Thermochimica Acta, 184 (1991) 269–294
Elsevier Science Publishers B.V., Amsterdam

Quantitative correlations of activation parameters and procedural factors—dependence on reaction type

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(Received 7 November 1990)

Abstract

The dependence of the correlation of kinetic parameters (energy of activation and pre-exponential factor) and procedural factors (sample mass and heating rate) on the type of reaction in non-isothermal thermogravimetry is established here for the first time. The effect of heating rate and sample mass on the stages of decomposition of diaquabis(ethylenediamine)copper(II) oxalate

$$[Cu(en)_2(H_2O)_2]C_2O_4 \xrightarrow[-2H_2O]{} [Cu(en)_2]C_2O_4 \xrightarrow[-en]{} Cu(en)C_2O_4 \xrightarrow[-CO_2\ -CO]{-en} CuO$$

has been studied non-isothermally. The kinetic parameters, calculated using both the mechanistic and non-mechanistic equations, show a systematic decrease with increase in either heating rate or sample mass for the dehydration and deamination reactions. For the decomposition reaction, the kinetic parameters are not appreciably affected by procedural factors. Mathematical correlations of high reliability are established between kinetic parameters and heating rate/sample mass using both the mechanistic and non-mechanistic equations for the dehydration and deamination reactions. Thus it has been found that the type of reaction is decisive in the correlation of kinetic parameters with procedural factors. The quantification follows a rectangular hyperbolic equation for the dehydration and a parabolic one for the deamination. No quantitative correlations were possible for the final decomposition of the oxalate to oxide.

For all three reaction types, the rate-controlling process is random nucleation with the formation of one nucleus on each particle. It is observed that the mechanism of these reactions is not affected by the variations in sample mass and heating rate, or by the reaction type.

INTRODUCTION

Results from TG curves are known to be affected by a number of experimental variables such as heating rate, sample mass, particle size, packing, atmosphere etc. [1–3]. Although the dependence of E and A on the sample mass and heating rate is well known, only comparatively recently

0040-6031/91/$03.50

have attempts been made to study the dependence quantitatively [4–12]. However, no effort seems to have been made so far to explore the possible relation between the type of reaction and the correlation of kinetic parameters with procedural factors.

In this paper we report the results of our attempts to evolve the mathematical correlations between the procedural factors and kinetic parameters for three reaction types, namely the successive dehydration, deamination and final decomposition reactions of diaquabis(ethylenediamine)copper(II) oxalate. The evaluation of kinetic parameters using mechanistic and non-mechanistic equations from non-isothermal TG curves is also discussed.

In view of the presence of ethylenediamine (en), one of the simplest chelating amines, and also the incorporation of two water molecules in the coordination sphere, $[Cu(en)_2(H_2O)_2]C_2O_4$ has been chosen as a model complex for studying the dependence of kinetic parameters on procedural factors for both the dehydration and deamination reactions. The complex also gives 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

Preparation of the complex

The $[Cu(en)_2(H_2O)_2]C_2O_4$ was prepared according to the procedures described in the literature [13]. The violet complex was characterized by spectral and chemical methods. The average particle size, determined by a Fisher sub-sieve sizer, was 50 μm. The copper content in the complex was analysed gravimetrically. Elemental analyses were carried out using a Carlo Erba microelemental analyser.

Instruments

The TG–DTG experiments were carried out with a DuPont 2000 thermal analyser in conjunction with a 951 thermogravimetric analyser. The experiments were carried out in pure dry nitrogen, purged at a rate of 50 cm^3 min^{-1}. In order to study the effect of heating rate, the TG experiments were carried out at eight heating rates (1, 2, 5, 10, 15, 20, 50 and 100 °C min^{-1}); the sample mass was kept constant at 10 ± 0.1 mg in these experiments. To study the effect of sample mass, the heating rate was made constant (10 °C min^{-1}) and eight sets of sample masses were employed. The samples were loaded directly onto the platinum sample pan of the TGA on which the mass was recorded directly. The particle size of the samples was the same in all the experiments, and the sample loading was done in as uniform a manner as possible. X-ray powder diffractograms were recorded using a Philips 1710 diffractometer with a PW 1729 X-ray generator using Cu Kα radiation. Computational work was done with an IBM–PC/XT using a FORTRAN 77 program.

RESULTS AND DISCUSSION

Typical TG–DTG curves of $[Cu(en)_2(H_2O)_2]C_2O_4$ are given in Fig. 1. The first stage in the TG corresponds to the dehydration ($-2H_2O$). The second stage involves the deamination ($-$en) of the bis(ethylenediamine) complex to form the mono(ethylenediamine)copper(II) oxalate. The third stage comprises the decomposition of the mono(amine) complex to CuO. The intermediates and the residue have been identified by X-ray diffraction analysis.

The temperature of inception (T_i), DTG peak temperature (T_s) and the temperature of completion of reaction (T_f) for each stage with different sample masses and heating rates are tabulated in Table 1. For any given temperature interval, the extent of decomposition is greater at a slow heating rate than at a faster heating rate. As the heating rate increases the initial procedural decomposition temperature T_i exhibits a tendency to increase. Similarly, the temperature of completion of reaction, T_f, also increases with increasing heating rate and sample mass. It is also observed that the reaction interval ($T_f - T_i$) increases as the heating rate is increased for both the dehydration and deamination reactions. Concerning the effect of sample mass, it can be observed that T_i was virtually constant for the dehydration and deamination stages. This observation is consistent with the literature

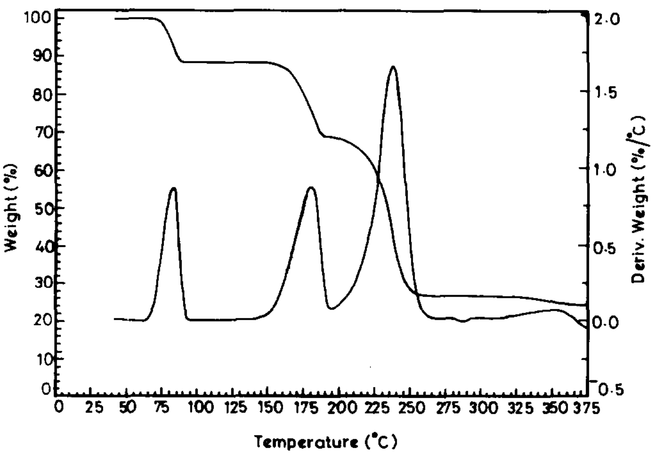

Fig. 1. TG–DTG curves of $[Cu(en)_2(H_2O)_2]C_2O_4$.

TABLE 1

Phenomenological data for the thermal decomposition of $[Cu(en)_2(H_2O)_2]C_2O_4$

Sample mass (mg)	T_i (°C)	T_f (°C)	T_s (°C)	Heating rate (°C min^{-1})	T_i (°C)	T_f (°C)	T_s (°C)
Dehydration							
1.076	85	105	96.3	1	70	90	82.3
2.487	65	102	91.2	2	80	100	90.6
4.885	70	107	99.2	5	75	104	95.2
7.436	70	115	101.4	10	94	126	99.0
10.00	70	105	99.0	15	80	132	113.8
12.494	73	123	107.4	20	90	143	118.5
15.206	86	128	112.4	50	96	183	134.7
20.743	78	130	113.2	100	100	205	152.4
Deamination							
1.076	170	197	191.2	1	155	190	179.6
2.487	170	202	193.2	2	159	194	185.6
4.885	177	210	202.9	5	166	203	194.2
7.436	175	215	204.5	10	169	212	190.0
10.00	160	205	190.0	15	183	232	217.5
12.494	170	219	206.1	20	175	230	214.8
15.206	173	221	209.8	50	183	240	225.3
20.743	170	224	211.5	100	205	290	249.3
Decomposition							
1.076	197	285	263.8	1	190	260	237.1
2.487	202	285	263.3	2	194	262	242.2
4.885	210	285	265.4	5	203	275	254.4
7.436	215	285	273.5	10	212	270	250.4
10.00	205	272	250.4	15	232	300	285.0
12.494	219	280	270.1	20	230	292	272.6
15.206	221	285	264.9	50	240	305	278.6
20.743	224	292	270.0	100	290	365	336.4

reports [14]. For all three stages of decomposition, T_f increases as the sample mass is increased. This is because once the decomposition reaction has begun, it generally does not take place uniformly on every particle throughout the entire mass of the sample [15]. Under such non-homogeneous conditions, it would be expected that the time required for complete decomposition of a powdered solid would increase with increased sample mass. Because the furnace heating rate is linear, there would be a resultant increase in the observed value of T_f [16].

Kinetic parameters

The kinetic parameters were calculated using four integral equations, namely Coats–Redfern, MacCallum–Tanner, Horowitz–Metzger and

TABLE 2

Kinetic parameters using non-mechanistic equations for different sample masses for the dehydration reaction of $[Cu(en)_2(H_2O)_2]C_2O_4$ ($n = 1.32$) [a]

Sample mass (mg)	CR			MT			MKN			HM		
	E (kJ mol^{-1})	*A* (s^{-1})	*r*	*E* (kJ mol^{-1})	*A* (s^{-1})	*r*	*E* (kJ mol^{-1})	*A* (s^{-1})	*r*	*E* (kJ mol^{-1})	*A* (s^{-1})	*r*
1.076	292.7	9.83×10^{39}	0.9969	292.5	9.31×10^{39}	0.9970	292.6	9.80×10^{39}	0.9969	299.2	8.02×10^{40}	0.9961
2.487	169.5	2.17×10^{22}	0.9984	168.3	1.32×10^{22}	0.9985	169.5	2.22×10^{22}	0.9984	173.1	6.95×10^{22}	0.9986
4.885	151.7	6.60×10^{19}	0.9984	150.3	3.79×10^{19}	0.9985	151.7	6.79×10^{19}	0.9984	164.2	3.93×10^{21}	0.9984
7.436	128.6	1.31×10^{16}	0.9979	127.2	7.48×10^{15}	0.9981	128.7	1.36×10^{16}	0.9979	136.9	1.82×10^{17}	0.9985
10.00	142.7	5.21×10^{18}	0.9975	141.2	2.88×10^{18}	0.9977	142.7	5.37×10^{18}	0.9975	157.2	6.20×10^{20}	0.9980
12.494	118.0	3.12×10^{14}	0.9982	116.5	1.77×10^{14}	0.9984	118.1	3.24×10^{14}	0.9982	128.0	7.53×10^{15}	0.9980
15.206	130.2	2.54×10^{16}	0.9979	128.8	1.45×10^{16}	0.9981	130.3	2.63×10^{16}	0.9979	146.5	4.55×10^{18}	0.9972
20.743	105.8	4.36×10^{12}	0.9984	104.3	2.48×10^{12}	0.9986	106.0	4.54×10^{12}	0.9984	117.9	1.89×10^{14}	0.9978

[a] CR, Coats–Redfern; MT, MacCallum–Tanner; MKN, Madhusudanan–Krishnan–Ninan; HM, Horowitz–Metzger.

TABLE 3

Kinetic parameters using non-mechanistic equations for different sample masses for the deamination reaction of $[Cu(en)_2(H_2O)_2]C_2O_4$ ($n = 1.18$) [a]

Sample mass (mg)	CR			MT			MKN			HM		
	E (kJ mol^{-1})	A (s^{-1})	r	E (kJ mol^{-1})	A (s^{-1})	r	E (kJ mol^{-1})	A (s^{-1})	r	E (kJ mol^{-1})	A (s^{-1})	r
1.076	277.9	6.04×10^{29}	0.9979	279.0	8.42×10^{29}	0.9980	277.9	6.11×10^{29}	0.9979	292.0	2.38×10^{31}	0.9974
2.487	251.5	4.97×10^{26}	0.9984	252.5	6.33×10^{26}	0.9985	251.6	5.06×10^{26}	0.9984	265.2	1.73×10^{28}	0.9985
4.885	235.8	2.54×10^{24}	0.9979	236.8	3.14×10^{24}	0.9980	235.8	2.59×10^{24}	0.9979	252.1	1.62×10^{26}	0.9982
7.436	216.1	1.19×10^{22}	0.9989	217.0	1.39×10^{22}	0.9990	216.2	1.22×10^{22}	0.9989	231.3	5.64×10^{23}	0.9989
10.00	204.3	2.75×10^{21}	0.9968	204.9	2.88×10^{21}	0.9971	204.5	2.82×10^{21}	0.9968	220.1	1.68×10^{23}	0.9966
12.494	194.8	4.30×10^{19}	0.9987	195.5	4.66×10^{19}	0.9988	194.9	4.42×10^{19}	0.9987	210.7	2.41×10^{21}	0.9986
15.206	194.3	2.69×10^{19}	0.9986	195.1	2.95×10^{19}	0.9987	194.4	2.77×10^{19}	0.9986	210.9	1.72×10^{21}	0.9986
20.743	185.3	2.44×10^{18}	0.9983	186.0	2.61×10^{18}	0.9984	185.4	2.51×10^{18}	0.9983	202.0	1.64×10^{20}	0.9984

[a] CR, Coats–Redfern; MT, MacCallum–Tanner; MKN, Madhusudanan–Krishnan–Ninan; HM, Horowitz–Metzger.

TABLE 4

Kinetic parameters using non-mechanistic equations for different sample masses for the decomposition reaction of $[Cu(en)_2(H_2O)_2]C_2O_4$ ($n = 1.05$) [a]

Sample mass (mg)	CR			MT			MKN			HM		
	E (kJ mol^{-1})	A (s^{-1})	r	E (kJ mol^{-1})	A (s^{-1})	r	E (kJ mol^{-1})	A (s^{-1})	r	E (kJ mol^{-1})	A (s^{-1})	r
1.076	234.8	1.55×10^{21}	0.9995	236.7	2.43×10^{21}	0.9995	234.9	1.59×10^{21}	0.9995	253.9	1.19×10^{23}	0.9999
2.487	228.6	2.78×10^{20}	0.9992	230.6	4.32×10^{20}	0.9993	228.7	2.86×10^{20}	0.9992	243.1	7.28×10^{21}	0.9984
4.885	244.6	8.49×10^{21}	1.0000	246.8	1.41×10^{22}	1.0000	244.7	8.70×10^{21}	1.0000	259.8	2.53×10^{23}	0.9997
7.436	226.0	9.23×10^{19}	0.9970	228.0	1.44×10^{20}	0.9972	226.1	9.49×10^{19}	0.9970	246.4	8.69×10^{21}	0.9979
10.00	212.9	3.05×10^{19}	0.9994	214.4	4.15×10^{19}	0.9995	213.0	3.14×10^{19}	0.9994	232.9	3.11×10^{21}	0.9994
12.494	234.7	9.11×10^{20}	0.9972	236.7	1.45×10^{21}	0.9974	234.8	9.35×10^{20}	0.9972	255.0	8.81×10^{22}	0.9979
15.206	258.1	1.91×10^{23}	0.9974	260.3	3.36×10^{23}	0.9975	258.1	1.95×10^{23}	0.9974	270.7	3.22×10^{24}	0.9962
20.743	267.8	1.43×10^{24}	0.9954	270.1	2.62×10^{24}	0.9957	267.8	1.46×10^{24}	0.9954	286.6	9.71×10^{25}	0.9970

[a] CR, Coats–Redfern; MT, MacCallum–Tanner; MKN, Madhusudanan–Krishnan–Ninan; HM, Horowitz–Metzger.

TABLE 5

Kinetic parameters using non-mechanistic equations for different heating rates for the dehydration reaction of $[Cu(en)_2(H_2O)_2]C_2O_4$ ($n = 1.32$) [a]

Heating rate (°C min^{-1})	CR			MT			MKN			HM		
	E (kJ mol^{-1})	A (s^{-1})	r	E (kJ mol^{-1})	A (s^{-1})	r	E (kJ mol^{-1})	A (s^{-1})	r	E (kJ mol^{-1})	A (s^{-1})	r
1	267.8	1.17×10^{37}	0.9978	267.1	9.28×10^{36}	0.9979	267.7	1.17×10^{37}	0.9978	277.1	2.81×10^{38}	0.9972
2	260.9	2.91×10^{35}	0.9985	260.3	2.35×10^{35}	0.9986	260.9	2.92×10^{35}	0.9985	269.1	4.40×10^{36}	0.9981
5	183.1	1.73×10^{24}	0.9975	181.9	1.08×10^{24}	0.9977	183.1	1.77×10^{24}	0.9975	193.6	5.41×10^{25}	0.9971
10	142.7	5.21×10^{18}	0.9975	141.2	2.88×10^{18}	0.9977	142.7	5.37×10^{18}	0.9975	157.2	6.20×10^{20}	0.9980
15	118.6	1.56×10^{14}	0.9984	117.3	9.49×10^{13}	0.9985	118.7	1.62×10^{14}	0.9984	125.1	1.15×10^{15}	0.9982
20	115.3	1.96×10^{14}	0.9982	113.8	1.13×10^{14}	0.9984	115.4	2.04×10^{14}	0.9983	129.9	1.87×10^{16}	0.9976
50	79.9	7.59×10^{8}	0.9965	78.7	5.08×10^{8}	0.9971	80.1	7.91×10^{8}	0.9965	87.1	6.00×10^{9}	0.9941
100	65.1	7.20×10^{6}	0.9971	64.0	5.37×10^{6}	0.9977	65.3	7.46×10^{6}	0.9972	73.9	8.25×10^{7}	0.9946

[a] CR, Coats–Redfern; MT, MacCallum–Tanner; MKN, Madhusudanan–Krishnan–Ninan; HM, Horowitz–Metzger.

TABLE 6

Kinetic parameters using non-mechanistic equations for different heating rates for the deamination reaction of $[Cu(en)_2(H_2O)_2]C_2O_4$ ($n = 1.18$) [a]

Heating rate (°C min^{-1})	CR			MT			MKN			HM		
	E (kJ mol^{-1})	A (s^{-1})	r	E (kJ mol^{-1})	A (s^{-1})	r	E (kJ mol^{-1})	A (s^{-1})	r	E (kJ mol^{-1})	A (s^{-1})	r
1	246.2	8.06×10^{25}	0.9987	246.9	9.45×10^{25}	0.9988	246.2	8.19×10^{25}	0.9987	260.1	3.29×10^{27}	0.9983
2	237.4	6.67×10^{24}	0.9985	238.1	7.78×10^{24}	0.9986	237.4	6.80×10^{24}	0.9985	251.1	2.49×10^{26}	0.9984
5	224.1	1.63×10^{23}	0.9982	224.9	1.88×10^{23}	0.9983	224.1	1.67×10^{23}	0.9982	238.2	6.38×10^{24}	0.9984
10	204.3	2.75×10^{21}	0.9968	204.9	2.88×10^{21}	0.9971	204.5	2.82×10^{21}	0.9968	220.1	1.68×10^{23}	0.9966
15	195.5	1.21×10^{19}	0.9986	196.5	1.43×10^{19}	0.9987	195.6	1.25×10^{19}	0.9987	205.2	1.27×10^{20}	0.9989
20	193.5	4.20×10^{19}	0.9987	194.2	4.61×10^{19}	0.9988	193.6	4.32×10^{19}	0.9987	213.5	6.24×10^{21}	0.9986
50	180.8	5.88×10^{17}	0.9940	181.8	6.82×10^{17}	0.9946	180.9	6.08×10^{17}	0.9940	189.8	5.15×10^{18}	0.9924
100	158.2	7.95×10^{14}	0.9904	159.5	9.48×10^{14}	0.9915	158.4	8.26×10^{14}	0.9905	168.0	7.49×10^{15}	0.9881

[a] CR, Coats–Redfern; MT, MacCallum–Tanner; MKN, Madhusudanan–Krishnan–Ninan; HM, Horowitz–Metzger.

TABLE 7

Kinetic parameters using non-mechanistic equations for different heating rates for the decomposition reaction of $[Cu(en)_2(H_2O)_2]C_2O_4$ ($n = 1.05$) [a]

Heating rate (°C min^{-1})	CR			MT			MKN			HM		
	E (kJ mol^{-1})	A (s^{-1})	r	E (kJ mol^{-1})	A (s^{-1})	r	E (kJ mol^{-1})	A (s^{-1})	r	E (kJ mol^{-1})	A (s^{-1})	r
1	247.1	3.28×10^{22}	0.9997	248.8	4.97×10^{22}	0.9997	247.2	3.36×10^{22}	0.9997	259.7	6.47×10^{23}	0.9992
2	238.6	5.41×10^{21}	0.9999	240.3	8.06×10^{21}	0.9999	238.7	5.54×10^{21}	0.9999	252.2	1.32×10^{23}	0.9996
5	250.3	4.87×10^{22}	0.9988	252.3	7.98×10^{22}	0.9989	250.3	4.99×10^{22}	0.9988	263.3	9.49×10^{23}	0.9978
10	212.9	3.05×10^{19}	0.9994	214.4	4.15×10^{19}	0.9995	213.0	3.14×10^{19}	0.9994	232.9	3.11×10^{21}	0.9994
15	238.3	6.71×10^{20}	0.9987	240.6	1.15×10^{21}	0.9988	238.4	6.89×10^{20}	0.9987	257.5	4.46×10^{22}	0.9985
20	260.6	3.20×10^{23}	0.9990	263.0	5.83×10^{23}	0.9991	260.7	3.27×10^{23}	0.9990	274.2	6.40×10^{24}	0.9982
50	206.3	2.09×10^{18}	0.9999	208.4	3.17×10^{18}	0.9999	206.5	2.15×10^{18}	0.9999	220.9	5.05×10^{19}	0.9998
100	215.9	3.41×10^{17}	0.9965	219.0	6.63×10^{17}	0.9968	216.0	3.53×10^{17}	0.9965	229.0	4.57×10^{18}	0.9948

[a] CR, Coats–Redfern; MT, MacCallum–Tanner; MKN, Madhusudanan–Krishnan–Ninan; HM, Horowitz–Metzger.

Madhusudanan–Krishnan–Ninan. The order parameter n was evaluated using the Coats–Redfern equation by an iteration method as described in our earlier publications [17,18]. The order parameters for each stage were chosen by taking the average of all the 16 values obtained for both the heating rate and sample mass variations. With the values of n thus obtained, the kinetic parameters were computed using the four non-mechanistic equations for the dehydration, deamination and decomposition reactions. The activation energy (E), the pre-exponential factor (A) and the correlation coefficients (r) for each stage evaluated from the TG curves for different sample masses and heating rates are given in Tables 2–7.

From Tables 2–7 it can be seen that both E and A calculated using all four non-mechanistic equations for the dehydration and deamination reactions are dependent on heating rate and sample mass—they decrease with increase in either heating rate or sample mass. Thus, so far as the kinetic parameters are concerned, an increase in heating rate for constant sample mass has the same qualitative effect as an increase in sample mass for constant heating rate. However, from Tables 4 and 7, it can be noted that the kinetic parameters are not appreciably affected by either heating rate or sample mass for the decomposition of $Cu(en)C_2O_4$ to CuO. The minor variations are rather irregular here.

The regular trend in these activation parameters relative to changes in heating rate and sample mass for the dehydration and deamination processes makes the data amenable to statistical analysis. Standard types of curve fits such as linear, rectangular hyperbolic, parabolic and exponential, were tried using various functions of these factors, and the best-fit curve was chosen. It was found that for all four kinetic equations the E or $\log A$ vs. sample mass or heating rate relationships for the dehydration stage could be best represented as a rectangular hyperbola of the type

$$y = a + b/x$$

that is

$$E = a + b/m \qquad \log A = a + b/m$$

and

$$E = a + b/\phi \qquad \log A = a + b/\phi$$

where a and b are empirical constants, different for the four non-mechanistic equations, and m and ϕ are sample mass and heating rate respectively. Similarly for the deamination stage, the relationships between the kinetic parameters E or $\log A$ and sample mass or heating rate are best represented by a second-degree equation (parabola), of the type

$$y = a + bx + cx^2$$

that is

$$E = a + bm + cm^2 \qquad \log A = a + bm + cm^2$$

TABLE 8

Curve-fit constants for the dehydration reaction using non-mechanistic equations [a]

	Sample mass				Heating rate			
	a	b	F	R^2	a	b	F	R^2
Correlation with E								
CR	107.25	194.22	173.10	0.9665	106.07	197.80	22.06	0.7862
MT	105.61	195.66	174.30	0.9667	104.75	198.56	22.17	0.7870
MKN	107.37	194.00	173.20	0.9665	106.21	197.55	22.06	0.7862
HM	119.89	185.38	96.80	0.9416	116.33	196.58	20.91	0.7770
Correlation with log A								
CR	13.13	28.23	147.02	0.9608	12.79	29.46	22.96	0.7929
MT	12.85	28.48	149.02	0.9613	12.59	29.58	23.26	0.7949
MKN	13.15	28.21	147.05	0.9608	12.81	29.44	22.96	0.7928
HM	14.88	27.02	86.99	0.9355	14.16	29.46	21.53	0.7820

[a] CR, Coats–Redfern; MT, MacCallum–Tanner; MKN, Madhusudanan–Krishnan–Ninan; HM, Horowitz–Metzger.

and

$$E = a + b\phi + c\phi^2 \qquad \log A = a + b\phi + c\phi^2$$

where a, b and c are empirical constants for different equations. The reliability of the curve fitting using the data obtained from four non-mechanistic equations was evaluated by the F-test [19]. The values of a and b along with the corresponding Fisher constant F and coefficient of determination R^2 for the dehydration stage, and the values of a, b and c

TABLE 9

Curve-fit constants for the deamination reaction using non-mechanistic equations [a]

	Sample mass					Heating rate				
	a	b	c	F	R^2	a	b	c	F	R^2
Correlation with E										
CR	282.37	−10.75	0.2991	131.01	0.9813	234.52	−1.96	0.0123	17.53	0.8752
MT	283.58	−10.82	0.3015	130.60	0.9812	235.22	−1.96	0.0122	17.23	0.8733
MKN	282.35	−10.73	0.2985	131.13	0.9813	234.58	−1.96	0.0122	17.57	0.8755
HM	296.19	−10.48	0.2929	114.56	0.9786	249.31	−2.04	0.0125	21.57	0.8961
Correlation with log A										
CR	30.26	−1.28	0.0349	116.13	0.9789	24.55	−0.2452	0.0015	18.22	0.8793
MT	30.41	−1.29	0.0354	117.88	0.9792	24.60	−0.2456	0.0015	18.04	0.8783
MKN	30.26	−1.28	0.0349	116.14	0.9789	24.55	−0.2450	0.0015	18.21	0.8793
HM	31.82	−1.26	0.0342	106.29	0.9770	26.24	−0.2574	0.0016	20.09	0.8894

[a] CR, Coats–Redfern; MT, MacCallum–Tanner; MKN, Madhusudanan–Krishnan–Ninan; HM, Horowitz–Metzger.

TABLE 10

The Fisher constant (F) and the coefficient of determination (R^2) for the dehydration reaction of $[Cu(en)_2(H_2O)_2]C_2O_4$ [a]

Fits		E			
		Sample mass		Heating rate	
		F	R^2	F	R^2
Linear	CR	6.60	0.5238	7.27	0.5479
	MT	6.57	0.5230	7.21	0.5457
	MKN	6.60	0.5238	7.27	0.5478
	HM	5.78	0.4907	7.70	0.5620
Hyperbola	CR	173.10	0.9665	22.06	0.7868
	MT	174.32	0.9667	22.17	0.7870
	MKN	173.17	0.9665	22.06	0.7862
	HM	96.77	0.9416	20.90	0.7770
Parabola	CR	6.01	0.7066	10.96	0.8144
	MT	6.01	0.7063	10.86	0.8129
	MKN	6.01	0.7066	10.96	0.8143
	HM	4.87	0.6611	12.04	0.8281
Exponential	CR	10.64	0.6396	16.03	0.7277
	MT	10.68	0.6403	15.99	0.7272
	MKN	10.63	0.6394	15.99	0.7272
	HM	8.42	0.5841	15.91	0.7263

[a] CR, Coats–Redfern; MT, MacCallum–Tanner; MKN, Madhusudanan–Krishnan–Ninan; HM, Horowitz–Metzger.

along with the Fisher constant and R^2 for the deamination stage are given in Tables 8 and 9. The critical values of the Fisher constants for the hyperbolic fit and parabolic fit, at 99% confidence levels, are 13.74 and 13.27 respectively for the dehydration and deamination processes. It was found that the F-statistic is significant at 99% confidence level for more than one fit for the dehydration and deamination stages. Therefore, to choose the best fit among them, the coefficient of determination R^2 was used [20]. The R^2 is a measure of association between a dependent variable and an optimal combination of two or more independent variables. It is the proportion of the dependent variables variance shared with the optimally weighted independent variables. The larger the R^2 the better the fit. The Fisher constant F and the coefficient of determination R^2 for the different fits for the dehydration and deamination stages are given in Tables 10–13. From Tables 10–13 it can be seen that R^2 has maximum values for a hyperbolic fit for the dehydration reaction and has maximum values for a parabolic fit for the deamination reaction. It is also observed that the confidence level of all the correlations is above 99%, indicating that the variables E and log A computed from the four non-mechanistic equations are best represented by

TABLE 11

The Fisher constant (F) and the coefficient of determination (R^2) for the dehydration reaction of $[Cu(en)_2(H_2O)_2]C_2O_4$ [a]

Fits		log A			
		Sample mass		Heating rate	
		F	R^2	F	R^2
Linear	CR	7.01	0.5390	7.18	0.5450
	MT	6.96	0.5372	7.06	0.5407
	MKN	7.01	0.5390	7.19	0.5452
	HM	6.20	0.5085	7.64	0.5603
Hyperbola	CR	147.02	0.9608	22.96	0.7929
	MT	149.02	0.9613	23.25	0.7949
	MKN	147.04	0.9608	22.95	0.7928
	HM	86.99	0.9355	21.52	0.7820
Parabola	CR	6.16	0.7114	11.07	0.8159
	MT	6.14	0.7107	10.88	0.8132
	MKN	6.16	0.7114	11.08	0.8160
	HM	5.02	0.6678	12.13	0.8292
Exponential	CR	12.14	0.6693	18.38	0.7539
	MT	12.16	0.6696	18.11	0.7512
	MKN	12.13	0.6692	18.37	0.7538
	HM	9.56	0.6144	18.05	0.7506

[a] CR, Coats–Redfern; MT, MacCallum–Tanner; MKN, Madhusudanan–Krishnan–Ninan; HM, Horowitz–Metzger.

a rectangular hyperbola for the dehydration stage and by a parabola for the deamination stage. By comparing the values for the Fisher constants and R^2 given in Tables 8 and 9, it can be inferred that the kinetic parameters are better correlated to sample mass than to heating rate.

Mechanism of the reaction

Similar quantitative correlations between the kinetic parameters and procedural factors have also been obtained using mechanisms invoking kinetic equations. The TG data for the different heating rates and sample masses were analysed using nine mechanism-based equations [21] and the results are given in Tables 14–19. Tables 14 and 15 give the kinetic parameters for the dehydration of diaquabis(ethylenediamine)copper(II) oxalate (to give bis(ethylenediamine)copper(II) oxalate) for different heating rates and sample masses respectively. Tables 16 and 17 give the corresponding values for the deamination process. The kinetic parameters for the decomposition reactions for different heating rates and sample masses are shown in Tables 18 and 19, respectively.

TABLE 12

The Fisher constant (F) and the coefficient of determination (R^2) for the deamination reaction of $[Cu(en)_2(H_2O)_2]C_2O_4$ [a]

Fits		E			
		Sample mass		Heating rate	
		F	R^2	F	R^2
Linear	CR	32.14	0.8427	17.41	0.7437
	MT	31.96	0.8419	17.14	0.7408
	MKN	32.19	0.8429	17.43	0.7440
	HM	31.02	0.8380	20.51	0.7737
Hyperbola	CR	31.70	0.8409	12.92	0.6830
	MT	31.68	0.8408	13.07	0.6854
	MKN	31.69	0.8408	12.91	0.6823
	HM	31.54	0.8402	10.89	0.6449
Parabola	CR	131.01	0.9813	17.53	0.8752
	MT	130.59	0.9812	17.22	0.8733
	MKN	131.12	0.9813	17.57	0.8755
	HM	114.56	0.9786	21.57	0.8961
Exponential	CR	42.26	0.8757	24.13	0.8009
	MT	41.94	0.8748	23.62	0.7975
	MKN	42.33	0.8759	24.14	0.8010
	HM	39.34	0.8677	28.51	0.8261

[a] CR, Coats–Redfern; MT, MacCallum–Tanner; MKN, Madhusudanan–Krishnan–Ninan; HM, Horowitz–Metzger.

From these tables it can be seen that in almost all cases the correlation coefficients are very close to unity, indicating near-perfect fits. A choice of the probable mechanism from the best-fit curve thus becomes difficult. In such a situation, Satava [21] has chosen the function $g(\alpha)$ which yielded kinetic parameters in agreement with those obtained by the numerical method he proposed. In the present case a comparison with the values obtained by the Coats–Redfern method will be more appropriate as this method was also used here for solving the exponential integral. The kinetic parameters computed from the Coats–Redfern equation together with those from the mechanistic equation (Mampel equation) for the dehydration, deamination and decomposition reactions are shown in Tables 20, 21 and 22, respectively. It was observed that the closest agreement was obtained using the Mampel equation for all three stages of decomposition. From these tables it can be observed that all three stages of decomposition follow the mechanism of random nucleation with the formation of one nucleus on each particle. The kinetic parameters calculated from the mechanistic equation for the decomposition reaction are not affected appreciably by either heating rate or sample mass. For the dehydration and deamination reactions the

TABLE 13

The Fisher constant (F) and the coefficient of determination (R^2) for the deamination reaction of $[Cu(en)_2(H_2O)_2]C_2O_4$ [a]

Fits		log A			
		Sample mass		Heating rate	
		F	R^2	F	R^2
Linear	CR	34.51	0.8519	18.23	0.7524
	MT	34.33	0.8512	18.02	0.7502
	MKN	34.50	0.8519	18.23	0.7524
	HM	33.95	0.8498	20.23	0.7713
Hyperbola	CR	31.66	0.8407	11.51	0.6575
	MT	31.79	0.8412	11.66	0.6602
	MKN	31.66	0.8407	11.51	0.6574
	HM	31.57	0.8403	9.73	0.6185
Parabola	CR	116.13	0.9789	18.21	0.8793
	MT	117.88	0.9792	18.04	0.8783
	MKN	116.14	0.9789	18.21	0.8793
	HM	106.29	0.9770	20.09	0.8894
Exponential	CR	49.48	0.8919	27.13	0.8189
	MT	49.28	0.8915	26.76	0.8169
	MKN	49.45	0.8918	27.12	0.8188
	HM	46.70	0.8862	29.65	0.8317

[a] CR, Coats–Redfern; MT, MacCallum–Tanner; MKN, Madhusudanan–Krishnan–Ninan; HM, Horowitz–Metzger.

kinetic parameters show a systematic trend — they decrease with increase in either heating rate or sample mass. These findings are quite similar to the trends observed in the case of mechanisms not invoking kinetic equations.

As in the case of the non-mechanistic approach, a statistical analysis was carried out to establish correlations of kinetic parameters (for stages I and II) from the mechanism-based equation with heating rate and sample mass. It was found that the curves of E or log A vs. heating rate or sample mass could be best fitted to a rectangular hyperbola for the dehydration reaction as

$$E = 96.82 + 164.06/m \qquad \log A = 8.55 + 23.89/m$$
$$E = 93.62 + 174.81/\phi \qquad \log A = 7.99 + 25.91/\phi$$

For the deamination reaction, the fit followed a parabolic relation

$$E = 263.15 - 9.7435m + 0.2684\ m^2$$
$$\log A = 25.01 - 1.1656m + 0.0314\ m^2$$

and

$$E = 219.59 - 1.8751\phi + 0.0116\phi^2$$
$$\log A = 19.75 - 0.2304\phi + 0.0014\phi^2$$

TABLE 14

Kinetic parameters using nine mechanistic equations for different heating rates for dehydration of $[Cu(en)_2(H_2O)_2]C_2O_4$ (sample mass, 10 ± 0.1 mg)

Heating rate [c]		1	2	3	4	5	6	7	8	9
1	E [a]	344.4	380.5	428.8	396.2	238.2	116.2	75.4	199.5	211.4
	A [b]	6.60×10^{44}	9.88×10^{49}	4.64×10^{56}	5.40×10^{51}	3.80×10^{29}	2.26×10^{11}	1.58×10^{5}	2.40×10^{23}	1.05×10^{25}
	r	0.96393	0.97500	0.98646	0.97937	0.99385	0.99360	0.99308	0.98100	0.98613
2	E	307.4	344.8	398.1	362.0	226.4	110.1	71.4	182.9	196.0
	A	3.52×10^{38}	6.38×10^{43}	1.11×10^{51}	5.05×10^{45}	2.18×10^{27}	2.28×10^{10}	4.22×10^{4}	3.56×10^{20}	2.15×10^{22}
	r	0.95710	0.97066	0.98553	0.97637	0.99451	0.99397	0.99364	0.97870	0.98498
5	E	234.9	259.6	293.1	270.5	162.2	78.1	50.0	135.2	143.5
	A	1.17×10^{28}	2.84×10^{31}	6.18×10^{35}	2.66×10^{32}	1.33×10^{18}	7.63×10^{5}	5.33×10^{1}	5.93×10^{13}	6.90×10^{14}
	r	0.96569	0.97693	0.98833	0.98136	0.99493	0.99459	0.99390	0.98279	0.98783
10	E	189.3	209.0	234.2	217.3	127.8	60.9	38.6	107.9	114.1
	A	7.85×10^{21}	3.65×10^{24}	5.20×10^{27}	1.44×10^{25}	2.93×10^{13}	4.55×10^{3}	2.08×10^{0}	1.36×10^{10}	8.08×10^{10}
	r	0.98373	0.98986	0.99522	0.99204	0.99740	0.99718	0.99700	0.99269	0.99500
15	E	156.1	172.2	193.7	179.2	105.5	49.5	30.8	88.3	93.6
	A	4.67×10^{15}	4.82×10^{17}	1.25×10^{20}	1.08×10^{18}	2.06×10^{9}	4.02×10^{1}	9.30×10^{-2}	3.37×10^{6}	1.31×10^{7}
	r	0.97554	0.98470	0.99339	0.98817	0.99771	0.99730	0.99683	0.98906	0.99288
20	E	143.0	160.1	183.1	167.6	101.1	47.4	29.5	82.7	88.4
	A	3.58×10^{14}	5.71×10^{16}	2.89×10^{19}	1.58×10^{17}	1.66×10^{9}	4.17×10^{1}	1.05×10^{-1}	1.57×10^{6}	7.25×10^{6}
	r	0.96763	0.97894	0.98996	0.98324	0.99597	0.99521	0.99445	0.98424	0.98924
50	E	100.8	113.0	129.2	118.3	70.1	31.7	18.8	57.2	61.2
	A	1.03×10^{8}	2.69×10^{9}	1.10×10^{11}	3.30×10^{9}	3.13×10^{4}	2.32×10^{-1}	4.11×10^{-3}	2.27×10^{2}	5.63×10^{2}
	r	0.95774	0.97090	0.98401	0.97595	0.99154	0.98939	0.98646	0.97573	0.98210
100	E	85.4	95.2	107.9	99.3	57.5	25.2	14.5	47.5	50.5
	A	6.80×10^{5}	7.71×10^{6}	9.92×10^{7}	6.47×10^{6}	6.18×10^{2}	4.21×10^{-2}	1.70×10^{-3}	1.15×10^{1}	2.13×10^{1}
	r	0.96433	0.97610	0.98746	0.98049	0.99346	0.99123	0.98783	0.97979	0.98541

[a] E, kJ mol^{-1}. [b] A, s^{-1}. [c] °C min^{-1}.

TABLE 15

Kinetic parameters using nine mechanistic equations for different sample masses for dehydration of $[Cu(en)_2(H_2O)_2]C_2O_4$ (heating rate, 10 °C min^{-1})

Sample mass [c]		1	2	3	4	5	6	7	8	9
1.076	E [a]	342.9	383.7	443.1	402.7	252.8	123.3	80.2	203.8	218.5
	A [b]	2.73×10^{43}	1.18×10^{49}	1.13×10^{57}	1.57×10^{51}	1.56×10^{31}	4.51×10^{12}	2.51×10^{6}	5.42×10^{23}	5.07×10^{25}
	r	0.94347	0.95928	0.97773	0.96616	0.98982	0.98936	0.98885	0.96901	0.97716
2.487	E	217.6	240.6	271.7	250.7	150.2	72.0	46.0	125.1	132.8
	A	3.83×10^{25}	4.97×10^{28}	4.47×10^{32}	3.49×10^{29}	2.91×10^{16}	1.52×10^{5}	2.25×10^{1}	2.68×10^{12}	2.50×10^{13}
	r	0.97602	0.98517	0.99391	0.98866	0.99808	0.99788	0.99784	0.98991	0.99357
4.885	E	205.2	224.9	250.6	233.3	136.3	65.1	41.4	115.9	122.2
	A	7.88×10^{23}	3.48×10^{26}	5.28×10^{29}	1.39×10^{27}	3.27×10^{14}	1.56×10^{4}	4.78×10^{0}	1.39×10^{11}	8.31×10^{11}
	r	0.98003	0.98772	0.99470	0.99051	0.99805	0.99798	0.99755	0.99147	0.99436
7.436	E	169.7	186.8	209.8	194.3	114.5	54.2	34.0	96.1	101.8
	A	1.92×10^{18}	3.38×10^{20}	1.84×10^{23}	9.55×10^{20}	1.06×10^{11}	2.54×10^{2}	2.90×10^{-1}	9.49×10^{7}	4.44×10^{8}
	r	0.98082	0.98879	0.99595	0.99165	0.99890	0.99878	0.99855	0.99265	0.99565
10.00	E	189.3	209.0	234.2	217.3	127.8	60.9	38.6	107.9	114.1
	A	7.85×10^{21}	3.65×10^{24}	5.20×10^{27}	1.44×10^{25}	2.93×10^{13}	4.55×10^{3}	2.08×10^{0}	1.36×10^{10}	8.08×10^{10}
	r	0.98373	0.98986	0.99522	0.99204	0.99740	0.99718	0.99700	0.99269	0.99500
12.494	E	153.1	169.6	191.4	176.7	104.7	49.2	30.7	87.2	92.6
	A	6.51×10^{15}	8.78×10^{17}	3.22×10^{20}	2.19×10^{18}	3.33×10^{9}	4.29×10^{1}	8.63×10^{-2}	4.16×10^{6}	1.76×10^{7}
	r	0.97441	0.98392	0.99279	0.98745	0.99727	0.99691	0.99651	0.98840	0.99231
15.206	E	167.4	185.6	209.9	193.5	115.3	54.6	34.3	95.9	101.9
	A	1.12×10^{18}	2.81×10^{20}	2.47×10^{23}	9.36×10^{20}	1.57×10^{11}	3.10×10^{2}	3.32×10^{-1}	9.77×10^{7}	5.14×10^{8}
	r	0.96810	0.97885	0.98951	0.98299	0.99542	0.99489	0.99422	0.98407	0.98880
20.743	E	142.8	157.2	175.7	163.3	94.9	44.3	27.4	80.1	84.7
	A	1.59×10^{14}	1.05×10^{16}	1.26×10^{18}	1.84×10^{16}	1.02×10^{8}	7.16×10^{0}	2.54×10^{-2}	3.28×10^{5}	1.05×10^{6}
	r	0.97617	0.98484	0.99281	0.98799	0.99700	0.99650	0.99576	0.98867	0.99222

[a] E, kJ mol^{-1}. [b] A, s^{-1}. [c] mg.

TABLE 16

Kinetic parameters using nine mechanistic equations for different heating rates for deamination of $[Cu(en)_2(H_2O)_2]C_2O_4$ (sample mass, 10 ± 0.1 mg)

Heating rate [c]		1	2	3	4	5	6	7	8	9
1	E [a]	339.1	373.0	418.5	387.8	230.8	111.7	72.0	194.3	205.5
	A [b]	1.61×10^{33}	9.99×10^{36}	6.72×10^{41}	1.35×10^{38}	1.09×10^{21}	9.45×10^{6}	1.64×10^{2}	2.04×10^{16}	3.13×10^{17}
	r	0.97621	0.98509	0.99348	0.98843	0.99774	0.99751	0.99756	0.98973	0.99331
2	E	317.2	351.7	398.5	366.9	221.5	107.0	68.8	183.9	195.4
	A	3.06×10^{30}	2.03×10^{34}	1.67×10^{39}	2.93×10^{35}	8.50×10^{19}	3.60×10^{6}	1.06×10^{2}	1.31×10^{15}	2.11×10^{16}
	r	0.97715	0.98620	0.99454	0.98954	0.99822	0.99810	0.99818	0.99086	0.99429
5	E	294.7	327.5	373.0	342.2	208.3	100.3	64.3	171.4	182.6
	A	4.57×10^{27}	1.65×10^{31}	7.97×10^{35}	1.97×10^{32}	2.26×10^{18}	8.90×10^{5}	5.52×10^{1}	4.93×10^{13}	6.95×10^{14}
	r	0.97767	0.98687	0.99545	0.99041	0.99859	0.99853	0.99849	0.99182	0.99521
10	E	297.0	322.5	356.3	333.5	193.1	92.7	59.3	166.0	174.3
	A	3.18×10^{28}	1.78×10^{31}	4.28×10^{34}	8.23×10^{31}	1.22×10^{17}	2.85×10^{5}	3.20×10^{1}	3.36×10^{13}	2.26×10^{14}
	r	0.97831	0.98620	0.99338	0.98908	0.99666	0.99636	0.99606	0.98998	0.99307
15	E	258.2	287.3	327.2	300.2	181.9	86.8	55.2	149.7	159.5
	A	1.71×10^{22}	1.54×10^{25}	9.46×10^{28}	9.55×10^{25}	3.59×10^{14}	1.72×10^{4}	5.30×10^{0}	4.33×10^{10}	3.70×10^{11}
	r	0.97983	0.98840	0.99619	0.99169	0.99899	0.99897	0.99890	0.99283	0.99607
20	E	266.0	293.5	330.1	305.4	181.3	86.7	55.1	152.1	161.1
	A	1.20×10^{24}	8.78×10^{26}	3.09×10^{30}	4.58×10^{27}	1.66×10^{15}	4.38×10^{4}	1.10×10^{1}	3.39×10^{11}	2.52×10^{12}
	r	0.98030	0.98835	0.99561	0.99130	0.99875	0.99857	0.99817	0.99230	0.99543
50	E	230.4	259.2	298.7	272.0	167.3	79.5	50.2	135.5	145.2
	A	2.93×10^{19}	2.28×10^{22}	1.15×10^{26}	1.32×10^{23}	1.88×10^{13}	6.83×10^{3}	4.13×10^{0}	2.73×10^{9}	2.21×10^{10}
	r	0.95118	0.96563	0.98093	0.97145	0.99022	0.98922	0.98798	0.97297	0.97981
100	E	200.5	226.5	262.0	238.1	146.3	68.8	43.0	117.9	126.7
	A	4.41×10^{15}	1.35×10^{18}	1.75×10^{21}	5.09×10^{18}	4.25×10^{10}	4.12×10^{2}	7.53×10^{-1}	1.88×10^{7}	1.09×10^{8}
	r	0.94234	0.95813	0.97496	0.96449	0.98561	0.98361	0.98136	0.96540	0.97327

[a] E, kJ mol^{-1}. [b] A, s^{-1}. [c] °C min^{-1}.

TABLE 17

Kinetic parameters using nine mechanistic equations for different sample masses for deamination of $[Cu(en)_2(H_2O)_2]C_2O_4$ (heating rate, 10 °C min^{-1})

Sample mass [c]		1	2	3	4	5	6	7	8	9
1.076	E [a]	384.6	422.5	473.2	439.0	260.9	126.6	81.8	220.3	232.7
	A [b]	2.37×10^{38}	3.32×10^{42}	6.42×10^{47}	6.37×10^{43}	6.08×10^{24}	2.31×10^{9}	1.40×10^{4}	5.04×10^{19}	9.93×10^{20}
	r	0.97316	0.98246	0.99167	0.98602	0.99665	0.99656	0.99621	0.98743	0.99132
2.487	E	325.1	362.7	415.1	379.7	233.3	112.8	72.6	190.8	203.7
	A	3.04×10^{31}	3.94×10^{35}	1.16×10^{41}	8.46×10^{36}	3.62×10^{21}	5.31×10^{7}	1.09×10^{3}	1.78×10^{16}	3.98×10^{17}
	r	0.97490	0.98490	0.99431	0.98875	0.99827	0.99819	0.99798	0.99019	0.99415
4.885	E	319.2	352.3	397.6	367.0	220.3	106.3	68.2	183.7	194.9
	A	1.43×10^{30}	4.84×10^{33}	1.81×10^{38}	5.36×10^{34}	4.07×10^{19}	5.40×10^{6}	2.32×10^{2}	1.14×10^{15}	1.51×10^{16}
	r	0.98087	0.98905	0.99633	0.99208	0.99868	0.99863	0.99847	0.99332	0.99617
7.436	E	295.2	326.3	367.5	339.8	202.5	97.3	62.3	169.7	179.8
	A	2.16×10^{27}	4.27×10^{30}	5.31×10^{34}	3.39×10^{31}	3.21×10^{17}	4.58×10^{5}	4.34×10^{1}	2.45×10^{13}	2.47×10^{14}
	r	0.98291	0.99030	0.99672	0.99297	0.99922	0.99911	0.99887	0.99389	0.99650
10.00	E	297.0	322.5	356.3	333.5	193.1	92.7	59.3	166.0	174.8
	A	3.18×10^{28}	1.78×10^{31}	4.28×10^{34}	8.23×10^{31}	1.22×10^{17}	2.85×10^{5}	3.20×10^{1}	3.36×10^{13}	2.26×10^{14}
	r	0.97831	0.98620	0.99338	0.98908	0.99666	0.99636	0.99606	0.98998	0.99307
12.494	E	274.7	301.6	336.5	313.0	183.5	87.8	55.9	155.7	164.3
	A	9.55×10^{24}	6.26×10^{27}	1.53×10^{31}	2.93×10^{28}	2.05×10^{15}	3.49×10^{4}	7.63×10^{0}	5.97×10^{11}	4.04×10^{12}
	r	0.98264	0.98977	0.99601	0.99229	0.99867	0.99856	0.99831	0.99317	0.99583
15.206	E	273.5	300.1	335.2	311.6	182.9	87.5	55.7	155.0	163.6
	A	4.29×10^{24}	2.51×10^{27}	5.94×10^{30}	1.15×10^{28}	1.27×10^{15}	2.72×10^{4}	6.42×10^{0}	3.72×10^{11}	2.48×10^{12}
	r	0.98286	0.99006	0.99645	0.99264	0.99888	0.99869	0.99849	0.99363	0.99619
20.743	E	255.6	281.7	316.7	293.1	173.7	82.9	52.6	145.8	154.4
	A	3.99×10^{22}	2.06×10^{25}	4.70×10^{28}	9.31×10^{25}	1.12×10^{14}	7.91×10^{3}	2.77×10^{0}	3.22×10^{10}	2.15×10^{11}
	r	0.98187	0.98964	0.99642	0.99241	0.99879	0.99864	0.99852	0.99331	0.99620

[a] E, kJ mol^{-1}. [b] A, s^{-1}. [c] mg.

TABLE 18

Kinetic parameters using nine mechanistic equations for different heating rates for decomposition of $[Cu(en)_2(H_2O)_2]C_2O_4$ (sample mass, 10 ± 0.1 mg)

Heating rate [c]		1	2	3	4	5	6	7	8	9
1	E [a]	355.6	392.0	440.4	407.8	242.7	117.1	75.2	204.0	216.0
	A [b]	1.63×10^{30}	6.34×10^{33}	2.08×10^{38}	6.85×10^{34}	1.11×10^{19}	8.67×10^{5}	3.10×10^{1}	3.87×10^{14}	4.98×10^{15}
	r	0.98249	0.98944	0.99617	0.99211	0.99936	0.99938	0.99898	0.99312	0.99599
2	E	342.2	377.8	425.1	393.3	234.4	112.9	72.4	196.7	208.3
	A	7.03×10^{28}	2.17×10^{32}	4.92×10^{36}	2.10×10^{33}	1.91×10^{18}	4.93×10^{5}	2.65×10^{1}	9.07×10^{13}	1.06×10^{15}
	r	0.98468	0.99138	0.99728	0.99381	0.99977	0.99962	0.99953	0.99482	0.99726
5	E	361.0	397.6	446.4	413.6	245.8	118.5	76.1	206.9	218.8
	A	1.76×10^{30}	5.53×10^{33}	1.35×10^{38}	5.45×10^{34}	1.68×10^{19}	2.31×10^{6}	1.01×10^{2}	7.38×10^{14}	8.76×10^{15}
	r	0.97685	0.98522	0.99356	0.98848	0.99820	0.99802	0.99810	0.98976	0.99327
10	E	333.5	357.1	390.1	367.7	209.7	100.6	64.2	182.6	190.8
	A	1.36×10^{28}	2.29×10^{30}	1.72×10^{33}	6.98×10^{30}	1.39×10^{16}	8.95×10^{4}	1.41×10^{1}	8.35×10^{12}	4.24×10^{13}
	r	0.98652	0.99227	0.99789	0.99455	0.99952	0.99946	0.99953	0.99547	0.99777
15	E	351.3	385.4	429.5	399.8	234.4	112.6	72.0	199.3	210.2
	A	1.36×10^{28}	1.63×10^{31}	8.54×10^{34}	9.85×10^{31}	2.77×10^{17}	4.81×10^{5}	4.89×10^{1}	4.38×10^{13}	3.59×10^{14}
	r	0.98528	0.99175	0.99696	0.99395	0.99887	0.99872	0.99854	0.99466	0.99691
20	E	358.4	399.5	456.1	417.9	255.4	123.2	79.1	209.6	223.5
	A	2.86×10^{29}	1.86×10^{33}	1.86×10^{38}	2.83×10^{34}	9.56×10^{19}	1.08×10^{7}	4.48×10^{2}	1.18×10^{15}	2.01×10^{16}
	r	0.97400	0.98393	0.99370	0.98781	0.99864	0.99854	0.99864	0.98928	0.99351
50	E	301.4	331.2	370.9	344.1	202.8	96.9	61.5	171.1	180.9
	A	8.21×10^{23}	4.04×10^{26}	8.26×10^{29}	1.75×10^{27}	9.30×10^{14}	4.79×10^{4}	1.50×10^{1}	2.94×10^{11}	1.89×10^{12}
	r	0.98714	0.99316	0.99829	0.99524	1.00000	1.00000	0.99997	0.99619	0.99810
100	E	299.0	333.9	381.0	349.2	211.6	100.8	63.8.	173.9	185.5
	A	1.74×10^{21}	1.27×10^{24}	5.12×10^{27}	6.91×10^{24}	1.41×10^{14}	2.43×10^{4}	1.15×10^{1}	2.53×10^{10}	1.94×10^{11}
	r	0.96660	0.97775	0.98906	0.98207	0.99583	0.99538	0.99490	0.98352	0.98855

[a] E, kJ mol^{-1}. [b] A, s^{-1}. [c] °C min^{-1}.

TABLE 19

Kinetic parameters using nine mechanistic equations for different sample masses for decomposition of $[Cu(en)_2(H_2O)_2]C_2O_4$ (heating rate, 10 °C min^{-1})

Sample mass [c]		1	2	3	4	5	6	7	8	9
1.076	E [a]	351.2	383.5	425.2	397.1	231.1	111.1	71.2	197.9	208.2
	A [b]	1.71×10^{29}	1.82×10^{32}	7.96×10^{35}	1.02×10^{33}	6.44×10^{17}	6.20×10^{5}	5.18×10^{1}	1.18×10^{14}	9.27×10^{14}
	r	0.99216	0.99648	0.99945	0.99775	0.99969	0.99973	0.99971	0.99838	0.99949
2.487	E	337.4	369.8	412.2	383.7	224.9	108.0	69.0	191.2	201.7
	A	4.62×10^{27}	4.87×10^{30}	2.33×10^{34}	2.83×10^{31}	1.14×10^{17}	2.56×10^{5}	2.82×10^{1}	1.93×10^{13}	1.54×10^{14}
	r	0.98106	0.98845	0.99537	0.99117	0.99894	0.99877	0.99861	0.99216	0.99516
4.885	E	363.5	397.5	441.9	412.0	240.7	115.9	74.3	205.6	216.5
	A	1.22×10^{30}	1.78×10^{33}	1.27×10^{37}	1.18×10^{34}	3.38×10^{18}	1.43×10^{6}	9.08×10^{1}	4.22×10^{14}	3.70×10^{15}
	r	0.98712	0.99284	0.99797	0.99496	0.99993	0.99996	0.99998	0.99574	0.99779
7.436	E	336.3	367.8	408.9	381.3	222.4	106.7	68.2	189.9	200.0
	A	1.78×10^{27}	1.43×10^{30}	4.58×10^{33}	78.35×10^{30}	3.97×10^{16}	1.48×10^{5}	1.95×10^{1}	9.39×10^{12}	6.79×10^{13}
	r	0.99319	0.99710	0.99919	0.99827	0.99757	0.99734	0.99727	0.99860	0.99923
10.00	E	333.5	357.1	390.1	367.7	209.7	100.6	64.2	182.6	190.8
	A	1.36×10^{28}	2.29×10^{30}	1.72×10^{33}	6.98×10^{30}	1.39×10^{16}	8.95×10^{4}	1.41×10^{1}	8.35×10^{12}	4.24×10^{13}
	r	0.98652	0.99227	0.99789	0.99455	0.99952	0.99946	0.99953	0.99547	0.99777
12.494	E	350.6	383.0	425.0	396.7	230.9	111.0	71.1	197.7	208.0
	A	7.24×10^{28}	7.39×10^{31}	3.04×10^{35}	4.09×10^{32}	3.77×10^{17}	4.71×10^{5}	4.26×10^{1}	7.37×10^{13}	5.65×10^{14}
	r	0.99223	0.99640	0.99874	0.99755	0.99757	0.99752	0.99720	0.99806	0.99870
15.206	E	361.5	401.0	454.9	418.5	253.1	122.1	78.4	209.7	223.0
	A	7.95×10^{29}	4.12×10^{33}	2.58×10^{38}	5.42×10^{34}	5.92×10^{19}	6.12×10^{6}	2.42×10^{2}	1.12×10^{15}	1.68×10^{16}
	r	0.96881	0.97951	0.99033	0.98367	0.99659	0.99641	0.99602	0.98521	0.98991
20.743	E	379.3	419.0	473.4	436.7	262.8	126.9	81.6	218.9	232.2
	A	3.49×10^{31}	1.82×10^{34}	1.22×10^{40}	2.44×10^{36}	4.48×10^{20}	1.71×10^{7}	4.86×10^{2}	7.79×10^{15}	1.19×10^{17}
	r	0.99461	0.99812	0.99937	0.99908	0.99628	0.99615	0.99590	0.99948	0.99942

[a] E, kJ mol^{-1}. [b] A, s^{-1}. [c] mg.

TABLE 20

Kinetic parameters for the dehydration reaction using Coats–Redfern and mechanism-based equations

Heating rate (°C min^{-1})	Coats–Redfern			Mampel equation		
	E (kJ mol^{-1})	A (s^{-1})	r	E (kJ mol^{-1})	A (s^{-1})	r
1	267.8	1.17×10^{37}	0.9978	238.2	3.80×10^{29}	0.9938
2	260.9	2.91×10^{35}	0.9985	226.4	2.18×10^{27}	0.9945
5	183.1	1.73×10^{24}	0.9975	162.2	1.33×10^{18}	0.9949
10	142.7	5.21×10^{18}	0.9975	127.8	2.93×10^{13}	0.9974
15	118.6	1.56×10^{14}	0.9984	105.5	2.06×10^{9}	0.9977
20	115.3	1.96×10^{14}	0.9982	101.1	1.66×10^{9}	0.9959
50	79.9	7.59×10^{8}	0.9965	70.1	3.13×10^{4}	0.9915
100	65.1	7.20×10^{6}	0.9971	57.5	6.18×10^{2}	0.9934
Sample mass (mg)						
1.076	292.7	9.83×10^{39}	0.9969	252.8	1.56×10^{31}	0.9898
2.487	169.5	2.17×10^{22}	0.9984	150.2	2.91×10^{16}	0.9980
4.885	151.7	6.60×10^{19}	0.9984	136.3	3.27×10^{14}	0.9980
7.436	128.6	1.31×10^{16}	0.9979	114.5	1.06×10^{11}	0.9989
10.00	142.7	5.21×10^{18}	0.9975	127.8	2.93×10^{13}	0.9974
12.494	118.0	3.12×10^{14}	0.9982	104.7	3.33×10^{9}	0.9972
15.206	130.2	2.54×10^{16}	0.9979	115.3	1.57×10^{11}	0.9954
20.743	105.8	4.36×10^{12}	0.9984	94.9	1.02×10^{8}	0.9970

TABLE 21

Kinetic parameters for the deamination reaction using Coats–Redfern and mechanism-based equations

Heating rate (°C min^{-1})	Coats–Redfern			Mampel equation		
	E (kJ mol^{-1})	A (s^{-1})	r	E (kJ mol^{-1})	A (s^{-1})	r
1	246.2	8.06×10^{25}	0.9987	230.8	1.09×10^{21}	0.9977
2	237.4	6.67×10^{24}	0.9985	221.5	8.50×10^{19}	0.9982
5	224.1	1.63×10^{23}	0.9982	208.3	2.26×10^{18}	0.9985
10	204.3	2.75×10^{21}	0.9968	193.1	1.22×10^{17}	0.9966
15	195.5	1.21×10^{19}	0.9986	181.9	3.59×10^{14}	0.9989
20	193.5	4.20×10^{19}	0.9987	181.3	1.66×10^{15}	0.9987
50	180.8	5.88×10^{17}	0.9940	167.3	1.88×10^{13}	0.9902
100	158.2	7.95×10^{14}	0.9904	146.3	4.25×10^{10}	0.9856
Sample mass (mg)						
1.076	277.9	6.04×10^{29}	0.9979	260.9	6.08×10^{24}	0.9966
2.487	251.5	4.97×10^{26}	0.9984	233.3	3.62×10^{21}	0.9982
4.885	235.8	2.54×10^{24}	0.9979	220.3	4.07×10^{19}	0.9986
7.436	216.1	1.19×10^{22}	0.9889	202.5	3.21×10^{17}	0.9992
10.00	204.3	2.75×10^{21}	0.9968	193.1	1.22×10^{17}	0.9966
12.494	194.8	4.30×10^{19}	0.9987	183.5	2.05×10^{15}	0.9986
15.206	194.3	2.69×10^{19}	0.9986	182.9	1.27×10^{15}	0.9988
20.743	185.3	2.44×10^{18}	0.9983	173.7	1.12×10^{14}	0.9987

TABLE 22

Kinetic parameters for the decomposition reaction using Coats–Redfern and mechanism-based equations

Heating rate (°C min^{-1})	Coats–Redfern			Mampel equation		
	E (kJ mol^{-1})	A (s^{-1})	r	E (kJ mol^{-1})	A (s^{-1})	r
1	247.1	3.28×10^{22}	0.9997	242.7	1.11×10^{19}	0.9993
2	238.6	5.41×10^{21}	0.9999	234.4	1.91×10^{18}	0.9997
5	250.3	4.87×10^{22}	0.9988	245.8	1.68×10^{19}	0.9982
10	212.9	3.05×10^{19}	0.9994	209.7	1.39×10^{16}	0.9995
15	238.3	6.71×10^{20}	0.9987	234.4	2.77×10^{17}	0.9988
20	260.6	3.20×10^{23}	0.9990	255.4	9.56×10^{19}	0.9986
50	206.3	2.09×10^{18}	0.9999	202.8	9.30×10^{14}	1.0000
100	215.9	3.41×10^{17}	0.9965	211.6	1.41×10^{14}	0.9958
Sample mass (mg)						
1.076	234.8	1.55×10^{21}	0.9995	231.1	6.44×10^{17}	0.9996
2.487	228.6	2.78×10^{20}	0.9992	224.9	1.14×10^{17}	0.9989
4.885	244.6	8.49×10^{21}	1.0000	240.7	3.38×10^{18}	0.9999
7.436	226.0	9.23×10^{19}	0.9970	222.4	3.97×10^{16}	0.9975
10.00	212.9	3.05×10^{19}	0.9994	209.7	1.39×10^{16}	0.9995
12.494	234.7	9.11×10^{20}	0.9972	230.9	3.77×10^{17}	0.9975
15.206	258.1	1.91×10^{23}	0.9974	253.1	5.92×10^{19}	0.9965
20.743	267.8	1.43×10^{24}	0.9954	262.8	4.48×10^{20}	0.9962

TABLE 23

The curve-fit constants for the dehydration and deamination reactions using the Mampel equation

	a	b	c	F	R^2
Dehydration					
Sample mass					
E	96.82	164.06	–	162.19	0.9664
log A	8.55	23.89	–	133.60	0.9570
Heating rate					
E	93.62	174.81	–	23.33	0.7955
log A	7.99	25.91	–	24.25	0.8017
Deamination					
Sample mass					
E	263.15	−9.7435	0.2684	89.74	0.9729
log A	25.01	−1.1656	0.0314	80.24	0.9698
Heating rate					
E	219.59	−1.8751	0.0116	19.80	0.8879
log A	19.75	−0.2304	0.0014	19.39	0.8858

The reliability of the fits was evaluated by the F-test and it was found that all correlations were above the 99% confidence level. The values of the empirical constants along with the corresponding Fisher constants for the dehydration and deamination processes using the mechanistic equation (Mampel) are given in Table 23.

Dependence of reaction mode

As reported earlier [14], all three thermal decomposition stages of diaquabis(ethylenediamine)copper(II) oxalate follow the same reaction mechanism described by the Mampel equation. For all three stages the reaction mechanism is not influenced by the variation in heating rate and sample mass. However, the values of kinetic parameters calculated using the four non-mechanistic and mechanistic-based equations show a different trend. For the dehydration process, they decrease systematically with increase in either heating rate or sample mass, the trend being represented by a rectangular hyperbolic equation. The kinetic parameters for the deamination process also show a systematic decrease; however, the dependence is best depicted by a different equation, a parabola. For the final decomposition of the mono(amine) complex to CuO, the kinetic parameters do not show any systematic variation. Thus it can be seen that the mode of dependence of the kinetic parameters on procedural factors is different for the three types of reaction.

ACKNOWLEDGEMENTS

We thank the authorities of Vikram Sarabhai Space Centre for providing the instrumental facilities. The help of Dr. K. Krishnan and Mr. G. Viswanathan Asari with the TG instrumental work is gratefully appreciated. One of the authors (S.M.) is thankful to the Council of Scientific and Industrial Research, New Delhi, for the award of a Senior Research Fellowship.

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