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THERMAL DECOMPOSITION STUDIES. PART XII. KINETICS OF DEHYDRATION OF CALCIUM OXALATE MONOHYDRATE. MULTIPLE CORRELATION WITH HEATING RATE AND SAMPLE MASS

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ABSTRACT

The kinetic parameters (energy of activation, E, and pre-exponential factor, A) from non-isothermal TG data have been correlated, for the first time, with simultaneous variations of both the procedural factors (heating rate and sample mass) by multiple regression analysis. The unique equation based on the mechanism of the reaction as well as three general mechanism-non-invoking integral equations were used to calculate E and A from the TG data for the dehydration of $CaC_2O_4 \cdot H_2O$. The kinetic parameters calculated using all four equations showed a systematic trend and the results can be expressed as

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

SYMBOLS

A	pre-exponential factor
α	fraction decomposed
ϕ	heating rate
E	energy of activation
m	sample mass
n	order parameter
R	gas constant
r	correlation coefficient
T_i	temperature of inception of reaction
T_f	temperature of completion of reaction
T_s	DTG peak temperature
θ	$T - T_s$
C—R	Coats—Redfern equation
M—T	MacCallum—Tanner equation
H—M	Horowitz—Metzger equation
M—B	The mechanism-based equation

INTRODUCTION

In one of our earlier publications [1], the kinetic parameters (energy of activation, E, and pre-exponential factor, A) for the dehydration of $CaC_2O_4 \cdot H_2O$ to CaC_2O_4 were evaluated from non-isothermal TG curves, using three well-known mechanism-non-invoking equations [2—4]. The studies were carried out at seven heating rates with a fixed sample mass and with seven sample masses at a fixed heating rate. It was observed that the kinetic parameters (E and $\log_{10}A$) showed a systematic decrease with increase in either heating rate or sample mass.

In another publication [5], we established from non-isothermal TG that the mechanism of the dehydration of $CaC_2O_4 \cdot H_2O$ is a phase boundary reaction with cylindrical symmetry having $g(\alpha) = 1 - (1 - \alpha)^{1/3}$. A kinetic equation was derived using this value of $g(\alpha)$. The kinetic parameters using this mechanism-based equation also showed a systematic decrease with increase in either heating rate (with fixed sample mass) or sample mass (at constant heating rate).

In the present study, it is attempted, for the first time, to evolve multiple correlations between heating rates, sample masses and the kinetic parameters for the dehydration reaction, calculated from non-isothermal TG curves, using both the mechanism-based and the mechanism-non-invoking equations. Such a study would enable one to predict the kinetic parameters for any combination of heating rate and sample mass.

EXPERIMENTAL

The details regarding the sample and the instruments used are the same as those described in our earlier publication [1]. Five heating rates (2, 5, 10, 20 and 50°C min^{-1}) were employed in this study, and for each heating rate five sample masses (2.5, 5.0, 7.5, 10 and 15 mg) were chosen. The entire study was carried out with material from the same batch. The samples were loaded on the platinum sample pan and suppression controls were employed so that the mass loss for the dehydration was recorded on more than 50% of the Y-axis. The temperature was measured by a chromel—alumel thermocouple positioned near the sample pan. The chart drive mode was time-base, and the chart speed was chosen in such a way that 1°C corresponded to 1 chart division on the X-axis. The furnace atmosphere was dry nitrogen purged at a flow rate of 50 cm^3 min^{-1}. Other experimental details were the same as those described in our earlier publication [1].

RESULTS AND DISCUSSION

The temperatures of inception (T_i) and completion (T_f) and the DTG peak temperature (T_s) obtained from the TG curves for the dehydration of $CaC_2O_4 \cdot H_2O$ to CaC_2O_4 for various heating rates and sample masses are given in Table 1. From this table, it can be seen that T_i is not much affected

TABLE 1

TG results for different heating rates and sample masses

Sample mass (mg)	Heating rate														
	2°C min^{-1}			5°C min^{-1}			10°C min^{-1}			20°C min^{-1}			50°C min^{-1}		
	T_i (°C)	T_f (°C)	T_s (°C)	T_i (°C)	T_f (°C)	T_s (°C)	T_i (°C)	T_f (°C)	T_s (°C)	T_i (°C)	T_f (°C)	T_s (°C)	T_i (°C)	T_f (°C)	T_s (°C)
2.5	114	146	139	106	155	146	116	172	162	105	184	174	117	225	191
5.0	114	154	146	110	167	156	117	188	173	115	201	183	121	232	206
7.5	112	154	145	109	171	159	125	190	176	115	208	187	118	240	205
10.0	111	155	147	110	172	162	121	195	181	105	212	191	105	256	214
15.0	108	158	151	113	179	166	117	201	184	116	227	203	116	273	224

by heating rate or sample mass. (The random fluctuations from 105 to 125°C are within the experimental scatter.) But both T_f and T_s increase steadily with increase in heating rate and sample mass. These values show the increase horizontally, vertically and diagonally in the table. Thus the T_f and T_s values for 2°C min^{-1} and 2.5 mg are 146°C and 139°C, respectively, and the corresponding value for 50°C min^{-1} and 15 mg are 273°C and 224°C, respectively, while the T_i values for these cases are 114 and 116°C. This trend is expected from our earlier work and the work of other authors [6].

The following three mechanism-non-invoking equations were used for the calculations of the kinetic parameters.

(1) Coats—Redfern equation

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

(2) MacCallum—Tanner equation

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

(3) Horowitz—Metzger equation

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

The order parameter, n, was established as 0.65 for this reaction in our earlier work [1] and the same value is used here.

Using the nine formulae listed by Satava [7], we have shown [2] that the mechanism of the conversion of $CaC_2O_4 \cdot H_2O$ to CaC_2O_4 is a phase boundary reaction with spherical symmetry. As done in our earlier work, solving the exponential integral for non-isothermal TG using the Coats—Redfern method we obtain the equation

$$\ln \frac{1-(1-\alpha)^{1/3}}{T^2} = \ln\left[\frac{AR}{\phi E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT}$$

for the above mechanism. This was the mechanism-based (M—B) equation used in the present work.

Using each of the above four equations, the energy of activation and the pre-exponential factor were calculated from the TG curves for the different heating rates and sample masses. The calculations were done with the computer and the correlation coefficiently, r, was also calculated in each case. The values of E, A and r obtained using the four equations are given in Tables 2—5.

From these tables, the following observations emerge.

(1) The correlation coefficients are very close to unity (>0.99 in all cases) indicating near-perfect fits.

(2) The kinetic parameters calculated using the approximation technique (H—M equation) are higher than the values obtained from the exact integral methods. The values from the exact integral methods vary only marginally.

TABLE 2

Kinetic parameters calculated using the Coats—Redfern equation

Sample mass (*mg*)	Heating rate														
	2°C min^{-1}			5°C min^{-1}			10°C min^{-1}			20°C min^{-1}			50°C min^{-1}		
	E [a]	A [b]	r	E [a]	A [b]	r	E [a]	A [b]	r	E [a]	A [b]	r	E [a]	A [b]	r
2.5	182.2	3.349×10^{21}	0.9950	135.5	7.151×10^{14}	0.9958	126.0	2.272×10^{13}	0.9960	96.71	4.492×10^{9}	0.9990	92.78	1.383×10^{9}	0.9981
5.0	151.8	3.067×10^{16}	0.9961	109.6	1.395×10^{11}	0.9981	106.8	3.757×10^{10}	0.9982	94.18	1.234×10^{9}	0.9986	87.41	1.487×10^{8}	0.9979
7.5	146.0	6.775×10^{15}	0.9979	108.1	7.249×10^{10}	0.9988	104.2	2.374×10^{10}	0.9990	83.80	5.829×10^{7}	0.9998	74.53	5.552×10^{6}	0.9997
10.0	131.9	8.367×10^{13}	0.9971	105.0	2.557×10^{10}	0.9996	99.83	3.712×10^{9}	0.9990	82.74	3.654×10^{7}	0.9996	71.76	1.659×10^{6}	0.9980
15.0	122.2	3.260×10^{12}	0.9997	101.9	8.159×10^{9}	0.9987	90.41	1.975×10^{8}	0.9988	74.82	2.507×10^{6}	0.9997	69.52	5.549×10^{5}	0.9983

[a] kJ mole^{-1}. [b] sec^{-1}.

TABLE 3

Kinetic parameters calculated using the MacCallum—Tanner equation

Sample mass (mg)	Heating rate														
	2°C min^{-1}			5°C min^{-1}			10°C min^{-1}			20°C min^{-1}			50°C min^{-1}		
	E [a]	A [b]	r	E [a]	A [b]	r	E [a]	A [b]	r	E [a]	A [b]	r	E [a]	A [b]	r
2.5	187.6	2.626×10^{21}	0.9954	134.6	4.950×10^{14}	0.9962	125.3	1.654×10^{13}	0.9964	95.95	3.322×10^{9}	0.9991	92.23	1.095×10^{9}	0.9984
5.0	151.1	2.224×10^{16}	0.9964	108.7	9.671×10^{10}	0.9984	106.1	2.796×10^{10}	0.9985	93.52	9.444×10^{8}	0.9988	87.03	1.247×10^{8}	0.9983
7.5	145.3	4.817×10^{15}	0.9981	107.2	5.136×10^{10}	0.9990	103.3	1.673×10^{10}	0.9992	83.10	4.550×10^{7}	0.9998	73.96	4.641×10^{6}	0.9998
10.0	131.1	5.802×10^{13}	0.9974	104.2	1.849×10^{10}	0.9997	99.22	2.847×10^{9}	0.9991	82.06	2.873×10^{7}	0.9997	71.35	1.462×10^{6}	0.9985
15.0	121.3	2.623×10^{12}	0.9979	101.0	5.853×10^{9}	0.9989	89.73	1.518×10^{8}	0.9990	74.25	2.089×10^{6}	0.9998	69.31	5.192×10^{5}	0.9987

[a] kJ mole^{-1}. [b] sec^{-1}.

TABLE 4

Kinetic parameters calculated using the Horowitz—Metzger equation

Sample mass (mg)	Heating rate														
	2°C min^{-1}			5°C min^{-1}			10°C min^{-1}			20°C min^{-1}			50°C min^{-1}		
	E [a]	A [b]	r	E [a]	A [b]	r	E [a]	A [b]	r	E [a]	A [b]	r	E [a]	A [b]	r
2.5	202.0	1.977×10^{23}	0.9940	150.2	4.327×10^{16}	0.9944	141.4	1.342×10^{15}	0.9944	112.2	2.839×10^{11}	0.9995	108.7	8.464×10^{10}	0.9958
5.0	165.7	1.709×10^{18}	0.9946	123.9	8.487×10^{12}	0.9966	121.8	2.289×10^{12}	0.9969	110.0	8.551×10^{10}	0.9972	104.0	1.003×10^{10}	0.9965
7.5	160.0	3.519×10^{17}	0.9969	122.2	3.961×10^{12}	0.9979	117.8	1.126×10^{12}	0.9919	99.44	3.684×10^{9}	0.9988	91.27	3.967×10^{8}	0.9980
10.0	145.9	4.663×10^{15}	0.9958	117.6	8.152×10^{11}	0.9996	115.0	1.784×10^{11}	0.9986	99.41	2.837×10^{9}	0.9986	87.69	9.643×10^{7}	0.9951
15.0	136.0	1.737×10^{14}	0.9964	116.0	4.772×10^{11}	0.9975	106.9	1.366×10^{10}	0.9969	91.48	1.772×10^{8}	0.9983	84.35	2.689×10^{7}	0.9952

[a] kJ mole^{-1}. [b] sec^{-1}.

TABLE 5

Kinetic parameters calculated using the mechanism-based equation

Sample mass (mg)	Heating rate														
	2°C min^{-1}			5°C min^{-1}			10°C min^{-1}			20°C min^{-1}			50°C min^{-1}		
	E^a	A^b	r	E^a	A^b	r	E^a	A^b	r	E^a	A^b	r	E^a	A^b	r
2.5	189.0	1.461×10^{21}	0.9952	136.2	2.929×10^{14}	0.9960	126.7	9.271×10^{12}	0.9961	97.22	1.744×10^{9}	0.9982	93.27	5.320×10^{8}	0.9982
5.0	152.5	1.290×10^{16}	0.9962	110.1	5.501×10^{10}	0.9982	107.4	1.481×10^{10}	0.9983	94.65	4.722×10^{8}	0.9986	87.85	5.621×10^{7}	0.9980
7.5	146.8	2.853×10^{15}	0.9980	108.6	2.895×10^{10}	0.9989	104.8	9.429×10^{9}	0.9991	84.25	2.219×10^{7}	0.9998	74.90	2.064×10^{6}	0.9998
10.0	132.6	3.411×10^{13}	0.9972	105.7	1.058×10^{10}	0.9996	100.4	1.480×10^{9}	0.9989	83.12	1.363×10^{7}	0.9996	72.13	6.151×10^{5}	0.9981
15.0	122.8	1.314×10^{12}	0.9978	102.4	3.197×10^{9}	0.9987	90.87	7.540×10^{7}	0.9988	75.20	9.338×10^{5}	0.9997	69.91	2.061×10^{5}	0.9984

[a] kJ mole^{-1}. [b] sec^{-1}.

Similar observations were made by us earlier [1,8].

(3) The values of E and A calculated using all the equations (mechanism-based and mechanism-non-invoking) are dependent on both heating rate and sample mass. As observed earlier [1,2], the variations are systematic. Both E and A decrease with increase in heating rate and sample mass. Thus we find a decrease vertically, horizontally and diagonally in the tables.

In our earlier work [1,2] it was found that the kinetic parameters are better correlated with heating rate than with sample mass and that the curves of E vs. heating rate and $\log_{10}A$ vs. heating rate could be best fitted as rectangular hyperbolae following the equation

$$E(\text{or } \log_{10}A) = \text{constant} + \frac{\text{constant}}{\text{heating rate}}$$

at fixed sample mass. Similar statistical analysis was also done here for each set of values obtained with the four equations. The reliability of the curve fitting was evaluated by the F-test. The equations for the curves are represented as

$$E = C_1 + \frac{C_2}{\phi}$$

$$\log_{10}A = C_3 + \frac{C_4}{\phi}$$

The values of C_1, C_2, C_3 and C_4 and the corresponding Fisher constants for the five sample masses, and for the four kinetic equations used, are listed in Tables 6—9.

The critical values of the Fisher constants at 99% and 95% confidence levels are 34.1 and 10.1, respectively. From Tables 6—9, it can be seen that, out of the 40 curves, the Fisher constants for 30 correspond to a confidence level of above 99%, while for the remaining 10, the confidence level is above 95% and often very close to 99%.

Another interesting observation that can be made from these tables is that the correlation constants C_1, C_2, C_3 and C_4 show a systematic decrease with increase in sample mass in all four cases. So a statistical analysis was done to establish the correlation between the sample mass. It was found that the curves of C_1, C_2, C_3 or C_4 vs. sample mass could be best fitted again as rectangular hyperbolae following the equation

$$C = A + \frac{B}{m}$$

The values of the correlation constants, A and B, along with the corresponding Fisher constants, F, for the four kinetic equations are given in Table 10. It can be seen from Table 10 that the confidence levels of all the correlations are above 99% (the critical value of F, for 99% confidence level, is 34.1).

It emerges from the above discussions that E and $\log_{10}A$ are related to the heating rate for a constant sample mass and *the constants for such correlations are, in turn, related to the sample mass.* It is, therefore, evident that the kinetic parameters can be correlated *simultaneously* to heating rate and sample mass. Multiple regression analysis was carried out using the computer

TABLE 6

Curve fit constants for kinetic parameters from the Coats—Redfern equation

Sample mass (mg)	Correlation for E			Correlation for $\log_{10} A$		
	C_1	C_2	F	C_3	C_4	F
2.5	94.22	193.2	68.22	9.330	25.15	71.39
5.0	82.47	148.8	357.8	7.584	19.11	335.4
7.5	79.41	137.5	44.62	7.245	17.65	50.76
10.0	78.69	112.4	27.56	7.004	14.56	34.54
15.0	73.61	104.4	30.42	6.224	13.50	32.85

TABLE 7

Curve fit constants for kinetic parameters from the MacCallum—Tanner equation

Sample mass (mg)	Correlation for E			Correlation for $\log_{10} A$		
	C_1	C_2	F	C_3	C_4	F
2.5	94.88	190.0	82.10	9.199	25.17	73.47
5.0	81.85	149.0	362.6	7.472	19.15	431.8
7.5	78.67	137.4	46.22	7.136	17.54	53.17
10.0	78.13	111.8	27.76	6.918	14.39	35.33
15.0	73.15	103.3	31.39	6.157	13.28	34.22

TABLE 8

Curve fit constants for kinetic parameters from the Horowitz—Metzger equation

Sample mass (mg)	Correlation for E			Correlation for $\log_{10} A$		
	C_1	C_2	F	C_3	C_4	F
2.5	110.0	189.0	65.85	11.12	25.11	72.31
5.0	98.80	144.9	402.6	9.452	18.89	470.2
7.5	94.91	133.5	58.46	9.034	17.46	57.70
10.0	94.42	107.4	28.57	8.746	14.41	39.40
15.0	89.49	100.3	26.97	8.017	13.39	29.94

TABLE 9

Curve fit constants for kinetic parameters from the mechanism-based equation

Sample mass (mg)	Correlation for E			Correlation for $\log_{10} A$		
	C_1	C_2	F	C_3	C_4	F
2.5	94.76	193.8	67.43	8.919	25.25	71.01
5.0	82.87	149.6	353.9	6.951	21.06	335.4
7.5	79.82	138.2	44.40	6.823	17.75	50.42
10.0	79.12	113.1	27.29	6.584	14.64	33.85
15.0	74.00	104.8	30.48	5.796	13.57	32.83

TABLE 10

Correlation constants for the equation

$$C_1, C_2, C_3, \text{ or } C_4 = A + \frac{B}{m}$$

Kinetic equation	Correlation for C_1			Correlation for C_2			Correlation for C_3			Correlation for C_4		
	A_1	B_1	F	A_2	B_2	F	A_3	B_3	F	A_4	B_4	F
C–R	71.34	57.45	129.8	92.51	259.7	70.06	5.938	8.551	97.21	11.85	34.13	88.93
M–T	70.32	61.21	157.8	92.87	252.3	54.57	5.867	8.387	101.2	11.64	34.83	84.12
H–M	87.14	57.69	151.3	88.14	260.4	65.21	7.722	8.624	117.1	11.66	34.42	100.4
M–B	71.70	57.86	128.9	93.11	259.9	68.52	5.479	8.533	67.9	12.20	34.73	35.39

TABLE 11

Multiple correlation of kinetic parameters with heating rate and sample mass

Kinetic equation	Correlation with E				Correlation with $\log_{10} A$			
	k_1	k_2	k_3	r	k_4	k_5	k_6	r
C—R	134.9	103.1	64.19	0.9550	17.46	14.54	4.988	0.9579
M—T	134.5	103.0	63.58	0.9549	17.35	14.49	4.897	0.9577
H—M	130.6	103.1	79.44	0.9549	17.33	14.65	6.757	0.9584
M—B	135.6	103.5	64.54	0.9549	17.55	14.60	4.557	0.9578

and it was found that for all the kinetic equations, the data could be best correlated to heating rate and sample mass as

$$E = \frac{k_1}{\phi} + \frac{k_2}{m} + k_3$$

$$\log_{10} A = \frac{k_4}{\phi} + \frac{k_5}{m} + k_6$$

where k_1 ... k_6 are empirical constants.

The multiple correlation coefficient, r, was also calculated in each case. The constants k_1—k_3 and k_4—k_6 and the corresponding values of r, obtained for the four kinetic equations used, are given in Table 11.

For all the above cases, the multiple correlation coefficients are above 0.95, indicating the validity of our assumptions for the correlation.

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