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A COMPREHENSIVE STUDY OF THE INFLUENCE OF SAMPLE MASS ON THE KINETIC PARAMETERS IN ISOTHERMAL DEHYDRATION REACTIONS

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ABSTRACT

Kinetic parameters, viz. activation energy, E, and pre-exponential factor, A, have been evaluated for the dehydration of zinc oxalate dihydrate from isothermal mass-loss measurements. Mechanistic and mechanism-free kinetic equations as well as a new equation incorporating the dependence of rate constant, k, on, the order parameter, n', and isothermal temperature, $T_{(iso)}$, have been used to calculate the kinetic parameters. The results obtained from all the three equations indicate the same trend. The kinetic parameters for the dehydration are mass dependent and they show a systematic decrease with increase in sample mass, m. The best fit correlation between E or log A and m can be expressed by a second-degree curve of the form

$$E = a_1 - a_2 m + a_3 m^2$$

$$\log_{10} A = b_1 - b_2 m + b_3 m^2$$

where a_1, a_2, a_3, and b_1, b_2, b_3 are empirical constants.

INTRODUCTION

The dependence of kinetic parameters on heating rate and sample mass is not new [1,2]. Several qualitative and quantitative studies relating kinetic parameters and experimental variables have been reported [3–8] for thermal decomposition reactions carried out under isothermal and dynamic conditions. Non-isothermal kinetic methods have always been a subject of controversy [9–11]. The advantages and disadvantages of isothermal and non-isothermal methods have been discussed [12].

The effect of the simultaneous variation of sample mass and heating rate on the dehydration kinetics of $ZnC_2O_4 \cdot 2\ H_2O$ has been reported [13,14]. However, in isothermal experiments the only variable is sample mass. In an

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earlier publication we had evaluated the kinetic parameters for the dehydration reaction from isothermal experiments using three different approaches and a new correlation between n', $T_{(iso)}$ and k was also established [15]. In this communication it is attempted to study the effect of sample mass on the dehydration kinetics of $ZnC_2O_4 \cdot 2\ H_2O$ from isothermal mass-loss measurements. Mathematical correlations between activation energy, pre-exponential factor (obtained from all the three methods) and sample mass are also presented in this paper.

EXPERIMENTAL

The sample of $ZnC_2O_4 \cdot 2\ H_2O$ used for this study had the same purity and particle size as reported earlier [13]. Isothermal mass-loss curves were recorded on a DuPont 990 thermal analyser. All the experiments were done in a dry nitrogen atmosphere purged at a rate of 50 $cm^3\ min^{-1}$. At each isothermal temperature, eight sets of sample mass (1.3, 2.5, 5.0, 10.0, 13.0, 15.0, 20.0 and 30.0 mg) were employed to study the variations of E and A with sample mass. Further experimental details are given in our earlier paper [15]. Computational work was done with a CDC computer using the FORTRAN IV program.

THEORETICAL

The kinetic parameters from isothermal mass-loss curves can be calculated by three different methods [15]. The general form of the kinetic equation for the thermal decomposition of solids under isothermal conditions is given by Šesták [16] as

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

where α is the fractional decomposition at time, t, $g(\alpha)$ is the integrated form of the fractional decomposition function $f(\alpha)$, and k is the rate constant. The rate constant can be expressed by the Arrhenius equation

$$k = A\ e^{-E/Rt} \tag{2}$$

$E_{(mean)}$ *and* $A_{(mean)}$

From i number of isothermal experiments, E and A (for α varying from 0.1 to 0.9) can be evaluated using the following mechanism-free kinetic equation (the derivation of this equation has been reported in our earlier paper [15]).

$$\log t_{ij} = -\log g_i(\alpha_j) - \log A + \frac{E}{2.303RT_i} \tag{3}$$

where t_{ij} is the time for the fractional decomposition, α_j (j ranging from 0.1 to 0.9) in each isothermal experiment.

$E_{(exp.)}$ *and* $A_{(exp.)}$

The E and A values can be calculated from a mechanism-based equation of the type given by Erofeev [17] as follows

$$\log[-\ln(1-\alpha)] = \frac{1}{n'}\log k + \frac{1}{n'}\log t \tag{4}$$

$E_{(calc.)}$ *and* $A_{(calc.)}$

A linear dependence of log n' versus $T_{(iso)}$ and log k versus log n' was also observed [15] and this was mathematically correlated as

$$\log k = \log k_0 + C\left[A + BT_{(iso)}\right] \tag{5}$$

where $\log k_0 = \log k$ when $n' = 1$ and A, B and C are constants. For isothermal experiments, the kinetic parameters for the three methods are evaluated by using the appropriate equations (3), (4) or (5).

RESULTS AND DISCUSSION

For the dehydration reaction, a total of 43 sets of isothermal experiments were carried out for different sample masses and the time–temperature data obtained were used for the computation of the kinetic parameters. The values of reaction time, t (s) and the corresponding isothermal temperatures for different α values are given in Table 1. Using these values, plots of log t versus $1/T_{(iso)}$ were made for all 43 curves. Figures 1 to 8 give these plots.

From the linear plots, the slopes, intercepts and corresponding values of E, log A and correlation coefficient, r, were calculated. These values are given in Table 2. The correlation coefficients for all the plots are above 0.99 indicating the goodness of the fit. The mean values of E and log A (for $\alpha = 0.1$–0.9) are given in Table 7, and it can be seen that they decrease as the sample mass increases from 1.3 to 30.0 mg.

Kinetic parameters were calculated from the same experimental data using the mechanistic equation (4). Log g(α) versus log t plots were drawn (where $g(\alpha) = [-\ln(1-\alpha)]$). These graphs are shown in Figs. 9 to 16. The values of slope, intercept, n', k and r, calculated from the plots, are given in Table 3. It can be seen that the values of n' increase with increasing $T_{(iso)}$. A similar trend is also observable for the rate constants.

The quantitative correlations between log n' and $T_{(iso)}$ as well as log k and log n' were established recently [15] for a constant sample mass. The validity

TABLE 1

α and t(s) values at different isothermal temperatures and sample masses

Sample mass (mg)	$T_{(iso)}$ (K)	Time (s)								
		$\alpha_{0.1}$	$\alpha_{0.2}$	$\alpha_{0.3}$	$\alpha_{0.4}$	$\alpha_{0.5}$	$\alpha_{0.6}$	$\alpha_{0.7}$	$\alpha_{0.8}$	$\alpha_{0.9}$
1.3	379	708	725	881	1035	1148	1259	1474	1640	1820
	384	363	457	550	646	733	818	881	955	1059
	389	216	285	351	417	479	525	582	631	700
	394	106	138	188	221	257	278	320	351	389
	399	51	74	100	120	139	155	176	195	219
2.5	362	1380	1860	2244	2676	2928	3276	3660	4302	4524
	366	1060	1380	1660	1885	2240	2550	2818	3097	3845
	372	396	576	726	876	1020	1176	1308	1488	1704
	376	246	354	471	576	666	780	888	1014	1170
	380	132	204	273	336	399	471	537	612	654
5.0	368	1782	2250	2682	3162	3534	3910	4167	4860	5430
	377	480	648	840	960	1128	1280	1380	1620	1842
	382	264	384	498	603	702	810	912	1056	1146
	387	162	249	321	384	480	545	631	684	822
	391	102	169	233	285	330	395	432	526	624
10.0	366	2520	3228	3960	4560	5196	5760	6480	7176	8100
	378	564	804	1020	1248	1428	1644	1884	2148	2508
	388	168	276	372	468	564	654	762	882	1050
	392	108	186	264	330	408	492	570	660	768
	397	57	114	168	222	276	339	396	468	540
	402	–	66	111	150	186	231	276	342	420

13.0	375	1080	1392	1716	2028	2340	2604	2916	3276	3708
	378	642	912	1164	1362	1596	1848	2088	2400	2712
	384	324	480	624	780	924	1068	1236	1386	1584
	388	205	313	447	557	646	775	912	1041	1188
	395	96	174	249	321	393	468	549	627	732
15.0	368	1500	2154	2664	3204	3756	4272	4860	5460	6061
	373	780	1152	1464	1800	2136	2472	2820	3227	3732
	377	444	720	1002	1200	1428	1680	1944	2220	2562
	382	331	528	696	876	1047	1237	1462	1660	2089
	386	204	342	462	588	720	858	1002	1170	1344
	392	110	210	297	390	476	570	672	786	918
20.0	376	1344	1920	2442	2916	3396	3900	4392	4980	5640
	381	785	1140	1513	1840	2180	2510	2818	3300	3630
	386	492	756	996	1236	1440	1698	1974	2256	2592
	390	342	534	696	876	1050	1236	1398	1614	1880
	396	198	336	468	594	720	858	1002	1170	1350
30.0	378	807	1110	1386	1653	1923	2181	2472	2781	3168
	383	570	810	1086	1290	1512	1732	1963	2220	2538
	388	294	453	600	738	891	1045	1218	1392	1566
	393	189	306	414	521	620	732	856	990	1176
	398	114	204	291	378	467	558	651	759	810
	405	–	105	168	227	289	354	425	506	606

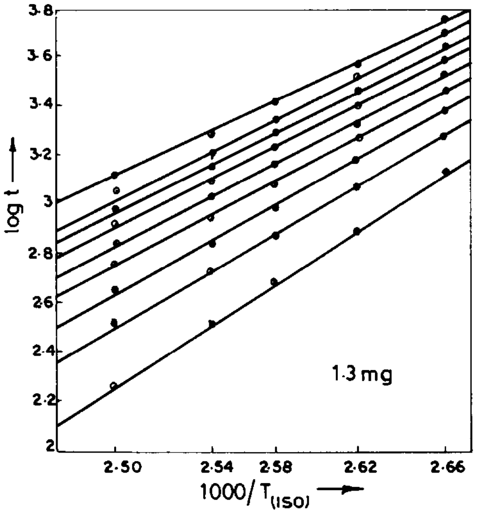

Fig. 1. Plots of log t versus $1000/T_{(iso)}$ for 1.3 mg.

of these relations is further confirmed by the data from different sample masses. Linear plots of log n' versus $T_{(iso)}$ and log k versus log n' were drawn (log k values are from eqn. 4). Figures 17 and 18 represent these plots. The values of the slope, intercept and coresponding correlation coefficient are given in Table 4. The results thus obtained from the plots are introduced in eqn. (5) and the rate constants were calculated for different sample masses. The values of these rate constants are given in Table 5. From the rate constants obtained from eqns. (4) and (5), kinetic parameters were

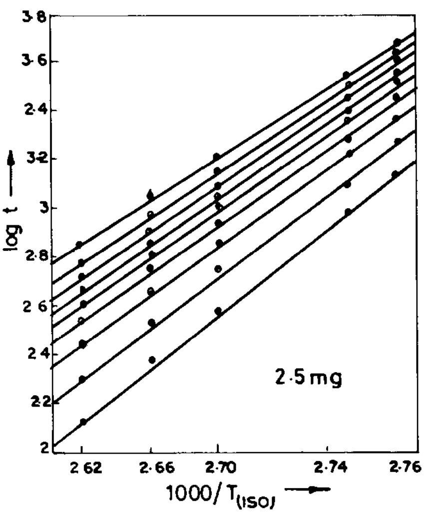

Fig. 2. Plots of log t versus $1000/T_{(iso)}$ for 2.5 mg.

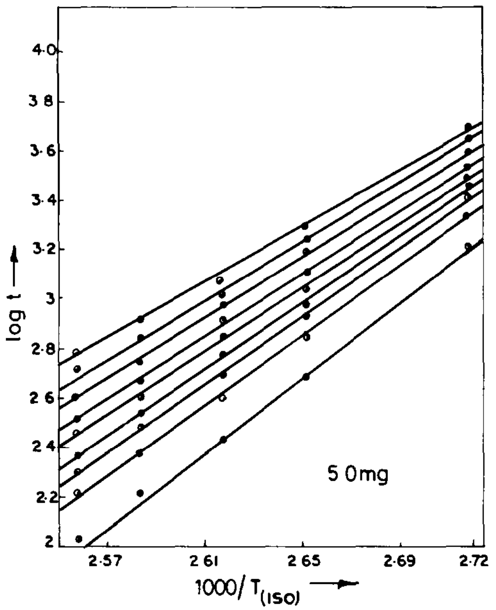

Fig. 3. Plots of log t versus $1000/T_{(\text{iso})}$ for 5.0 mg.

calculated using Arrhenius plots. The values of E, A and r thus calculated are given in Table 6. Figures 19 and 20 show the corresponding log k versus $1/T_{(\text{iso})}$ plots, for the k values using eqns. (4) and (5). Table 7 gives the

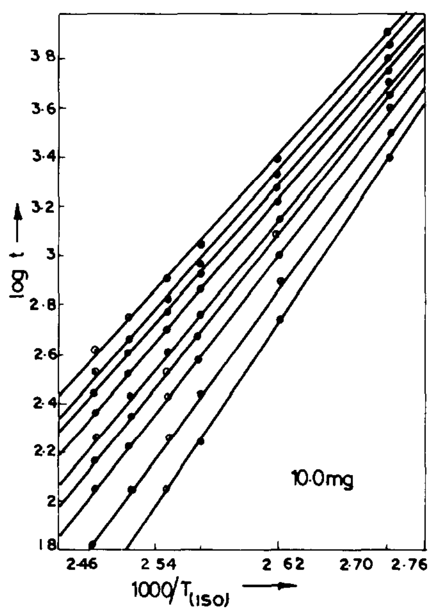

Fig. 4. Plots of log t versus $1000/T_{(\text{iso})}$ for 10.0 mg.

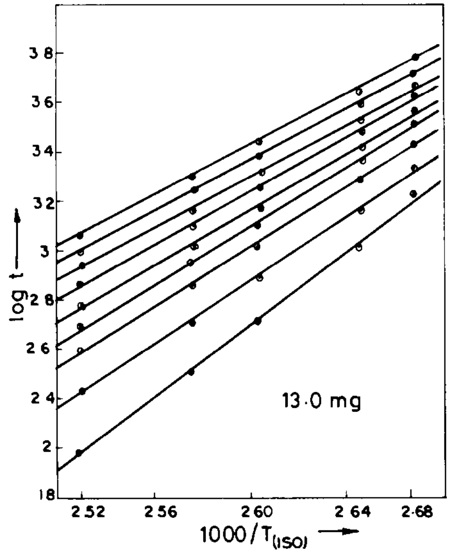

Fig. 5. Plots of log t versus $1000/T_{(\mathrm{iso})}$ for 13.0 mg.

values of E and log A obtained from all the three methods. It can be seen from this table that both E and log A decrease with increasing sample mass. Therefore, statistical analyses were carried out to establish the correlation between kinetic parameters and sample mass. Different types of curve fitting (such as linear, parabola, rectangular hyperbola, exponential, etc.) were tried

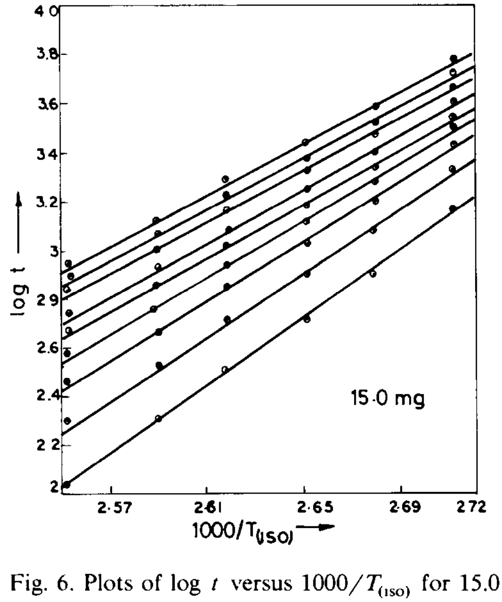

Fig. 6. Plots of log t versus $1000/T_{(\mathrm{iso})}$ for 15.0 mg.

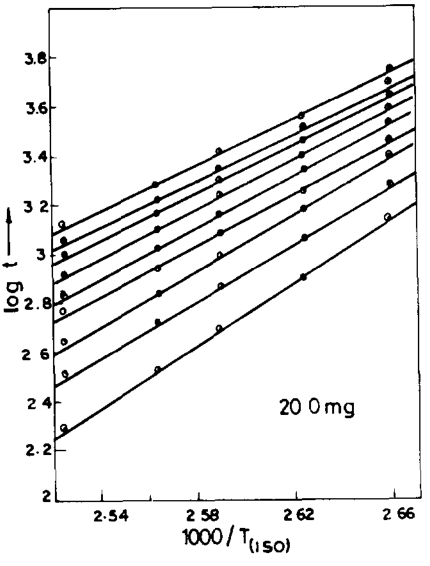

Fig. 7. Plots of log t versus $1000/T_{(\mathrm{iso})}$ for 20.0 mg.

and it was found that the curves of E versus sample mass and log A versus sample mass could be best represented by second-degree curves (parabolae). The corresponding plots are shown in Figs. 21 and 22. The equations representing these curves are given below.

$$E_{(\mathrm{mean})} = 33.344 - 6.839 \times 10^{-1} m + 1.080 \times 10^{-2} m^2$$

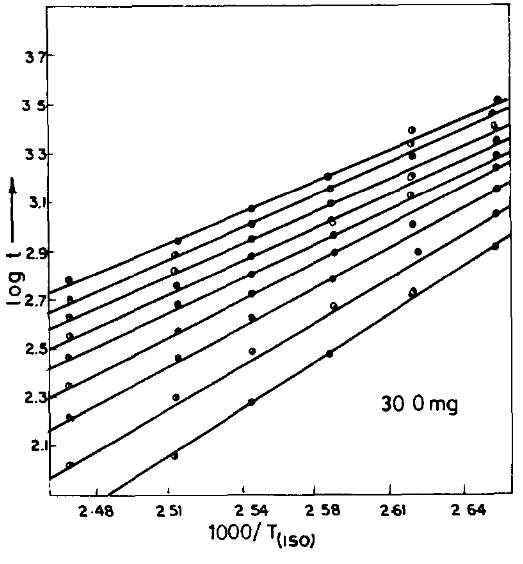

Fig. 8. Plots of log t versus $1000/T_{(\mathrm{iso})}$ for 30.0 mg.

TABLE 2

Results of log t versus $1/T_{(iso)}$ plots for different sample masses

Sample mass (mg)	α	Slope	Intercept	E (kcal mol^{-1})	log A	r
1.3	0.1	8.5192	−19.6118	38.9842	18.6345	0.9976
	0.2	7.5529	−17.0256	34.5623	16.3724	0.9941
	0.3	7.1156	−15.7972	32.5614	15.3495	0.9955
	0.4	7.0570	−15.5733	32.2931	15.2816	0.9955
	0.5	6.9184	−15.1594	31.6588	15.0002	0.9945
	0.6	6.9113	−15.0994	31.6266	15.1615	0.9950
	0.7	6.9093	−15.0419	31.6174	15.1225	0.9967
	0.8	6.9077	−14.9976	31.6101	15.2043	0.9975
	0.9	6.8778	−14.8748	31.4734	15.2370	0.9977
2.5	0.1	8.0329	−18.9905	36.7509	18.0132	0.9978
	0.2	7.5139	−17.4427	34.3839	16.7913	0.9976
	0.3	7.1117	−16.2564	32.5436	15.8087	0.9975
	0.4	6.9277	−15.1695	31.7017	15.3907	0.9973
	0.5	6.7609	−14.8511	30.9384	15.0103	0.9990
	0.6	6.5808	−14.6217	30.1119	14.5837	0.9967
	0.7	6.4908	−14.3296	29.7021	14.4102	0.9969
	0.8	6.2561	−13.6065	28.6283	13.8132	0.9969
	0.9	6.2405	−13.6110	28.5567	13.9733	0.9976
5.0	0.1	7.7004	−17.7056	35.2374	16.7283	0.9978
	0.2	6.9741	−15.6385	31.9137	14.9875	0.9960
	0.3	6.6529	−14.6495	30.4438	14.2018	0.9969
	0.4	6.5305	−14.2878	29.8840	13.9961	0.9960
	0.5	6.3427	−13.7263	29.0247	13.5671	0.9959
	0.6	6.1894	−13.2641	28.3229	13.2261	0.9955
	0.7	6.0970	−12.9645	27.9126	13.0481	0.9990
	0.8	6.0490	−12.7886	27.6807	12.9953	0.9955
	0.9	5.8696	−12.2589	26.8598	12.6211	0.9945
10.0	0.1	7.7698	−17.8338	35.5250	16.8565	0.9988
	0.2	6.8436	−15.1931	31.3167	14.5417	0.9999
	0.3	6.3195	−13.6883	28.9134	13.2406	0.9997
	0.4	6.0630	−12.9302	27.7444	12.6385	0.9995
	0.5	5.8903	−12.4132	26.9543	12.2540	0.9992
	0.6	5.6970	−11.8350	26.0653	11.7970	0.9986
	0.7	5.6040	−11.5329	25.6443	11.6135	0.9989
	0.8	5.4390	−11.0377	24.8849	11.2444	0.9982
	0.9	5.3400	−10.7131	24.4319	11.0753	0.9980
13.0	0.1	7.6327	−17.3546	34.9277	16.3773	0.9983
	0.2	6.6625	−14.6528	30.4880	14.0014	0.9977
	0.3	6.1505	−13.1941	28.1451	12.7464	0.9978
	0.4	5.8395	−12.2951	26.7219	12.0034	0.9939
	0.5	5.6936	−11.8436	26.0542	11.6844	0.9969
	0.6	5.4880	−11.2432	25.1134	11.2052	0.9979
	0.7	5.3210	−10.7467	24.3492	10.8273	0.9981
	0.8	5.2935	−10.6200	24.2234	10.8267	0.9982
	0.9	5.1978	−10.3122	23.7855	10.6744	0.9980

TABLE 2 (continued)

Sample mass (mg)	α	Slope	Intercept	E (kcal mol^{-1})	log A	r
15.0	0.1	6.6879	−15.0143	30.6044	14.0370	0.9978
	0.2	5.9756	−12.9362	27.3446	12.2848	0.9976
	0.3	5.6443	−11.9446	25.8288	11.4969	0.9975
	0.4	5.5275	−11.2759	24.8365	10.9842	0.9973
	0.5	5.3437	−10.9714	24.4531	10.8122	0.9990
	0.6	5.1734	−10.4598	23.6735	10.4218	0.9967
	0.7	5.1042	−10.2068	23.3572	10.2874	0.9969
	0.8	4.9725	−9.9061	22.7538	10.0128	0.9969
	0.9	4.8985	−9.5474	22.4157	9.9096	0.9976
20.0	0.1	6.1929	−13.3563	28.3390	12.3790	0.9990
	0.2	5.6130	−11.6611	25.6856	11.0097	0.9989
	0.3	5.3764	−10.9246	24.6027	10.4769	0.9986
	0.4	5.1710	−10.3001	23.6626	10.0084	0.9987
	0.5	5.0522	−9.9184	23.1190	9.7594	0.9985
	0.6	4.9246	−9.5197	22.5353	9.4817	0.9984
	0.7	4.8144	−9.1763	22.0311	9.2569	0.9976
	0.8	4.7545	−8.5894	21.7560	8.7961	0.9958
	0.9	4.5970	−8.4903	21.0355	8.8525	0.9979
30.0	0.1	5.9212	−14.4071	27.0957	13.4298	0.9965
	0.2	5.7926	−12.6057	26.5084	11.9543	0.9963
	0.3	5.3377	−10.9542	24.4257	10.5068	0.9980
	0.4	5.0103	−10.0185	22.9273	9.7268	0.9965
	0.5	4.7966	−9.3900	21.9494	9.2208	0.9972
	0.6	4.6038	−8.8263	21.0675	8.7883	0.9966
	0.7	4.4681	−8.4139	20.4461	8.4945	0.9964
	0.8	4.3312	−8.0021	19.8197	8.2088	0.9968
	0.9	4.2859	−7.8284	19.6127	8.1906	0.9945

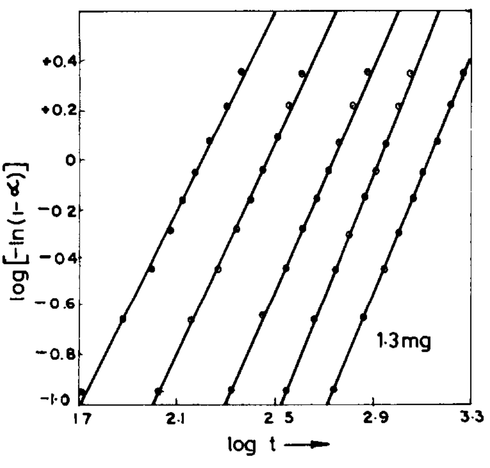

Fig. 9. Plots of log[− ln(1 − α)] versus log t for 1.3 mg.

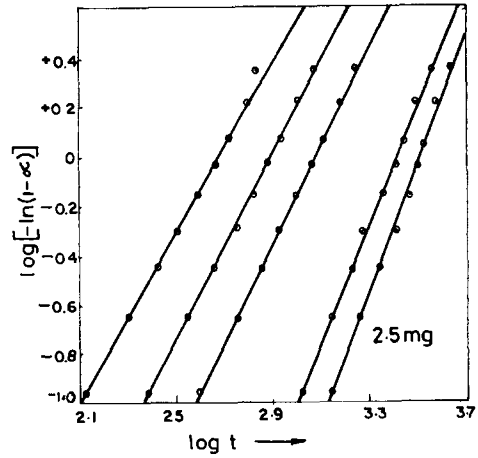

Fig. 10. Plots of log[− ln(1 − α)] versus log t for 2.5 mg.

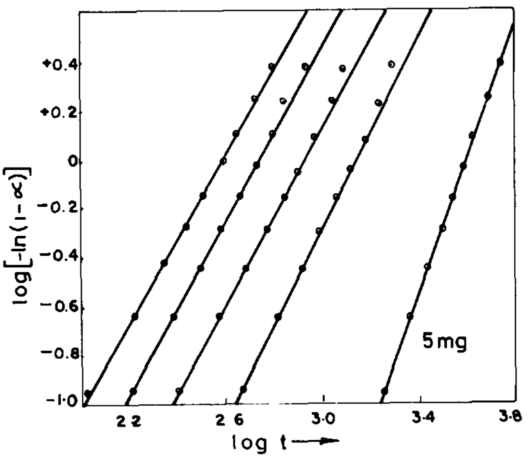

Fig. 11. Plots of log[− ln(1 − α)] versus log t for 5.0 mg.

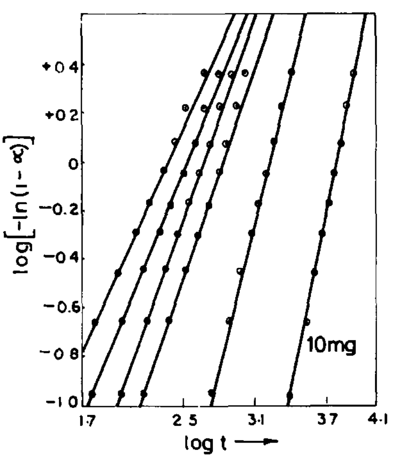

Fig. 12. Plots of log[− ln(1 − α)] versus log t for 10.0 mg.

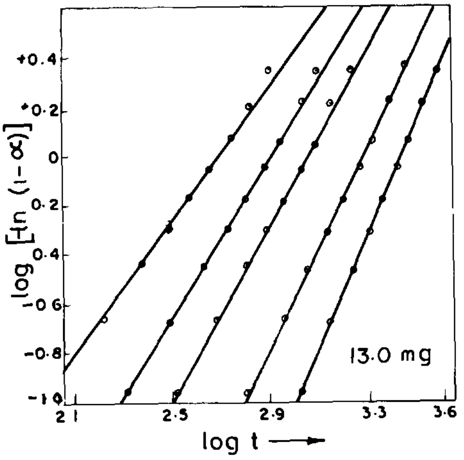

Fig. 13. Plots of log[– ln(1 – α)] versus log *t* for 13.0 mg.

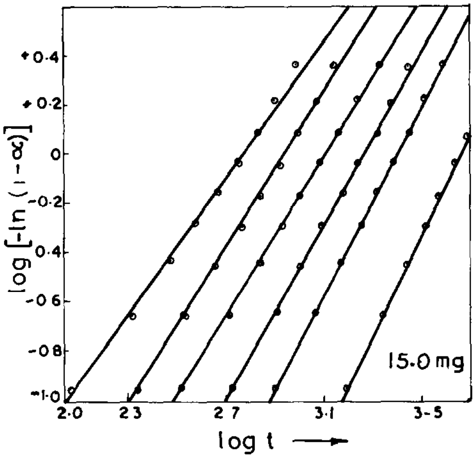

Fig. 14. Plots of log[– ln(1 – α)] versus log *t* for 15.0 mg.

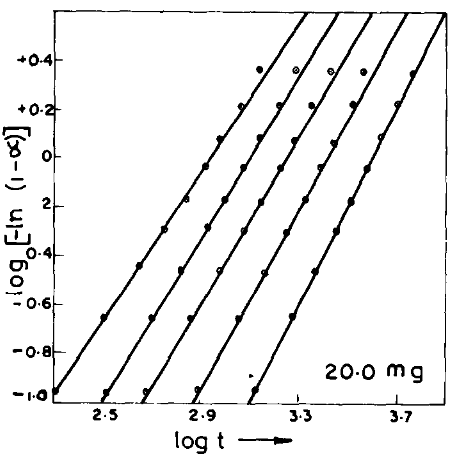

Fig. 15. Plots of log[– ln(1 – α)] versus log *t* for 20.0 mg.

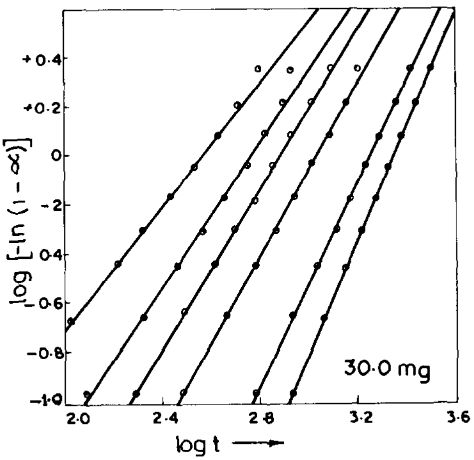

Fig. 16. Plots of log[− ln(1 − α)] versus log t for 30.0 mg.

$$E_{(\text{exp.})} = 32.428 - 7.301 \times 10^{-1} m + 1.190 \times 10^{-2} m^2$$

$$E_{(\text{calc.})} = 31.905 - 6.984 \times 10^{-1} m + 1.130 \times 10^{-2} m^2$$

$$\log_{10} A_{(\text{mean})} = 16.288 - 4.458 \times 10^{-1} m + 7.600 \times 10^{-3} m^2$$

$$\log_{10} A_{(\text{exp.})} = 15.806 - 4.582 \times 10^{-1} m + 7.600 \times 10^{-3} m^2$$

$$\log_{10} A_{(\text{calc})} = 15.481 - 4.397 \times 10^{-1} m + 7.305 \times 10^{-3} m^2$$

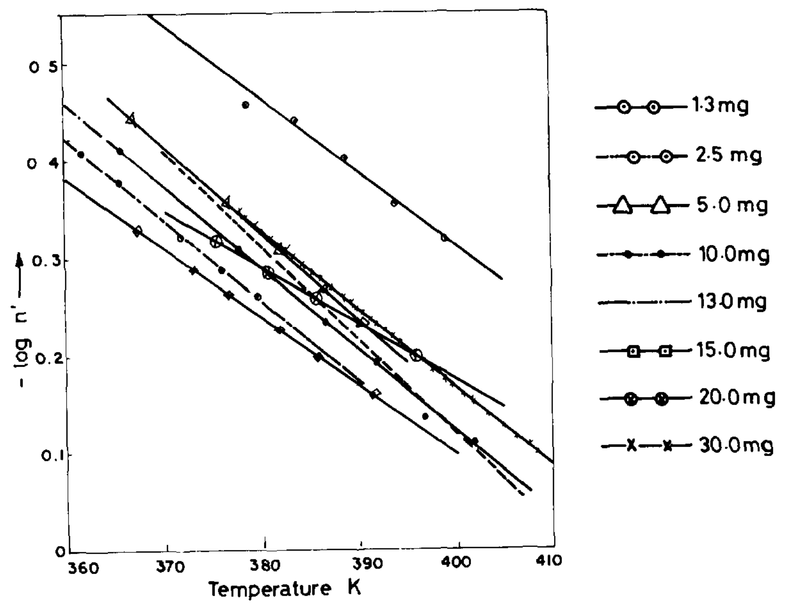

Fig. 17. Plots of log n' versus $T_{(\text{iso})}$ for different sample masses.

TABLE 3

Results of log[− ln(1 − α)] versus log t plots for different $T_{(iso)}$ values and sample masses

Sample mass (mg)	$T_{(iso)}$ (K)	Slope, $1/n'$	n'	Intercept, $\log k/n'$	log k	r
1.3	379	2.8236	0.3542	−8.8322	−3.1280	0.9900
	384	2.7554	0.3629	−8.0193	−2.9104	0.9972
	389	2.5255	0.3960	−6.8816	−2.7251	0.9970
	394	2.2533	0.4438	−5.5407	−2.4589	0.9951
	399	2.0621	0.4849	−4.5357	−2.1995	0.9954
2.5	362	2.5654	0.3898	−9.0472	−3.5266	0.9990
	366	2.4096	0.4150	−8.2183	−3.4107	0.9939
	372	2.0829	0.4801	−6.4054	−3.0752	0.9989
	376	1.9300	0.5181	−5.5975	−2.9003	0.9988
	380	1.8335	0.5451	−4.8976	−2.6712	0.9950
5.0	368	2.8052	0.3565	−10.1144	−3.6056	0.9988
	377	2.2550	0.4434	−7.5000	−3.1134	0.9959
	382	2.0218	0.4946	−7.0229	−2.9142	0.9967
	387	1.8654	0.5361	−5.8918	−2.7445	0.9978
	391	1.7158	0.5828	−4.4680	−2.6040	0.9975
10.0	366	2.5740	0.3885	−9.7129	−3.7734	0.9995
	378	2.0475	0.4884	−6.6160	−3.2313	0.9997
	388	1.6835	0.5940	−4.7659	−2.8310	0.9986
	392	1.5537	0.6436	−4.1894	−2.6964	0.9967
	297	1.3451	0.7430	−3.2769	−2.4362	0.9944
	462	1.2741	0.7850	−3.0266	−2.3766	0.9940
13.0	375	2.4169	0.4136	−8.2835	−3.4273	0.9989
	378	2.1021	0.4757	−6.8837	−3.2747	0.9993
	384	1.8817	0.5314	−5.7131	−3.0361	0.9981
	388	1.6959	0.5986	−4.9153	−2.8983	0.9972
	395	1.4893	0.6714	−4.8418	−2.6753	0.9947
15.0	368	2.1446	0.4663	−7.8024	−3.6381	0.9984
	373	1.9323	0.5175	−6.5735	−3.4019	0.9991
	377	1.8670	0.5356	−6.0560	−3.2438	0.9969
	382	1.6798	0.5953	−5.2229	−3.1092	0.9995
	386	1.5791	0.6253	−4.7015	−2.9401	0.9977
	392	1.4385	0.6952	−3.9760	−2.7640	0.9950
20.0	376	2.1028	0.4756	−7.5672	−3.5987	0.9990
	381	1.9383	0.5159	−6.6013	−3.4057	0.9976
	386	1.8142	0.5512	−5.8787	−3.2403	0.9986
	390	1.7395	0.5749	−5.3864	−3.0964	0.9984
	396	1.5733	0.6354	−4.6292	−2.9414	0.9971
30.0	378	2.2158	0.4513	−7.4208	−3.3490	0.9993
	383	2.0442	0.4892	−6.5189	−3.2477	0.9983
	388	1.7883	0.5592	−5.4109	−3.0258	0.9970
	393	1.6717	0.5982	−4.8098	−2.8772	0.9987
	398	1.4979	0.6676	−4.1110	−2.7445	0.9930
	405	1.3203	0.7574	−3.3725	−2.5543	0.9934

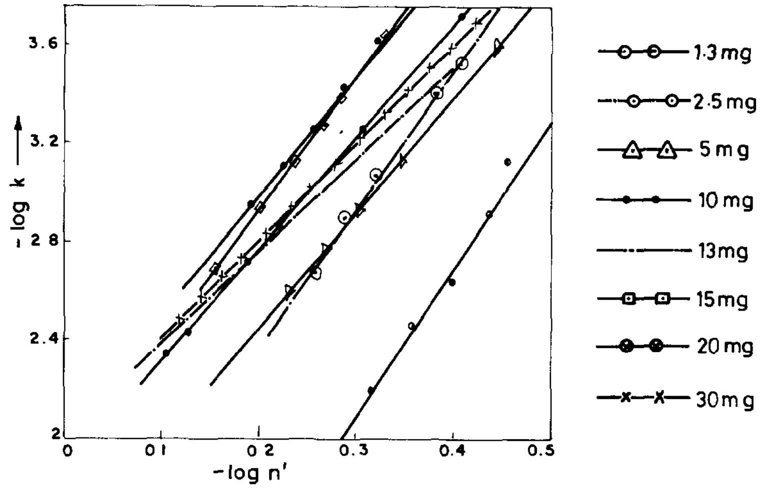

Fig. 18. Plots of log k versus log n' for different sample masses.

TABLE 4

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

Sample mass (mg)	Plot No. [a]	Slope	Intercept	r
1.3	A	0.0072	−3.1960	0.9833
	B	6.2339	−1.2402	0.9885
2.5	A	0.0085	−3.4828	0.9952
	B	5.6489	−1.2425	0.9930
5.0	A	0.0091	−3.8253	0.9971
	B	4.7098	−1.4779	0.9970
10.0	A	0.0087	−3.6006	0.9951
	B	4.5874	−1.8401	0.9940
13.0	A	0.0102	−4.1942	0.9960
	B	3.6007	−2.0711	0.9954
15.0	A	0.0071	−2.9370	0.9968
	B	5.0200	−1.9482	0.9940
20.0	A	0.0061	−2.6207	0.9981
	B	5.3722	−1.8531	0.9945
30.0	A	0.0084	−3.5267	0.9979
	B	3.6079	−2.1061	0.9980

[a] A = log n' versus $T_{(iso)}$ plots, B = log k versus log n' plots.

TABLE 5

Calculated rate constants (log k) from $\log k = \log k_0 + C[A + BT_{(iso)}]$ for different $T_{(iso)}$ values

Sample mass (mg)							
1.3	2.5	5.0	10.0	13.0	15.0	20.0	30.0
−3.1527	−3.5348	−3.6877	−3.7506	−3.4065	−3.5757	−3.6104	−3.3743
−2.9283	−3.3428	−3.3011	−3.2217	−3.2967	−3.3975	−3.4465	−3.2227
−2.7038	−3.0547	−3.0863	−2.8726	−3.0756	−3.2549	−3.2827	−3.0712
−2.4794	−2.8626	−2.8716	−2.7129	−2.9290	−3.0767	−3.1516	−2.9197
−2.2550	−2.6705	−2.6998	−2.5134	−2.6719	−2.9341	−2.9550	−2.7681
			−2.3138		−2.7203		−2.5560

TABLE 6

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

Sample mass (mg)	Plot No. [a]	Slope	Intercept	E (kcal mol^{-1})	A_1 (s^{-1})	r
1.3	A	6.9781	15.2603	31.9322	1.8210×10^{15}	0.9966
	B	6.7933	14.7751	31.0866	5.9583×10^{14}	0.9998
2.5	A	6.6438	14.7869	30.4024	6.1221×10^{14}	0.9956
	B	6.6012	14.6985	30.2075	4.9639×10^{14}	0.9998
5.0	A	6.2213	13.3398	28.4691	2.1870×10^{13}	0.9950
	B	6.1750	13.0854	28.2574	1.2174×10^{13}	0.9997
10.0	A	5.8869	12.3294	26.9386	2.1350×10^{12}	0.9975
	B	5.8642	12.2566	26.8350	1.8013×10^{12}	0.9998
13.0	A	5.5239	11.3279	25.2779	2.1275×10^{11}	0.9977
	B	5.4339	11.0796	24.8657	1.2012×10^{11}	0.9998
15.0	A	5.1742	10.4516	23.6776	2.8288×10^{10}	0.9971
	B	5.1401	10.3846	23.5214	2.4244×10^{10}	0.9998
20.0	A	4.9259	9.5159	22.5415	3.2805×10^{9}	0.9982
	B	4.8780	9.3588	22.3220	2.2845×10^{9}	0.9999
30.0	A	4.6497	8.9368	21.2773	8.6457×10^{8}	0.9970
	B	4.6374	8.8866	21.2213	7.7011×10^{8}	0.9998

[a] A = log k versus $1/T_{(iso)}$ (exp.), B = log k versus $1/T_{(iso)}$ (calc.).

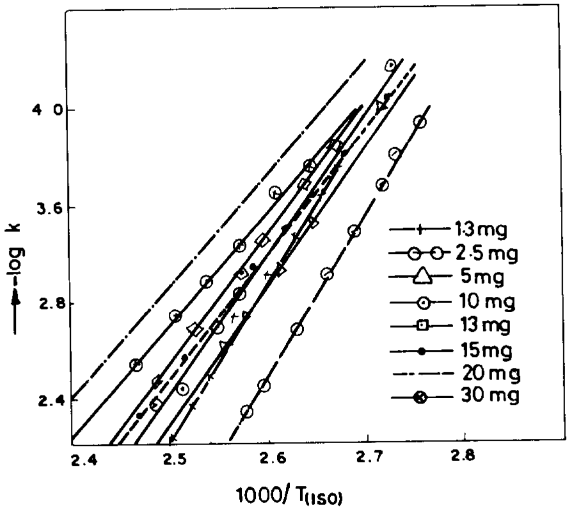

Fig. 19. Plots of log k (exp.) versus $1000/T_{(iso)}$ for different sample masses.

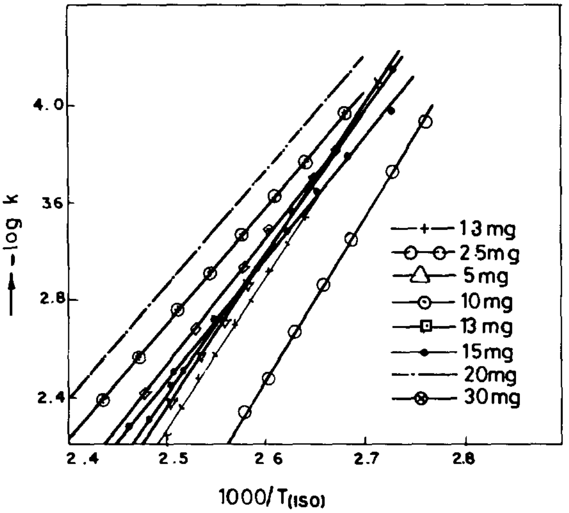

Fig. 20. Plots of log k (calc.) versus $1000/T_{(\mathrm{iso})}$ for different sample masses.

TABLE 7

Kinetic parameters from three different methods

Sample mass (mg)	Mean from $\alpha = 0.1$ to 0.9		Experimental		Calculated	
	E (kcal mol^{-1})	$\log_{10}A$	E (kcal mol^{-1})	$\log_{10}A$	E (kcal mol^{-1})	$\log_{10}A$
1.3	32.9315	15.6961	31.9322	15.2603	31.0866	14.7751
2.5	31.3039	15.3105	30.4024	14.7869	30.2075	14.6958
5.0	29.6977	13.9302	28.4691	13.3398	28.4691	13.0855
10.0	27.9480	12.8068	26.9386	12.3293	26.8350	12.2556
13.0	27.0898	12.2552	25.2779	11.3279	24.8657	11.0796
15.0	25.0297	11.1385	23.6776	10.4516	23.5214	10.3848
20.0	23.6408	10.0023	22.5415	9.5159	22.3220	9.3519
30.0	22.6502	9.8356	21.2773	8.9368	21.2213	8.8866

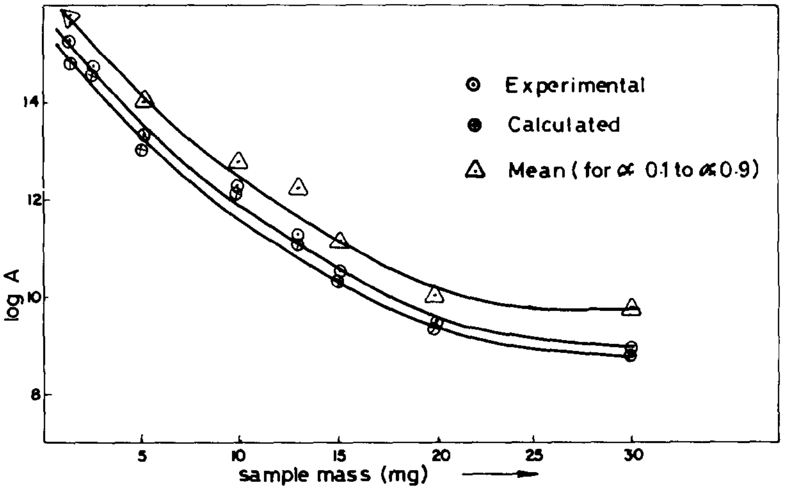

Fig. 21. Plots of log A versus sample mass.

TABLE 8

Empirical constants from E versus m and $\log_{10}A$ versus m plots

Eqn. no.	E versus m					$\log_{10}A$ versus m				
	a_1	$a_2 \times 10^{-1}$	$a_3 \times 10^{-2}$	Minimum residue	Fisher constant	b_1	$b_2 \times 10^{-1}$	$b_3 \times 10^{-3}$	Minimum residue	Fisher constant
3	33.344	6.839	1.080	1.77	129.72	16.288	4.458	7.600	0.59	147.66
4	32.428	7.301	1.190	1.36	183.68	15.806	4.582	7.600	0.36	263.93
5	31.905	6.984	1.130	1.06	217.30	15.481	4.397	7.305	0.52	170.39

Critical value $F_{0.99}(\nu_1 = 2.\ \nu_2 = 5) = 13.30$.

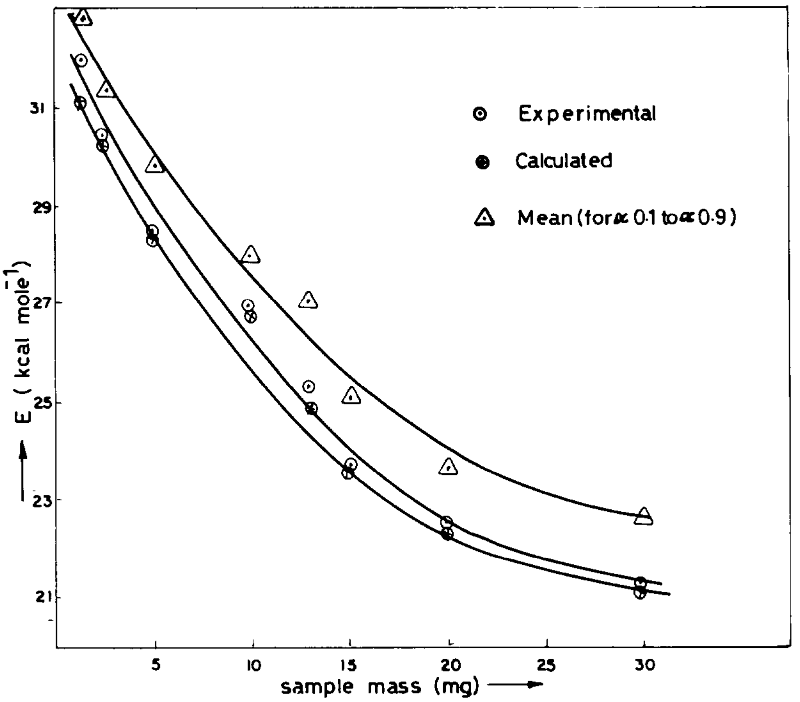

Fig. 22. Plots of E versus sample mass.

The reliability of the curves was established by the F-test [18]. The values of empirical constants, Fisher constants and sum of the minimum residuals calculated for the curves are given in Table 8. It is found that the computed Fisher values are much higher than the critical Fisher values for the 99% confidence level (13.30), indicating that the variations of E or log A are best represented by a quadratic curve for all the three methods employed.

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