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THERMAL DECOMPOSITION KINETICS. XIII. EFFECT OF SAMPLE MASS ON THE THERMAL DECOMPOSITION KINETICS OF $CaC_2O_4 \cdot H_2O$ FROM ISOTHERMAL MASS-LOSS DATA

K.N. NINAN

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

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ABSTRACT

The kinetic parameters for the first two stages of the thermal decomposition of calcium oxalate monohydrate

$$CaC_2O_4 \cdot H_2O \underset{\text{(stage I)}}{\overset{-H_2O}{\rightarrow}} CaC_2O_4 \underset{\text{(stage II)}}{\overset{-CO}{\rightarrow}} CaCO_3$$

have been established from isothermal mass-change studies. For the decomposition of calcium oxalate to carbonate, the kinetic parameters are not appreciably affected by the sample mass in the ranges studied. For the dehydration of $CaC_2O_4 \cdot H_2O$, they show a systematic decrease with increase in sample mass, and the curves of E or $\log A$ vs. sample mass can be best fitted as parabolae following an equation of the type

$$E(\text{or } \log A) = \text{constant} - (\text{constant}) \times (\text{mass}) + (\text{constant}) \times (\text{mass})^2$$

SYMBOLS USED

A = pre-exponential factor (s^{-1});
α = fraction decomposed;
E = energy of activation (kJ mol^{-1});
m = sample mass (mg);
n = order parameter;
r = correlation coefficient;
T = temperature (K).

INTRODUCTION

In an earlier publication [1], the kinetic parameters (E, A and n) for the dehydration of $CaC_2O_4 \cdot H_2O$ and the decomposition of the resultant CaC_2O_4 to $CaCO_3$ and CO were evaluated from TG curves using three mechanism-non-invoking kinetic equations. The studies were carried out at seven different heating rates with a fixed sample mass and with seven different sample masses at a fixed heating rate. It was observed that the kinetic parameters were not appreciably affected for the decomposition of CaC_2O_4, whereas for the dehydration reaction, they showed a systematic decrease with increase in either heating rate or sample mass. Mathematical correlations of high reliability between the kinetic parameters and procedural factors were also evolved for the dehydration step.

Non-isothermal kinetic methods have always been a subject of controversy and criticism [2–5]. So, it was considered worthwhile to extend the studies on calcium oxalate monohydrate, using isothermal methods as well, to see whether the kinetic parameters obtained from isothermal methods are subject to the fluctuations and trends, observed in the case of the results from non-isothermal methods. In the non-isothermal experiments, seven different heating rates and seven different sample masses were used. Obviously, the only variable in isothermal experiments is the sample mass, and therefore, we have studied the effect of the seven sample masses on the isothermal kinetic parameters from the first two stages of the thermal decomposition of $CaC_2O_4 \cdot H_2O$, carried out in a nitrogen atmosphere. Correlations between kinetic parameters and sample mass have been reported [6] from isothermal mass-loss studies of $CaCO_3$. So, it is attempted here to evolve mathematical correlations between sample mass and kinetic parameters from this study.

EXPERIMENTAL

Sample

Calcium oxalate monohydrate powder of 99.9% purity and 5 μm average particle size from the same lot was used in the entire study.

Instruments

The isothermal mass-loss curves were recorded on a DuPont 990 thermal analyser (2 pen) in conjunction with a 951 thermogravimetric analyser. Computational work was done with an IBM-360 computer using a FORTRAN IV program.

Procedure

All the measurements were done in an atmosphere of dry nitrogen purged at a rate of 50 cm^3 min^{-1}. The mass loss was recorded on the y-axis and the temperature on the y'-axis. The temperature was always steady for the entire span of the experiment, or at least the fluctuations were too small to be revealed on the recorder, which gave a perfect straight line.

The furnace was initially stabilised at the required temperature for about 30 min before introducing the sample. Even though the temperature programme was pre-set to a gap of 10 K for successive experiments, the actual sample temperature, as recorded by the thermocouple, sometimes rose above or dipped below the set point. The temperatures given in the tables in this communication are those recorded by the thermocouple.

As the set temperature was increased to higher values, it was observed that the sample underwent some reaction during the initial lag period, when it was raised to the furnace temperature. This is an inherent disadvantage of isothermal techniques [7]. So, the isothermal mass-loss curves could be recorded only at 4–6 different temperatures in the range 380–430 K for stage I, and 690–750 K for stage II. Mass supression controls were used to expand the mass loss, recorded on the y-axis.

Time was recorded on the x-axis and the chart speed was adjusted to obtain an amplified recorder output for the two stages of decomposition. The initial time, t_0, was noted by extrapolation to the zero mass-loss point on the y-axis. In each experiment, as soon as the dehydration reaction was over, the furnace temperature was raised to the value required for the stage II reaction, and the recording was continued until a well-defined plateau was obtained.

Seven sample masses (1.1, 2.5, 5.0, 7.5, 10, 15 and 20 mg) were employed in this study. Sample loading was done carefully to obtain the actual masses ± 0.1 mg of these nominal values. A total of 67 mass-loss curves were recorded for the two stages of decomposition (33 for stage I and 34 for stage II).

RESULTS AND DISCUSSION

The kinetic analysis of the mass-loss data was carried out with the general mechanism-non-invoking isothermal equation, the integral form of which can be given as

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = kt$$

In an earlier publication [1], the values of n were established as 0.65 for stage I and 0.50 for stage II. Using these values of n, the rate constants were calculated by plotting the left-hand side of the above equation against time, t. The values of the rate constants and the corresponding correlation coefficients at different temperatures and for different sample masses for the dehydration of $CaC_2O_4 \cdot H_2O$ are given in Table 1. Similar values for the decomposition of the resultant CaC_2O_4 to $CaCO_3$ and CO are given in Table

TABLE 1

Rate constants at different temperatures and for different sample masses for dehydration of $CaC_2O_4 \cdot H_2O$ (T in K and k in s^{-1})

1.1 mg			2.5 mg		
T	k	r	T	k	r
383	0.1827×10^{-3}	0.9995	403	0.8002×10^{-3}	0.9986
393	0.4907×10^{-3}	0.9777	412	0.2229×10^{-2}	0.9975
402	0.1826×10^{-2}	0.9917	423	0.7939×10^{-2}	0.9885
412	0.4062×10^{-2}	0.9851	433	0.1147×10^{-1}	0.9820
418	0.7363×10^{-2}	0.9830	437	0.2255×10^{-1}	0.9863
5.0 mg			7.5 mg		
T	k	r	T	k	r
381	0.1213×10^{-3}	0.9929	388	0.1643×10^{-3}	0.9994
389	0.2077×10^{-3}	0.9960	402	0.5062×10^{-3}	0.9961
399	0.8279×10^{-3}	0.9936	417	0.1997×10^{-2}	0.9920
408	0.1500×10^{-2}	0.9884	424	0.2705×10^{-2}	0.9881
420	0.3393×10^{-2}	0.9916	434	0.7008×10^{-2}	0.9873
10 mg			15 mg		
T	k	r	T	k	r
391	0.2380×10^{-3}	0.9934	392	0.1647×10^{-3}	0.9998
413	0.1247×10^{-2}	0.9958	412	0.6206×10^{-3}	0.9977
423	0.2029×10^{-2}	0.9928	422	0.1176×10^{-2}	0.9948
430	0.3877×10^{-2}	0.9901	442	0.3842×10^{-2}	0.9866
20 mg					
T	k	r			
392	0.2658×10^{-3}	0.9938			
408	0.8933×10^{-3}	0.9922			
412	0.7425×10^{-3}	0.9974			
418	0.1182×10^{-2}	0.9923			
431	0.2789×10^{-2}	0.9924			

2. From these tables it can be seen that the correlation coefficients are close to unity in almost all cases, indicating near-perfect fits.

Using each set of values of T and k, given in Tables 1 and 2, linear plots of $\ln k$ vs. $1/T$ were drawn and E and A were calculated from the slope and intercept, respectively. The values of E and A along with the corresponding correlation coefficients are given in Tables 3 and 4. Table 3 gives the kinetic parameters for different sample masses for the dehydration reaction and Table 4 gives similar values for the decomposition of CaC_2O_4. The correlation coefficients are also near unity in these cases.

TABLE 2

Rate constants at different temperatures and for different sample masses, for decomposition of CaC_2O_4 (T in K and k in s^{-1})

1.1 mg			2.5 mg		
T	k	r	T	k	r
693	0.1157×10^{-2}	0.9991	694	0.3551×10^{-3}	0.9955
701	0.2013×10^{-2}	0.9989	706	0.4910×10^{-3}	0.9971
708	0.2465×10^{-2}	0.9989	716	0.9960×10^{-3}	0.9975
722	0.5924×10^{-2}	0.9873	725	0.2006×10^{-2}	0.9991
			735	0.2622×10^{-2}	0.9986
			750	0.5371×10^{-2}	0.9997
5.0 mg			7.5 mg		
T	k	r	T	k	r
695	0.2708×10^{-3}	0.9967	690	0.1981×10^{-3}	0.9997
706	0.5254×10^{-3}	0.9995	701	0.4053×10^{-3}	0.9993
713	0.6858×10^{-3}	0.9998	710	0.6765×10^{-3}	0.9992
725	0.1288×10^{-2}	0.9996	721	0.1325×10^{-2}	0.9995
736	0.2904×10^{-2}	0.9997	731	0.2267×10^{-2}	0.9994
750	0.4682×10^{-2}	0.9984			
10 mg			15 mg		
T	k	r	T	k	r
690	0.1615×10^{-3}	0.9994	708	0.5844×10^{-3}	0.9991
703	0.5249×10^{-3}	0.9990	719	0.8969×10^{-3}	0.9994
721	0.1153×10^{-2}	0.9993	728	0.1562×10^{-2}	0.9986
723	0.1114×10^{-2}	0.9985	732	0.1787×10^{-2}	0.9997
			744	0.2811×10^{-2}	0.9984
20 mg					
T	k	r			
703	0.3281×10^{-3}	0.9967			
712	0.6139×10^{-3}	0.9989			
722	0.1025×10^{-2}	0.9990			
749	0.4757×10^{-2}	0.9993			

TABLE 3

Kinetic parameters for different sample masses for dehydration of $CaC_2O_4 \cdot H_2O$

Sample mass (mg)	E (kJ mol^{-1})	A (s^{-1})	r
1.1	142.7	5.125×10^{15}	0.9966
2.5	136.7	4.662×10^{14}	0.9891
5.0	118.3	1.985×10^{12}	0.9916
7.5	113.2	2.724×10^{11}	0.9978
10.0	97.37	2.431×10^{9}	0.9972
15.0	90.78	2.035×10^{8}	1.0000
20.0	82.02	2.272×10^{7}	0.9826

E *and* A *for stage II*

From Table 4, it can be observed that the kinetic parameters for stage II are not appreciably affected by sample mass. The values of E and A are in the range 197–252 kJ mol^{-1} and 2×10^{11} to 2×10^{15} s^{-1}, respectively. The variations are irregular in nature. It is interesting to note that these values are in the same range as those obtained in our non-isothermal studies [1].

E *and* A *for stage I*

From Table 3 it can be observed that the values of E and A for the dehydration reaction are strongly dependent on sample mass: they show a systematic decrease with increase in sample mass. Here again, the trend is similar to the one observed for non-isothermal kinetics [1].

Figure 1 shows the curves of E and log A vs. sample mass. Using a computer, different types of curve fittings (e.g., exponential, parabola and rectangular hyperbola) were worked out and it was found that the curves of

TABLE 4

Kinetic parameters for different sample masses for decomposition of CaC_2O_4

Original sample mass (mg)	E (kJ mol^{-1})	A (s^{-1})	r
1.1	222.0	6.441×10^{13}	0.9938
2.5	220.8	1.332×10^{13}	0.9903
5.0	229.9	5.116×10^{13}	0.9962
7.5	249.4	1.516×10^{15}	0.9998
10.0	239.0	2.335×10^{14}	0.9793
15.0	196.9	1.953×10^{11}	0.9955
20.0	251.8	1.741×10^{15}	0.9995

E or $\log A$ vs. sample mass could best be fitted as parabolae, using the following equations

$$E = 149.9 - 4.806\, m + 0.1567\, m^2$$

$$\log A = 16.69 - 0.9243\, m + 0.02313\, m^2$$

The reliability of these equations was assessed by the F test [8] and the Fisher constants for the two worked out to be 142.4 and 232.2, respectively, corresponding to a confidence level of above 99% in both cases. (The critical value of the Fisher constant [8] for the system at 99% confidence level is 18.) It is interesting to note that similar equations correlating kinetic parameters with sample mass were obtained in the case of the non-isothermal method also [1].

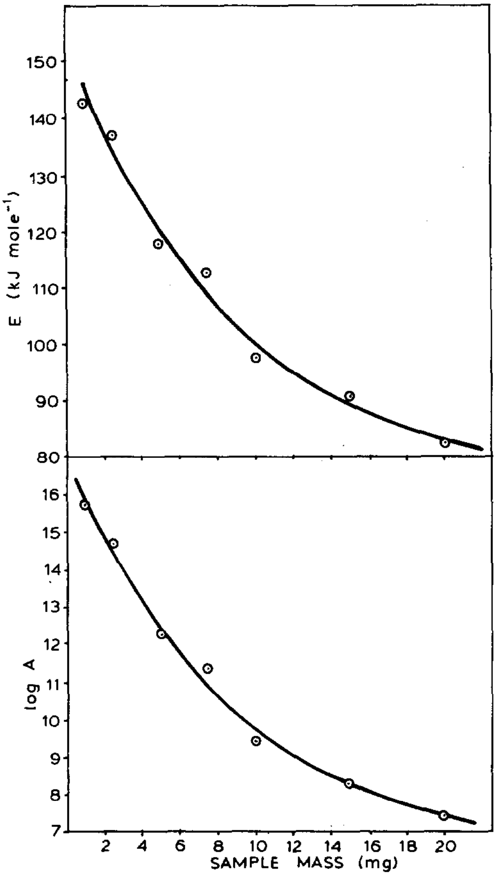

Fig. 1. Plots of $E/\log A$ vs. sample mass.

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