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THERMAL DECOMPOSITION KINETICS. PART XI. MECHANISM OF THERMAL DECOMPOSITION OF CALCIUM OXALATE MONOHYDRATE FROM A THERMOGRAVIMETRIC STUDY — THE EFFECTS OF HEATING RATE AND SAMPLE MASS ON KINETIC PARAMETERS FROM MECHANISTIC EQUATIONS

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ABSTRACT

The mechanisms of the first two stages of the thermal decomposition of calcium oxalate monohydrate

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

have been established from non-isothermal thermogravimetric studies. For both stages, the rate-controlling processes are phase boundary reactions; the dehydration step assumes spherical symmetry whereas the decomposition step follows cylindrical symmetry. The kinetic parameters calculated from mechanistic equations show the same trend as those from mechanism-non-invoking equations. Thus, for the decomposition of CaC_2O_4 the kinetic parameters are not appreciably affected by heating rate or sample mass. For the dehydration step they show a systematic decrease with increase in either heating rate or sample mass. The best fit correlations can be expressed as follows

E(or, log A) = (Constant/Heating rate) + Constant, (at fixed sample mass)
E(or, log A) = (Constant) × (Mass)^2 − (Constant) × (Mass) + Constant, (at fixed heating rate)

SYMBOLS USED

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 = temperature in K.

INTRODUCTION

In an earlier publication[1] we had evaluated E, A and n for the dehydration of $CaC_2O_4 \cdot H_2O$ and the decomposition of CaC_2O_4 to $CaCO_3$ and CO, using three well-known integral equations[2-4]. Mathematical correlations of high reliability between heating rate or sample mass on the one hand, and the kinetic parameters on the other, were also evolved for the dehydration step.

Non-isothermal TG experiments have recently been used to study the mechanism of thermal decomposition of solid state reactions[5-8]. In the present study it is attempted to establish the mechanisms of the first two stages of the thermal decomposition of $CaC_2O_4 \cdot H_2O$, using non-isothermal TG experiments. A search through the available literature did not reveal any earlier attempt made to correlate kinetic parameters obtained from mechanism-based equations with heating rate and sample mass. Such mathematical correlations are also presented in this paper.

EXPERIMENTAL DATA

Seven heating rates (1, 2, 5, 10, 20, 50 and 100 °C min^{-1}) at constant sample mass (5±0.1 mg) and seven sample masses (1.1, 2.5, 5.1, 7.4, 10.0, 15.0 and 20.2 mg) at constant heating rate (10 °C min^{-1}) were employed in our earlier study[1] and the twenty-eight sets of values of α and T obtained in that study have been used for the present calculations.

The TG experiments were carried out in a nitrogen atmosphere using a Dupont 990 Thermal Analyser with 951 Thermogravimetric Analyser. Computational work was done with IBM-360 Computer. Further details are given in our earlier paper[1].

MATHEMATICAL TREATMENT OF DATA

Kinetic parameters are evaluated from non-isothermal TG curves by the application of the Arrhenius equation

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\phi} e^{-E/RT} dT$$

The usual mechanism-non-invoking kinetic equations are merely extensions of those used in homogenous kinetics, wherein it is assumed that $f(\alpha) = (1 - \alpha)^n$. In contrast, mechanism-invoking kinetic studies are based on the assumption that the form of $f(\alpha)$ depends on the reaction mechanism. A series of $f(\alpha)$ forms are proposed and the

TABLE 1

MECHANISTIC EQUATIONS

Eqn. No.	*Form of g(α)*	*Rate-controlling process*
1	α^2	One-dimensional diffusion
2	$\alpha + (1 - \alpha) \ln (1 - \alpha)$	Two-dimensional diffusion
3	$[1 - (1 - \alpha)^{\frac{1}{3}}]^2$	Three-dimensional diffusion, spherical symmetry — Jander equation
4	$(1 - \frac{2}{3}\alpha) - (1 - \alpha)^{\frac{2}{3}}$	Three-dimensional diffusion, spherical symmetry — Ginstling–Brounshtein equation
5	$- \ln (1 - \alpha)$	Random nucleation — one nucleus on each particle
6	$[- \ln (1 - \alpha)]^{\frac{1}{2}}$	Random nucleation — Avrami equation I
7	$[- \ln (1 - \alpha)]^{\frac{1}{3}}$	Random nucleation — Avrami equation II
8	$1 - (1 - \alpha)^{\frac{1}{2}}$	Phase boundary reaction — cylindrical symmetry
9	$1 - (1 - \alpha)^{\frac{1}{3}}$	Phase boundary reaction — spherical symmetry

mechanism is obtained from the one that gives the best representation of the experimental data.

In this study, kinetic parameters are calculated using the integral method. The integral forms of

$$\int_0^\alpha d\alpha/f(\alpha) = g(\alpha)$$

for nine probable reaction mechanisms, listed by Satava[9], are given in Table 1. The Coats–Redfern method[2] was used for solving the exponential integral, as it is one of the best approaches recommended by several authors[10–12].

Using the computer, linear plots of the nine forms of $g(\alpha)/T^2$ vs. $1/T$ were drawn by the method of least squares, and the corresponding correlation coefficients were also evaluated. E and A were calculated in each case from the slope and the intercept, respectively.

RESULTS AND DISCUSSION

For the two stages of decomposition, a total of $28 \times 9 = 252$ sets of values of E, A and r were calculated and are presented in Tables 2–5.

Tables 2 and 3 give the kinetic parameters for dehydration of $CaC_2O_4 \cdot H_2O$ to CaC_2O_4, for different heating rates and sample masses, respectively. Tables 4 and 5 give the corresponding values for the decomposition of CaC_2O_4 to $CaCO_3$ (in a nitrogen atmosphere). From these tables it can be readily seen that in almost all cases the correlation coefficients are very close to unity, indicating near-perfect fits. A similar observation was made by earlier workers[8] for the decomposition of $Mg(OH)_2$.

TABLE 2

KINETIC PARAMETERS FOR DIFFERENT HEATING RATES FOR CONVERSION OF $CaC_2O_4 \cdot H_2O$ TO CaC_2O_4 (Sample mass = 5 ± 0.1 mg)

Heating rate (°C min^{-1})		*E(kJ mole^{-1}), A(sec^{-1}) and r for mechanistic equations (1–9)*								
		1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
1	*E*	386.9	425.1	475.7	441.6	262.4	127.8	82.95	222.0	234.5
	A	1.86×10^{46}	9.86×10^{50}	9.65×10^{56}	3.24×10^{52}	6.33×10^{30}	2.64×10^{13}	3.59×10^{7}	1.48×10^{25}	4.36×10^{28}
	r	0.9816	0.9893	0.9953	0.9919	0.9968	0.9966	0.9964	0.9928	0.9952
2	*E*	258.4	281.7	311.9	291.6	169.0	81.1	51.8	145.1	152.5
	A	4.82×10^{29}	3.0×10^{32}	6.47×10^{35}	1.35×10^{33}	6.05×10^{18}	2.95×10^{7}	4.24×10^{3}	1.98×10^{15}	1.29×10^{16}
	r	0.9846	0.9913	0.9964	0.9935	0.9975	0.9973	0.9971	0.9942	0.9962
5	*E*	188.8	205.6	227.2	212.7	121.9	57.47	36.01	104.8	110.1
	A	4.99×10^{20}	4.22×10^{22}	6.53×10^{24}	8.04×10^{22}	6.02×10^{12}	3.95×10^{4}	6.34×10^{1}	1.61×10^{10}	5.50×10^{10}
	r	0.9894	0.9949	0.9983	0.9985	0.9979	0.9977	0.9974	0.9970	0.9982
10	*E*	182.9	199.8	221.9	207.1	119.5	56.15	35.05	101.9	107.4
	A	2.41×10^{19}	1.79×10^{21}	2.59×10^{23}	3.32×10^{21}	1.60×10^{12}	2.76×10^{4}	6.12×10^{1}	4.40×10^{9}	1.48×10^{10}
	r	0.9899	0.9953	0.9984	0.9987	0.9971	0.9968	0.9964	0.9973	0.9983
20	*E*	163.7	178.1	196.6	184.2	104.7	48.72	30.06	90.10	94.65
	A	9.47×10^{16}	3.17×10^{18}	1.53×10^{20}	4.11×10^{18}	2.76×10^{10}	4.78×10^{3}	2.31×10^{1}	1.84×10^{8}	4.72×10^{8}
	r	0.9919	0.9964	0.9987	0.9976	0.9972	0.9968	0.9963	0.9979	0.9986
50	*E*	152.4	165.9	183.3	171.6	97.29	44.85	27.37	83.58	87.85
	A	1.52×10^{15}	3.48×10^{16}	1.01×10^{18}	3.82×10^{16}	2.47×10^{9}	2.11×10^{3}	1.75×10^{1}	2.49×10^{7}	5.62×10^{7}
	r	0.9917	0.9958	0.9981	0.9970	0.9971	0.9967	0.9961	0.9972	0.9980
100	*E*	132.0	142.8	156.4	147.3	81.73	36.90	22.07	70.99	74.35
	A	4.16×10^{12}	4.21×10^{13}	4.12×10^{14}	3.25×10^{13}	3.52×10^{7}	3.26×10^{2}	6.18×10^{0}	8.48×10^{5}	1.46×10^{6}
	r	0.9970	0.9982	0.9974	0.9983	0.9932	0.9921	0.9906	0.9980	0.9972

TABLE 3

KINETIC PARAMETERS FOR DIFFERENT SAMPLE MASSES FOR CONVERSION OF $CaC_2O_4 \cdot H_2O$ TO CaC_2O_4 (Heating rate = 10°C min^{-1})

Sample mass (mg)		*E(kJ mole^{-1}), A(sec^{-1}) and r for mechanistic equations (1–9)*								
		1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
1.1	*E*	209.2	228.7	254.0	237.0	137.4	65.27	41.23	117.3	123.6
	A	7.51×10^{23}	1.44×10^{26}	6.99×10^{28}	3.97×10^{26}	1.80×10^{15}	1.03×10^{6}	7.27×10^{2}	1.89×10^{12}	8.56×10^{12}
	r	0.9932	0.9972	0.9985	0.9981	0.9956	0.9952	0.9947	0.9983	0.9985
2.5	*E*	214.1	234.1	260.4	242.7	141.2	67.08	42.39	120.2	126.7
	A	7.47×10^{23}	1.48×10^{26}	8.36×10^{28}	4.22×10^{26}	2.17×10^{15}	1.12×10^{6}	7.64×10^{2}	1.97×10^{12}	9.27×10^{12}
	r	0.9845	0.9914	0.9963	0.9936	0.9966	0.9962	0.9958	0.9942	0.9961
5.1	*E*	182.9	199.8	221.9	207.1	119.5	56.15	35.05	101.9	107.4
	A	2.41×10^{19}	1.79×10^{21}	2.59×10^{23}	3.32×10^{21}	1.60×10^{12}	2.76×10^{4}	6.12×10^{1}	4.40×10^{9}	1.48×10^{10}
	r	0.9899	0.9953	0.9984	0.9987	0.9971	0.9968	0.9964	0.9973	0.9983
7.4	*E*	194.9	215.3	242.7	224.3	132.9	62.85	39.49	111.0	117.7
	A	5.83×10^{20}	1.11×10^{23}	6.81×10^{25}	3.26×10^{23}	6.32×10^{13}	1.80×10^{5}	2.18×10^{2}	5.14×10^{10}	2.48×10^{11}
	r	0.9930	0.9975	0.9990	0.9986	0.9956	0.9951	0.9946	0.9988	0.9990
10.0	*E*	166.1	184.0	208.2	191.8	114.0	53.36	33.14	94.48	100.4
	A	1.28×10^{17}	1.17×10^{19}	2.87×10^{21}	2.53×10^{19}	2.35×10^{11}	1.02×10^{4}	3.09×10^{1}	3.85×10^{8}	1.48×10^{9}
	r	0.9928	0.9975	0.9990	0.9987	0.9946	0.9940	0.9931	0.9989	0.9989
15.0	*E*	157.2	171.0	189.0	176.9	100.8	46.74	28.73	86.43	90.87
	A	6.76×10^{15}	1.92×10^{17}	8.10×10^{18}	2.38×10^{17}	4.18×10^{9}	1.29×10^{3}	7.59	3.04×10^{7}	7.54×10^{7}
	r	0.9904	0.9959	0.9990	0.9972	0.9974	0.9970	0.9966	0.9978	0.9988
20.2	*E*	153.4	167.5	185.4	173.4	98.62	45.58	27.90	84.57	88.97
	A	9.67×10^{14}	2.78×10^{16}	1.01×10^{18}	3.30×10^{16}	1.26×10^{9}	6.86×10^{2}	4.90	1.08×10^{7}	2.57×10^{7}
	r	0.9926	0.9968	0.9991	0.9980	0.9982	0.9980	0.9976	0.9983	0.9991

TABLE 4

KINETIC PARAMETERS FOR DIFFERENT HEATING RATES FOR DECOMPOSITION OF CaC_2O_4 TO $CaCO_3$ (Original sample mass = 5 ± 0.1 mg)

Heating rate (°C min^{-1})		*E(kJ mole^{-1}), A(sec^{-1}) and r for mechanistic equations (1–9)*								
		1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
1	*E*	408.7	451.7	508.1	470.2	279.2	133.8	85.33	234.4	248.3
	A	8.47×10^{26}	9.57×10^{29}	5.10×10^{33}	5.77×10^{30}	4.82×10^{17}	4.45×10^{6}	7.92×10^{2}	7.44×10^{13}	6.09×10^{14}
	r	0.9915	0.9963	0.9996	0.9979	0.9994	0.9994	0.9993	0.9985	0.9996
2	*E*	459.5	502.1	557.8	520.3	303.4	145.7	93.14	259.2	272.9
	A	5.55×10^{29}	4.42×10^{32}	1.45×10^{36}	2.28×10^{33}	8.90×10^{18}	2.72×10^{7}	3.34×10^{3}	2.03×10^{15}	1.47×10^{16}
	r	0.9915	0.9963	0.9997	0.9979	0.9994	0.9993	0.9993	0.9985	0.9996
5	*E*	457.7	507.4	573.0	528.8	316.4	152.1	97.26	264.2	280.3
	A	1.76×10^{29}	3.79×10^{32}	5.07×10^{36}	3.08×10^{33}	5.70×10^{19}	1.08×10^{8}	1.13×10^{4}	4.17×10^{15}	4.28×10^{16}
	r	0.9917	0.9969	0.9999	0.9985	0.9986	0.9985	0.9984	0.9990	0.9999
10	*E*	453.3	490.4	537.3	505.8	287.9	137.8	87.71	250.9	262.5
	A	6.09×10^{28}	1.54×10^{31}	8.80×10^{33}	4.51×10^{31}	5.31×10^{17}	1.41×10^{7}	3.55×10^{3}	5.17×10^{14}	2.44×10^{15}
	r	0.9987	0.9998	0.9984	0.9997	0.9942	0.9937	0.9932	0.9995	0.9985
20	*E*	426.8	462.9	508.8	478.0	273.1	130.3	82.75	236.9	248.2
	A	1.14×10^{27}	2.39×10^{29}	1.12×10^{32}	6.54×10^{29}	7.43×10^{16}	7.22×10^{6}	2.82×10^{3}	8.39×10^{13}	3.76×10^{14}
	r	0.9984	0.9975	0.9939	0.9966	0.9871	0.9860	0.9847	0.9958	0.9937
50	*E*	418.8	452.6	496.6	467.0	266.1	126.7	80.20	231.1	241.9
	A	1.36×10^{26}	1.75×10^{28}	5.17×10^{30}	4.08×10^{28}	1.99×10^{18}	5.71×10^{6}	3.20×10^{3}	3.08×10^{13}	1.24×10^{14}
	r	0.9951	0.9975	0.9983	0.9981	0.9961	0.9957	0.9953	0.9982	0.9982
100	*E*	439.2	475.9	522.8	491.3	280.3	133.6	84.68	243.3	254.8
	A	1.07×10^{27}	1.86×10^{29}	6.94×10^{31}	4.73×10^{29}	1.12×10^{17}	1.91×10^{7}	8.98×10^{3}	1.50×10^{14}	6.38×10^{14}
	r	0.9950	0.9979	0.9990	0.9986	0.9972	0.9969	0.9967	0.9988	0.9990

TABLE 5

KINETIC PARAMETERS FOR DIFFERENT SAMPLE MASSES FOR DECOMPOSITION OF CaC_2O_4 TO $CaCO_3$ (Heating rate = 10°C min^{-1})

Sample mass (mg)		*E(kJ mole^{-1}), A(sec^{-1}) and r for mechanistic equations (1-9)*								
		1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
1.1	*E*	402.2	438.6	485.3	453.9	262.0	125.0	79.28	225.1	236.6
	A	9.36×10^{25}	2.48×10^{28}	1.67×10^{31}	7.64×10^{28}	2.54×10^{16}	3.02×10^{6}	1.26×10^{3}	2.11×10^{13}	1.04×10^{14}
	r	0.9986	0.9992	0.9973	0.9989	0.9922	0.9915	0.9907	0.9985	0.9972
2.5	*E*	387.9	420.6	461.9	434.1	247.3	117.6	74.34	214.7	224.9
	A	5.53×10^{24}	7.64×10^{26}	2.04×10^{29}	1.74×10^{27}	1.61×10^{15}	7.36×10^{5}	4.83×10^{2}	2.85×10^{12}	1.11×10^{13}
	r	0.9986	0.9981	0.9950	0.9974	0.9887	0.9876	0.9864	0.9967	0.9948
5.1	*E*	453.3	490.4	537.3	505.8	287.9	137.8	87.71	250.9	262.9
	A	6.09×10^{28}	1.54×10^{31}	8.80×10^{33}	4.51×10^{31}	5.31×10^{17}	1.41×10^{7}	3.55×10^{3}	5.17×10^{14}	2.44×10^{15}
	r	0.9987	0.9998	0.9985	0.9997	0.9942	0.9937	0.9932	0.9995	0.9985
7.4	*E*	413.1	446.4	487.9	460.1	260.1	123.9	78.52	227.6	237.8
	A	1.38×10^{26}	1.93×10^{28}	4.72×10^{30}	4.29×10^{28}	7.30×10^{15}	1.58×10^{6}	8.10×10^{2}	1.42×10^{13}	5.43×10^{13}
	r	0.9987	0.9982	0.9953	0.9975	0.9896	0.9886	0.9876	0.9968	0.9950
10.0	*E*	423.0	461.3	510.1	477.3	275.4	131.5	83.54	236.8	248.9
	A	5.07×10^{26}	1.56×10^{29}	1.23×10^{32}	5.06×10^{29}	7.41×10^{16}	5.14×10^{6}	1.79×10^{3}	5.49×10^{13}	2.81×10^{14}
	r	0.9973	0.9991	0.9986	0.9993	0.9948	0.9943	0.9938	0.9992	0.9985
15.0	*E*	382.6	414.5	454.9	427.8	243.1	115.4	72.79	211.3	221.2
	A	6.39×10^{23}	7.01×10^{25}	1.39×10^{28}	1.45×10^{26}	3.48×10^{14}	3.33×10^{5}	2.80×10^{2}	7.80×10^{11}	2.83×10^{12}
	r	0.9981	0.9979	0.9953	0.9973	0.9897	0.9887	0.9876	0.9967	0.9951
20.2	*E*	388.9	425.6	473.7	441.3	257.1	122.3	77.38	218.8	230.6
	A	1.40×10^{24}	3.29×10^{26}	2.26×10^{29}	1.01×10^{27}	2.99×10^{15}	9.96×10^{5}	5.87×10^{2}	2.34×10^{12}	1.15×10^{13}
	r	0.9979	0.9991	0.9975	0.9990	0.9919	0.9911	0.9903	0.9987	0.9934

TABLE 6

KINETIC PARAMETERS FROM COATS-REDFERN AND MECHANISTIC EQUATIONS FOR DIFFERENT HEATING RATES AND SAMPLE MASSES FOR THE CONVERSION OF $CaC_2O_4 \cdot H_2O$ TO CaC_2O_4

Heating rate (°C min^{-1})	*Kinetic parameters using equations:*				*Sample mass* (mg)	*Kinetic parameters using equations:*			
	Coats–Redfern		*Mechanistic Equation No. 9*			*Coats–Redfern*		*Mechanistic Equation No. 9*	
	E ($kJ\ mole^{-1}$)	*A* (sec^{-1})	*E* ($kJ\ mole^{-1}$)	*A* (sec^{-1})		*E* ($kJ\ mole^{-1}$)	*A* (sec^{-1})	*E* ($kJ\ mole^{-1}$)	*A* (sec^{-1})
1	233.2	8.84×10^{26}	234.5	4.36×10^{28}	1.1	122.9	2.11×10^{13}	123.6	8.56×10^{12}
2	151.8	3.07×10^{16}	152.5	1.29×10^{16}	2.5	126.0	2.27×10^{13}	126.7	9.27×10^{12}
5	109.6	1.39×10^{11}	110.1	5.50×10^{10}	5.1	106.8	3.75×10^{10}	107.4	1.48×10^{10}
10	106.8	3.75×10^{10}	107.4	1.48×10^{10}	7.4	117.0	6.06×10^{11}	117.7	2.48×10^{11}
20	94.2	1.23×10^{9}	94.65	4.72×10^{8}	10.0	99.8	3.71×10^{9}	100.4	1.48×10^{9}
50	87.4	1.49×10^{8}	87.85	5.62×10^{7}	15.0	90.4	1.96×10^{8}	90.87	7.54×10^{7}
100	74.0	3.98×10^{6}	74.35	1.46×10^{6}	20.2	88.5	6.76×10^{7}	88.97	2.57×10^{7}

TABLE 7

KINETIC PARAMETERS FROM COATS–REDFERN AND MECHANISTIC EQUATIONS FOR DIFFERENT HEATING RATES AND SAMPLE MASSES FOR THE DECOMPOSITION OF CaC_2O_4 TO $CaCO_3$

Heating rate (°C min^{-1})	*Kinetic parameters using equations:*				*Sample mass (mg)*	*Kinetic parameters using equations:*			
	Coats–Redfern		*Mechanistic Equation No. 8*			*Coats–Redfern*		*Mechanistic Equation No. 8*	
	E (kJ mole^{-1})	*A (sec^{-1})*	*E (kJ mole^{-1})*	*A (sec^{-1})*		*E (kJ mole^{-1})*	*A (sec^{-1})*	*E (kJ mole^{-1})*	*A (sec^{-1})*
1	234.4	1.49×10^{14}	234.4	7.44×10^{13}	1.1	225.1	4.22×10^{13}	225.1	2.11×10^{13}
2	259.2	4.05×10^{15}	259.2	2.03×10^{15}	2.5	214.7	5.70×10^{12}	214.7	2.85×10^{12}
5	264.2	8.34×10^{15}	264.2	4.17×10^{15}	5.1	250.9	1.04×10^{15}	250.9	5.17×10^{14}
10	250.9	1.04×10^{15}	250.9	5.17×10^{14}	7.4	227.6	2.84×10^{13}	227.6	1.42×10^{13}
20	236.9	1.68×10^{14}	236.9	8.39×10^{13}	10.0	236.8	1.10×10^{14}	236.8	5.49×10^{13}
50	231.1	6.17×10^{13}	231.1	3.08×10^{13}	15.0	211.1	1.56×10^{12}	211.3	7.80×10^{11}
100	243.3	3.00×10^{14}	243.3	1.50×10^{14}	20.2	218.8	4.67×10^{12}	218.8	2.34×10^{12}

A choice of the probable mechanism from the best-fit curve, thus, becomes difficult. In such instances the above authors[8] have chosen the function $g(\alpha)$ which yielded kinetic parameters in agreement with those obtained by the numerical method proposed by them. In the present case a comparison with the values obtained by the Coats–Redfern method will be more appropriate as the same method was used here for solving the exponential integral. The kinetic parameters calculated for the same experimental data with the Coats–Redfern equation are taken from our earlier work[1], and the comparison with the mechanistic equation which gives the nearest values of E and A, is given in Tables 6 and 7.

From these tables the following observations emerge.

(i) Both stages of decomposition follow the mechanism of phase boundary reaction. The dehydration of $CaC_2O_4 \cdot H_2O$ to CaC_2O_4 assumes spherical symmetry (eqn. 9, Table 1), while the decomposition of CaC_2O_4 to $CaCO_3$ follows cylindrical symmetry (eqn. 8, Table 1). The kinetic parameters calculated from the mechanistic equation for the decomposition of CaC_2O_4 to $CaCO_3$ are not appreciably affected by either heating rate or sample mass. For the conversion of $CaC_2O_4 \cdot H_2O$ to CaC_2O_4, the 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 reported by us earlier[1], concerning the kinetic parameters obtained from mechanism-non-invoking equations.

As in our earlier work[1], a statistical analysis was carried out to establish correlations of kinetic parameters with heating rate and sample mass. It was found that the curves of E vs. heating rate and log A vs. heating rate could be best fitted to rectangular hyperbolae following the equations

$$E = 82.866 + 149.62/\phi$$
$$\log_{10}A = 6.9504 + 21.062/\phi$$

The reliability of the fits was evaluated by the F-test and the Fisher constants worked out to be 353.9 and 335.5, respectively, corresponding to a confidence level of above 99% in both cases.

The best-fit curves for kinetic parameters and sample mass are parabolae, following the equations

$$E = 130.01 - 3.3388\, m + 0.0614\, m^2$$
$$\log_{10}A = 13.719 - 0.5441\, m + 0.0113\, m^2$$

The Fisher constants are 13.96 and 20.34, respectively, corresponding to a confidence level of above 95 and 99%, respectively.

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