THERMAL DECOMPOSITION STUDIES

PART X[*]. THERMAL DECOMPOSITION KINETICS OF CALCIUM OXALATE MONOHYDRATE — CORRELATIONS WITH HEATING RATE AND SAMPLE MASS

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ABSTRACT

Quantitative correlations between kinetic parameters (energy of activation E, pre-exponential factor A) and procedural factors (heating rate, sample mass) in non-isothermal thermogravimetry have been made for the first time. The effect of heating rate and sample mass on the first two stages of thermal decomposition of calcium oxalate monohydrate in a nitrogen atmosphere

$$(CaC_2O_4 \cdot H_2O \overset{H_2O}{\rightarrow} CaC_2O_4 \overset{-CO}{\rightarrow} CaCO_3)$$

has been evaluated in detail using non-isothermal thermogravimetry. Kinetic parameters are calculated from the TG curves using three integral methods (two "exact" and one "approximate"). The values obtained by the "approximate" method are higher than the corresponding values from the "exact" integral methods. For the decomposition of calcium oxalate to carbonate, the kinetic parameters are not much affected by heating rates or sample masses in the ranges studied. For the dehydration of $CaC_2O_4 \cdot H_2O$, the parameters show a systematic decrease with increase in either heating rate or sample mass. The values of E and log A obtained by all three equations are best correlated to heating rate as rectangular hyperbolae of the type:

$$E \text{ (or log } A) = \frac{\text{constant}}{\text{heating rate}} + \text{constant}$$

The best fits for correlation to sample mass are parabolae of the type
$$E \text{ (or log } A) = \text{constant} \times (\text{mass})^2 - \text{constant} \times \text{mass} + \text{constant}$$

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SYMBOLS USED

A = pre-exponential factor
α = fraction decomposed
ϕ = heating rate in deg min^{-1}
E = energy of activation
n = order parameter
R = gas constant
T_i = temperature of inception of reaction
T_f = temperature of completion of reaction
T_s = DTG peak temperature
$\Delta T = T - T_s$

INTRODUCTION

The results from dynamic non-isothermal thermogravimetry are affected by experimental conditions like heating rate, sample mass, sample particle size, packing and atmosphere[1,2]. Calcium oxalate monohydrate has been widely used as a standard substance for studying the effect of several such parameters[3-5].

Dharwadkar and Karkhanavala[6] studied the variations in energy of activation for the dehydration of $CaC_2O_4 \cdot H_2O$, caused by changes in heating rate and sample mass; and using Horowitz–Metzger[7] equation, they obtained the values in the range of 73–160 kJ mol^{-1}. Activation energy values in the range of 85–113 kJ mol^{-1} have been reported by a number of authors[7-11]. Recently, Segal and Vlad[12] have used a non-linear temperature programme to obtain the kinetic parameters as: $E = 96$ kJ mol^{-1} and $A = 7.32 \times 10^6$.

Coats and Redfern[8] have reported the energy of activation as 259 kJ mol^{-1} for the decomposition of CaC_2O_4 to $CaCO_3$ and CO. Higher values (310–322 kJ mol^{-1}) have been reported[10,11] for the decomposition in air where the products are $CaCO_3$ and CO_2. In this communication, we wish to present the results of our detailed studies on both the dehydration of $CaC_2O_4 \cdot H_2O$ and the decomposition of CaC_2O_4 to $CaCO_3$ and CO, carried out in a nitrogen atmosphere, for different heating rates and sample masses. It is attempted to evolve, for the first time, mathematical correlations between heating rates/sample masses and the kinetic parameters calculated from non-isothermal TG curves (Since these reactions are well known, the DTA experiments were not done. Also, the TG curves are not reproduced here.)

EXPERIMENTAL

Sample

Calcium oxalate monohydrate [$CaC_2O_4 \cdot H_2O$] powder (DuPont), purity 99.9%, was used.

Instruments

The TG experiments were carried out with DuPont 990 thermal analyser (2 pen) in conjunction with 951 thermogravimetric analyser. Computational work was done with IBM-360 computer using Fortran IV programme.

Procedure

Six heating rates (1, 2, 5, 10, 20 and 100°C min^{-1}) were employed to study their effect; and the sample mass was kept constant at 5 ± 0.1 mg in these experiments. To study the effect of sample mass, the heating rate was constant (10°C min^{-1}) and six sample masses (1.1, 2.5, 5.1, 7.4, 10.0, 15.0 and 20.2 mg) were chosen.

The samples were directly loaded onto the platinum sample pan of the TGA on which the mass was directly recorded. 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. The sample mass was shown on the Y-axis of the recorder. Suppression controls were used in such a way that the first two stages of decomposition of $CaC_2O_4 \cdot H_2O$ were recorded on the entire span of the Y-axis. To expand the X-axis the chart-drive mode was time base, and the speed was chosen to obtain 1 in. chart corresponding to 10°C rise in temperature in all the cases. Y-axis was used as an independent check of sample temperature measured by a chromel–alumel thermocouple positioned near the sample pan. The atmosphere was dry nitrogen purged at a rate of 50 cm^3 min^{-1}.

RESULTS AND DISCUSSION

The first and second stages of thermal decomposition of calcium oxalate mono-hydrate correspond to dehydration of $CaC_2O_4 \cdot H_2O$ to CaC_2O_4 and to the conversion of CaC_2O_4 to $CaCO_3$, respectively. The values of T_i, T_f and T_s as obtained from the

TABLE 1

TG RESULTS FOR DIFFERENT HEATING RATES

Sample mass $= 5 \pm 0.1$ mg

Heating rate (°C min^{-1})	Stage I			Stage II		
	$T_i(°C)$	$T_f(°C)$	$T_s(°C)$	$T_i(°C)$	$T_f(°C)$	$T_s(°C)$
1	118	145	140	379	456	439
2	114	154	146	391	485	467
5	110	167	156	402	498	483
10	117	188	173	403	513	496
20	115	201	183	407	512	498
50	121	232	206	428	541	518
100	116	276	223	447	570	541

TABLE 2

TG RESULTS FOR DIFFERENT SAMPLE MASSES

Heating rate -- $10^{\circ}C$ min^{-1}

Sample mass (mg)	Stage I			Stage II		
	$T_i(^{\circ}C)$	$T_f(^{\circ}C)$	$T_s(^{\circ}C)$	$T_i(^{\circ}C)$	$T_f(^{\circ}C)$	$T_s(^{\circ}C)$
1.1	111	159	152	390	493	475
2.5	116	172	162	391	497	480
5.1	117	188	173	403	513	496
7.4	125	190	176	401	508	491
10.0	121	195	181	405	512	494
15.0	117	201	184	400	520	496
20.2	125	213	199	410	520	500

TG experiments are given in Tables 1 and 2. Table 1 gives the values of T_i, T_f and T_s for different heating rates with constant sample mass, and Table 2 gives the corresponding values for different sample masses at a constant heating rate.

From these tables, it can be seen that the temperature of inception of decomposition of both the stages is not much affected by changes in heating rate and sample mass (except that, at high heating rates, T_i for the decomposition of CaC_2O_4 shows some increase). Both T_f and T_s of the dehydration reaction steadily increase with both heating rate and sample mass. Similar trends were observed earlier also[6]. For the decomposition of calcium oxalate to carbonate, there is a similar increase, but to a lesser extent.

Kinetic parameters

The kinetic parameters, viz., energy of activation and pre-exponential factor were calculated from the non-isothermal TG curves using the integral method. Three well-known equations (two "exact" and one "approximate") were chosen. They are:

(1) Coats–Redfern equation[8]

$$\ln \frac{1 - (1 - \alpha)^{1-n}}{(1 - n) T^2} = \ln \left[\frac{AR}{\phi E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT}$$

(2) MacCallum–Tanner equation[13]

$$\log_{10} \frac{1 - (1 - \alpha)^{1-n}}{1 - n} = \log_{10} \frac{AE}{\phi R} - 0.485E^{0.435} - \frac{(0.449 + 0.217E) \times 10^3}{T}$$

(3) Horowitz–Metzger equation[7]

$$\ln \frac{1 - (1 - \alpha)^{1-n}}{1 - n} = \ln \left(\frac{ART_s^2}{\phi E} \right) - \frac{E}{RT_s} + \frac{E\phi}{RT_s^2}$$

The order parameter, n, was evaluated for both the stages of decomposition using the Coats–Redfern equation by a computational procedure. Using the computer, linear plots of

$$\ln \frac{1 - (1 - \alpha)^{1-n}}{(1 - n)\, T^2} \text{ vs. } \frac{1}{T}$$

were drawn by the method of least squares taking the $(1 - \alpha)$ and the corresponding T values for the two stages of decomposition from a typical TG curve. Curves were drawn for different values of n in the range of 0 to 3 and the order parameters were fixed from the two values of n which gave the best fit lines for the two stages. The values were $n = 0.65$ for the conversion of $CaC_2O_4 \cdot H_2O$ to CaC_2O_4 and $n = 0.50$ for the decomposition of CaC_2O_4 to $CaCO_3$.

With these values of n and using each of the three kinetic equations, energy of activation and pre-exponential factor for the two stages of decomposition of $CaC_2O_4 \cdot H_2O$ were calculated from the TG curves for different heating rates and sample masses. The calculations were done with the computer and the correlation coefficient, r, was determined in each case. Table 3 gives the values of E, A and r calculated from the TG curves for different heating rates, using the three equations, for the dehydration of $CaC_2O_4 \cdot H_2O$. The values for different sample masses are given in Table 4. Similar values for the decomposition of CaC_2O_4 to $CaCO_3$ are given in Tables 5 and 6, which show the effect of heating rate and sample masses, respectively.

In all these cases, the values of the correlation coefficients are almost unity indicating nearly perfect fits. Kinetic parameters calculated using the "approximate" method (Horowitz–Metzger equation) are higher than the corresponding values calculated using the "exact" methods (Coats–Redfern and MacCallum–Tanner equations). Similar observations have also been made by us earlier[1,2].

TABLE 3

KINETIC PARAMETERS FOR DIFFERENT HEATING RATES FOR THE CONVERSION OF $CaC_2O_4 \cdot H_2O$ TO CaC_2O_4

Sample mass $- 5 \pm 0.1$ mg $n = 0.65$.

Heating rate ($^\circ C$ min^{-1})	Kinetic parameter using equations								
	Coats–Redfern			MacCallum–Tanner			Horowitz–Metzger		
	E^a	A	r	E^a	A	r	E^a	A	r
1	233.2	8.84×10^{24}	0.995	233.0	8.20×10^{24}	0.995	246.2	4.05×10^{25}	0.994
2	151.8	3.07×10^{14}	0.996	151.1	2.22×10^{14}	0.996	165.7	1.71×10^{18}	0.995
5	109.6	1.39×10^{11}	0.998	108.7	9.67×10^{10}	0.998	123.9	8.49×10^{12}	0.997
10	106.8	3.75×10^{10}	0.998	106.1	2.80×10^{10}	0.999	121.8	2.29×10^{12}	0.997
20	94.2	1.23×10^{9}	0.999	93.5	9.44×10^{8}	0.999	110.0	8.55×10^{10}	0.997
50	87.4	1.49×10^{8}	0.998	87.0	1.25×10^{8}	0.998	104.0	1.00×10^{10}	0.997
100	74.0	3.98×10^{6}	0.997	73.7	3.36×10^{6}	0.998	92.3	4.04×10^{8}	0.999

^{a} Values of E are in kJ mol^{-1}.

TABLE 4

KINETIC PARAMETERS FOR DIFFERENT SAMPLE MASSES FOR THE CONVERSION OF $CaC_2O_4 \cdot H_2O$ TO CaC_2O_4

Heating rate $= 10°C$ min^{-1}, $n = 0.65$.

Sample mass (mg)	Kinetic parameter using equations								
	Coats–Redfern			MacCallum–Tanner			Horowitz–Metzger		
	E^a	A	r	E^a	A	r	E^a	A	r
1.1	122.9	2.11×10^{13}	0.998	122.0	1.46×10^{13}	0.999	138.1	1.41×10^{15}	0.998
2.5	126.0	2.27×10^{13}	0.996	125.3	1.65×10^{13}	0.996	141.4	1.34×10^{15}	0.994
5.1	106.8	3.75×10^{10}	0.998	106.1	2.80×10^{10}	0.999	121.8	2.29×10^{12}	0.997
7.4	117.0	6.06×10^{11}	0.999	116.5	4.64×10^{11}	0.999	132.5	3.23×10^{13}	0.999
10.0	99.8	3.71×10^{9}	0.999	99.2	2.85×10^{9}	0.999	115.0	1.78×10^{11}	0.999
15.0	90.4	1.96×10^{8}	0.999	89.7	1.52×10^{8}	0.999	106.0	1.37×10^{10}	0.997
20.2	88.5	6.76×10^{7}	0.999	88.0	5.47×10^{7}	0.999	105.8	4.77×10^{9}	0.998

^{a} Values of E are in kJ mol^{-1}.

TABLE 5

KINETIC PARAMETERS FOR DIFFERENT HEATING RATES FOR THE DECOMPOSITION OF CaC_2O_4 TO $CaCO_3$

Original sample mass 5 ± 0.1 mg, $n = 0.50$.

Heating rate ($°C$ min^{-1})	Kinetic parameters calculated using equations								
	Coats–Redfern			MacCallum–Tanner			Horowitz–Metzger		
	E^a	A	r	E^a	A	r	E^a	A	r
1	234.4	1.49×10^{14}	0.999	239.1	4.12×10^{14}	0.999	256.5	6.67×10^{15}	0.998
2	259.2	4.05×10^{15}	0.999	264.5	1.32×10^{16}	0.999	284.9	2.58×10^{17}	0.997
5	264.2	8.34×10^{15}	0.999	269.8	2.93×10^{16}	0.999	287.4	3.68×10^{17}	0.998
10	250.9	1.04×10^{15}	1.000	256.5	3.49×10^{15}	1.000	280.7	1.04×10^{17}	1.000
20	236.9	1.68×10^{14}	0.996	242.5	5.42×10^{14}	0.996	265.2	1.74×10^{16}	0.998
50	231.1	6.17×10^{13}	0.998	236.9	2.05×10^{14}	0.998	259.5	6.23×10^{15}	0.998
100	243.3	3.00×10^{14}	0.999	249.6	1.11×10^{15}	0.999	272.6	2.67×10^{16}	0.999

^{a} Values of E are in kJ mol^{-1}.

TABLE 6

KINETIC PARAMETERS FOR DIFFERENT SAMPLE MASSES FOR THE DECOMPOSITION OF CaC_2O_4 TO $CaCO_3$

Heating rate $10°C$ min^{-1}, $n = 0.50$.

Sample mass (mg)	Kinetic parameters calculated using equations								
	Coats–Redfern			MacCallum–Tanner			Horowitz–Metzger		
	E^a	A	r	E^a	A	r	E^a	A	r
1.1	225.1	4.22×10^{13}	0.999	230.2	1.23×10^{14}	0.999	251.5	3.35×10^{15}	1.000
2.5	214.7	5.70×10^{12}	0.997	219.8	1.61×10^{13}	0.997	242.2	5.65×10^{14}	0.992
5.1	250.9	1.04×10^{15}	1.000	256.5	3.49×10^{15}	1.000	287.4	3.68×10^{17}	0.998
7.4	227.6	2.84×10^{13}	0.997	232.9	2.84×10^{13}	0.997	256.6	3.07×10^{15}	0.999
10.0	236.8	1.10×10^{14}	0.999	242.4	3.52×10^{14}	0.999	263.8	8.41×10^{15}	1.000
15.0	211.1	1.56×10^{12}	0.997	216.6	4.54×10^{12}	0.997	239.6	1.60×10^{14}	0.999
20.2	218.8	4.67×10^{12}	0.999	224.2	1.42×10^{13}	0.999	246.3	3.48×10^{14}	1.000

^{a} Values of E are in kJ mol^{-1}.

A distinction between the decomposition (stage II) and dehydration (stage I)

From Tables 5 and 6, it can be noted that the kinetic parameters are not much affected by either heating rate or sample mass for the decomposition of CaC_2O_4 to $CaCO_3$. The minor variations are rather irregular here. However, Tables 3 and 4 show that for the conversion to $CaC_2O_4 \cdot H_2O$ to CaC_2O_4, both E and A calculated using all the three equations are strongly dependent on both heating rate and sample mass — they decrease with increase in either heating rate or sample mass. A similar observation was made by earlier workers also[6]. Thus, so far as the kinetic parameters are concerned, an increase in heating rate for constant sample mass has qualitatively the same effect as an increase in sample mass for constant heating rate.

Quantitative correlations

An attempt was made, for the first time, to make quantitative correlations between kinetic parameters and procedural factors, in the case of the dehydration step. The regular trends of kinetic parameters in this case, relative to changes in heating rate and sample mass, make the data amenable to statistical treatment. Different curve fittings were worked out, using computer, with various functions of these factors, and the best fit curve giving the correlation coefficient nearest to unity was chosen. It is found that for all the three kinetic equations, the curves of activation energy for the dehydration reaction vs. the heating rate are best fitted as rectangular hyperbolae of the type:

$$E = \frac{C_1}{\text{heating rate}} + C_2$$

where C_1 and C_2 are different constants for different equations. Their values are given in Table 7 which gives the correlation coefficient of the corresponding curve also.

TABLE 7

CONSTANTS FOR THE CORRELATIONS OF HEATING RATE AND E (dehydration stage)

Kinetic equation	C_1	C_2	r
Coats–Redfern	148.77	82.47	0.993
MacCallum–Tanner	149.02	81.85	0.993
Horowitz–Metzger	144.90	88.79	0.994

For the pre-exponential factors, the best fits are obtained as rectangular hyperbolae for the curves of log A vs. heating rate. The equation of the curve is of the type:

$$\log_{10} A = \frac{C_1}{\text{heating rate}} + C_2$$

TABLE 8

CONSTANTS FOR THE CORRELATIONS OF HEATING RATE AND $\log_{10}A$ (dehydration stage)

Kinetic equation	C_1	C_2	r
Coats–Redfern	19.05	7.56	0.994
MacCallum–Tanner	19.16	7.47	0.994
Horowitz–Metzger	18.89	9.45	0.995

TABLE 9

CONSTANTS FOR CORRELATIONS OF SAMPLE MASS AND E (dehydration stage)

Kinetic equation	k_1	k_2	k_3	r
Coats–Redfern	0.0618	3.33	129.3	0.934
MacCallum–Tanner	0.0606	3.29	128.4	0.932
Horowitz–Metzger	0.0724	3.46	144.8	0.925

TABLE 10

CONSTANTS FOR CORRELATIONS OF SAMPLE MASS AND $\log_{10}A$ (dehydration stage)

Kinetic equation	k_1	k_2	k_3	r
Coats–Redfern	0.0113	0.543	14.11	0.954
MacCallum–Tanner	0.0113	0.542	13.97	0.953
Horowitz–Metzger	0.0124	0.562	15.93	0.956

The values of C_1, C_2 and r for the three kinetic equations are given in Table 8.

The best fit curves for the kinetic parameters and sample masses are parabolas. Here again, E is directly related, whereas it is log A that is related to sample mass. The equations for the curves are:

$$E = k_1 (\text{mass})^2 - k_2 \text{ mass} \div k_3$$
$$\log_{10}A = k_1 (\text{mass})^2 - k_2 \text{ mass} \div k_3$$

where k_1, k_2 etc. are different constants for different kinetic equations. Their values and the corresponding correlation coefficients are given in Tables 9 and 10.

For all the above curves, the correlation coefficients are very near unity, indicating the validity of our assumptions for the correlations. It can also be noted that a more regular trend is obtained with heating rate than with sample mass.

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