

# Quantitative correlation of kinetic parameters and procedural factors in non-isothermal thermogravimetry-dependence of heating rate and sample mass

K. S. Rejitha · Suresh Mathew

Received: 21 April 2009 / Accepted: 18 December 2009 / Published online: 12 January 2010  
© Akadémiai Kiadó, Budapest, Hungary 2010

**Abstract** Dependence of kinetic parameters (activation energy and pre-exponential factor) and procedural factors (sample mass and heating rate) independent of the reversibility and the type of reactions in non-isothermal thermogravimetry have been established. Tris(ethylenediamine)nickel(II) oxalate dihydrate has been selected as a model complex and experiments were carried out at different heating rates and sample masses to study the dependence quantitatively. The kinetic parameters calculated using mechanistic and non-mechanistic equations show a systematic decrease with increase in either sample mass or heating rate for the dehydration and deamination reactions. For the decomposition reaction, the kinetic parameters are not influenced by the procedural factors. Mathematical correlations of high reliability are established between kinetic parameters and heating rate/sample mass using both mechanistic and non-mechanistic equations for dehydration and deamination reactions. The quantification follows an exponential decay of second order relation with respect to heating rate and a sigmoidal relation with regard to sample mass for both the dehydration and deamination reactions. No quantitative correlation is possible for the final decomposition stage. Thus, it is found that independent of the type of reaction (deamination or dehydration) the kinetic parameters have a particular dependence on the procedural variables. The equations for exponential decay and sigmoidal dependence can be represented as  $y = y_0 + A_1 e^{-x/t_1} + A_2 e^{-x/t_2}$  and

$y = \frac{A_1 - A_2}{1 + e^{(x-x_0)/dx}} + A_2$  respectively, where  $y$  represents kinetic parameters ( $E$  or  $A$ ) and  $x$  represents the procedural variables ( $\varphi$  or  $m$ ). Mechanism of the dehydration reaction is found to be random nucleation with the formation of one nucleus on each particle and the deamination is a phase boundary reaction. It is observed that the mechanism of these reversible reactions is not affected by the variation in sample mass and heating rate.

**Keywords** Exponential decay · Kinetic parameters · Thermal decomposition · Tris(ethylenediamine)nickel(II) oxalate dihydrate

## Introduction

Thermal decomposition studies of oxalate systems present an interesting problem and have long been studied. Oxalate compounds give well defined decomposition pattern on heating and hence it is always used as model compounds to investigate the influence of many experimental variables [1]. Recently, thermal decomposition studies of various oxalate compounds have been reported [2, 3]. Precursor nano synthesis and the dielectric studies of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  have also been reported [4]. Mathew et al. have investigated the deamination kinetics of nickel amine complex [5] and the effect of procedural parameters like sample mass and heating rate on the kinetics and mechanism of solid state decomposition using diaquobis(ethylenediamine)copper(II) oxalate as the model system [6].

It is well known that the results from TG curves are affected by procedural parameters like furnace heating rate, furnace atmosphere, geometry of the sample holder and furnace, sensitivity of recording mechanism, composition of sample container, amount of sample etc. Amongst these, the

**Electronic supplementary material** The online version of this article (doi:10.1007/s10973-009-0670-7) contains supplementary material, which is available to authorized users.

K. S. Rejitha · S. Mathew (✉)  
School of Chemical Sciences, Mahatma Gandhi University, P.D.  
Hills, Kottayam 686 560, Kerala, India  
e-mail: sureshmathews@sancharnet.in

major experimental variables are heating rate and sample mass. Investigations on the effect of these experimental variables are very important and the results are often used to optimise the experimental conditions in quality assessment of petroleum products [7]. Although the dependence of  $E$  and  $A$  on the sample mass and heating rate is well known [8–11], not much work has been done so far to study the dependence quantitatively.

In this paper, we report the results of our attempts to evolve a mathematical correlation between the procedural factors and the kinetic parameters for three reaction types viz., reversible deamination, reversible dehydration and the irreversible decomposition reaction. Kinetic parameters derived from both the mechanistic (model fitting) and non-mechanistic equations from non-isothermal analysis is utilised for the investigation.

In the present work, tris(ethylenediamine)nickel(II) oxalate dihydrate was used as the model complex, which gave non-overlapping and clear cut stoichiometric reactions of three reaction types, i.e. a reversible dehydration, followed by a reversible deamination, followed by a non-reversible decomposition reaction.

## Experimental

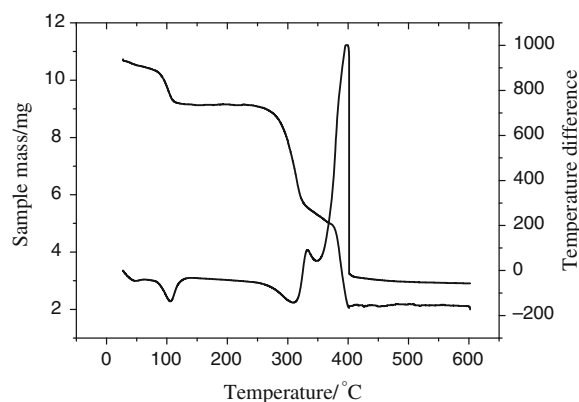
The complex was synthesized as per the procedure reported in the literature [12] and was characterised by various spectral and chemical means. Nickel content in the complex was determined by means of gravimetry [13].

### Instrumentations

Thermogravimetric analyses were carried out using Shimadzu DTG-60 instrument connected to a TA-60 online analyser. The experiments were conducted in flowing air with a flow rate of 50 mL min<sup>-1</sup>. In order to study the effect of heating rate, eight experiments were conducted at different heating rates (1, 2, 5, 10, 15, 20, 50 and 90 °C min<sup>-1</sup>). Samples were loaded in a platinum crucible of cylindrical geometry with a diameter of 5 mm and the mass was kept constant around 10 ± 0.1 mg. To investigate the effect of sample mass, seven sample masses (2.5, 5, 7, 10, 12, 15.6, 20 mg) were used and the heating rate was kept constant (10 °C min<sup>-1</sup>). All the samples were loaded in a platinum crucible in a uniform manner. The particles were sieved through a Fisher sub-sieve sizer to make the particle size uniform so that the effect of particle size can be avoided. The average particle size was 50 μm.

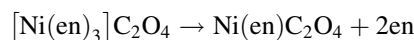
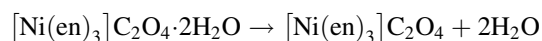
## Results and discussion

The TG/DTA plot for the complex at 10 °C min<sup>-1</sup> is given in Fig. 1. The first stage of decomposition corresponds to



**Fig. 1** TG/DTA plot for the decomposition of tris(ethylenediamine)nickel(II) oxalate dihydrate ( $\varphi = 10\text{ }^{\circ}\text{C min}^{-1}$ )

the loss of two water molecules to give tris(ethylenediamine)nickel(II) oxalate. The second stage corresponds to the loss of two en molecules to give mono ethylenediamine complex. The final stage corresponds to the decomposition of mono(ethylenediamine)nickel(II) oxalate to give NiO as the final residue. The intermediates were separated and identified by means of XRD and SEM. The stages of thermal decomposition are as shown below. Under oxidising condition, ethylenediamine is oxidised instantaneously and the oxides of nitrogen and carbon are evolved as the gaseous products and the exothermicity due to oxidation is seen in the DTA.



The shapes of the TG curves remain unchanged with increase in either heating rate or sample mass while there is a noticeable increase in the temperature of inception ( $T_i$ ) and final temperature ( $T_f$ ). The decomposition starts at low temperature for slow heating rate and ends at low temperature. It is observed that the reaction interval ( $T_f - T_i$ ) is increased with increase in heating rate. For all three decomposition stages,  $T_f$  increases with sample mass and heating rate. With increase in sample mass there is an increase in the concentration of the gaseous products in the surrounding atmosphere, which in turn retards the forward reaction thereby shifting the reaction to higher temperature. Also, the increase of the mass leads to a larger change of the temperature profile due to the self-cooling (or self-heating) process, caused by the heat of the reaction [14]. Since the furnace heating rate is linear, there is a resultant increase in the value of  $T_f$  [15]. The phenomenological data for the thermal decomposition of the model complex are given in Table 1.

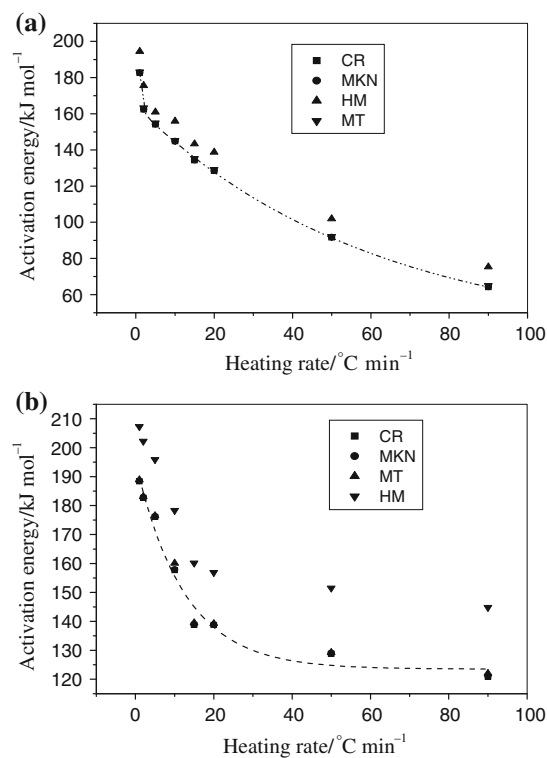
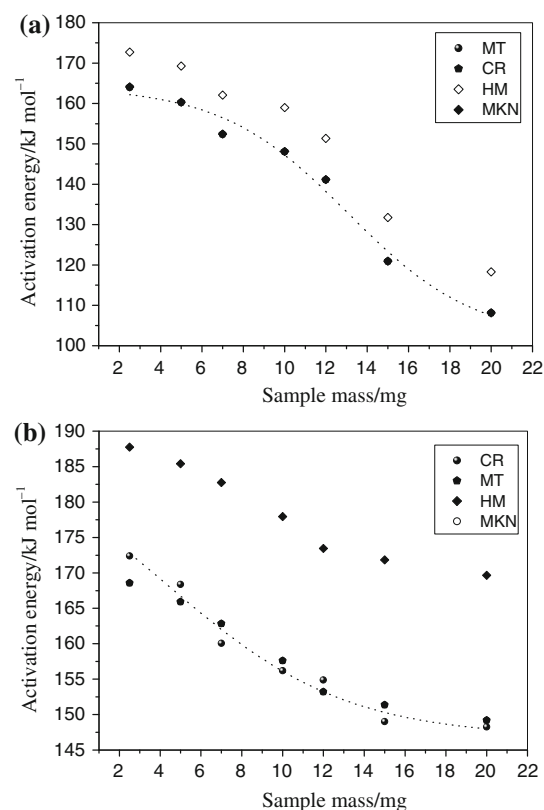
**Table 1** Phenomenological data for the thermal decomposition of  $[\text{Ni}(\text{en})_3]\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ 

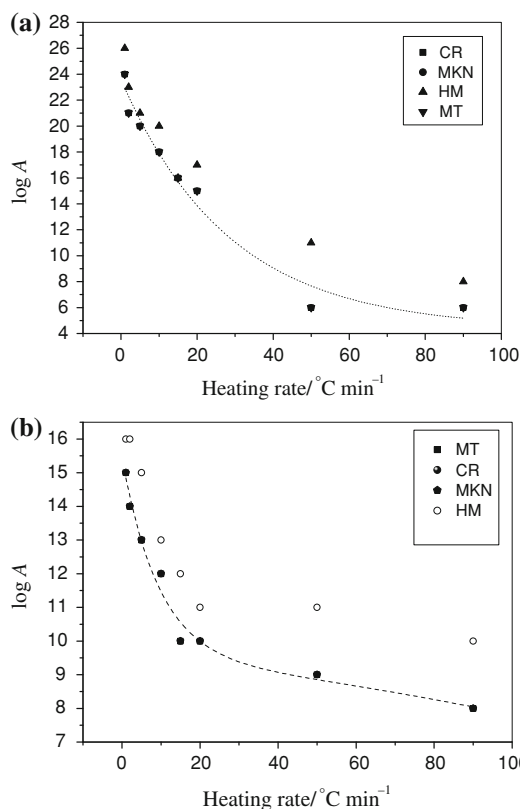
	Dehydration/ $^{\circ}\text{C}$			Deamination/ $^{\circ}\text{C}$			Decomposition/ $^{\circ}\text{C}$		
	$T_i$	$T_f$	$T_s$	$T_i$	$T_f$	$T_s$	$T_i$	$T_f$	$T_s$
Sample mass/mg									
2.5	77	138	90	242	317	290	318	380	370
5	80	152	98	248	326	310	327	387	378
7	82	158	103	250	330	313	331	397	390
10	82	161	105	252	332	313	333	400	392
12	81	165	109	256	335	314	336	407	396
15.6	81	170	112	263	341	316	342	412	398
20	85	174	114	268	348	330	349	422	406
Heating rate, $\rho/^{\circ}\text{C min}^{-1}$									
1	58	106	82	224	283	274	284	340	325
2	61	115	84	234	302	300.5	303	360	358
5	66	106	97.7	247	308	298	309	387	380
10	74	136	101	250	331	312	332	404	396
15	76	140	113	255	344	322	345	410	408
20	78	144	115	258	350	334	351	418	412
50	81	164	142	276	373	348.5	374	475	470
90	80	184	153	280	402	375	403	520	450

### Kinetic parameters

The kinetic parameters were calculated using four non-mechanistic equations viz., Coats–Redfern, MacCallum–Tanner, Horowitz–Metzger and MKN [16–19] equations. The order parameter  $n$  was determined using the Coats–Redfern equation by an iteration method. Linear plots of  $\ln[g(\alpha)/T^2]$  vs.  $1/T$  were plotted by least square method, taking  $\alpha$  and  $T$  values from the TG curve. Linear curves were drawn for different values of  $n$  ranging from 0 to 2, in increment of 0.01. The value of  $n$  was selected from the best fit having maximum correlation coefficient. The order parameters for each stage were chosen by taking the average of all values obtained for both heating rate and sample mass variations. With the values of  $n$  thus obtained, the kinetic parameters were computed using four non-mechanistic equations for deamination and dehydration reactions [6].

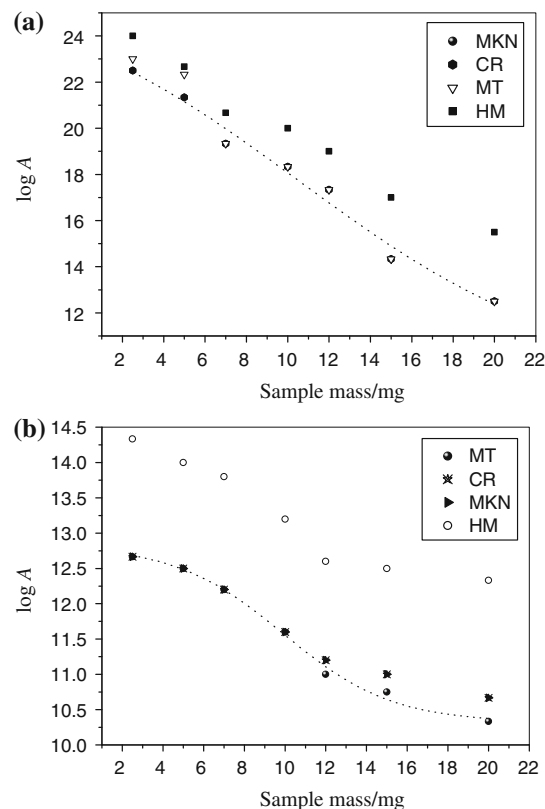
The variations of the kinetic parameters with heating rate and sample mass for the dehydration and deamination stages are given in Figs. 2, 3, 4 and 5. From the figures, it can be seen that the activation energy ( $E$ ) and pre-exponential factor ( $A$ ) are found to decrease with increase in sample mass or heating rate. Thus, as far as the kinetic parameters are concerned, an increase in heating rate at constant sample mass has the same quantitative trend as an increase in the sample mass at constant heating rate. Whereas for the final decomposition reaction no particular trend is observed, i.e. the variations are irregular.

**Fig. 2** Variation of activation energy with heating rate for **a** dehydration and **b** deamination reaction**Fig. 3** Variation of activation energy with sample mass for **a** dehydration and **b** deamination reaction



**Fig. 4** Variation of  $\log A$  with heating rate for **a** dehydration and **b** deamination reaction

The regular trend of these kinetic parameters relative to changes in heating rate and sample mass for the dehydration and deamination reactions makes the data amenable to statistical analysis. Standard types of curve fits such as exponential decay of 1st, 2nd and 3rd orders, exponential growth and sigmoidal (Boltzmann) were tried and the best fit was chosen (Figs. 2, 3, 4, 5). It is found that for all the four non-mechanistic equations the variation of  $E$  and  $A$



**Fig. 5** Variation of  $\log A$  with sample mass for **a** dehydration and **b** deamination reaction

values with heating rates for the dehydration and the deamination reaction can be represented as an exponential decay of 2nd order.

$$E = y_0 + A_1 e^{-\varphi/t_1} + A_2 e^{-\varphi/t_2}$$

$$\log A = y_0 + A_1 e^{-\varphi/t_1} + A_2 e^{-\varphi/t_2}$$

where  $y_0$ ,  $A_1$ ,  $A_2$ ,  $t_1$  and  $t_2$  are fit parameters for exponential decay of order two and represents offset, amplitudes and

**Table 2** Curve fit constants for the reversible reactions (exponential decay second order equation) using non-mechanistic equations

	Dehydration					Deamination				
	$y_0$	$A_1$	$A_2$	$t_1$	$t_2$	$y_0$	$A_1$	$A_2$	$t_1$	$t_2$
Correlation with $E$										
CR	35.4	128.7	60	173.1	0.47	-7.9	7.9	56.9	2.7	9.1
MKN	35.7	128.6	60	172.4	0.47	-2.2	2.2	57.1	7.6	9.1
MT	34.7	127.8	59.7	172.1	0.45	-6.2	5.4	54.2	6.5	8.1
HM	43.1	81.2	64.7	128.7	0.84	-1.7	1.7	57.5	9.4	7.3
Correlation with $\log A$										
CR	3.9	17.7	40.9	43.8	0.37	10.9	-1.4	5.9	-122.5	9.5
MKN	4.4	19.6	40.9	42.8	0.36	10.9	-1.4	5.9	-122.5	9.5
MT	3.8	17.5	43.1	41.1	0.35	10.3	-2.3	5.4	-111.1	9.8
HM	6.6	14.6	14.5	36.9	0.69	10.3	-3.3	3.3	-110.3	11.1

**Table 3** Curve fit constants for the reversible reactions (sigmoidal) equation using non-mechanistic equations

	Dehydration				Deamination			
	A <sub>1</sub>	A <sub>2</sub>	x <sub>0</sub>	dx	A <sub>1</sub>	A <sub>2</sub>	x <sub>0</sub>	dx
Correlation with <i>E</i>								
CR	164.2	101.5	13.1	3.1	170.4	148.8	8.6	2.8
MKN	164.3	101.4	13.1	3.1	170.4	148.8	8.6	2.8
MT	164.5	102.3	13.2	3.4	168.2	145.2	7.6	3.1
HM	171.8	112.9	13.3	2.8	189.3	169.5	8.9	2.7
Correlation with log <i>A</i>								
CR	26.6	8.9	10.5	6.8	12.8	10.3	9.9	2.7
MKN	26.6	8.9	10.5	6.8	12.9	10.7	9.2	2.8
MT	23.4	9.1	10.4	5.9	12.4	10.2	7.2	2.9
HM	167.5	6.7	-4.5	23.7	14.4	12.3	8.9	2.2

decay constants respectively for a second order exponential decay curve and  $\varphi$  is the heating rate.

The variation of *E* and *A* values with sample mass for the dehydration and deamination reaction can be best represented as a sigmoidal (Boltzman fit) curve of the type

$$E = \frac{A_1 - A_2}{1 + e^{(m-x_0)/dx}} + A_2$$

$$\log A = \frac{A_1 - A_2}{1 + e^{(m-x_0)/dx}} + A_2$$

where *A*<sub>1</sub>, *A*<sub>2</sub>, *x*<sub>0</sub>, and *dx* are fit parameters which represents the initial value, final value, centre (point of inflection) and time constant (the change in *X* corresponding to the most significant change in *Y* values), respectively, of a sigmoidal curve and *m* is the sample mass. The fit constants that are different for the four non-mechanistic equations and are given in Tables 2 and 3. The fitted curves are given in Figs. 2, 3, 4 and 5.

The reliability of the fits were assessed by means of *R*<sup>2</sup> (coefficient of determination) and chi square ( $\chi^2$ ) value. Chi square test is to measure the discrepancy existing between the observed and the expected frequencies. The smaller the value of chi square the better will be the fit. *R*<sup>2</sup> is a statistics that will give information about the goodness of a model. An *R*<sup>2</sup> of 1.0 indicates a perfect fit [20, 21]. The goodness of the models was also checked by *F* test. The fisher constant at 99% confidence level, the values of chi square and *R*<sup>2</sup> for various fits are given in Tables 4, 5, 6 and 7. The fit with higher *R*<sup>2</sup> and lower chi square values is selected as the best fit.

Mechanism of the reactions

Quantitative correlations between the kinetic parameters and procedural factors have also been obtained using mechanism

**Table 4** The fisher constant, chi square ( $\chi^2$ ) and coefficient of determination (*R*<sup>2</sup>) for the various fits between heating rate ( $\varphi$ )/sample mass (*m*) with activation energy for the dehydration reaction using four non-mechanistic equations

Fits	Activation energy, <i>E</i>					
	Heating rate			Sample mass		
	<i>F</i>	<i>R</i> <sup>2</sup>	$\chi^2$	<i>F</i>	<i>R</i> <sup>2</sup>	$\chi^2$
Exponential decay I						
CR	685.8	0.9778	46.13	581.2	0.9624	24.01
MKN	685.8	0.9778	46.13	580.2	0.9731	17.19
MT	671.1	0.9778	46.13	571.1	0.9745	16.65
HM	581.2	0.9722	58.31	502.1	0.9545	27.63
Exponential decay II						
CR	1047.2	0.9997	0.8950	-	-	-
MKN	1047.2	0.9997	0.8944			
MT	1025.3	0.9998	0.8943			
HM	1016.7	0.9989	4.56			
Exponential decay III						
CR	1044.6	0.9997	2.55	-	-	-
MKN	1044.6	0.9997	2.54			
MT	1035.2	0.9997	2.54			
HM	1016.7	0.9987	13.68			
Exponential growth						
CR	685.8	0.9778	46.13	621.1	0.9624	24.01
MKN	685.8	0.9778	46.01	621.1	0.9731	17.19
MT	690.1	0.9776	47.31	613.4	0.9745	16.65
HM	581.2	0.9722	58.31	582.2	0.9545	27.63
Sigmoidal						
CR	674	0.9774	58.71	654.1	0.9862	11.74
MKN	674	0.9774	58.56	653.5	0.9861	11.84
MT	674	0.9773	59.01	650.2	0.9877	11.89
HM	572.9	0.9718	73.8	632.1	0.9870	10.50

invoking equation. The kinetic parameters obtained for mechanism invoking equation for different heating rates and sample masses are given in Tables 8 and 9.

The correlation coefficients obtained are very close to unity in almost all cases, indicating nearly perfect fit. A choice of the probable mechanism from the best fit curve thus becomes difficult. In such a situation, Satava [22] has chosen the function *g*( $\alpha$ ) which yield kinetic parameters in agreement with those kinetic parameters by numerical method. In the present case, comparison with the values obtained from Coats–Redfern method is more appropriate as this method was also used for solving the exponential integral. It is found that the rate controlling process for dehydration reaction is random nucleation while the rate controlling process for the deamination process is phase boundary reaction. Kinetic parameters were also calculated from the mechanistic equations. For the dehydration and

**Table 5** The fisher constant, chi square ( $\chi^2$ ) and coefficient of determination ( $R^2$ ) for the various fits between heating rate ( $\varphi$ )/sample mass ( $m$ ) with log  $A$  for the dehydration reaction using four non-mechanistic equations

Fits	Log $A$					
	Heating rate			Sample mass		
	$F$	$R^2$	$\chi^2$	$F$	$R^2$	$\chi^2$
Exponential decay I						
CR	461.4	0.9805	0.9539	521.2	0.9831	0.33
MKN	466.1	0.9805	0.9539	521.1	0.9831	0.33
MT	453.2	0.9801	0.9831	518.2	0.9878	0.43
HM	306.4	0.9661	1.73	472.3	0.9859	0.2508
Exponential decay II						
CR	657.5	0.9997	0.1851	534.2	0.9831	0.6541
MKN	657.5	0.9997	0.1851	532.1	0.9831	0.33
MT	612.3	0.9989	0.15	530.6	0.9845	0.143
HM	462	0.9849	1.29	521.1	0.9859	0.3759
Exponential decay III						
CR	640.2	0.9902	0.2418	516.1	0.9831	–
MKN	466.1	0.9902	0.2418	517.9	0.9831	–
MT	524.2	0.9896	1.78	510.0	0.9832	–
HM	416.6	0.9849	3.77	482.1	0.9859	–
Exponential growth						
CR	461.4	0.9805	0.9539	521.7	0.9831	0.33
MKN	466.1	0.9805	0.9539	521	0.9831	0.33
MT	420.3	0.9801	1.73	513.2	0.9878	0.43
HM	306.4	0.9661	2.98	498.7	0.9859	0.2508
Sigmoidal						
CR	452.7	0.9801	6.23	576.2	0.9847	0.39
MKN	466.1	0.9801	1.54	576.3	0.9847	0.39
MT	403.2	0.9834	7.89	570.9	0.9894	0.23
HM	300.9	0.9657	2.19	555.2	0.9859	0.1879

**Table 6** The fisher constant, chi square ( $\chi^2$ ) and coefficient of determination ( $R^2$ ) for the various fits between heating rate ( $\varphi$ )/sample mass ( $m$ ) with activation energy for the deamination reaction using four non-mechanistic equations

Fits	Activation energy, $E$					
	Heating rate			Sample mass		
	$F$	$R^2$	$\chi^2$	$F$	$R^2$	$\chi^2$
Exponential decay I						
CR	123.6	0.9640	39.76	624.3	0.9745	2.17
MKN	124.2	0.9637	40.22	624.4	0.9748	2.16
MT	131.1	0.9641	41.01	620.9	0.9788	2.34
HM	78	0.9791	17.75	602.1	0.9712	2.16
Exponential decay II						
CR	230.2	0.9794	37.93	625.1	0.9745	4.35
MKN	232.4	0.9793	38.21	624.3	0.9748	4.31
MT	228.1	0.981	38.21	618.2	0.9812	3.21
HM	78	0.9791	29.88	588.4	0.9712	4.33
Exponential decay III						
CR	229.2	0.9793	114.59	625.1	0.9745	–
MKN	216.4	0.9771	123.59	624.3	0.9748	–
MT	225.5	0.9791	120.9	618.2	0.9732	–
HM	78	0.9693	190.1	588.4	0.9712	–
Exponential growth						
CR	123.6	0.9640	39.76	625.1	0.9745	2.17
MKN	124.2	0.9637	40.22	624.3	0.9748	2.16
MT	120.5	0.9645	39.8	618.2	0.9744	2.17
HM	78	0.935	46.2	588.4	0.9712	2.16
Sigmoidal						
CR	120.7	0.9638	40.02	1014.2	0.9973	0.305
MKN	121.4	0.9641	39.76	1014.2	0.9974	0.301
MT	118.6	0.9637	50.1	100.2	0.9978	0.31
HM	50.2	0.9335	60.9	989.7	0.9959	0.406

deamination reaction the kinetic parameters decrease with increase in heating rate or sample mass (Tables 8, 9). The mechanism of these reversible reactions remains unchanged with the change in sample mass and heating rate. Where as the kinetic parameter obtained from the mechanism invoking equation for the decomposition reaction is not affected by either sample mass or heating rate.

Regular variations of the kinetic parameters obtained from mechanistic equation were subjected to statistical analysis as in the case of non-mechanistic equations. Equations corresponding to exponential decay of order 1, 2, 3, exponential growth and sigmoidal relations were tried for curve fitting. The variation of kinetic parameters with heating rate for the dehydration and deamination reaction can be represented as exponential decay of order two while the variation of kinetic parameters with sample mass for the dehydration and deamination reaction can be represented as sigmoidal curve.

Exponential decay of order 2 can be represented as

$$E = 14.1 + 519.8e^{(-\varphi/0.49)} + 112.8e^{(-\varphi/82.9)}$$

$$\log A = -1.4 + 71.2e^{(-\varphi/19.7)} + 0.56e^{(-\varphi/117.9)}$$

$$E = -4.4 + 4.4e^{(-\varphi/1.3)} + 54.8e^{(-\varphi/10.2)}$$

$$\log A = 2.6 - 5.3e^{(-\varphi/11.2)} + 2.6e^{(-\varphi/1.8)}$$

Sigmoidal equations are

$$E = \frac{188.8}{1 + e^{(m-28.4)/10.4}} - 41.5$$

$$\log A = \frac{312.7}{1 + e^{(m-129.9)/142.6}} - 200.7$$

$$E = \frac{18.9}{1 + e^{(m-8.2)/2.6}} + 154$$

$$\log A = \frac{2.2}{1 + e^{(m-9.5)/2.9}} + 14$$

**Table 7** The fisher constant, chi square ( $\chi^2$ ) and coefficient of determination ( $R^2$ ) for the various fits between heating rate ( $\phi$ )/sample mass ( $m$ ) with log  $A$  for the deamination reaction using four non-mechanistic equations

Fits	Log $A$					
	Heating rate			Sample mass		
	$F$	$R^2$	$\chi^2$	$F$	$R^2$	$\chi^2$
<b>Exponential decay I</b>						
CR	92.7	0.9766	0.2054	635.1	0.9684	0.039
MKN	92.9	0.9766	0.2054	635.3	0.9723	0.025
MT	90.7	0.9763	0.2031	628.8	0.9732	0.031
HM	73.1	0.9747	0.2028	592.4	0.9531	0.045
<b>Exponential decay II</b>						
CR	141.8	0.9833	0.2439	635.1	0.9684	0.078
MKN	141.9	0.9833	0.2431	635.3	0.9723	0.051
MT	129.1	0.9834	0.2434	628.8	0.9732	0.045
HM	73.1	0.9747	0.3379	592.4	0.9531	0.091
<b>Exponential decay III</b>						
CR	137.9	0.9823	0.7755	635.1	0.9684	–
MKN	136.5	0.9823	0.7755	635.3	0.9723	–
MT	132.1	0.9822	0.7745	628.8	0.9732	–
HM	73.1	0.9747	1.01	592.4	0.9531	–
<b>Exponential growth</b>						
CR	92.9	0.9766	0.2054	635.1	0.9684	0.0395
MKN	92.9	0.9766	0.2054	635.3	0.9723	0.0252
MT	89.9	0.9765	0.21	628.8	0.9732	0.0231
HM	73.1	0.9727	0.2028	592.4	0.9531	0.0453
<b>Sigmoidal</b>						
CR	90.6	0.9764	0.2589	978.2	0.9946	0.009
MKN	90.1	0.9764	0.2589	978.2	0.9959	0.005
MT	89.7	0.9764	0.261	967.5	0.9959	0.0034
HM	73.1	0.974	0.1525	911.2	0.9896	0.0134

**Table 8** Kinetic parameters for reversible reactions at various heating rates obtained from mechanistic equations

Heating rate, $\phi/^\circ\text{C min}^{-1}$	Dehydration (Mampel equation)		Deamination (phase boundary equation)	
	$E/\text{kJ mol}^{-1}$	$A/\text{s}^{-1}$	$E/\text{kJ mol}^{-1}$	$A/\text{s}^{-1}$
1	195.7	$1.5 \times 10^{30}$	192.7	$5.3 \times 10^{18}$
2	133.8	$3.9 \times 10^{20}$	189.9	$1.9 \times 10^{18}$
5	116.9	$9.9 \times 10^{17}$	184.8	$8.5 \times 10^{17}$
10	115.7	$5.6 \times 10^{17}$	166.7	$1.4 \times 10^{16}$
15	109.6	$5.6 \times 10^{16}$	145.7	$1.3 \times 10^{14}$
20	105.8	$1.7 \times 10^{16}$	147.2	$1.6 \times 10^{14}$
50	72.4	$2.7 \times 10^{11}$	134.3	$1.2 \times 10^{13}$
90	53.3	$8 \times 10^8$	125.4	$1.2 \times 10^{12}$

**Table 9** Kinetic parameters obtained for the reversible reactions at various sample masses from mechanistic equations

Sample mass/mg	Dehydration (Mampel equation)		Deamination (phase boundary equation)	
	$E/\text{kJ mol}^{-1}$	$A/\text{s}^{-1}$	$E/\text{kJ mol}^{-1}$	$A/\text{s}^{-1}$
2.45	135.8	$9 \times 10^{22}$	189.9	$7.6 \times 10^{18}$
5.14	134.2	$2.2 \times 10^{21}$	163.3	$7.7 \times 10^{15}$
6.96	119	$8.3 \times 10^{17}$	158.6	$1.9 \times 10^{15}$
10	115.7	$5.6 \times 10^{17}$	166.7	$1.4 \times 10^{16}$
12.09	134.9	$1.9 \times 10^{20}$	147.8	$1.7 \times 10^{14}$
15.55	104.8	$9.6 \times 10^{15}$	164.2	$4.3 \times 10^{15}$
20.09	75.4	$2.1 \times 10^{11}$	148	$9.6 \times 10^{13}$

**Table 10** The curve fit constants for the reversible reactions (exponential decay second order equation) using the mechanistic equations

	$y_0$	$A_1$	$A_2$	$t_1$	$t_2$	$F$	$R^2$	$\chi^2$
<b>Dehydration (Mampel equation)</b>								
Correlation with $E$	14.1	519.8	112.8	0.49	82.9	656	0.9969	12.8
Correlation with log $A$	–1.4	71.2	0.56	19.7	117.9	621	0.9959	0.4
<b>Deamination (phase boundary equation)</b>								
Correlation with $E$	–4.4	4.4	54.8	1.3	10.2	215.2	0.9735	0.1241
Correlation with log $A$	2.6	–5.3	2.6	11.2	1.8	231	0.9766	0.1342

The curve fit constants for the dehydration and deamination reaction using mechanism based equations (Mampel and phase boundary equations) are given in Tables 10 and 11.

Dependence of procedural factors

The investigation reveals that independent of reversibility and type of the reaction, the kinetic parameters have a

**Table 11** The curve fit constants for the reversible reactions (sigmoidal) equation using the mechanistic equations

	$A_1$	$A_2$	$x_0$	$dx$	$F$	$R^2$	$\chi^2$
Dehydration (Mampel equation)							
Correlation with $E$	147.3	-41.5	28.4	10.4	650.3	0.9873	2.12
Correlation with $\log A$	112	-200.7	129.9	142.6	567.3	0.9776	12.1
Deamination (Phase boundary equation)							
Correlation with $E$	172.9	154	8.2	2.6	670	0.9987	0.2921
Correlation with $\log A$	16.2	14	9.5	2.9	643.2	0.9921	0.2112

dependence on the procedural variables. Mathew et al. [6] have evolved mathematical correlation between activation parameters and procedural factors and its dependence on reaction type. It is found that for both the dehydration and deamination reactions, quantitative correlation can be evolved between a particular procedural variable ( $\varphi$  or  $m$ ) and kinetic parameters.

## Conclusions

The effect of kinetic parameters on procedural parameters like heating rate and sample mass during the thermal decomposition have been studied using tris(ethylenediamine)nickel(II) oxalate dihydrate as a model complex. The complex yields clear cut thermal decomposition pattern consists of reversible dehydration, reversible deamination and irreversible decomposition. For the dehydration and deamination reaction the kinetic parameters decrease with increase in sample mass or heating rate while for the decomposition reaction the variations are irregular. The mechanism of these reversible reactions remains unchanged with variations in procedural factors (heating rate and sample mass). Quantitative correlations between the kinetic parameters and procedural variables, independent of the type of the reaction have been evolved. The dependence of kinetic parameters on heating rate can be best described as a second order exponential decay for the deamination and dehydration reaction. While the dependence of kinetic parameters on sample mass can be expressed as a sigmoidal equation for the deamination and dehydration reaction. No quantitative correlation is possible for decomposition reaction.

## References

- Krishnan K, Ninan KN, Madhusudanan PM. Effect of simultaneous variation of sample mass and heating rate on the mechanism of dehydration of zinc oxalate dihydrate. *Thermochim Acta*. 1985;89:295–305.
- Ubaladini A, Artini C, Costa GA, Carnasciali MM, Masini R. Synthesis and thermal decomposition of mixed Gd–Nd oxalates. *J Therm Anal Calorim*. 2008;91:797–803.
- Su TT, Zhai YC, Jiang H, Gong H. Studies on the thermal decomposition kinetics and mechanism of ammonium niobium oxalate. *J Therm Anal Calorim*. 2009;98:449–455.
- Thomas P, Dwarakanath K, Varma KBR, Kutty TRN. Synthesis of nanoparticles of the giant dielectric material,  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  from a precursor route. *J Therm Anal Calorim*. 2009;95:267–72.
- Rejitha KS, Mathew S. Thermal deamination kinetics of tris(ethylenediamine)nickel(II) sulphate in the solid-state. *J Therm Anal Calorim*. 2008;93:213–7.
- Mathew S, Nair CGR, Ninan KN. Quantitative correlations of activation parameters and procedural factors-dependence on reaction type. *Thermochim Acta*. 1991;184:269–94.
- Shishkin YL. The effect of sample mass and heating rate on DSC results when studying the fractional composition and oxidative stability of lube base oils. *Thermochim Acta*. 2006;444:26–34.
- Bigda R, Mianowsky A. Influence of heating rate on kinetic quantities of solid phase thermal decomposition. *J Therm Anal Calorim*. 2006;84:453–65.
- Olszak-Humienik M, Mozejko J. Eyring parameters of dehydration processes. *Thermochim Acta*. 2003;405:171–81.
- Liu Y, Zhao J, Zhang H, Zhu Y, Wang Z. Thermal decomposition of basic zinc carbonate in nitrogen atmosphere. *Thermochim Acta*. 2004;414:121–3.
- Samtani M, Dollimore D, Alexander KS. Comparison of dolomite decomposition kinetics with related carbonates and the effect of procedural variables on its kinetic parameters. *Thermochim Acta*. 2002;392–393:135–45.
- Haschke JM, Wendlandt WW. The thermal decomposition of metal ethylenediamine complexes. *Anal Chim Acta*. 1965;32:386–93.
- Vogel AG. Text book of quantitative inorganic analysis. 4th ed. London: Longman; 1978.
- Maciejewski M. Somewhere between fiction and reality—the usefulness of kinetic data of solid-state reactions. *J Therm Anal*. 1992;38:51–70.
- Wendlandt WW. Thermal methods of analysis. 3rd ed. New York: Wiley-Interscience; 1986.
- Coats AW, Redfern JP. Kinetic parameters from thermogravimetric data. *Nature*. 1964;201:68–9.
- MacCallum JR, Tanner J. The kinetics of thermogravimetry. *Eur Polym J*. 1970;6:1033–9.
- Horowitz HH, Metzger G. A new analysis of thermo gravimetric traces. *Anal Chem*. 1963;35:1464–8.
- Madhusudanan PM, Krishnan K, Ninan KN. New approximation for the  $p(x)$  function in the evaluation of non-isothermal kinetic data. *Thermochim Acta*. 1986;97:189–201.
- Spiegel MR. Theory and problems of statistics in SI units. 1st ed. New York: McGraw-Hill; 1972.
- Freud JE. Mathematical statistics. 5th ed. New Jersey: Prentice Hall Inc; 1992.
- Satava V. Mechanism and kinetics from non-isothermal TG traces. *Thermochim Acta*. 1971;2:423–8.