J Therm Anal Calorim (2012) 109:89–96
DOI 10.1007/s10973-011-1557-y

Kinetics of the thermal dehydration of potassium titanium oxalate, $K_2TiO(C_2O_4)_2 \cdot 2H_2O$

K. Muraleedharan · P. Labeeb

Received: 8 February 2011 / Accepted: 31 March 2011 / Published online: 11 April 2011

Abstract The thermal dehydration reaction of potassium titanium oxalate, $K_2TiO(C_2O_4)_2 \cdot 2H_2O$, has been studied by means of thermogravimetry (TG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) in nitrogen atmosphere at different heating rates. $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ dehydrates in a single step through a practically irreversible process. The activation energy involved and its dependence on the conversion degree were estimated by evaluating the thermogravimetric data according to model-free methods, and values of activation energy were determined for the dehydration reaction. Activation energy values were also evaluated from DSC data using isoconversional methods. The complexity of the dehydration of $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ is illustrated by the dependence of E on the extent of conversion, α $(0.05 \leq \alpha \leq 0.95)$.

Keywords Dehydration kinetics · Differential scanning calorimetry · Kinetic parameters · Potassium titanium oxalate · Thermogravimetry

Introduction

The dehydration kinetics of metal oxalates has been the subject for a number of thermogravimetric studies, both from practical and theoretical viewpoints [1–5]. The studies on the thermal decomposition of manganese (II) oxalate dihydrate and manganese (II) oxalate trihydrate using TG, DTA, and X-ray diffraction techniques have been reported [6]. The thermal decomposition behavior of strontium oxalate hydrate ($SrC_2O_4 \cdot 1.25H_2O$) has been studied by TG–DTA-derivative thermogravimetry (DTG) techniques, in air, up to the formation of strontium oxide (SrO) [7].

Kinetic studies on the thermal dehydration reactions of several compounds are reported in the literature [8–21]. For instance, Torres-Garcia et al. [8] studied the dehydration process of divalent transition metal nitroprussides by TG and DSC and observed that the copper complex dehydrates in a single step through a practically irreversible process in contrast to cadmium and cobalt complexes which shows two stages—in the first stage, only the zeolitic waters are removed, by a diffusion mechanism, while in the second stage the strongly bonded water molecules are dehydrated. They estimated the values of activation energy and its dependence on the conversion degree by evaluating the thermogravimetric data. Chambré et al. [9] studied the dehydration step due to elimination of osmotic water and hydrogen bounded water with the carboxylic groups under non-isothermal conditions for some carboxylic resins with acrylic–divinylbenzene matrix, evaluated the kinetic parameters by means of isoconversional methods, and observed that the apparent kinetic parameters are dependent on the cross-linking degree, granulation, exchange capacity, and heating rate. Logvinenko et al. [10] studied the dehydration processes of series of rhenium cluster compounds by TG and DSC, evaluated the kinetic parameters of the dehydration reaction by model-free methods and discussed the role of water molecules in the stability of cluster compounds. The dehydration kinetics of $VOSO_4 \cdot 2H_2O$ have been studied under non-isothermal conditions on a derivatograph and the kinetic parameters of the dehydration process using different kinetic models have been determined [11].

K. Muraleedharan (✉) · P. Labeeb
Department of Chemistry, University of Calicut,
Calicut 673635, Kerala, India
e-mail: kmuralika@gmail.com

Boonchom et al. [12] investigated the thermal decomposition of aluminum phosphate monohydrate, $AlPO_4 \cdot H_2O$-H_4, in air using TG-DTG/DTA, calculated the values of activation energy (E) for the dehydration reaction through the isoconversional methods of Ozawa and Kissinger–Akahira–Sunose and the possible conversion functions have been estimated through the comparative methods. They observed that the activation energy values calculated for the decomposition of $AlPO_4 \cdot H_2O$–H_4 by different methods and techniques were consistent with those of the kinetic models that better described the dehydration reaction by simple *n*-order reaction. Jankovic et al. [13] investigated the isothermal dehydration of equilibrium swollen poly(acrylic acid) hydrogel in the temperature range 306–361 K, calculated the kinetic parameters using *initial rate* and *stationary point* methods of Johnson–Mehl–Avrami. They determined the reaction models for the dehydration using the *model-fitting* method and reported that both, the reaction model and activation parameters of the hydrogel dehydration were completely different for the isothermal process than for the non-isothermal one. They also observed that the increase in dehydration temperature lead to the changes in isothermal kinetic model. Neacsu et al. [14] studied the dehydration of irradiated and non-irradiated asparagine monohydrate by means of DSC in isothermal conditions and static atmosphere at four different temperatures, viz. 358, 363, 368, and 373 K. They analyzed the isothermal kinetics via the common factorized rate equation and observed that Šesták–Berggren conversion function was found to best fit the experimental data. Model-free approach has been used for the study of the dehydration kinetics of cluster compound $[\{Mg(H_2O)_5\}_2Re_6S_8(OH)_6] \cdot H_2O$, and it has been observed that linear and non-linear regression methods give more accurate and full kinetic description of the process [15].

The dehydration of $LiCl \cdot H_2O$ was studied under inert helium atmosphere by DTA/TG for different heating rates [16]. It has been found that the dehydration of $LiCl \cdot H_2O$ proceeds through a two-step reaction between 99–110 and 160–186 °C, leading to the formation of $LiCl \cdot 0.5H_2O$ as intermediate compound, with activation energies of 240 kJ mol^{-1} (step 1) and 137 kJ mol^{-1} (step 2), respectively. It has been reported that the thermal dehydration of $Al_2(SO_4)_3 \cdot 18H_2O$ occurs through four major stages, all of endothermic, and some of these major stages are composed of sub-stages [17]. Çilgi and Cetisli [17] reported that the first three major stages are dehydration reactions in which two, ten, and six moles of water are lost, respectively, and the last major stage is that of sulfate decomposition. They calculated the kinetic parameters of the major and sub-stages by integral and differential methods and investigated the alterations of activation energies with respect to the decomposition ratio and to the method adopted. Boonchom et al. [18] studied the thermal decomposition of synthetic serrabrancaite ($MnPO_4 \cdot H_2O$) in N_2 atmosphere using TG–DTG–DTA and reported that the decomposition occurs in two stages, which are assigned to the dehydration and the reduction processes with $Mn_2P_2O_7$ as the final product, which was identified by X-ray powder diffraction, FT-IR, and FT-Raman techniques. They performed the kinetic analysis of both the dehydration and reduction reactions of $MnPO_4 \cdot H_2O$ under non-isothermal condition through isoconversional methods of Flynn–Wall–Ozawa and Kissinger–Akahira–Sunose and showed the dependences of activation energies on the extent of conversions.

In another study Boonchom and Kongtaweelert [19] investigated the kinetics of the thermal dehydration of aluminum phosphate monohydrate, $AlPO_4 \cdot H_2O$, using thermogravimetry (TG–DTG–DTA) at four heating rates in dry air atmosphere and calculated the activation energy values of the dehydration step of $AlPO_4 \cdot H_2O$ through the methods of Friedman and Flynn–Wall–Ozawa. They observed that the activation energy values are independent of extent of conversions, suggested a single kinetic mechanism for the dehydration reaction for $AlPO_4 \cdot H_2O$, and reported that the kinetic and thermodynamic functions calculated for the dehydration reaction by different techniques and methods were found to be consistent. Foppoli et al. [20] studied the kinetics of the dehydration reaction of hydrated form of theophylline-7-acetic acid, obtained by recrystallization from water, by fitting the dehydration data to various solid-state reaction models. They observed that the dehydration reaction follows a three-dimensional phase boundary reaction proceeding from the surface of the crystal inward along three dimensions with an activation energy value of 173 kJ mol^{-1}. Danvirutai et al. [21] studied the dehydration kinetics of ammonium manganese phosphate monohydrate ($NH_4MnPO_4 \cdot H_2O$) by the method proposed by Kissinger, under non-isothermal conditions, and observed an activation energy value of 180.77 kJ mol^{-1}.

Potassium titanium oxalate (PTO) and similar type of compounds have attracted much attention due to their technological importance, for instance, as precursor of nanostructured titanates. Titanate-based ceramics have many applications in material science for different reasons [22]. PTO shows an overall dehydration of the type $A \rightarrow B + C$, where A and B are solid phases and C is $H_2O_{(g)}$. Even though PTO has many chemical [23] and pharmaceutical [24, 25] applications, no kinetic studies on its thermal dehydration were reported in the literature.

The rate of the processes leading to property changes of high energetic materials during storage depends on the intrinsic properties of the materials, such as kinetic parameters of the dehydration process. A sound knowledge of the temperature dependence of the dehydration rate is required for the prediction of safe storage and service life of high energetic materials. The objective of the present investigation is to study the thermal dehydration kinetics of PTO, which is very important because industry needs measurements of kinetic parameter for the accurate design of installation and treatment conditions, and augmentation of temperature or elongation of reaction time means more cost. The results of the kinetic investigations can also be applied to problems such as useful lifetime of certain components, oxidative and thermal stability, and quality control [26].

Experimental

Materials

AnalaR grade potassium titanium oxalate of E merck is dissolved in water, recrystallized, dried, powdered in an agate mortar, sieved to fix the particle size in the range, 90–106 μm, and kept in a vacuum desiccator.

Methods

TG analyses of PTO samples were carried out on a SETARAM made Labsys TG–DTA-1600 at four different heating rates, viz, 5, 10, 15, and 20° min^{-1}. The operational characteristics of the TG–DTA system are—sample mass: 10 mg, sample pan: silica, and atmosphere: flowing nitrogen (flow rate $= 6 \times 10^{-2}$ L min^{-1}). The DSC analyses of PTO samples were carried out on a Mettler Toledo DSC 822e with a measurement resolution of 0.04 mW at room temperature. Duplicate runs were made under similar conditions (for both TG–DTA and DSC) and found that the data overlap with each other, indicating satisfactory reproducibility.

Kinetic analyses of TG and DSC data

The most common experimental technique employed to study kinetics of thermally activated reactions is thermogravimetry, under isothermal and/or non-isothermal conditions. In non-isothermal TG, two methods, model-fitting and model-free analyses have been used for the evaluation of kinetic parameters. Model-fitting methods were among the first and most popular methods for kinetic description, because it requires only a single heating rate experiment to calculate the kinetic parameters. However, the popularity of this method has been declined in favor of isoconversional method of model-free approach [27–29].

The basic form of the equation used for analysis of non-isothermal TG data is given below [30]:

$$\ln g(\alpha) = \ln[AE/\beta R] + \ln p(x) \qquad (1)$$

where $g(\alpha)$ is a function of α, which depends on the mechanism of the reaction; A is the pre-exponential factor; β is the heating rate; R is the universal gas constant; and $p(x) = \int_x^\infty (\mathrm{e}^{-x}/x^2)\mathrm{d}x$ and $x = E/RT$. This equation can be readily applied once the form of the function $p(x)$ is established.

For kinetic analyses, the main task is to derive the solution for the above temperature integral. Several methods are available under different approaches, viz., integral, differential, and approximation, for the evaluation of the temperature integral. However, most of these methods neglect the low temperature end of the temperature integral. The macroscopic kinetics is inherently complex, because they include information about multiple steps that are occurring simultaneously. Unscrambling the complex kinetics presents a serious challenge that can only be met by kinetic methods that provide means of detecting and treating multistep processes. Isoconversional methods, based on multiple heating programs, are the most popular methods that can meet this challenge [31]. Isoconversional kinetics rely upon evaluating a dependence of the effective activation energy on conversion or temperature and using this dependence for making kinetic predictions and for exploring the mechanism of thermal processes.

The conventional model-fitting approach assuming a fixed mechanism throughout the reaction and extract a single values of the apparent activation energy and pre-exponential factor and was found to be too simplistic. The values of Arrhenius parameters obtained in such a way are in fact an average that does not reflect changes in the reaction mechanism and kinetics with the extent of conversion. The model-free approach allows for a change of mechanism and activation energy during the course of a reaction and is therefore more realistic. The isoconversional method suggested by Flynn–Wall–Ozawa [32] use approximation of the integral equation, which leads to simple linear equation for evaluation of activation energy:

$$\ln \beta = \ln(AE/R) - \ln g(\alpha) - 5.3305 - 1.052(E/RT) \qquad (2)$$

A plot of $\ln \beta$ versus $1/T$ will give a straight line with a slope of $-1.052E/R$.

If the values of activation energy determined for the various values of α, are almost constant, then certainly the reaction involves only a single step. On the contrary, a change in E with increasing degree of conversion is an indication of a complex reaction mechanism that invalidates the separation of variables involved in the Ozawa–Flynn–Wall analysis [33].

Model-free kinetics rest on evaluating the E_α dependence [34]. This dependence is adequate for both theoretical and practical purposes of kinetic predictions. Normally, model-free kinetics do not concern with evaluating A and $g(\alpha)$ or $f(\alpha)$ because they are not needed for performing kinetic predictions. Also, these values are hardly suitable for theoretical interpretation because of the strong ambiguity associated with them. However, these values can be determined in the frameworks of model-free kinetics.

The contribution of DSC techniques for determining kinetic parameters of thermal dehydration processes prompted us for the evaluation of kinetic parameters by applying different isoconversional methods on DSC data of the endothermic dehydration process of PTO. In DSC, the conversion degree α is assumed to satisfy a n-order rate equation where the rate constant is expressed in Arrhenius form as

$$d\alpha/dt = Ae^{-E/RT}(1-\alpha)^n \tag{3}$$

where n is the overall reaction order with respect to unreacted material.In DSC experiments, the conversion degree α is defined by the ratio between the partial enthalpy and the total heat of reaction:

$$\alpha = \Delta H_{\mathrm{partial}}/\Delta H_{\mathrm{total}} \tag{4}$$

where H is the enthalpy of the reaction. By introducing $\beta = dT/dt$ in Eq. 3 and on integration, one obtains

$$g(\alpha) = [AE/\beta R]\,p(x) \tag{5}$$

This is the basic equation used for the evaluation of kinetic parameters from DSC data for which various approximation methods are available. In Kissinger's method, the conversion degree is supposed to be constant at the top of the DSC peak, whatever α may be, and $p(x)$ is assumed to be expressed by Kissinger's approximation [35]. With these two assumptions, Eq. 5 can be written as

$$\ln\left(\beta/T_{\mathrm{p}}^2\right) = \ln(AR/E) - \left(E/RT_{\mathrm{p}}\right) - \ln g\left(\alpha_{\mathrm{p}}\right) \tag{6}$$

where α_{p} is the conversion degree reached at the peak top temperature T_{p}.

A plot of ln (β/T_{p}^2) versus $1/T_{\mathrm{p}}$ should be linear and the activation energy might be obtained from the slope $(-E/R)$. Even though Kissinger's method was initially developed for first-order reactions, it has been reported that this equation holds good for any kinetic model [36] and Hatakeyama et al. [37] reported that activation energy values are obtained with a good accuracy if four or more scanning rates are tested.

The method of Ozawa [34] was also employed for the estimation of kinetic parameters from the DSC data of the dehydration process of PTO. Ozawa's method is usually performed using the top of the temperature peak T_{p}, at this point, it is assumed that A, α, and E are independent of the scanning rate β, while A and E are independent of α. So using Doyle's approximation [38], Eq. 5 may be expressed as

$$\ln g\left(\alpha_{\mathrm{p}}\right) = \ln(AR/E) - \ln\beta - 2.315 - 0.4567\left(E/RT_{\mathrm{p}}\right) \tag{7}$$

The apparent activation energy can be obtained from a plot of ln β against $1/T_{\mathrm{p}}$. Although this method is often applied to the peak top temperature, another conversion degree could be used, such as any isoconversion method [39].

Results and discussion

Broadbent et al. [40] reported the results of thermogravimetric and differential thermo analytical studies on PTO and potassium aluminium oxalate under non-isothermal conditions in air, nitrogen, and carbon dioxide atmospheres. They reported that the dehydration of PTO starts at 70 °C and proceeds in several stages until completion at 200 °C. It has been shown that PTO is less stable than potassium oxalate [41].

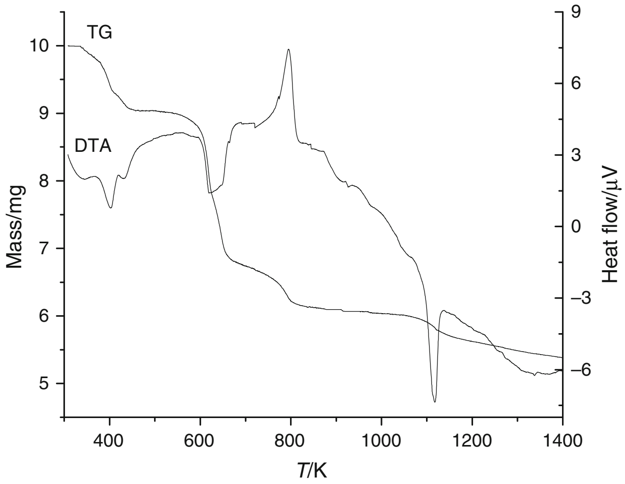

Fig. 1 Simultaneous TG–DTA curve for PTO at a heating rate of 10 K min^{-1}

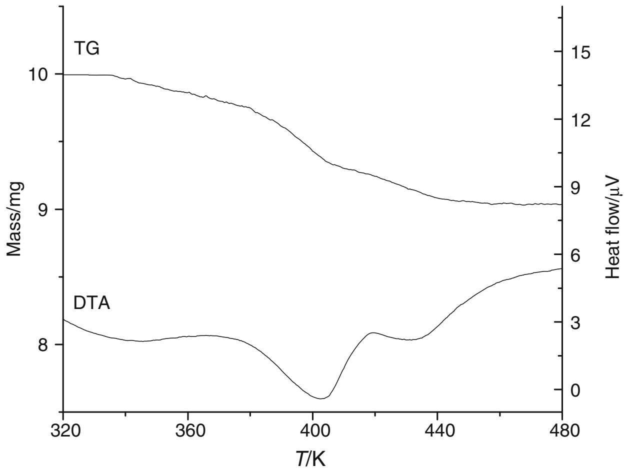

Fig. 2 Typical TG and DTA curves for the thermal dehydration of PTO at a heating rate of 10° min^{-1}

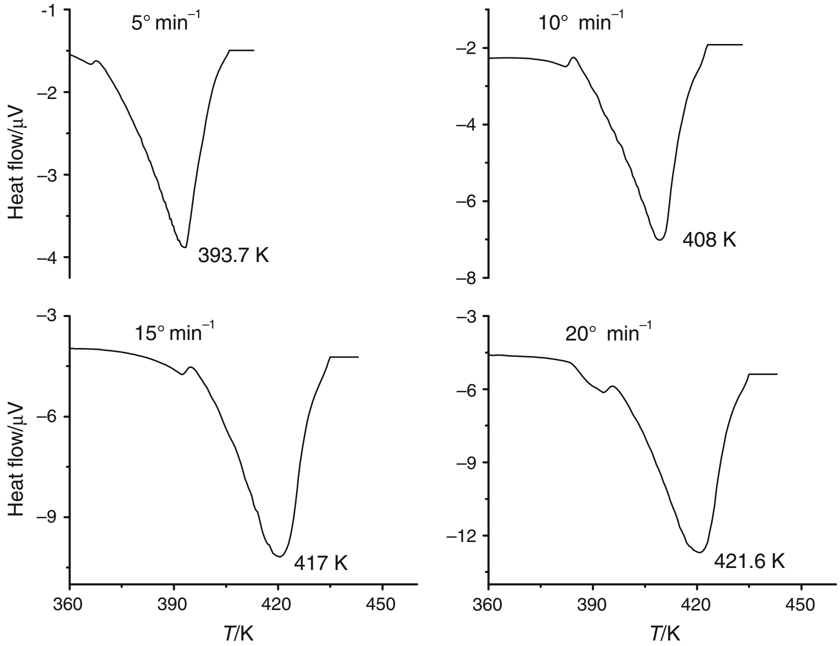

Fig. 3 DSC curves for the thermal dehydration of PTO at different heating rates

It has been observed that PTO decomposes through five stages as:

$K_2TiO(C_2O_4)_2{\cdot}2H_2O \rightarrow K_2TiO(C_2O_4)_2 + 2H_2O$ (ambient−140°C)

$2K_2TiO(C_2O_4)_2 \rightarrow K_4Ti_2O_2(C_2O_4)_3{\cdot}CO_3 + CO$ (140−220°C)

$K_4Ti_2O_2(C_2O_4)_3{\cdot}CO_3 \rightarrow K_4Ti_2O_5CO_3 \cdot CO_2 + 2CO_2 + 3CO$ (250−420°C)

$K_4Ti_2O_5CO_3 \cdot CO_2 \rightarrow K_4Ti_2O_5CO_3 + CO_2$ (420−600°C)

$K_4Ti_2O_5CO_3 \rightarrow 2K_2TiO_3 + CO_2$ (600−860°C)

Several authors [3, 22, 24] observed this type of phenomena in the decomposition of other titanyl oxalates, e.g., Barium titanium oxalate and strontium titanium oxalate. Figure 1 shows the simultaneous TG–DTA curve for PTO at a heating rate of 10 K min^{-1} in nitrogen atmosphere. Similar curves were obtained at all other heating rates (not shown).

The dehydration of PTO undergoes in the temperature range ambient–140 °C. Figure 2 shows the TG–DTA curve for the dehydration of PTO at a heating rate of 10° min^{-1} in nitrogen atmosphere. Similar curves were obtained at all other heating rates (not shown). The DSC curves for the dehydration of PTO at different heating rates are shown in Fig. 3.

Figure 4 shows the α–T curves with values of DSC peak temperature (T_p) for the thermal dehydration of PTO at different heating rates. The energetic and kinetics of the dehydration reaction of PTO has been studied through model-free methods from TG data. The apparent activation energy values were estimated using the isoconversion method suggested by Ozawa, Flynn, and Wall [38] at different percentages of conversion by fitting the plot of ln β versus $1/T$, and the values are given in Table 1. Plots of ln β versus $1/T$ under isoconversional method for the dehydration of PTO samples at all percentages of conversions give high values of correlation coefficient ($r < -0.99$) with activation energy values in the range 68.3–70.3 kJ mol^{-1}. Typical isoconversional plots for the dehydration of PTO are shown in Fig. 5. The apparent activation energy values determined for the various values of α of the dehydration

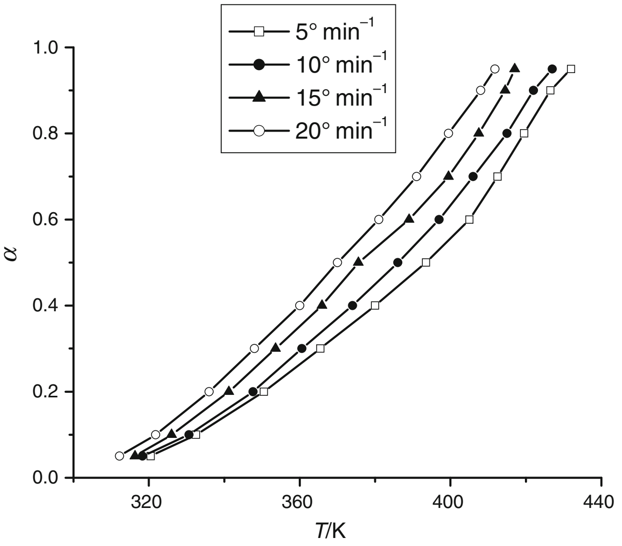

Fig. 4 α–T curves for the thermal dehydration of PTO at different heating rates

reaction are found to be consistent (69.3 ± 1 kJ mol^{-1}), which indicates that the dehydration occurs through a single step. The dependence of *E* on conversion is shown in Fig. 6.

The temperature ranges for the dehydration of PTO and values of peak temperature (T_p) obtained from the DSC, at different heating rates, are given in Table 2. The DSC data of the endothermic dehydration process of PTO were also subjected to kinetic analyses through isoconversional methods proposed by Ozawa [34] and Kissinger [35]. Both these isoconversional methods give consistent values of *E* with good correlation. The activation energy values obtained as per the method of Ozawa (69.2 kJ mol^{-1}) and Kissinger (69.8 kJ mol^{-1}) from DSC data are found to be in close agreement with those obtained through isoconversional method applied to TG data (69.3 ± 1 kJ mol^{-1}). The isoconversional plots for the methods of Ozawa and Kissinger are shown, respectively, in Figs. 7 and 8. The values of activation energy and correlation coefficient (*r*) are also given in Figs. 7 and 8.

Table 1 Values of *E* and *r*, obtained from TG data through isoconversional method, for the dehydration of PTO

Conversion/α	*E*/kJ mol^{-1}	$-r$
0.05	69.5	0.9994
0.10	68.3	0.9998
0.20	69.2	0.9996
0.30	68.7	0.9999
0.40	68.9	0.9995
0.50	70.2	0.9994
0.60	70.1	0.9998
0.70	70.3	0.9994
0.80	69.4	0.9997
0.90	69.8	0.9991
0.95	68.6	0.9993

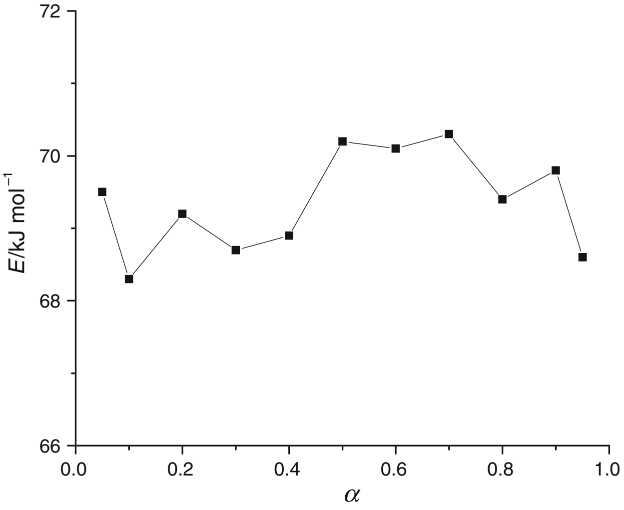

Fig. 6 Dependence of *E* on conversion for the thermal dehydration of PTO

Fig. 5 Typical isoconversional plots for the thermal dehydration of PTO

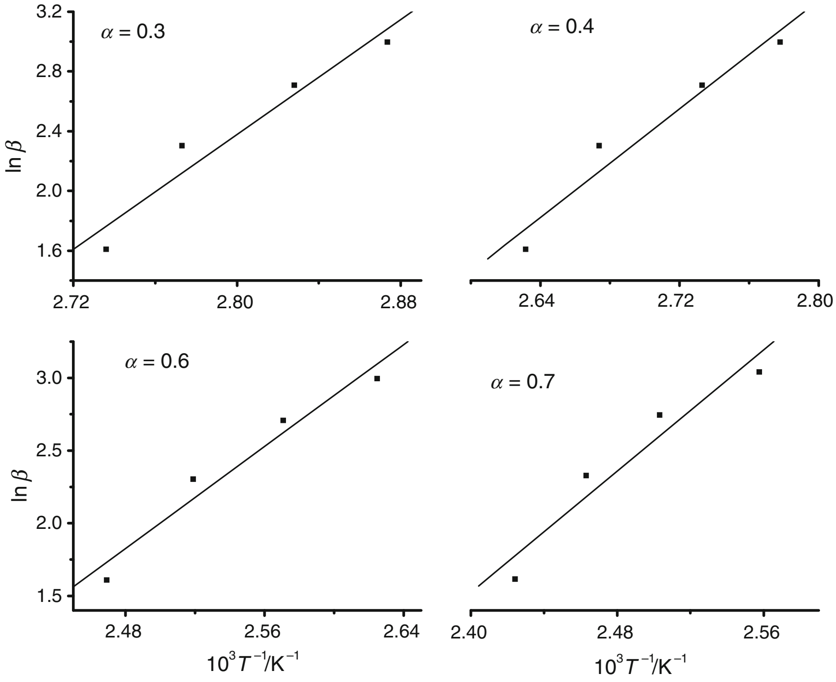

Table 2 Temperature range for the dehydration of PTO and values of T_p, from DSC, at different heating rates

Heating rate/° min^{-1}	Temperature range/K	Peak temperature (T_p)/K
5	360–406	393.7
10	382–423	408
15	387–434	417
20	392–437	421.6

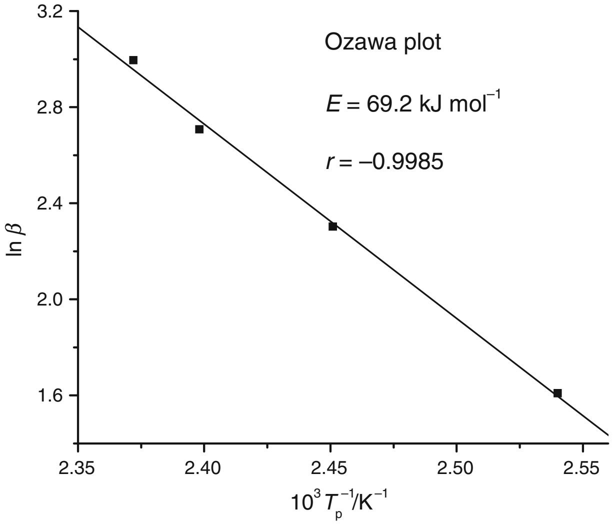

Fig. 7 Ozawa's method applied on the top of the peak

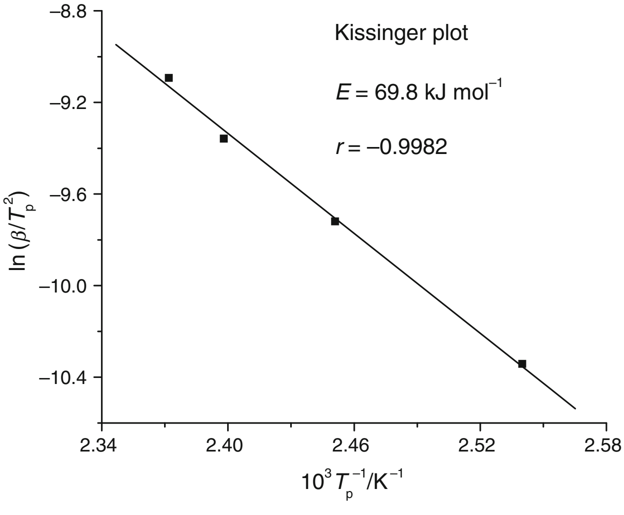

Fig. 8 Kissinger's method applied on the top of the peak

Conclusions

We observed that the activation energy values obtained through the isoconversional method applied to the TG data during the entire dehydration process ($\alpha = 0.05 \leq \alpha \leq 0.95$) of PTO are approximately constant. Further, the activation energy values calculated for the thermal dehydration of PTO by different methods and techniques were found to be consistent. The activation energy involved and its dependence on the conversion degree were estimated by evaluating the TG data according to an isoconversional model. From the dependence of the values of activation energy obtained for the extent of conversions and from different methods, it could be concluded that the thermal dehydration of PTO is a single-step irreversible process.

Acknowledgements The authors express their thanks to KSCSTE for the provision of instrumental facility.

References

1. Gopalakrishnamurhty HS, Rao MS, Kutty TRN. Thermal decomposition of titanyl oxalates. II. Kinetics of decomposition of barium titanyl oxalate. J Inorg Nucl Chem. 1975;37:1875–8.
2. Patra BS, Otta S, Battamisra SD. A kinetic and mechanistic study of thermal decomposition of strontium titanyl oxalate. Thermochim Acta. 2006;441:84–8.
3. Duval C. Inorganic thermogravimetric analysis. 2nd ed. Amsterdam: Elsevier; 1963.
4. Galwey AK, Brown ME. An appreciation of the chemical approach of V. V. Boldyrev to the study of the decomposition of solids. J Therm Anal Calorim. 2007;90:9–22.
5. Majumdar S, Sharma IG, Bidaye AC, Suri AK. A study on isothermal kinetics of thermal decomposition of cobalt oxalate to cobalt. Thermochim Acta. 2008;473:45–9.
6. Donkora B, Mehandjiev D. Mechanism of decomposition of manganese (II) oxalate dihydrate and manganese (II) oxalate trihydrate. Thermochim Acta. 2004;421:141–9.
7. Al-Newaiser FA, Al-Thabaiti SA, Al-Youbi AO, Obaid AY, Gabal MA. Thermal decomposition kinetics of strontium oxalate. Chem Pap. 2007;61:370–5.
8. Torres-Garcia J, Balmaseda J, del Castillo LF, Reguera E. Thermal evolution of microporous nitroprussides on their dehydration process. J Therm Anal Calorim. 2006;86:371–7.
9. Chambré D, Iditoiu C, Segal E. Non-isothermal dehydration kinetics of acrylic ion-exchange resins. J Therm Anal Calorim. 2007;88:673–9.
10. Logvinenko V, Fedorov V, Mironov Yu, Drebushchak V. Kinetic and thermodynamic stability of cluster compounds under heating. J Therm Anal Calorim. 2007;88:687–92.
11. Vlaev LT, Georgieva VG, Genieva SD. Products and kinetics of non-isothermal decomposition of vanadium(IV) oxide compounds. J Therm Anal Calorim. 2007;88:805–12.
12. Boonchom B, Youngme S, Srithanratana T, Danvirutai C. Synthesis of $AlPO_4$ and kinetics of thermal decomposition of $AlPO_4 \cdot H_2O–H_4$ precursor. J Therm Anal Calorim. 2008;91:511–6.
13. Jankovic B, Adnadevic B, Jovanovic J. Isothermal kinetics of dehydration of equilibrium swollen poly(acrylic acid) hydrogel. J Therm Anal Calorim. 2008;92:821–7.
14. Neacsu A, Contineanu I, Popa VT, Contineanu M. Dehydration of irradiated and non-irradiated *L*-a-asparagine monohydrate. J Therm Anal Calorim. 2008;94:405–10.
15. Logvinenko V. Model-free approach in the study of decomposition kinetics for cluster compounds and coordination compounds. J Therm Anal Calorim. 2008;93:805–9.

16. Masset PJ. Thermogravimetric study of the dehydration reaction of LiCl·H_2O. J Therm Anal Calorim. 2009;96:439–41.
17. Çilgi GK, Cetisli H. Thermal decomposition kinetics of aluminum sulfate hydrate. J Therm Anal Calorim. 2009;98:855–61.
18. Boonchom B, Danvirutai C, Thongkam M. Non-isothermal decomposition kinetics of synthetic serrabrancaite ($MnPO_4 \cdot H_2O$) precursor in N_2 atmosphere. J Therm Anal Calorim. 2010;99: 357–62.
19. Boonchom B, Kongtaweelert S. Study of kinetics and thermodynamics of the dehydration reaction of $AlPO_4 \cdot H_2O$. J Therm Anal Calorim. 2010;99:531–8.
20. Foppoli A, Zema L, Maroni A, Sangalli ME, Caira MR, Gazzaniga A. Dehydration kinetics of theophylline-7-acetic acid monohydrate. J Therm Anal Calorim. 2010;99:649–54.
21. Danvirutai C, Noisong P, Youngme S. Some thermodynamic functions and kinetics of thermal decomposition of $NH_4MnPO_4 \cdot H_2O$ in nitrogen atmosphere. J Therm Anal Calorim. 2010;100:117–24.
22. Ischenko V, Pippel E, Köferstein R, Abicht HP, Woltersdorf J. Barium titanate via thermal decomposition of Ba,Ti-precursor complexes: the nature of the intermediate phases. Solid State Sci. 2007;9:21–6.
23. Gopalakrishnamurhty HS, Rao MS, Kutty TRN. Thermal decomposition of titanyl oxalates. I. Barium titanyl oxalate. J Inorg Nucl Chem. 1975;37:1891–8.
24. Kuntic V, Pejic N, Misic S, Vukojevic V, Vujic Z, Malesev D. Determination of quercetin in pharmaceutical formations via its reaction with potassium titanyloxalate. Determination of the stability constants of the quercetin titanyloxalato complex. J Serb Chem Soc. 2005;70:753–63.
25. Pejic N, Kuntic V, Malesev D. Potassium titanyloxalate as analytical reagents for micro-quantitative determination of quercetin. Pharmazie. 2001;56:216–7.
26. Celis K, Van Driessche I, Mouton R, Vanhoyland G, Hoste S. Thermomicroscopy as a tool to study the kinetics of consecutive reactions in the solid state. Meas Sci Rev. 2001;1:177–80.
27. Vyazovkin S, Wight CA. Kinetics in solids. Annu Rev Phys Chem. 1997;48:125–49.
28. Khawam A, Flanagan DR. Role of isoconversional methods in varying activation energies of solid-state kinetics. I. Isothermal kinetic studies. Thermochim Acta. 2005;429:93–102.
29. Khawam A, Flanagan DR. Complementary use of model-free and modelistic methods in the analysis of solid-state kinetics. J Phys Chem. 2005;109B:10073–80.
30. Muraleedharan K, Labeeb P, Abdul Mujeeb VM, Aneesh MH, Ganga Devi T, Kannan MP. Effect of particle size on the thermal decomposition kinetics of potassium titanium oxalate. Z Phys Chem. doi:10.1524/zpch.2011.0051.
31. Brown ME, Gallagher PK, editors. Handbook of thermal analysis and calorimetry, vol. 5, recent advances, techniques and applications. Amsterdam: Elsevier; 2008.
32. Ozawa T. A new method of analyzing thermogravimetric data. Bull Chem Soc Jpn. 1965;38:1881–6.
33. Vyazovkin S. Model-free kinetics staying free of multiplying entities without necessity. J Therm Anal Calorim. 2006;83:45–51.
34. Ozawa T. Kinetic analysis of derivative curves in thermal analysis. J Therm Anal. 1970;2:301–24.
35. Kissinger HE. Reaction kinetics in differential thermal analysis. Anal Chem. 1957;29:1702–6.
36. Sbirrazzuoli N, Girault Y, Elegant L. Simulations for evaluation of kinetic methods in differential scanning calorimetry. Part 3. Peak maximum evolution methods and isoconversional methods. Thermochim Acta. 1997;293:25–37.
37. Hatakeyama T, Zhenhai L. Handbook of thermal analysis. Chichester: Wiley; 1998. p. 47–9.
38. Doyle CD. Estimating isothermal life from thermogravimetric data. J Appl Polym Sci. 1962;6:639–46.
39. Leoni E, Tomi P, Khoumeri B, Balbi N, Bernardini AF. Thermal degradation of pinus pinaster needles by DSC. Part 1. Dehydration kinetics. J Fire Sci. 2001;19:379–97.
40. Broadbent D, Dollimore D, Dollimore J. Thermogravimetry and differential thermal analysis studies on potassium titanyl oxalate and potassium aluminium oxalate and related oxalates. Analyst. 1969;94:543–53.
41. Papazian HA, Pizzolato PJ, Patrick JA. Thermal decomposition of oxalates of ammonium and potassium. J Am Cer Soc. 1971;54: 250–4.