Thermochimica Acta, 98 (1986) 221–236
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION KINETICS. PART XIV. KINETICS AND MECHANISM OF ISOTHERMAL DECOMPOSITION OF CALCIUM OXALATE MONOHYDRATE AND CORRELATION WITH SAMPLE MASS

K.N. NINAN

Analytical and Spectroscopy Division, Vikram Sarabhai Space Centre,
Trivandrum 695 022 (India)

(Received 6 August 1985)

ABSTRACT

The mechanisms of the first two stages of the thermal decomposition of calcium oxalate monohydrate have been established from isothermal mass-loss studies. For both stages, the rate-controlling process is phase boundary reaction with cylindrical symmetry. The isothermal kinetic parameters computed from the mechanism-based equation show the same trend as those from the mechanism-non-invoking approach. For the decomposition of calcium oxalate to calcium carbonate and carbon monoxide, the kinetic constants are not appreciably affected by sample mass, while for the dehydration of calcium oxalate monohydrate, they show a systematic decrease with increase in sample mass. The bestfit correlations have been represented as:

E (or $\log A$) $= C_1 - C_2 m + C_3 m^2$

INTRODUCTION

In an earlier publication [1], the kinetic parameters (E and A) for the dehydration of calcium oxalate monohydrate and for the decomposition of the resultant calcium oxalate to calcium carbonate and carbon monoxide were evaluated from isothermal mass-loss measurements using the general mechanism-non-invoking integral equation. The isothermal experiments were carried out with seven sample masses. It was observed that the kinetic parameters were not appreciably affected for the decomposition of calcium oxalate; whereas for the dehydration reaction, they showed a systematic decrease with increasing sample mass and the values of E and $\log A$ were mathematically correlated to sample mass.

In another publication [2] it was pointed out that the mechanism of a thermal decomposition reaction cannot be evaluated by curve-fitting the TG data alone, since almost all the mechanism-based equations, which were tried out, gave linear plots for the first two stages of thermal decomposition of

0040-6031/86/$03.50

calcium oxalate monohydrate. From a theoretical analysis using the Avrami–Erofeev equation, Criado and Morales [3] came to the same conclusion and pointed out that at least one isothermal experiment is required to assign the proper reaction mechanism. This was later proven experimentally by Dharwadkar et al. [4] from a study of the thermal decomposition of cadmium carbonate. It was therefore also considered worthwhile to analyse the isothermal mass-loss data [1] using mechanism-based equations. The results obtained are presented in this communication which forms the last part of one aspect of these studies using the model compound, calcium oxalate monohydrate. The concluding remarks given in this paper also cover certain aspects of earlier publications [1,2,5,6].

EXPERIMENTAL DATA

Details regarding the sample, instruments and experimental procedure are given in an earlier publication [1]. Seven sample masses (1.1, 2.5, 5.0, 7.5, 10, 15 and 20 ± 0.1 mg) were employed in the study and a total of 67 mass-loss curves were recorded for the first two stages of isothermal decomposition of calcium oxalate monohydrate (33 for the dehydration step and 34 for the decomposition of the resultant calcium oxalate to calcium carbonate and carbon monoxide in a nitrogen atmosphere). The α–t values obtained from those curves are used for the present calculations.

MATHEMATICAL TREATMENT OF DATA

The basic kinetic equation for isothermal experiments is given by:

$$\frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = k\,\mathrm{d}t$$

the integrated form of which can be represented as:

$$\mathrm{g}(\alpha) = kt$$

Mechanism-based kinetic studies are based on the assumption that the form of $\mathrm{f}(\alpha)$ or $\mathrm{g}(\alpha)$ depends on the reaction mechanism. The $\mathrm{g}(\alpha)$ forms corresponding to nine probable reaction mechanisms have been proposed [7] and the mechanism is obtained from that which gives the best representation of the experimental data. The forms of $\mathrm{g}(\alpha)$ corresponding to the rate-controlling processes for the nine reaction mechanisms (numbered 1 to 9) are given in Table 1.

Using the 69 sets of α–t values corresponding to the first two stages of thermal decomposition of calcium oxalate monohydrate, linear plots of the nine forms of $\mathrm{g}(\alpha)$ versus t were made by the method of least squares, and

TABLE 1

Mechanism-based 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	$[1-(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion, spherical symmetry, Jander equation
4	$(1-\frac{2}{3}\alpha)-(1-\alpha)^{2/3}$	Three-dimensional diffusion, spherical symmetry, Ginstling–Brounshtein equation
5	$-\ln(1-\alpha)$	Random nucleation, one nucleus on each particle
6	$[-\ln(1-\alpha)]^{1/2}$	Random nucleation, Avrami eqn. I
7	$[-\ln(1-\alpha)]^{1/3}$	Random nucleation, Avrami eqn. II
8	$1-(1-\alpha)^{1/2}$	Phase boundary reaction, cylindrical symmetry
9	$1-(1-\alpha)^{1/3}$	Phase boundary reaction, spherical symmetry

the corresponding correlation coefficients were also calculated. The rate constant, k, was calculated from the slope in each case. From the Arrhenius equation:

$$\ln k = \ln A - \frac{E}{RT}$$

the plot of $\ln k$ versus $1/T$ gives a straight line with a slope of $-E/R$ and intercept of $\ln A$.

RESULTS AND DISCUSSION

For the dehydration step (Stage I) there are a total of $33 \times 9 = 297$ linear plots of g(α) versus t. The values of rate constant, k, and correlation coefficient, r, for these plots are given in Tables 2–8 (corresponding to the seven sample masses). Similarly, for the decomposition of calcium oxalate to calcium carbonate and carbon monoxide (Stage II), there are $34 \times 9 = 306$ linear plots of g(α) versus t, and the computed values of k and r for these plots are given in Tables 9–15.

Choice of reaction mechanism

Since the reaction mechanism has to be inferred from the best linear curves of g(α) versus t, the 297 curves obtained with the nine mechanism-based equations for Stage I and the 306 corresponding curves for Stage II have been classified on the basis of their correlation coefficients and are tabulated in Table 16. The curves have been classified into three categories having correlation coefficients above 0.999, between 0.999 and 0.990, and

TABLE 2

Rate constants at different temperatures for dehydration of $CaC_2O_4 \cdot H_2O$ with mechanism-based equations (sample mass =1.1 mg)

Eqn. No.	383 K		393 K		402 K		412 K		418 K	
	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r
1	0.1008×10^{-3}	0.9978	0.2603×10^{-3}	0.9777	0.9848×10^{-3}	0.9913	0.2212×10^{-2}	0.9814	0.4090×10^{-2}	0.9807
2	0.8291×10^{-4}	0.9881	0.2209×10^{-3}	0.9475	0.8133×10^{-3}	0.9718	0.1804×10^{-2}	0.9546	0.3327×10^{-2}	0.9538
3	0.3548×10^{-4}	0.9527	0.1035×10^{-3}	0.8747	0.3517×10^{-3}	0.9211	0.7782×10^{-3}	0.8889	0.1416×10^{-2}	0.8921
4	0.2280×10^{-4}	0.9788	0.6230×10^{-4}	0.9268	0.2243×10^{-3}	0.9577	0.4964×10^{-3}	0.9361	0.9122×10^{-3}	0.9360
5	0.2726×10^{-3}	0.9878	0.7796×10^{-3}	0.9275	0.2676×10^{-2}	0.9663	0.6076×10^{-2}	0.9470	0.1096×10^{-1}	0.9474
6	0.1459×10^{-3}	0.9930	0.3946×10^{-3}	0.9886	0.1396×10^{-2}	0.9969	0.3282×10^{-2}	0.9943	0.5812×10^{-2}	0.9928
7	0.1031×10^{-3}	0.9790	0.2751×10^{-3}	0.9949	0.9737×10^{-3}	0.9953	0.2330×10^{-2}	0.9959	0.4065×10^{-2}	0.9979
8	0.7816×10^{-4}	0.9990	0.2063×10^{-3}	0.9894	0.7559×10^{-3}	0.9980	0.1741×10^{-2}	0.9936	0.3153×10^{-2}	0.9915
9	0.6200×10^{-4}	0.9994	0.1669×10^{-3}	0.9761	0.6022×10^{-3}	0.9921	0.1378×10^{-2}	0.9839	0.2497×10^{-2}	0.9818

TABLE 3

Rate constants at different temperature for dehydration of $CaC_2O_4 \cdot H_2O$ with mechanism-based equations (sample mass = 2.5 mg)

Eqn. No.	403 K		412 K		423 K		433 K		437 K	
	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r
1	0.4735×10^{-3}	0.9980	0.1267×10^{-3}	0.9925	0.4557×10^{-2}	0.9892	0.6462×10^{-2}	0.9738	0.1319×10^{-1}	0.9876
2	0.3799×10^{-3}	0.9881	0.1039×10^{-2}	0.9820	0.3811×10^{-2}	0.9704	0.5149×10^{-2}	0.9483	0.1093×10^{-1}	0.9682
3	0.1512×10^{-3}	0.9591	0.4323×10^{-3}	0.9547	0.1644×10^{-2}	0.9267	0.2075×10^{-2}	0.9005	0.4599×10^{-2}	0.9266
4	0.1023×10^{-3}	0.9802	0.2837×10^{-3}	0.9744	0.1053×10^{-2}	0.9578	0.1390×10^{-2}	0.9338	0.2996×10^{-2}	0.9560
5	0.1157×10^{-2}	0.9883	0.3289×10^{-2}	0.9861	0.1210×10^{-1}	0.9638	0.1648×10^{-1}	0.9551	0.3392×10^{-1}	0.9629
6	0.6084×10^{-3}	0.9980	0.1736×10^{-2}	0.9998	0.6012×10^{-2}	0.9944	0.9151×10^{-2}	0.9941	0.1691×10^{-1}	0.9925
7	0.4196×10^{-3}	0.9942	0.1210×10^{-2}	0.9962	0.4081×10^{-2}	0.9983	0.6503×10^{-2}	0.9984	0.1145×10^{-1}	0.9974
8	0.3445×10^{-3}	0.9995	0.9547×10^{-3}	0.9990	0.3358×10^{-2}	0.9946	0.4972×10^{-2}	0.9894	0.9573×10^{-2}	0.9925
9	0.2713×10^{-3}	0.9984	0.7563×10^{-3}	0.9972	0.2697×10^{-2}	0.9877	0.3887×10^{-2}	0.9810	0.7658×10^{-2}	0.9854

TABLE 4

Rate constants at different temperatures for dehydration of $CaC_2O_4 \cdot H_2O$ with mechanism-based equations (sample mass = 5 mg)

Eqn. No.	381 K		389 K		399 K		408 K		420 K	
	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r
1	0.6789×10^{-4}	0.9852	0.1174×10^{-3}	0.9903	0.4646×10^{-3}	0.9875	0.8370×10^{-3}	0.9796	0.1902×10^{-2}	0.9840
2	0.5482×10^{-4}	0.9666	0.9373×10^{-4}	0.9736	0.3716×10^{-3}	0.9689	0.6642×10^{-3}	0.9546	0.1496×10^{-2}	0.9605
3	0.2261×10^{-4}	0.9265	0.3766×10^{-4}	0.9346	0.1509×10^{-3}	0.9285	0.2675×10^{-3}	0.9057	0.5935×10^{-3}	0.9096
4	0.1491×10^{-4}	0.9549	0.2529×10^{-4}	0.9625	0.1006×10^{-3}	0.9572	0.1792×10^{-3}	0.9399	0.4017×10^{-3}	0.9456
5	0.1768×10^{-3}	0.9725	0.2980×10^{-3}	0.9787	0.1194×10^{-2}	0.9739	0.2146×10^{-2}	0.9626	0.4810×10^{-2}	0.9674
6	0.9676×10^{-4}	0.9990	0.1664×10^{-3}	0.9981	0.6623×10^{-3}	0.9980	0.1210×10^{-2}	0.9969	0.2747×10^{-2}	0.9978
7	0.6864×10^{-4}	0.9962	0.1189×10^{-3}	0.9919	0.4715×10^{-3}	0.9948	0.8669×10^{-3}	0.9961	0.1976×10^{-2}	0.9948
8	0.5228×10^{-4}	0.9973	0.8999×10^{-4}	0.9991	0.3583×10^{-3}	0.9978	0.6513×10^{-3}	0.9946	0.1478×10^{-2}	0.9969
9	0.4112×10^{-4}	0.9923	0.7038×10^{-4}	0.9955	0.2806×10^{-3}	0.9930	0.5080×10^{-3}	0.9875	0.1149×10^{-2}	0.9909

TABLE 5

Rate constants at different temperatures for dehydration of $CaC_2O_4 \cdot H_2O$ with mechanism-based equations (sample mass = 7.5 mg)

Eqn. No.	388 K		402 K		417 K		424 K		434 K	
	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r
1	0.9300×10^{-4}	0.9950	0.2827×10^{-3}	0.9926	0.1115×10^{-2}	0.9863	0.1488×10^{-2}	0.9841	0.3844×10^{-2}	0.9823
2	0.7129×10^{-4}	0.9829	0.2303×10^{-3}	0.9743	0.8927×10^{-3}	0.9627	0.1216×10^{-2}	0.9583	0.3127×10^{-2}	0.9588
3	0.2683×10^{-4}	0.9560	0.9644×10^{-4}	0.9305	0.3647×10^{-3}	0.9114	0.5190×10^{-3}	0.8994	0.1368×10^{-2}	0.9060
4	0.1884×10^{-4}	0.9750	0.6293×10^{-4}	0.9617	0.2419×10^{-3}	0.9476	0.3340×10^{-3}	0.9412	0.8744×10^{-3}	0.9435
5	0.2254×10^{-3}	0.9920	0.7459×10^{-3}	0.9760	0.2889×10^{-2}	0.9669	0.4024×10^{-2}	0.9555	0.1050×10^{-1}	0.9569
6	0.1341×10^{-3}	0.9943	0.4031×10^{-3}	0.9962	0.1605×10^{-2}	0.9972	0.2177×10^{-2}	0.9954	0.5626×10^{-2}	0.9962
7	0.9755×10^{-4}	0.9835	0.2851×10^{-3}	0.9878	0.1146×10^{-2}	0.9933	0.1546×10^{-2}	0.9937	0.3986×10^{-2}	0.9965
8	0.7236×10^{-4}	0.9997	0.2174×10^{-3}	0.9993	0.8641×10^{-3}	0.9973	0.1160×10^{-2}	0.9953	0.2995×10^{-2}	0.9944
9	0.5556×10^{-4}	0.9993	0.1717×10^{-3}	0.9955	0.6769×10^{-3}	0.9912	0.9179×10^{-3}	0.9870	0.2378×10^{-2}	0.9863

TABLE 6

Rate constants at different temperatures for dehydration of $CaC_2O_4 \cdot H_2O$ with mechanism-based equations (sample mass = 10 mg)

Eqn.	391 K		413 K		423 K		430 K	
No.	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r
1	0.1325×10^{-3}	0.9889	0.7057×10^{-3}	0.9931	0.1149×10^{-2}	0.9868	0.2202×10^{-2}	0.9888
2	0.1089×10^{-3}	0.9701	0.5811×10^{-3}	0.9779	0.9189×10^{-3}	0.9678	0.1811×10^{-2}	0.9691
3	0.4613×10^{-4}	0.9268	0.2451×10^{-3}	0.9393	0.3715×10^{-3}	0.9279	0.7691×10^{-3}	0.9235
4	0.2988×10^{-4}	0.9576	0.1593×10^{-3}	0.9670	0.2484×10^{-3}	0.9561	0.4971×10^{-3}	0.9560
5	0.3535×10^{-3}	0.9711	0.1856×10^{-2}	0.9773	0.2926×10^{-2}	0.9729	0.5811×10^{-2}	0.9652
6	0.1893×10^{-3}	0.9980	0.9712×10^{-3}	0.9987	0.1606×10^{-2}	0.9984	0.2992×10^{-2}	0.9961
7	0.1337×10^{-3}	0.9945	0.6757×10^{-3}	0.9960	0.1135×10^{-2}	0.9973	0.2062×10^{-2}	0.9986
8	0.1019×10^{-3}	0.9980	0.5325×10^{-3}	0.9991	0.8775×10^{-3}	0.9972	0.1653×10^{-2}	0.9959
9	0.8076×10^{-4}	0.9927	0.4231×10^{-3}	0.9953	0.6876×10^{-3}	0.9921	0.1316×10^{-2}	0.9893

TABLE 7

Rate constants at different temperatures for dehydration of $CaC_2O_4 \cdot H_2O$ with mechanism-based equations (sample mass = 15 mg)

Eqn.	392 K		412 K		422 K		442 K	
No.	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r
1	0.9233×10^{-4}	0.9970	0.3453×10^{-3}	0.9953	0.6711×10^{-3}	0.9920	0.2189×10^{-2}	0.9871
2	0.7673×10^{-4}	0.9885	0.2879×10^{-3}	0.9815	0.5493×10^{-3}	0.9757	0.1785×10^{-2}	0.9623
3	0.3290×10^{-4}	0.9596	0.1257×10^{-3}	0.9381	0.2289×10^{-3}	0.9370	0.7512×10^{-3}	0.9036
4	0.2115×10^{-4}	0.9808	0.7971×10^{-4}	0.9698	0.1500×10^{-3}	0.9646	0.4883×10^{-3}	0.9454
5	0.2475×10^{-3}	0.9900	0.9438×10^{-3}	0.9778	0.1740×10^{-2}	0.9759	0.5724×10^{-2}	0.9545
6	0.1289×10^{-3}	0.9951	0.4861×10^{-3}	0.9977	0.9122×10^{-3}	0.9987	0.2968×10^{-2}	0.9939
7	0.8990×10^{-4}	0.9833	0.3375×10^{-3}	0.9911	0.6337×10^{-3}	0.9973	0.2050×10^{-2}	0.9980
8	0.7011×10^{-4}	0.9993	0.2635×10^{-3}	0.9999	0.5034×10^{-3}	0.9985	0.1642×10^{-2}	0.9940
9	0.5591×10^{-4}	0.9997	0.2108×10^{-3}	0.9972	0.3991×10^{-3}	0.9942	0.1304×10^{-2}	0.9855

TABLE 8

Rate constants at different temperatures for dehydration of $CaC_2O_4 \cdot H_2O$ with mechanism-based equations (sample mass = 20 mg)

Eqn.	392 K		408 K		412 K		418 K		431 K	
No.	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r
1	0.1487×10^{-3}	0.9901	0.5024×10^{-3}	0.9851	0.4195×10^{-3}	0.9937	0.6675×10^{-3}	0.9897	0.1541×10^{-2}	0.9899
2	0.1212×10^{-3}	0.9709	0.3967×10^{-3}	0.9624	0.3431×10^{-3}	0.9799	0.5505×10^{-3}	0.9705	0.1294×10^{-2}	0.9722
3	0.5081×10^{-4}	0.9231	0.1580×10^{-3}	0.9142	0.1437×10^{-3}	0.9413	0.2335×10^{-3}	0.9256	0.5755×10^{-3}	0.9264
4	0.3313×10^{-4}	0.9574	0.1067×10^{-3}	0.9482	0.9380×10^{-4}	0.9693	0.1512×10^{-3}	0.9575	0.3602×10^{-3}	0.9594
5	0.3923×10^{-3}	0.9701	0.1272×10^{-2}	0.9693	0.1099×10^{-2}	0.9807	0.1766×10^{-2}	0.9687	0.4298×10^{-2}	0.9666
6	0.2110×10^{-3}	0.9977	0.7182×10^{-3}	0.9981	0.5817×10^{-3}	0.9990	0.9214×10^{-3}	0.9976	0.2177×10^{-2}	0.9976
7	0.1489×10^{-3}	0.9942	0.5139×10^{-3}	0.9955	0.4065×10^{-3}	0.9943	0.6405×10^{-3}	0.9972	0.1501×10^{-2}	0.9980
8	0.1141×10^{-3}	0.9983	0.3886×10^{-3}	0.9972	0.3180×10^{-3}	0.9997	0.5045×10^{-3}	0.9973	0.1180×10^{-2}	0.9975
9	0.9017×10^{-4}	0.9931	0.3026×10^{-3}	0.9915	0.2519×10^{-3}	0.9970	0.4013×10^{-3}	0.9916	0.9480×10^{-3}	0.9916

TABLE 9

Rate constants at different temperatures for decomposition of CaC_2O_4 with mechanism-based equations (original sample mass = 1.1 mg)

Eqn.	693 K		701 K		708 K		722 K	
No.	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r
1	0.7801×10^{-3}	0.9963	0.1337×10^{-2}	0.9923	0.1630×10^{-2}	0.9923	0.3722×10^{-2}	0.9888
2	0.6548×10^{-3}	0.9905	0.1087×10^{-2}	0.9797	0.1347×10^{-2}	0.9789	0.3767×10^{-2}	0.9745
3	0.2825×10^{-3}	0.9643	0.4477×10^{-3}	0.9467	0.5710×10^{-3}	0.9442	0.1301×10^{-2}	0.9393
4	0.1810×10^{-3}	0.9840	0.2958×10^{-3}	0.9705	0.3698×10^{-3}	0.9692	0.8421×10^{-3}	0.9646
5	0.2079×10^{-2}	0.9893	0.3435×10^{-2}	0.9820	0.4313×10^{-2}	0.9799	0.9899×10^{-2}	0.9766
6	0.1042×10^{-2}	0.9988	0.1827×10^{-2}	0.9996	0.2249×10^{-2}	0.9997	0.5222×10^{-2}	0.9995
7	0.7116×10^{-3}	0.9943	0.1276×10^{-2}	0.9972	0.1563×10^{-2}	0.9975	0.3652×10^{-2}	0.9985
8	0.5786×10^{-3}	0.9991	0.1007×10^{-2}	0.9989	0.1232×10^{-2}	0.9989	0.2840×10^{-2}	0.9976
9	0.4645×10^{-3}	0.9990	0.7950×10^{-3}	0.9982	0.9804×10^{-3}	0.9957	0.2255×10^{-2}	0.9937

TABLE 10

Rate constants at different temperatures for decomposition of CaC_2O_4 with mechanism-based equations (original sample mass = 2.5 mg)

Eqn. No.	694 K		706 K		716 K	
	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r
1	0.2325×10^{-3}	0.9945	0.3212×10^{-3}	0.9955	0.6434×10^{-3}	0.9937
2	0.1974×10^{-3}	0.9945	0.2696×10^{-3}	0.9933	0.5432×10^{-3}	0.9913
3	0.8833×10^{-4}	0.9677	0.1185×10^{-3}	0.9670	0.2440×10^{-3}	0.9624
4	0.5513×10^{-4}	0.9890	0.7485×10^{-4}	0.9876	0.1517×10^{-3}	0.9852
5	0.6519×10^{-3}	0.9931	0.8855×10^{-3}	0.9927	0.1823×10^{-2}	0.9905
6	0.3290×10^{-3}	0.9927	0.4548×10^{-3}	0.9936	0.9325×10^{-3}	0.9956
7	0.2273×10^{-3}	0.9788	0.3162×10^{-3}	0.9804	0.6494×10^{-3}	0.9833
8	0.1775×10^{-3}	0.9955	0.2455×10^{-3}	0.9971	0.4980×10^{-3}	0.9975
9	0.1432×10^{-3}	0.9993	0.1968×10^{-3}	0.9998	0.4006×10^{-3}	0.9997
Eqn. No.	725 K		735 K		750 K	
	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r
1	0.1327×10^{-2}	0.9937	0.1721×10^{-2}	0.9941	0.3552×10^{-2}	0.9956
2	0.1134×10^{-2}	0.9864	0.1443×10^{-2}	0.9881	0.3079×10^{-2}	0.9868
3	0.5150×10^{-3}	0.9515	0.6349×10^{-3}	0.9558	0.1437×10^{-2}	0.9471
4	0.3181×10^{-3}	0.9780	0.4006×10^{-3}	0.9804	0.8709×10^{-3}	0.9770
5	0.3758×10^{-2}	0.9820	0.4739×10^{-2}	0.9879	0.1035×10^{-1}	0.9775
6	0.1839×10^{-2}	0.9998	0.2419×10^{-2}	0.9975	0.4936×10^{-2}	0.9994
7	0.1251×10^{-2}	0.9963	0.1675×10^{-2}	0.9878	0.3325×10^{-2}	0.9971
8	0.1003×10^{-2}	0.9991	0.1311×10^{-2}	0.9986	0.2685×10^{-2}	0.9997
9	0.8136×10^{-3}	0.9980	0.1052×10^{-2}	0.9995	0.2197×10^{-2}	0.9975

below 0.990. Equations which gave correlation coefficients below 0.990 were discarded, and the one which gave a maximum number of curves with correlation coefficient above 0.999 was chosen.

Stage I

Referring to Table 16, eqns. (1)–(5) can be directly discarded. Of the remaining four equations, eqn. (8) has given the maximum number of good linear curves (r of 10 curves has a value above 0.999 and of 22 curves is between 0.999 and 0.990) and, therefore, this equation represents the mechanism of the reaction. Thus, the dehydration of calcium oxalate monohydrate is a phase boundary reaction with cylindrical symmetry, following the equation:

$$1-(1-\alpha)^{1/2}=kt$$

This is contrary to the deductions made from our TG studies [2], from which it was inferred that the reaction mechanism is a phase boundary reaction with spherical symmetry (eqn. 9). However, this inference was arbitrary, i.e., by comparison with a mechanism-non-invoking equation.

TABLE 11

Rate constants at different temperatures for decomposition of CaC_2O_4 with mechanism-based equations (original sample mass = 5 mg)

Eqn. No.	695 K		706 K		713 K	
	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r
1	0.1784×10^{-3}	0.9937	0.3403×10^{-3}	0.9908	0.4521×10^{-3}	0.9935
2	0.1482×10^{-3}	0.9908	0.2671×10^{-3}	0.9782	0.3656×10^{-3}	0.9806
3	0.6357×10^{-4}	0.9672	0.1048×10^{-3}	0.9469	0.1499×10^{-3}	0.9473
4	0.4084×10^{-4}	0.9854	0.7151×10^{-4}	0.9695	0.9931×10^{-4}	0.9713
5	0.4783×10^{-3}	0.9935	0.8492×10^{-3}	0.9877	0.1161×10^{-2}	0.9852
6	0.2486×10^{-3}	0.9951	0.4856×10^{-3}	0.9978	0.6255×10^{-3}	0.9990
7	0.1730×10^{-3}	0.9844	0.3490×10^{-3}	0.9889	0.4393×10^{-3}	0.9929
8	0.1354×10^{-3}	0.9967	0.2627×10^{-3}	0.9995	0.3428×10^{-3}	0.9998
9	0.1080×10^{-3}	0.9991	0.2039×10^{-3}	0.9983	0.2700×10^{-3}	0.9980
Eqn. No.	725 K		736 K		750 K	
	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r
1	0.8446×10^{-3}	0.9941	0.1924×10^{-2}	0.9942	0.3044×10^{-2}	0.9884
2	0.6923×10^{-3}	0.9847	0.1581×10^{-2}	0.9827	0.2430×10^{-2}	0.9729
3	0.2900×10^{-3}	0.9544	0.6618×10^{-3}	0.9515	0.9780×10^{-3}	0.9366
4	0.1894×10^{-3}	0.9768	0.4325×10^{-3}	0.9740	0.6561×10^{-3}	0.9626
5	0.2220×10^{-2}	0.9878	0.5027×10^{-2}	0.9849	0.7751×10^{-2}	0.9795
6	0.1190×10^{-2}	0.9977	0.2649×10^{-2}	0.9994	0.4323×10^{-2}	0.9998
7	0.8398×10^{-3}	0.9883	0.1847×10^{-2}	0.9949	0.3082×10^{-2}	0.9965
8	0.6442×10^{-3}	0.9996	0.1452×10^{-2}	0.9997	0.2341×10^{-2}	0.9984
9	0.5099×10^{-3}	0.9990	0.1152×10^{-2}	0.9977	0.1830×10^{-2}	0.9951

Thus, the present studies confirm the views of earlier workers [3,4] that the appropriate reaction mechanism can be inferred only from isothermal studies.

Stage II

Referring to Table 16, eqns. (2)–(5) can be directly discarded. Equations (1) and (7) are also of secondary importance. Out of the remaining three equations, eqn. (8) has given the maximum number of good linear curves (r of 20 curves has a value above 0.999, and of 14 curves is between 0.999 and 0.990), and, therefore, this equation should represent the reaction mechanism. Thus, the decomposition of CaC_2O_4 to $CaCO_3$ and CO is a phase boundary reaction with cylindrical symmetry, following the equation:

$$1-(1-\alpha)^{1/2}=kt$$

The same inference was made from our TG studies [2].

E *and* A *values*

Stage II

From Tables 2–8, seven sets of values of T and k were taken and, using a

TABLE 12

Rate constants at different temperatures for decomposition of CaC_2O_4 with mechanism-based equations (original sample mass = 7.5 mg)

Eqn. No.	690 K		701 K		710 K		721 K		731K	
	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r
1	0.1298×10^{-3}	0.9954	0.2652×10^{-3}	0.9965	0.4426×10^{-3}	0.9955	0.8643×10^{-3}	0.9926	0.1468×10^{-2}	0.9906
2	0.1078×10^{-3}	0.9852	0.2184×10^{-3}	0.9874	0.3681×10^{-3}	0.9877	0.7158×10^{-3}	0.9822	0.1168×10^{-2}	0.9765
3	0.4654×10^{-4}	0.9482	0.9277×10^{-4}	0.9526	0.1588×10^{-3}	0.9588	0.3072×10^{-3}	0.9526	0.4687×10^{-3}	0.9426
4	0.2975×10^{-4}	0.9757	0.5998×10^{-4}	0.9784	0.1016×10^{-3}	0.9803	0.1972×10^{-3}	0.9741	0.3149×10^{-3}	0.9670
5	0.3511×10^{-3}	0.9845	0.7068×10^{-3}	0.9879	0.1197×10^{-2}	0.9893	0.2330×10^{-2}	0.9855	0.3738×10^{-2}	0.9829
6	0.1829×10^{-3}	0.9972	0.3742×10^{-3}	0.9960	0.6243×10^{-3}	0.9972	0.1224×10^{-2}	0.9991	0.2098×10^{-2}	0.9988
7	0.1276×10^{-3}	0.9878	0.2625×10^{-3}	0.9852	0.4354×10^{-3}	0.9880	0.8568×10^{-3}	0.9925	0.1500×10^{-2}	0.9929
8	0.9904×10^{-4}	0.9997	0.2026×10^{-3}	0.9993	0.3383×10^{-3}	0.9992	0.6624×10^{-3}	0.9995	0.1134×10^{-2}	0.9994
9	0.7901×10^{-4}	0.9989	0.1609×10^{-3}	0.9996	0.2698×10^{-3}	0.9994	0.5273×10^{-3}	0.9980	0.8850×10^{-3}	0.9968

TABLE 13

Rate constants at different temperatures for decomposition of CaC_2O_4 with mechanism-based equations (original sample mass =10 mg)

Eqn. No.	690 K		703 K		721 K		723 K	
	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r
1	0.1064×10^{-3}	0.9965	0.3427×10^{-3}	0.9922	0.7623×10^{-3}	0.9941	0.7460×10^{-3}	0.9946
2	0.8969×10^{-4}	0.9898	0.2781×10^{-3}	0.9819	0.6326×10^{-3}	0.9860	0.6251×10^{-3}	0.9899
3	0.3977×10^{-4}	0.9588	0.1145×10^{-3}	0.9524	0.2692×10^{-3}	0.9596	0.2710×10^{-3}	0.9643
4	0.2496×10^{-4}	0.9823	0.7566×10^{-4}	0.9739	0.1740×10^{-3}	0.9790	0.1729×10^{-3}	0.9838
5	0.2946×10^{-3}	0.9875	0.8888×10^{-3}	0.9873	0.2024×10^{-2}	0.9887	0.2004×10^{-2}	0.9904
6	0.1485×10^{-3}	0.9968	0.4846×10^{-3}	0.9989	0.1056×10^{-2}	0.9988	0.1008×10^{-2}	0.9989
7	0.1023×10^{-3}	0.9877	0.3433×10^{-3}	0.9924	0.7350×10^{-3}	0.9922	0.6900×10^{-3}	0.9934
8	0.8073×10^{-4}	0.9994	0.2625×10^{-3}	0.9990	0.5764×10^{-3}	0.9993	0.5572×10^{-3}	0.9985
9	0.6497×10^{-4}	0.9996	0.2067×10^{-3}	0.9980	0.4591×10^{-3}	0.9987	0.4471×10^{-3}	0.9992

TABLE 14

Rate constants at different temperatures for decomposition of CaC_2O_4 with mechanism-based equations (original sample mass =15 mg)

Eqn. No.	708 K		719 K		728 K		732 K		744 K	
	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r
1	0.3800×10^{-3}	0.9923	0.5898×10^{-3}	0.9939	0.1007×10^{-2}	0.9891	0.1210×10^{-2}	0.9962	0.1934×10^{-2}	0.9961
2	0.3100×10^{-3}	0.9838	0.4957×10^{-3}	0.9837	0.8389×10^{-3}	0.9731	0.1013×10^{-2}	0.9864	0.1630×10^{-2}	0.9931
3	0.1305×10^{-3}	0.9533	0.2183×10^{-3}	0.9504	0.3674×10^{-3}	0.9326	0.4369×10^{-3}	0.9553	0.7026×10^{-3}	0.9746
4	0.8484×10^{-4}	0.9761	0.1377×10^{-3}	0.9749	0.2324×10^{-3}	0.9617	0.2798×10^{-3}	0.9780	0.4507×10^{-3}	0.9886
5	0.1007×10^{-2}	0.9873	0.1623×10^{-2}	0.9840	0.2785×10^{-2}	0.9743	0.3216×10^{-2}	0.9846	0.5095×10^{-2}	0.9938
6	0.5408×10^{-3}	0.9984	0.8237×10^{-3}	0.9994	0.1457×10^{-2}	0.9995	0.1602×10^{-2}	0.9998	0.2492×10^{-2}	0.9989
7	0.3812×10^{-3}	0.9906	0.5679×10^{-3}	0.9940	0.1020×10^{-2}	0.9960	0.1089×10^{-2}	0.9975	0.1678×10^{-2}	0.9949
8	0.2922×10^{-3}	0.9991	0.4485×10^{-3}	0.9994	0.7811×10^{-3}	0.9986	0.8937×10^{-3}	0.9997	0.1405×10^{-2}	0.9984
9	0.2311×10^{-3}	0.9987	0.3601×10^{-3}	0.9981	0.6236×10^{-3}	0.9945	0.7176×10^{-3}	0.9979	0.1133×10^{-2}	0.9993

TABLE 15

Rate constants at different temperatures for decomposition of CaC_2O_4 with mechanism-based equations (original sample mass = 20 mg)

Eqn. No.	703 K		712 K		722 K		749 K	
	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r	k (s^{-1})	r
1	0.2205×10^{-3}	0.9958	0.4117×10^{-3}	0.9961	0.6919×10^{-3}	0.9948	0.3285×10^{-2}	0.9971
2	0.1804×10^{-3}	0.9931	0.3441×10^{-3}	0.9917	0.5812×10^{-3}	0.9885	0.2794×10^{-2}	0.9868
3	0.7492×10^{-4}	0.9704	0.1482×10^{-3}	0.9698	0.2521×10^{-3}	0.9609	0.1223×10^{-2}	0.9547
4	0.4922×10^{-4}	0.9878	0.9501×10^{-4}	0.9864	0.1608×10^{-3}	0.9817	0.7763×10^{-3}	0.9781
5	0.5673×10^{-3}	0.9953	0.1098×10^{-2}	0.9920	0.1852×10^{-2}	0.9877	0.8774×10^{-2}	0.9807
6	0.2952×10^{-3}	0.9951	0.5537×10^{-3}	0.9992	0.9224×10^{-3}	0.9997	0.4215×10^{-2}	0.9988
7	0.2040×10^{-3}	0.9858	0.3788×10^{-3}	0.9950	0.6278×10^{-3}	0.9962	0.2820×10^{-2}	0.9994
8	0.1641×10^{-3}	0.9967	0.3070×10^{-3}	0.9989	0.5126×10^{-3}	0.9990	0.2378×10^{-2}	0.9993
9	0.1301×10^{-3}	0.9994	0.2460×10^{-3}	0.9993	0.4121×10^{-3}	0.9986	0.1927×10^{-2}	0.9962

TABLE 16

Classification of mechanism based kinetic curves on the basis of the correlation coefficients

Eqn. No.	Stage I: No. of curves with correlation coefficients			Stage II: No. of curves with correlation coefficients		
	Above 0.999	0.999–0.990	Below 0.990	Above 0.999	0.999–0.990	Below 0.990
1	–	13	20	–	31	3
2	–	–	33	–	8	26
3	–	–	33	–	–	34
4	–	–	33	–	–	34
5	–	2	31	–	7	27
6	2	30	1	14	20	–
7	–	29	4	1	22	11
8	10	22	1	20	14	–
9	3	19	11	13	21	–

TABLE 17

Kinetic parameters for different sample masses for dehydration of $CaC_2O_4 \cdot H_2O$ with eqn. (8)

Sample mass (mg)	E (kJ mol^{-1})	A (s^{-1})	r
1.1	142.9	2.346×10^{15}	0.9971
2.5	136.5	1.878×10^{14}	0.9901
5.0	118.6	9.468×10^{11}	0.9917
7.5	112.4	9.404×10^{10}	0.9976
10.0	97.42	1.055×10^{9}	0.9975
15.0	90.94	9.072×10^{7}	0.9999
20.0	81.42	8.158×10^{6}	0.9814

TABLE 18

Kinetic parameters for different sample masses for decomposition of CaC_2O_4 with eqn. (8)

Original sample mass (mg)	E (kJ mol^{-1})	A (s^{-1})	r
1.1	222.0	3.193×10^{13}	0.9938
2.5	220.8	6.664×10^{12}	0.9903
5.0	229.9	2.561×10^{13}	0.9962
7.5	249.4	7.643×10^{14}	0.9998
10.0	239.1	1.183×10^{14}	0.9793
15.0	196.9	9.713×10^{10}	0.9955
20.0	251.8	8.635×10^{14}	0.9995

computer, linear plots of ln k versus $1/T$ were made. E and A, calculated from the slope and intercept of these curves, respectively, along with the corresponding correlation coefficients, are given in Table 17. Comparing this with earlier results [1], it can be seen that E and A values calculated from the mechanism-based equation are very close to those obtained from the mechanism-non-invoking method. Here again, E and A are not greatly affected by sample mass, they fluctuate randomly in the range 197–252 kJ mol^{-1} for E and in the range of 1×10^{11} to 9×10^{14} s^{-1} for A.

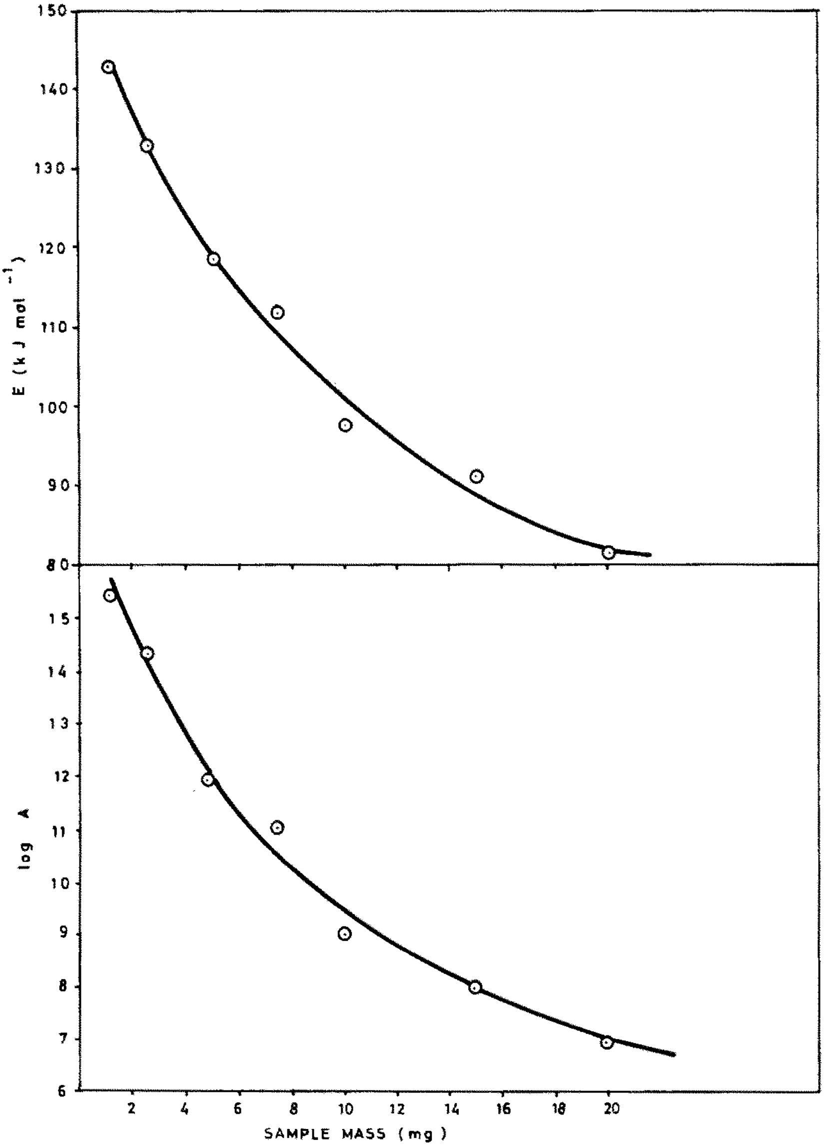

Fig. 1. Plots of E and log A versus sample mass.

Stage I

The seven sets of values of rate constants, calculated with eqn. (8) and the corresponding values of T were taken from Tables 9–15. From linear plots of ln k versus $1/T$, E and A were calculated. These values, along with the correlation coefficients, are given in Table 18. Comparing the data with an earlier publication [1], it can be observed that the kinetic parameters calculated using the mechanism-based equation are very close to those from the mechanism-non-invoking equation. Here again, the kinetic constants show the same trend, i.e., they decrease systematically with increase in sample mass.

As done earlier [1], a statistical analysis was carried out to establish the correlation of the kinetic parameters with sample mass. Figure 1 shows plots of E and log A versus sample mass. By trying out various curve-fits, using a computer, it was found that the best-fit curves of the kinetic parameters versus sample mass could be represented as:

$$E = 150.0 - 6.488m + 0.1560m^2$$

$$\log A = 16.32 - 0.9247m + 0.02301m^2$$

The reliability of the fits was evaluated by the F-test [8] and the Fisher constants were found to be 162.3 and 275.5, respectively, corresponding to a confidence level of above 99% in both cases. (The critical value of the Fisher constant for the system at 99% confidence level is 18.) Similar equations correlating the kinetic parameters with sample mass were also obtained in the case of the mechanism-non-invoking method [1].

SOME CONCLUDING REMARKS

The more important conclusions that can be drawn from the present study and our earlier studies [1,2,5,6,] on the first two stages of the thermal decomposition of calcium oxalate monohydrate can be summarised as follows:

(1) The mechanism of a thermal decomposition reaction cannot be assigned unequivocally from the mathematical curve fitting of the TG data alone, whereas from isothermal mass-loss data, one can find the reaction mechanism. In this regard, the isothermal method is superior to the non-isothermal method.

(2) So far as the values of the kinetic parameters are concerned, there is no significant difference between isothermal and non-isothermal methods or between mechanism-based and mechanism-non-invoking approaches, in the sense that they show the same degree of fluctuation and the same trend, as the case may be. Thus, for the purpose of calculating the kinetic constants, the TG method (which has the advantage of simplicity) can be used, after ascertaining the effect of procedural factors on the kinetic parameters.

(3) The values of the kinetic parameters are not appreciably affected by heating rate or sample mass in the case of the decomposition of calcium oxalate. However, in the case of the dehydration of calcium oxalate monohydrate, they decrease systematically with increasing heating rate or sample mass.

Calcium oxalate decomposition is an irreversible reaction and is, therefore, not appreciably affected by the concentration of the reaction products in the gas phase. Thus, procedural factors, within certain limits, exert a very minor influence on the reaction [9].

The dehydration of calcium oxalate monohydrate is an easily reversible reaction. Thus, any increase in partial pressure of H_2O will increase the reaction temperature. The larger the sample, the longer is the diffusion path for H_2O and, consequently, the partial pressure is more likely to build up. In dynamic TG experiments, the effect of time and temperature are superimposed which may be manifested as a systematic increase in T_f (temperature of completion of reaction) with increasing heating rate. For higher heating rates, the thermal inertia of the sample and the diffusion rate of the gaseous products play opposing roles. The overall effect of all these factors results in an enlarged temperature interval of the reaction and a reduced slope of the TG curve. In terms of kinetic parameters, this means a decreasing activation energy [10]. Since E and $\log A$ are linearly related by the kinetic compensation effect [11], there will also be an equivalent effect of heating rate and sample mass on $\log A$. In such cases it is not sufficient to calculate E and A from a single TG curve.

(4) The effect of the individual procedural factors on E or $\log A$ may be superimposed to get multiple correlations which would enable one to predict the kinetic parameters for any combination of the procedural factors.

ACKNOWLEDGEMENTS

The author thanks Dr. Vasant Gowariker and Prof. C.G.R. Nair for their encouragement.

LIST OF SYMBOLS

A	pre-exponental factor (s^{-1})
α	fraction decomposed
C	constant
E	energy of activation (kJ mol^{-1})
k	rate constant
m	sample mass (mg)
R	gas constant

r correlation coefficient
T temperature (K)
t time (s)

REFERENCES

1 K.N. Ninan, Thermochim. Acta, 74 (1984) 143.
2 K.N. Ninan and C.G.R. Nair, Thermochim. Acta, 30 (1979) 25.
3 J.M. Criado and J. Morales, Thermochim. Acta, 16 (1976) 382.
4 S.D. Dharwadkar, S.M. Chandrasekharaiah and M.D. Karkhanawala, Thermochim. Acta, 25 (1978) 372.
5 C.G.R. Nair and K.N. Ninan, Thermochim. Acta, 23 (1978) 161.
6 K.N. Ninan and C.G.R. Nair, Thermochim. Acta, 37 (1980) 161.
7 V. Satava, Thermochim. Acta, 2 (1971) 423.
8 C. Mack, Essentials of Statistics for Scientists and Technologists, Plenum Press, New York, 1967, p. 106.
9 H. Juntgen and K.H. Van Heek, in H.G. Weidemann (Ed.), Thermal Analysis, Vol. 2, Proc 3rd ICTA, Davos, 1971, Birkhauser Verlag, Basel, 1972, p. 423.
10 J. Zsako, E. Kekedy and Cs. Verhelyi, in H.G. Weidemann (Ed.), Thermal Analysis, Vol. 2, Proc. 3rd ICTA, Davos, 1971, Birkhauser Verlag, Basel, 1972, p. 492.
11 P.D. Garn, J. Therm. Anal., 10 (1976) 99.