THE EFFECT OF THE SIMULTANEOUS VARIATION OF SAMPLE MASS AND HEATING RATE IN DTA AND DSC

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ABSTRACT

Quantitative correlations between kinetic parameters (energy of activation, E), procedural factors (sample mass, m, and heating rate, ϕ) and the dependent variables (the temperature of inception of reaction, T_i, and temperature T_α at which a constant fraction α has decomposed) have been derived for differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The relations have the same form as those derived from earlier TG studies. The dependent variables T_i and T_α are related to m, ϕ and E by the equations

$$T_i = \left(\frac{C_3}{\phi} \right) m^{C_2/E}$$

where C_3 and C_2 are constants, and

$$T_\alpha = \left(\frac{C_4}{\phi} \right) m^{C_5/E}$$

where C_4 and C_5 are constants for a given α. The variation of C_5 with α is given by

$$C_5 = a + b\alpha$$

where a and b are constants. The equations are applicable to TG, DTA and DSC.

INTRODUCTION

The results from thermoanalytical studies are known [1–3] to be affected by a number of procedural factors such as heating rate, sample mass, sample particle size, atmosphere, etc. A few equations relating to kinetic parameters and procedural factors have been published recently [4–7]. From our TG studies on the dehydration of zinc oxalate dihydrate [8], we have derived multi-parameter equations correlating T_i or T_α with m, ϕ and E. The above study is now extended to DTA and DSC and the results are presented in this communication.

TABLE 1

Effect of sample mass and heating rate on temperature of inception of reaction

Experiment No.	Sample mass (mg)	Heating rate ($^\circ$C min^{-1})	T_i(K)	
			DTA	DSC
1	4	1	368	364
2	6	2	372	367
3	8	5	378	371
4	10	10	384	375
5	12	20	391	380
6	14	50	405	387

EXPERIMENTAL

Zinc oxalate dihydrate of 99.9% purity (BDH) was used. The particle size of the samples was kept in the range 25–37 μm. The experiments were carried out using a Du Pont 990 thermal analyzer in conjunction with Cell Base Module II, 1200°C DTA and 902 DSC. The atmosphere was dry nitrogen purged at a rate of 50 cm^3 min^{-1}. Six sets of sample mass and heating rate (given in Table 1) were employed to study the effect of their simultaneous variation on DTA and DSC results.

All the DTA and DSC curves were plotted on a time base linear chart and the chart speed was adjusted to obtain each small division of the chart corresponding to 1°C on the x-axis. The sample temperature was measured from the millivolt output of the corresponding thermocouples of the DTA and DSC, recorded on the y-axis of the two-pen recorder.

The fractional decomposition, α, was determined from the ratio of the fractional and total area under the curve. Numerical integration techniques (Simpson and Trapezoidal) were used for the purpose and the difference between the two methods was < 0.5% in all cases. Calculations were done with an IBM 360 computer using FORTRAN IV program.

RESULTS AND DISCUSSION

The values of the temperature of inception (T_i) of the dehydration reaction obtained from DTA and DSC experiments are given in Table 1. Similarly, the values of T_α (the temperature at which a constant fraction α has decomposed) from DTA and DSC are given in Tables 2 and 3, respectively.

The kinetic parameters were calculated from the DTA and DSC curves using the Coats and Redfern equation [9]. The order parameter, n, was determined by an iteration method described previously [8]. The best-fit

TABLE 2

Variation of T_α with sample mass and heating rate for various α values for DTA

Experiment No.	T_α(K) for various α values								
$\alpha =$	0.15	0.25	0.35	0.45	0.55	0.65	0.75	0.85	0.95
1	384.0	387.0	389.0	391.0	393.0	394.5	396.5	398.0	400.0
2	395.5	398.0	400.0	401.5	403.0	404.5	406.0	407.5	409.0
3	401.0	405.0	408.0	410.0	413.0	415.0	417.0	419.5	422.0
4	415.0	421.0	425.0	428.0	431.0	434.0	437.0	440.0	443.5
5	428.0	434.0	440.0	444.0	448.0	452.0	456.0	461.0	468.0
6	445.5	453.0	460.5	466.0	473.0	478.0	485.5	493.0	503.0

TABLE 3

Variation of T_α with sample mass and heating rate for various α values for DSC

Experiment No.	T_α(K) for various α values								
$\alpha =$	0.15	0.25	0.35	0.45	0.55	0.65	0.75	0.85	0.95
1	365.0	367.0	368.0	369.5	371.0	372.0	373.0	374.0	375.0
2	373.5	376.0	378.0	380.0	381.5	383.0	384.5	386.0	387.5
3	380.5	385.5	389.0	391.0	393.5	395.5	398.0	400.0	403.0
4	390.5	396.0	400.0	403.0	406.0	408.0	411.0	413.5	416.0
5	401.0	408.0	413.0	417.0	421.0	424.5	428.0	431.5	435.0
6	425.0	433.0	440.0	445.0	450.0	455.0	460.0	465.5	473.0

value was found to be unity in almost all the cases. Similar results were also obtained in our TG studies. The values of the energy of activation, E, and pre-exponential factor, A, calculated (with $n = 1$) from the DTA and DSC curves are given in Tables 4 and 5, respectively.

From Tables 1–5, it can be seen that as sample mass and heating rate increase, T_i or T_α increases. In the case of the kinetic parameters (E and A) a reverse trend is observed. These regular trends make the data amenable for statistical analysis. Curves of different combinations were, therefore, plotted and it was found that plots of $\log \phi\, T_i$ vs. $(\log m)/E$ gave straight lines for both DTA and DSC. Figure 1 shows these linear plots, whose correlation coefficients are 0.9989 and 0.9993, respectively, for DTA and DSC. These linear relations can be represented as

$$\log \phi T_i = C_1 + C_2 \frac{\log m}{E} \tag{1}$$

where C_1 and C_2 are constants. Equation (2) can be put in the form

$$T_i = \left(\frac{C_3}{\phi} \right) m^{C_2/E} \tag{2}$$

where $C_1 = \log C_3$. The constants C_3 and C_2 were found to be 220.7 and 47.88, respectively, for DTA, and 209.2 and 41.77, respectively, for DSC.

TABLE 4

Kinetic parameters for the dehydration of $ZnC_2O_4 \cdot 2\,H_2O$ from DTA

Experiment No.	E(kcal mole^{-1})	A(s^{-1})	r
1	96.40	3.99×10^{52}	0.9979
2	75.01	4.33×10^{38}	0.9980
3	48.80	4.19×10^{23}	0.9987
4	40.60	1.95×10^{18}	0.9989
5	32.46	2.64×10^{13}	0.9989
6	27.68	2.37×10^{10}	0.9981

TABLE 5

Kinetic parameters for the dehydration of $ZnC_2O_4 \cdot 2\,H_2O$ from DSC

Experiment No.	E(kcal mole^{-1})	A(s^{-1})	r
1	86.78	1.02×10^{49}	0.9982
2	64.93	1.52×10^{35}	0.9983
3	40.32	1.35×10^{20}	0.9986
4	34.46	2.97×10^{16}	0.9988
5	27.57	6.77×10^{11}	0.9994
6	24.69	1.94×10^{9}	0.9996

Similarly, for a fixed value of α, $\log \phi T_\alpha$ vs. $(\log m)/E$ gave straight lines. Therefore,

$$T_\alpha = \left(\frac{C_4}{\phi} \right) m^{C_5/E} \tag{3}$$

where C_4 and C_5 are constants. Three typical plots of $\log(\phi T_\alpha)$ vs. $(\log m)/E$
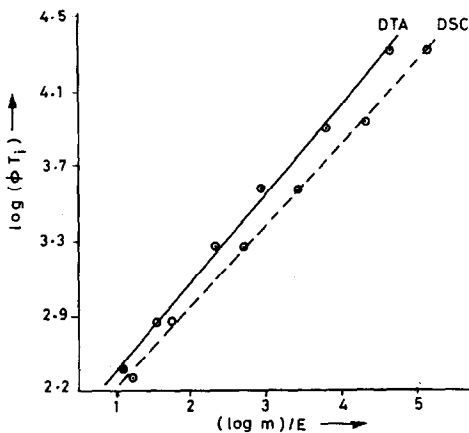
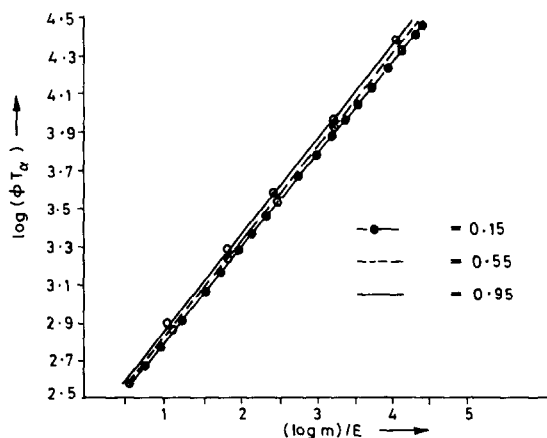Fig. 1. Plot of $\log (\phi T_i)$ vs. $(\log m)/E$ for DTA and DSC.

Fig. 2. Plot of $\log(\phi T_\alpha)$ vs. $(\log m)/E$ for fixed α values (DTA).

for constant α values (0.15, 0.55 and 0.95) are given in Figs. 2 and 3, respectively, for DTA and DSC. Nine such linear plots were drawn in both cases and the corresponding values of slope intercept and correlation coefficient, r, are given in Tables 6 and 7. It can be seen that when α is varied, C_4 and C_5 are not constants in both cases. C_5 varies linearly with α and Fig. 4 gives these plots. The linear variation can be represented by an equation

$$C_5 = a + b\alpha \tag{4}$$

where a and b are constants, whose values were found to be 48.33 and 1.22, respectively, for DTA, and 42.55 and 0.98, respectively, for DSC. The correlation coefficients are 0.9955 for DTA and 0.9950 for DSC. No correlations could be obtained between C_4 and α. Equation (3) can be written as
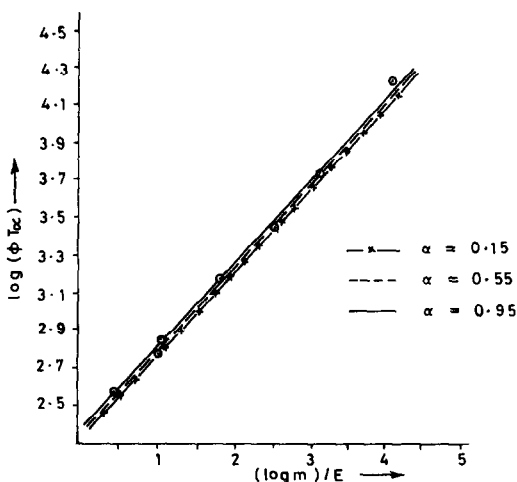

Fig. 3. Plot of $\log(\phi T_\alpha)$ vs. $(\log m)/E$ for fixed α values (DSC).

TABLE 6

Slopes and intercepts of $\log(\phi T_\alpha)$ vs. $(\log m)/E$ plots for various α values for DTA

α	Slope C_5	Intercept	r
0.15	48.51	2.361	0.9967
0.25	48.64	2.363	0.9967
0.35	48.79	2.364	0.9968
0.45	48.88	2.365	0.9968
0.55	48.99	2.365	0.9968
0.65	49.09	2.366	0.9970
0.75	49.21	2.366	0.9970
0.85	49.35	2.367	0.9971
0.95	49.55	2.366	0.9972

TABLE 7

Slopes and intercepts of $\log(\phi T_\alpha)$ vs. $(\log m)/E$ plots for various α values for DSC

α	Slope C_5	Intercept	r
0.15	42.64	2.315	0.9968
0.25	42.79	2.316	0.9967
0.35	42.93	2.317	0.9969
0.45	43.00	2.318	0.9969
0.55	43.09	2.319	0.9968
0.65	43.17	2.319	0.9968
0.75	43.26	2.320	0.9968
0.85	43.35	2.320	0.9968
0.95	43.46	2.320	0.9970

$$T_\alpha = \left(\frac{C_4}{\phi}\right) m^{(a+b\alpha)/E} \tag{5}$$

From Tables 4 and 5 it can be seen that A also shows a decrease with increase in m and ϕ, as in the case of E, and $\log A$ varies linearly with E, which can be attributed to the kinetic compensation effect [10].
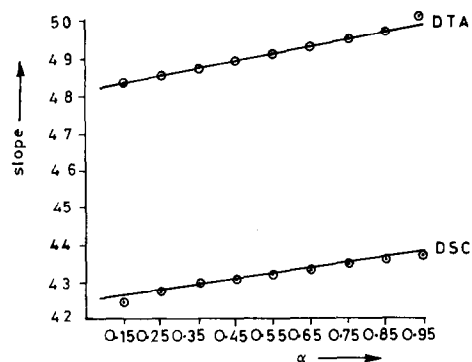
Fig. 4. Plot of slope vs. α for DTA and DSC.

Equations (1)–(5) are of the same form as those obtained from our earlier TG studies [8]. However, as compared to DTA and DSC, correlation coefficients for the linear plots of the above equations are generally higher in the case of TG, which in turn shows that the data obtained from TG are more quantitative than those from DTA and DSC.

CONCLUSION

From DTA and DSC studies, the independent variables, viz., sample mass and heating rate, have been mathematically correlated with the dependent variables, viz., T_i or T_α and energy of activation by multi-parameter equations involving T_i or T_α, m, ϕ and E. The equations derived earlier showing the relation between procedural factors and kinetic parameters for TG have the advantage of applicability to DTA and DSC which in turn give closer values. The greater precision of the values obtained from TG is attributable to the accuracy in measurement of mass. DTA and DSC give closer values, as the inherent errors are comparable in both the techniques [11].

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