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KINETICS OF ISOTHERMAL DEHYDRATION OF ZINC OXALATE DIHYDRATE

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ABSTRACT

A method is proposed for the determination of kinetic parameters from isothermal experiments which eliminates the use of the integrated form of fractional decomposition function, g(α), and, hence, the kinetic assumption concerning the mechanism of reaction. This method is used to calculate the kinetic parameters, viz., energy of activation, E, and pre-exponential factor, A, for the dehydration of $ZnC_2O_4 \cdot 2\ H_2O$ from isothermal mass loss measurements. The results obtained are comparable with those given by other methods. A relation between the order parameter, n, and the isothermal temperature, $T_{(iso)}$, has been obtained, and the experimentally determined values of the rate constant, k, and $T_{(iso)}$ have been correlated by the equation

$$\log k = \log k_0 + C\left[A + BT_{(iso)}\right]$$

The values of E and A thus obtained are comparable with those from mechanism-based and mechanism-free kinetic equations.

INTRODUCTION

Several studies on the dehydration of hydrated salts are reported in the literature [1–4]. Both isothermal and non-isothermal methods have been used to evaluate kinetic parameters and for the elucidation of the mechanism of dehydration reactions [5–7]. Mechanism-based and non-mechanistic rate equations have been employed for this purpose [8–13]. The advantages and disadvantages of both isothermal and non-isothermal methods have also been reported [14]. Several qualitative, and a few quantitative, studies on the dehydration of zinc oxalate dihydrate have been published [15–18]. The kinetics of dehydration of $ZnC_2O_4 \cdot 2\ H_2O$ using TG, DTA and DSC have been recently established and multiparameter equations involving the energy of activation (E), heating rate (ϕ), sample mass (m), the temperature of

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inception of reaction (T_i) and the temperature at which a constant fraction, α, has decomposed (T_α) have also been evolved [19,20]. The present investigation is an attempt to study some aspects of the isothermal dehydration of $ZnC_2O_4 \cdot 2\ H_2O$ and propose certain new approaches in evaluating kinetic parameters therefrom.

EXPERIMENTAL

The sample of $ZnC_2O_4 \cdot 2\ H_2O$ used for this study had the same particle size and purity as previously reported [19,20]. The isothermal mass-loss measurements were made using a DuPont 990 thermal analyser in conjunction with a 951 thermogravimetric analyser. All experiments were carried out in dry nitrogen atmosphere purged at a rate of 50 cm^3 min^{-1}. The sample mass was 10 ± 0.1 mg in all cases. The mass loss was recorded on the Y-axis and the temperature on the Y'-axis. The furnace was initially heated and stabilised at the required isothermal temperature for 30 min before introducing the sample. The temperature was noted from the millivolt output of the thermocouple. Time was recorded on the X-axis.

THEORETICAL

The integral form of the general kinetic equation for the thermal decomposition reaction of solids under isothermal conditions can be represented as [21]

$$g(\alpha) = kt \tag{1}$$

where α is the fractional decomposition at time t, $g(\alpha)$ is the integrated form of fractional decomposition function $f(\alpha)$, and k is the reaction rate constant.

If i isothermal experiments are carried out at different temperatures, T_i (where $i = 1, 2, 3\ldots$), then eqn. (1) can be written as

$$g_i(\alpha) = k_i t_i \tag{2}$$

Assuming that α_j (where $\alpha_j = 0.1, 0.2, 0.3\ldots$) is the constant fraction decomposed at time t_i, eqn. (2) becomes

$$g_i(\alpha_j) = k_{ij} t_{ij} \tag{3}$$

where k_{ij} is the temperature dependent rate constant, which can be written in the form of the Arrhenius expression as

$$k_{ij} = A_{ij} \exp(-E/RT_i) \tag{4}$$

Combining eqns. (3) and (4), we get

$$g_i(\alpha_j) = A_{ij} \exp(-E/RT_i) t_{ij} \tag{5}$$

As α values vary from 0.1 to 0.9 for each of the i isothermal runs, the value t_{ij} will also vary, while $g_i(\alpha_j)$ remains the same. Taking logarithms and transposing, eqn. (5) becomes

$$\log t_{ij} = \log g_i(\alpha_j) - \log A_{ij} + \frac{E}{2.303RT_i} \tag{6}$$

Assuming that the pre-exponential factor, A_{ij}, does not vary with temperature, eqn. (6) can be written as

$$\log t_{ij} = \log g_i(\alpha_j) - \log A + \frac{E}{2.303RT_i} \tag{7}$$

Thus, the plot of log t_{ij} vs. reciprocal isothermal absolute temperature will be linear. The slope of the plot gives the value of E. For a set of i isothermal experiments, each value will give one value of E, depending on the choice of α_j. The intercept of the above plot yields (log $g_i(\alpha_j)$ − log A) from which A can be determined, if the correct form of $g_i(\alpha_j)$ is known.

The mean values of E and A computed from eqn. (7) can be compared with the values obtained from the mechanism-based equation of the type (Erofeev) [22]

$$[g(\alpha)]^{n'} = kt \tag{8}$$

where $g(\alpha) = -\ln(1-\alpha)$ and $n' = 1/n$. Taking logarithms,

$$n' \log[-\ln(1-\alpha)] = \log k + \log t \tag{9}$$

Dividing both sides by n', eqn. (9) becomes

$$\log[-\ln(1-\alpha)] = \frac{1}{n'} \log k + \frac{1}{n'} \log t \tag{10}$$

A plot of the left-hand side of eqn. (10) against log t will give straight lines from which n' and k can be determined.

RESULTS AND DISCUSSION

The isothermal experimental data for the dehydration of $ZnC_2O_4 \cdot 2\,H_2O$ were used to calculate the kinetic parameters by the proposed mechanism-eliminating method (eqn. 7), and they are presented in Table 1. Table 2 gives the slopes, intercepts and the corresponding correlation coefficients for the plots of log t_i vs. reciprocal isothermal absolute temperature, and Fig. 1 shows these plots. Nine such linear plots were drawn. The correlation coefficients for the above plots are > 0.998, indicating the linearity of the fits. The values of E decreased from 35.5250 to 24.4319 kcal mol^{-1} as α

TABLE 1

α, t (s) and log t values at different isothermal temperatures

α	$T_{(iso)} = 366$ K		378 K		388 K		392 K		397 K		402 K	
	t	log t	t	log t	t	log t	t	log t	t	log t	t	log t
0.1	2520.0	3.4014	564.0	2.7513	168.0	2.2253	108.0	2.0334	57.0	1.7559	–	–
0.2	3228.0	3.5089	804.0	2.9053	276.0	2.4409	186.0	2.2695	114.0	2.0569	66.0	1.8195
0.3	3960.0	3.5975	1020.0	3.0086	372.0	2.5701	264.0	2.4216	168.0	2.2253	111.0	2.0453
0.4	4560.0	3.6590	1248.0	3.0962	468.0	2.6703	330.0	2.5165	222.0	2.3464	150.0	2.1761
0.5	5196.0	3.7157	1428.0	3.1547	564.0	2.7513	408.0	2.6107	276.0	2.4409	186.0	2.2695
0.6	5760.0	3.7604	1644.0	3.2759	654.0	2.8156	492.0	2.6920	339.0	2.5302	231.0	2.3636
0.7	6480.0	3.8116	1884.0	3.2751	762.0	2.8820	570.0	2.7554	396.0	2.5977	276.0	2.4409
0.8	7176.0	3.8559	2148.0	3.3320	882.0	2.9455	660.0	2.8195	468.0	2.6702	342.0	2.5340
0.9	8100.0	3.9084	2508.0	3.3993	1050.0	3.0212	768.0	2.8854	540.0	2.7324	420.0	2.6232

TABLE 2

Results of log t vs. $1/T_{(iso)}$ plots

α	Slope	Intercept	E (kcal mol^{-1})	A (s^{-1})	r
0.1	7.7698	−17.8338	35.5250	7.1875×10^{16}	0.9988
0.2	6.8436	−15.1931	31.3167	3.4809×10^{14}	0.9999
0.3	6.3195	−13.6883	28.9134	1.7402×10^{13}	0.9997
0.4	6.0630	−12.9302	27.7444	4.3501×10^{12}	0.9995
0.5	5.8903	−12.4132	26.9543	1.7947×10^{12}	0.9992
0.6	5.6970	−11.8350	26.0653	6.2661×10^{11}	0.9986
0.7	5.6040	−11.5329	25.6443	4.1581×10^{11}	0.9989
0.8	5.4390	−11.0377	24.8849	1.7555×10^{11}	0.9982
0.9	5.3400	−10.7131	24.4319	1.1986×10^{11}	0.9980

ranged from 0.1 to 0.9. The mean value of E obtained is 27.941 kcal mol^{-1}, which is in good agreement with the value of E for the dehydration of $ZnC_2O_4 \cdot 2\ H_2O$ reported earlier [19,20]. The only disadvantage of this method, as reported by other workers [23], is that A cannot be obtained directly. However, the value of A can be calculated from the known values of g(α). The values of A thus calculated have the same trend as in the case of E and vary from 7.1895×10^{16} to 1.1986×10^{11} s^{-1}. The geometric mean value of A is 6.4093×10^{12} s^{-1}, the usual range of frequency factor for solid-state reactions [24].

The same experimental data were used for the evaluation of kinetic parameters from the mechanism-based equation (eqn. 10). Plots of log g(α)

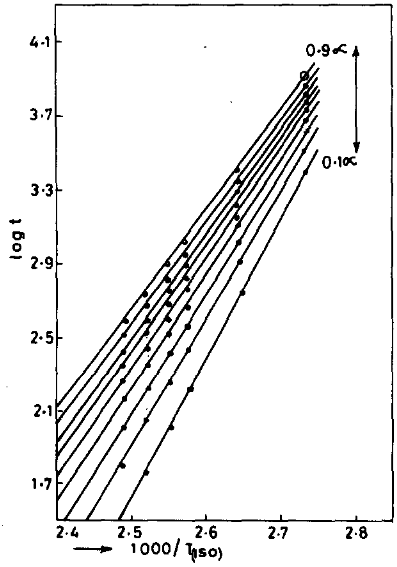

Fig. 1. Plots of log t vs. $1000/T_{(iso)}$.

TABLE 3

Results of $\log[-\ln(1-\alpha)]$ vs. $\log t$ plots for different $T_{(\mathrm{iso})}$ values

T(K)	Slope ($1/n'$)	n'	Intercept [($\log k$)/n']	$\log k$	k (s^{-1})	r
366	2.5740	0.3885	−9.7129	−3.7734	1.8475×10^{-4}	0.9995
378	2.0475	0.4884	−6.6160	−3.2313	5.8708×10^{-4}	0.9997
388	1.6835	0.5940	−4.7659	−2.8310	1.4757×10^{-3}	0.9986
392	1.5537	0.6436	−4.1894	−2.6964	2.0118×10^{-3}	0.9967
397	1.3451	0.7430	−3.2769	−2.4362	3.6626×10^{-3}	0.9944
402	1.2741	0.7850	−3.0266	−2.3766	4.2111×10^{-3}	0.9940

vs. log t were made and are shown in Fig. 2. Table 3 gives the results (slopes, intercepts, n', k and the correlation coefficients) of these plots. From the table, it can be seen that the value of n' increases from 0.389 to 0.785 when the isothermal temperature varies from 366 to 402 K. A similar trend can also be observed in the case of the rate constant k. The linear variation of log n' vs. $T_{(\mathrm{iso})}$ and log k vs. log n' are shown in Figs. 3 and 4, respectively. It has been reported that the value of n is temperature dependent [25], but a search through the available literature did not reveal any earlier mathematical correlations. The linear dependence of log n' with $T_{(\mathrm{iso})}$ or log k can be mathematically represented as

$$\log n' = A + BT_{(\mathrm{iso})} \tag{11}$$

where A and B are constants. Similarly

$$\log k = \log k_0 + C \log n' \tag{12}$$

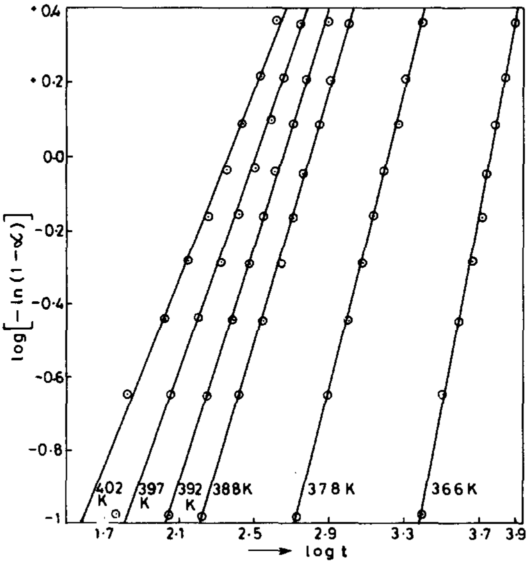

Fig. 2. Plots of log g(α) vs. log t.

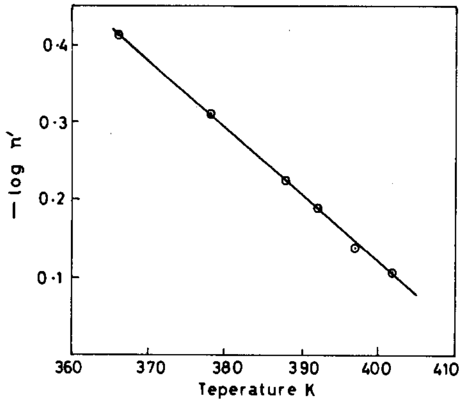

Fig. 3. Plot of log n' vs. $T_{(\mathrm{iso})}$.

where C is a constant and $\log k_0 = \log k$ when $n' = 1$. Combining eqns. (11) and (12)

$$\log k = \log k_0 + C\left[A + BT_{(\mathrm{iso})}\right] \tag{13}$$

The results obtained from the plots (Figs. 3 and 4) are given in Table 4. The values of slope and intercept thus obtained are introduced into eqn. (13) to get

$$\log k = -1.8401 + 4.5874\left[-3.6006 + 0.0087T_{(\mathrm{iso})}\right] \tag{14}$$

The values of rate constants, k, calculated using eqn. (14) are given in Table 5. These values of k are almost equal to those obtained from the mechanism-based equation (eqn. 10).

The kinetic parameters were calculated from the Arrhenius plot of log k (from both eqs. 10 and 14) vs. reciprocal isothermal absolute temperature. The values of slopes, intercepts and the corresponding correlation coeffi-

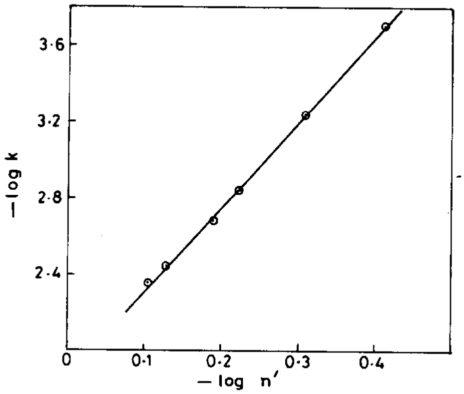

Fig. 4. Plot of log k vs. log n'.

TABLE 4

Results of log n' vs. $T_{(iso)}$ and log k vs. log n' plots

	log n' vs. $T_{(iso)}$	log k vs. log n'
Slope	0.0087	4.5874
Intercept	−3.6006	−1.8401
r	0.9951	0.9940

cients are given in Table 6 and the above plots are shown in Fig. 5.

The very close agreement between experimental and calculated values of E and A indicate the validity of the assumptions in our method. These values

TABLE 5

Rate constants calculated from eqn. (14)

T(K)	log k (calc)	k (s^{-1})	log n' (exp)
366	−3.7506	1.7758×10^{-4}	−0.4106
378	−3.2217	5.3493×10^{-4}	−0.3112
388	−2.8726	1.3409×10^{-3}	−0.2262
392	−2.7129	1.9368×10^{-3}	−0.1914
397	−2.5134	3.0662×10^{-3}	−0.1290
402	−2.3138	4.8555×10^{-3}	−0.1052

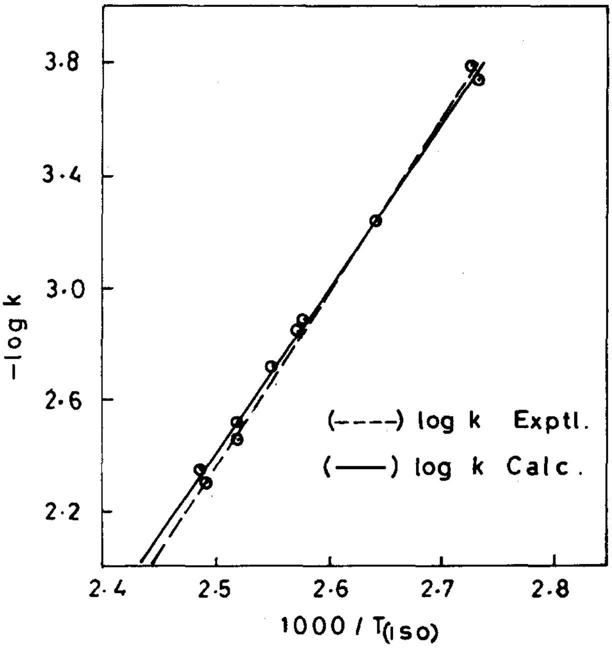

Fig. 5. Plot of log k vs. $1000/T_{(iso)}$.

TABLE 6

Results of log k vs. $1/T_{(iso)}$ plots

Plot	Slope	Intercept	E (kcal mol^{-1})	A (s^{-1})	r
log $k_{(expt)}$ vs. $1/T_{(iso)}$	5.8869	12.3294	26.9386	2.1350×10^{12}	0.9975
log $k_{(calcd)}$ vs. $1/T_{(iso)}$	5.8642	12.2566	26.8350	1.8013×10^{12}	0.9998

are, in turn, very close to the mean values of E and A obtained from the proposed mechanism-eliminating method (eqn. 7).

CONCLUSION

As the values of E and A are dependent on the choice of α, it is suggested that for the accurate determination of E and A, the whole range of α values (0.1–0.9) have to be studied, and $E_{(mean)}$ and $A_{(mean)}$ have to be reported instead of the values of E or A at a particular α value, as done by earlier workers [26]. Another advantage of this method is that neither the kinetic form nor the value of n need be known, if we have to calculate the energy of activation alone.

The linear variation of the order parameter with the isothermal temperature is incorporated in the equation to evaluate the reaction rate constant. The values of the activation energy based on the Erofeev equation and the proposed equation, taking into account the variation of n and $T_{(iso)}$, differs by 0.38% only and A has the same order of magnitude, confirming the validity of the assumption employed in the method. The proposed mechanism-eliminating equation also gives comparable values for $E_{(mean)}$ and $A_{(mean)}$. Studies on the effect of sample mass on similar variations of n, k and $T_{(iso)}$ are in progress.

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