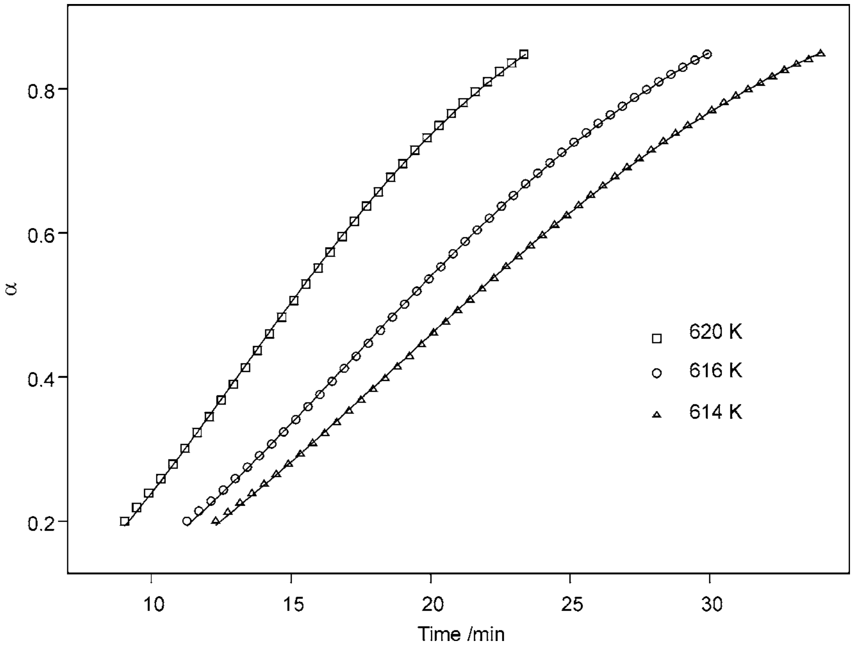

Fig. 4. $\alpha(t)$ for isothermal decomposition of ZnC_2O_4 at different temperatures (points—experimental data, lines—plot of Eq. (5) with estimated parameters).

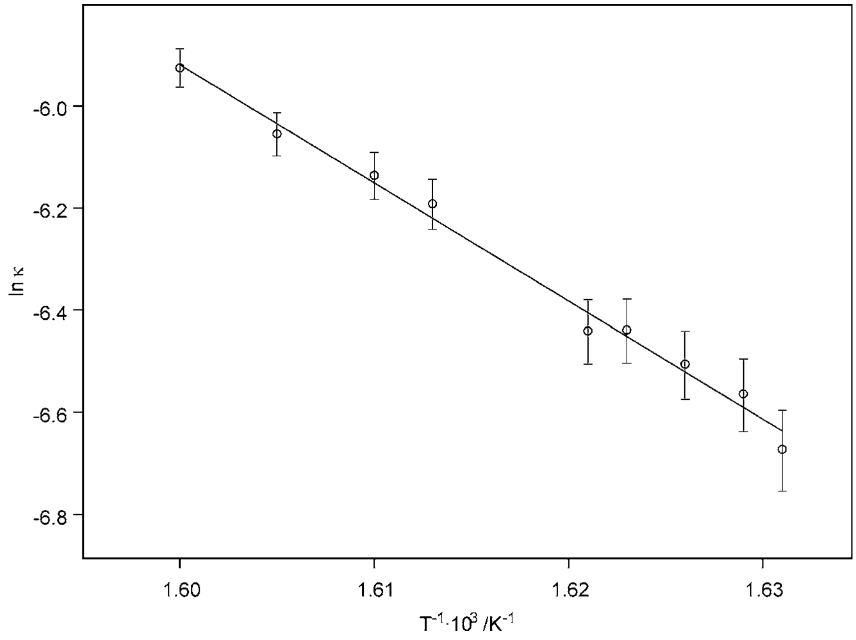

Fig. 5. Plot of $\ln\kappa$ vs. inverse temperature.

Table 2
Estimated parameters of Eq. (5) for isothermal experiments

T (K)	$\ln k$	n
613	−15.477	2.089
614	−15.425	2.110
615	−15.740	2.163
616	−14.924	2.081
617	−14.560	2.036
620	−14.196	2.054
621	−14.145	2.062
623	−14.070	2.074
625	−13.986	2.098

oxalate decomposition and the plots of Eq. (5) with the obtained parameters n and k for several temperatures.

The n and k values were used to calculate the reaction rate constants from Eq. (6). The plot of $\ln\kappa$ versus $1/T$ (Fig. 5) is a straight line. The activation energy calculated from the slope is $E_a = 190.8\,\mathrm{kJ\,mol^{-1}}$ (confidence interval 172.3–201.3 $\mathrm{kJ\,mol^{-1}}$) and $\ln\kappa_0 = 30.77$ (confidence interval 27.17–34.46) at a level of confidence 95%.

The difference between n found for isothermal and non-isothermal measurements is about 5% and can result from estimating parameters by different forms of the kinetic equation (integral and differential form). As all calculated values of n are in the range of statistical error we draw the conclusion that this parameter is the same for isothermal and non-isothermal conditions of decomposition. According to Erofeev the values of $n = 2$ or $3 > n > 2$ are connected with two-dimensional growth of nuclei. The activation energy of decomposition for non-isothermal measurements is about 5–10 $\mathrm{kJ\,mol^{-1}}$ lower than that estimated for isothermal measurements but both values are inside the range of error. The kinetic parameters are close to those obtained for isothermal decomposition in the atmosphere of decomposition products [7]. In conclusion, it can be stated that kinetics of decomposition of ZnC_2O_4 proceeds with the same mechanism in isothermal and non-isothermal conditions.

4. Conclusions

The thermal decomposition of ZnC_2O_4 in helium atmosphere was examined in isothermal and non-isothermal conditions. It was stated that it is a one stage process with ZnO as solid product. In the beginning the rate of decomposition is determined by nucleation of new phase. The kinetics of decomposition in the range of conversion $0.2 < \alpha < 0.85$ were described in terms of Avrami–Erofeev equation with the same parameter $n \approx 2$ for isothermal and non-isothermal measurements. This means that the rate of reaction is controlled by the two-dimensional growth of nuclei. The energy of activation found was 181.4–186.5 and 190.8 $\mathrm{kJ\,mol^{-1}}$ for non-isothermal and isothermal conditions, respectively.

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