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KINETICS AND MECHANISM OF THE THERMAL DEHYDRATION OF CALCIUM OXALATE MONOHYDRATE

HARUHIKO TANAKA *

Chemistry Laboratory, Faculty of School Education, Hiroshima University, Hiroshima (Japan)

SATOSHI OHSHIMA, SUMIO ICHIBA and HISAO NEGITA

Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima (Japan)

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ABSTRACT

The kinetics and mechanism of the thermal dehydration of $CaC_2O_4 \cdot H_2O$ were studied by means of thermogravimetry, both at constant temperature and linearly increasing temperature. The dehydration mechanism was determined as a random nucleation and subsequent growth mechanism, an Avrami—Erofeyev law with $m \simeq 2$. The mechanistic equation could be expressed as

$$[-\ln(1-\alpha)]^{1/1.904} = kt$$

where α is the fraction dehydrated at time t and k is the rate constant. The plausibility of the Avrami—Erofeyev mechanism in the thermal dehydration of $CaC_2O_4 \cdot H_2O$ is discussed.

INTRODUCTION

The kinetics of thermal dehydration of calcium oxalate monohydrate has been examined extensively by many workers [1—22]. The dehydration mechanism of the monohydrate was estimated exclusively as an nth order-type reaction with n having the value of either ca. 2/3 or unity in the equation

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{1}$$

where α is the fraction dehydrated, t is the time, and k is the rate constant. In these studies, however, no other type of equation such as those of Avrami—Erofeyev seems to have been examined except in the study by Ninan and Nair [21]. These authors selected a phase boundary reaction of a spherical symmetry from nine mechanistic equations, including those of Avrami—Erofeyev and diffusion-controlled reactions.

* To whom correspondence should be addressed.

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The possibility that an Avrami—Erofeyev mechanism regulates the dehydration of $CaC_2O_4 \cdot H_2O$ seems not to be eliminated, however, because the correlation coefficients for this mechanism are very close to unity and reasonable kinetic parameters are obtained, especially at lower heating rates. TG traces at lower heating rates are supposed to give more reliable kinetic parameters since the temperature in the sample is practically homogeneous, especially for the small amount of sample. It becomes probable that the Avrami—Erofeyev mechanism controls the dehydration of $CaC_2O_4 \cdot H_2O$ if we can assume that the value of m in the equation

$$[-\ln(1-\alpha)]^{1/m} = kt$$

should actually be scanned from unity to four [23].

In view of these considerations, it is of interest to reinvestigate the kinetics and mechanism of the thermal dehydration of $CaC_2O_4 \cdot H_2O$. The present paper deals with the dehydration mechanism and kinetic parameters evaluated by means of dynamic TG as well as TG at constant temperatures.

EXPERIMENTAL

Calcium oxalate monohydrate was prepared by the double decomposition of reagent grade ammonium oxalate and calcium chloride in dilute aqueous solution. The monohydrate was identified by means of IR and TG. It was ground in a mortar with a pestle and sieved and the fraction passing through the 280 mesh sieve was used as a sample.

TG—DSC measurements at various heating rates were carried out in air, using a Rigaku Thermoflex TG-DSC 8085 E1 type instrument. About 10.0 mg of the sample were weighed into a platinum crucible of 2.5 × 5 mm diameter, without pressing, which was tapped a few times on a desk. α-Alumina was used as a reference material. TG traces for three particle size fractions (48—100, 200—280, and 350—400 mesh) were obtained at a fixed heating rate.

TG traces at various constant temperatures were also recorded under the same sample conditions as those in the dynamic TG. The isothermal runs for different sample weights of 5, 10, 15, and 20 mg were performed.

Computer work was done with an Apple II microcomputer. Graphical plots were obtained using a Watanabe Sokki Co. plotter connected to the computer.

RESULTS AND DISCUSSION

Isothermal method

For the isothermal dehydration of $CaC_2O_4 \cdot H_2O$, the equation

$$F(\alpha) = kt \tag{2}$$

is assumed where $F(\alpha)$ is a function depending on the dehydration mecha-

TABLE 1

Various mechanistic functions

$F(\alpha)$	Symbol	Rate-controlling process
α^2	D_1	One-dimensional diffusion
$\alpha + (1-\alpha)\ln(1-\alpha)$	D_2	Two-dimensional diffusion
$[1-(1-\alpha)^{1/3}]^2$	D_3	Three-dimensional diffusion (Jander function)
$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}$	D_4	Three-dimensional diffusion (Ginstling—Broushtein function)
$\ln[\alpha/(1-\alpha)]$	A_u	Autocatalytic reaction (Prout—Tompkins function)
$1-(1-\alpha)^{1/n}$	R_n	Phase boundary reaction; n = 1, 2, and 3(one-, two-, and three-dimensional, respectively)
$(-\ln(1-\alpha)^{1/m}$	A_m	Random nucleation; m = 1 Random nucleation and subsequent growth; m = 1.5, 2, 3, and 4 (Avrami—Erofeyev functions)

nism. Various $F(\alpha)$ were derived on the basis of theoretical models [24,25]. The appropriate $F(\alpha)$ for the dehydration may be found by plotting it against t; the appropriate $F(\alpha)$ should give a straight line with a slope k. The $F(\alpha)$ functions examined in the present study are listed in Table 1.

Typical TG—DSC traces obtained simultaneously at a constant temperature for the dehydration of $CaC_2O_4 \cdot H_2O$ are given in Fig. 1. Plots of various $F(\alpha)$ against t are shown in Fig. 2. It is confirmed from Fig. 2 that either an R_n ($n = 2$) or A_m ($m = 1.5 \sim 2$) mechanism controls the dehydration. The retardation of $F(\alpha)$ values at $\alpha > 0.85$ may be due to the fact that the effect of the reverse reaction may not be negligible when α is close to unity [26]. TG traces at various constant temperatures are shown in Fig. 3.

The most appropriate values of n and m at a given temperature, those which give a straight line in the plots of $F(\alpha)$ against t, were obtained by scanning the n and m values using the microcomputer with plotter. The values of n and m obtained at different temperatures are given in Table 2, together with the corresponding k values and the correlation coefficient r in

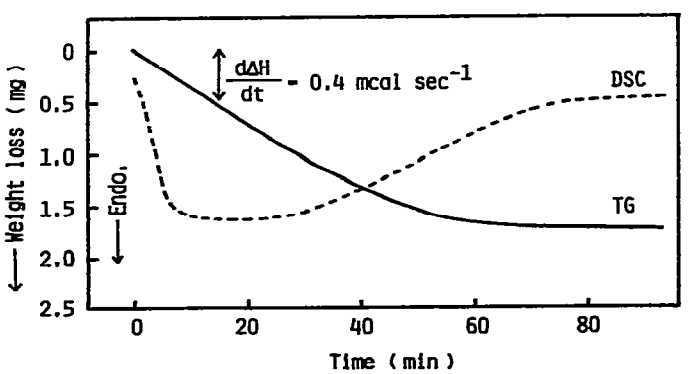

Fig. 1. Typical traces of TG (solid line) and DSC (broken line) obtained simultaneously for the isothermal dehydration of $CaC_2O_4 \cdot H_2O$.

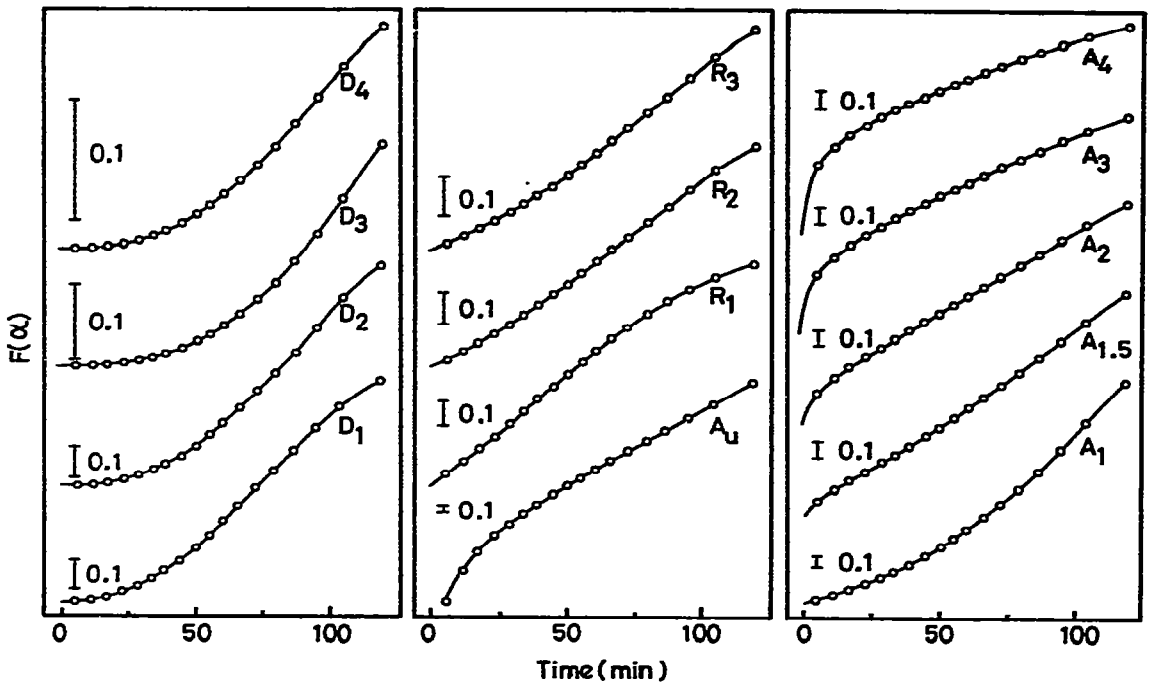

Fig. 2. Plots of F(α) vs. t for the isothermal dehydration of $CaC_2O_4 \cdot H_2O$.

the plots of F(α) against t. The mean values of n and m over the temperature range 140—165°C are found to be 2.018 ± 0.053 and 1.904 ± 0.056, respectively. The activation energy, E, and the frequency factor, A, obtained from the Arrhenius plot are given in Table 3. The Arrhenius plot is shown in Fig. 4.

Although the effect of sample weight on the n and m values were examined in the range 5—20 mg, no meaningful difference was found in the present study.

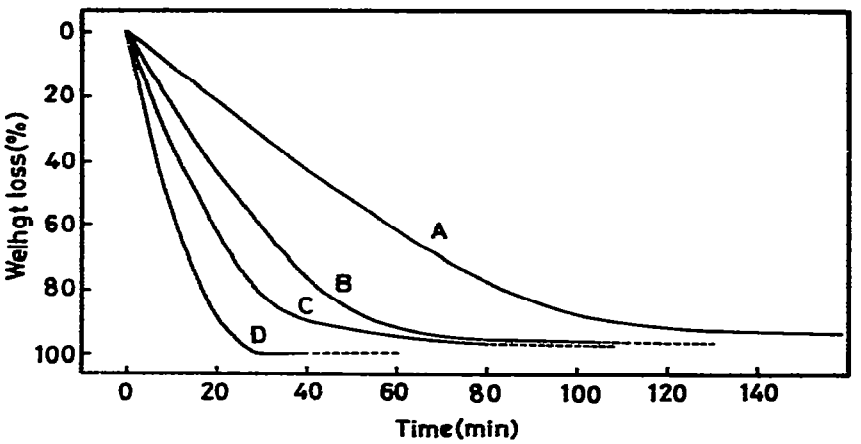

Fig. 3. TG traces for the isothermal dehydration of $CaC_2O_4 \cdot H_2O$ at various temperatures. A, 150.5°C; B, 156.2°C; C, 161.1°C; D, 165.4°C.

TABLE 2

The order parameters n and m with the corresponding k and r values

Temp. (°C)	R_n [a]			A_m [b]		
	n	k (s^{-1}) × 10^4	r	m	k (s^{-1}) × 10^4	r
140.6	2.17	1.006	0.9995	1.92	1.894	0.9999
143.2	2.13	1.138	0.9998	1.79	2.215	0.9999
146.2	1.82	1.654	0.9997	1.69	3.083	0.9997
147.6	1.82	1.997	0.9997	1.96	3.344	0.9999
150.5	1.75	2.310	0.9996	1.75	4.092	0.9996
152.9	1.69	3.586	0.9999	2.44	4.660	0.9999
155.1	1.79	3.907	0.9998	2.33	5.467	0.9999
157.7	1.92	4.149	0.9997	2.08	6.651	0.9997
159.8	2.00	4.321	0.9998	1.47	9.603	0.9995
162.6	2.33	5.435	0.9998	1.79	11.17	0.9999
165.1	2.78	5.734	0.9997	1.72	13.40	0.9998

[a] $R_n = 1 - (1 - \alpha)^{1/n}$.
[b] $A_m = [-\ln(1 - \alpha)]^{1/m}$.

TABLE 3

The kinetic parameters and the corresponding correlation coefficient r from the isothermal gravimetric method

$F(\alpha)$	E (k cal $mole^{-1}$)	$\log A$ (s^{-1})	$-r$
$R_{2.018}$	28.31 ± 0.26	10.97 ± 0.13	0.9910
$A_{1.904}$	28.23 ± 0.28	11.19 ± 0.14	0.9895

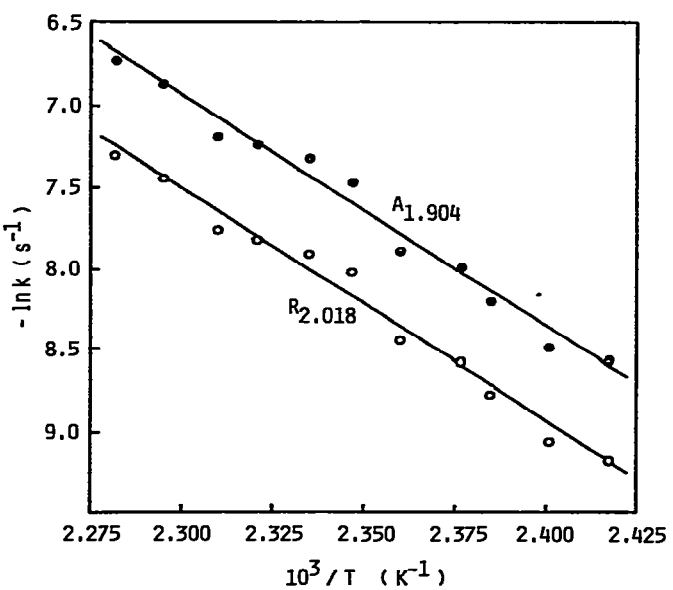

Fig. 4. Arrhenius plots for the isothermal dehydration of $CaC_2O_4 \cdot H_2O$.

Dynamic method

It seems that the Coats and Redfern method [5] extended to include any F(α) is one of the most reliable methods of evaluating kinetic parameters by means of dynamic TG [27]. The general equation for obtaining the parameters is

$$\ln\{F(\alpha)/T^2\} = \ln\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]-\frac{E}{RT} \tag{3}$$

where F(α) is a function depending on the mechanism of the non-isothermal dehydration, T is the absolute temperature, R is the gas constant, and a is the linear heating rate. The kinetic parameters, E and A, can be obtained by plotting $\ln\{F(\alpha)/T^2\}$ against $1/T$. Such plots for all the functions listed in Table 1 are shown in Fig. 5. Typical TG—DSC traces obtained simultaneously for the thermal dehydration of $CaC_2O_4 \cdot H_2O$ are given in Fig. 6. The kinetic parameters for all the functions are listed in Table 4. In the light of the reasonable order of magnitude of the parameters and correlation coefficient in Table 4, especially at the lowest heating rate, it is likely that either an R_n or A_m mechanism should regulate the dehydration of $CaC_2O_4 \cdot H_2O$. It seems to be difficult to select the correct mechanism from the two at this stage.

If we can assume here, however, that the function F(α) estimated from the isothermal method can be used for the dynamic method [28], the parameters listed in Table 5 are obtained. From the values at the lowest heating rate, which are considered as the most reliable, the values for $A_{1.904}$

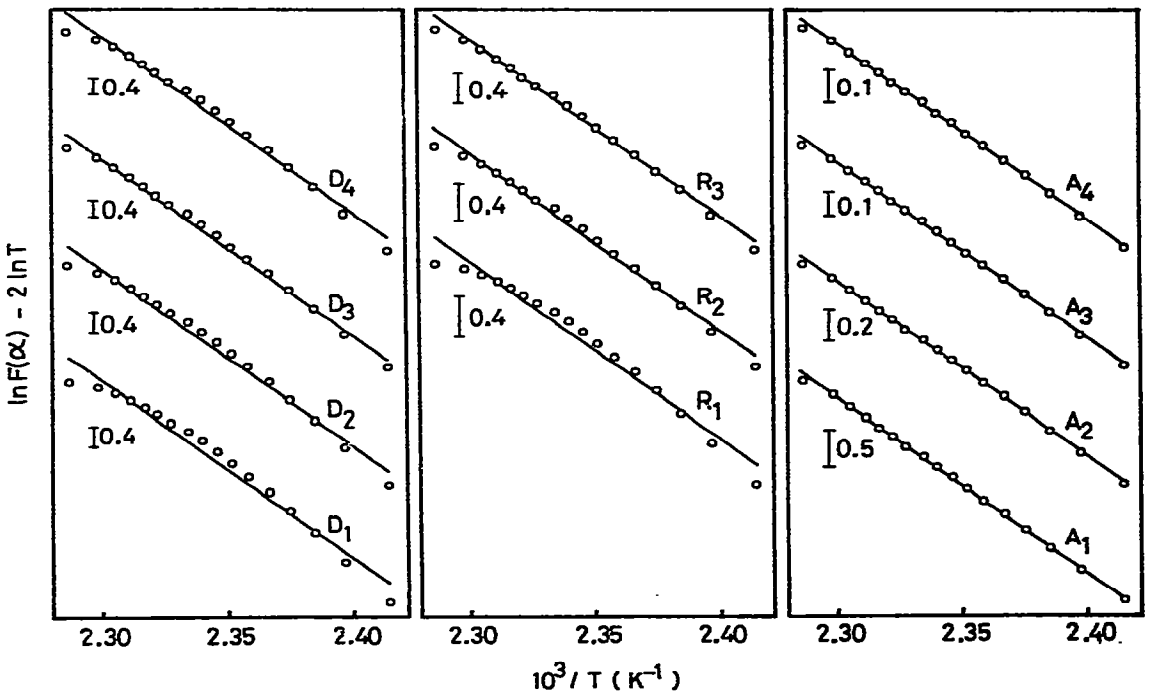

Fig. 5. Plots of $\ln\{F(\alpha)/T^2\}$ vs. $1/T$ for the non-isothermal dehydration of $CaC_2O_4 \cdot H_2O$.

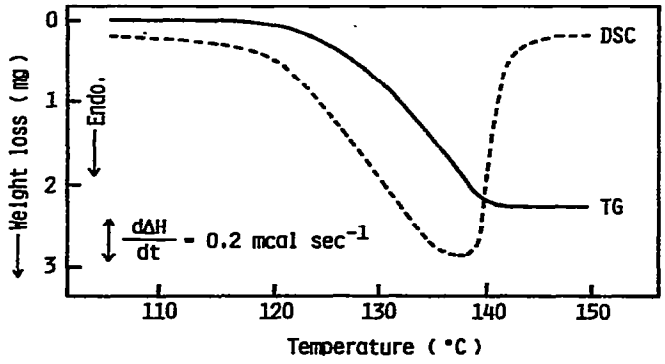

Fig. 6. Typical traces of TG (solid line) and DSC (broken line) obtained simultaneously for the non-isothermal dehydration of $CaC_2O_4 \cdot H_2O$.

are found to be compatible with those of isothermal method. This suggests that the dehydration of $CaC_2O_4 \cdot H_2O$ should be regulated by the $A_{1.904}$ mechanism.

The assumed $A_{1.904}$ mechanism could be checked by comparing the rate constant k for various particle sizes. The rate constant k is proved to be practically unaffected by the particle size, which is shown in Table 6. This result supports the $A_{1.904}$ mechanism, because the rate constant k should decrease with increasing radius of the particle in the case of a phase-boundary reaction [24].

It may be noted here that other mechanisms, like a phase-boundary controlled reaction, can not always be ruled out since the appropriate mechanism should be adopted according to the sample and measuring conditions such as pretreatment, particle size, sample size, packing, atmosphere, temperature, and so on [23,29].

The dehydration mechanism deduced in the present study resulted, in part at least, from the fact that the crystalline $CaC_2O_4 \cdot H_2O$ powder prepared from a hot solution was ground to very fine particles in a mortar with a pestle [30]. The role of advancement of reactant—product interface, if it occurs at all, may not be so great in the course of decomposition of these fine particles [31]. In addition, such particles have so much strain energy and various defects that the nucleation of the product may become possible inside the particle as well as on the surface and at the phase boundary [23,32].

It is also interesting to note that the kinetic parameters, E and A, for any function $F(\alpha)$ decrease with increasing linear heating rate. This trend was also found for the dehydration of $CaC_2O_4 \cdot H_2O$ by other workers [7,11,18,21]. The change in the parameters was attributed to the accompanying variation of the temperature range; the temperature of inception of dehydration is nearly constant irrespective of the heating rate whereas the temperature of completion becomes higher with increase in the heating rate [7]. Such change may also be explained in terms of a kinetic compensation effect [33] or the change of the distribution of the thermal flux [11,34]. In view of this, it is stressed that the kinetic parameters should be obtained at

TABLE 4

The values of E (kcal mole^{-1}) and log$A$ (s^{-1}) and the corresponding correlation coefficient r from the dynamic TG method

F(α)	Heating rate (°C min^{-1})								
	0.55			1.16			2.36		
	E	log$A$	$-r$	E	log$A$	$-r$	E	log$A$	$-r$
D_1	68.7	31.7	0.9858	62.8	28.5	0.9793	54.4	24.1	0.9724
D_2	76.4	35.5	0.9920	69.9	31.9	0.9869	60.6	27.0	0.9809
D_3	86.1	40.0	0.9971	79.0	36.0	0.9938	68.6	30.5	0.9891
D_4	79.6	36.5	0.9941	72.9	32.8	0.9896	63.2	27.7	0.9841
R_1	33.5	13.8	0.9850	30.5	12.3	0.9781	26.3	10.2	0.9705
R_2	39.8	16.8	0.9949	36.4	15.1	0.9905	31.5	12.6	0.9849
R_3	42.2	17.9	0.9970	38.6	16.1	0.9935	33.4	13.4	0.9885
A_1	47.4	21.2	0.9995	43.5	19.1	0.9976	37.7	16.2	0.9940
$A_{1.5}$	31.1	12.7	0.9994	31.1	11.4	0.9974	24.6	9.51	0.9937
A_2	22.9	8.41	0.9994	20.9	7.51	0.9974	18.0	6.15	0.9934
A_3	14.7	4.08	0.9994	13.4	3.57	0.9971	11.4	2.74	0.9926
A_4	10.6	1.88	0.9993	9.59	1.57	0.9969	8.12	1.01	0.9918

TABLE 5

The kinetic parameters, E and A, obtained from the analysis of dynamic TG in terms of the isothermally determined F(α)

Heating rate (°C min^{-1})	Dehydration temp. (°C)		R_n (n = 2.018)		
	T_{eo} [a]	T_p [b]	E (kcal mole^{-1})	log$A$ (s^{-1})	$-r$
0.55	136.7	157.3	39.87 ± 0.17	16.85 ± 0.09	0.9949
1.16	140.0	164.3	36.54 ± 0.21	15.15 ± 0.11	0.9905
2.36	145.2	172.8	31.50 ± 0.23	12.60 ± 0.12	0.9850
4.71	149.1	178.2	28.22 ± 0.10	11.06 ± 0.05	0.9965
9.33	153.8	187.8	24.59 ± 0.04	9.31 ± 0.02	0.9991
18.94	156.0	198.2	21.57 ± 0.08	7.87 ± 0.04	0.9966

[a] The temperature where the base line of the simultaneous DSC trace intersects the tangent of the maximum slope of peak.
[b] The peak temperature of the simultaneous DSC trace.

TABLE 6

The effect of particle size on the rate constant k for the functions $R_{2.018}$ and $A_{1.094}$ at a heating rate of 1.12°C min^{-1}.

F(α)	$k \times 10^4$ (s^{-1}) [a]		
	48—100 mesh	200—280 mesh	350—400 mesh
$R_{2.018}$	5.12	5.01	5.95
$A_{1.904}$	8.71	8.69	9.37

[a] The value at 160°C.

4.71			9.33			18.94		
E	log$A$	$-r$	E	log$A$	$-r$	E	log$A$	$-r$
49.1	21.4	0.9885	43.1	18.3	0.9939	37.9	15.7	0.9885
54.6	24.0	0.9940	47.9	20.5	0.9977	42.2	17.6	0.9941
61.5	26.9	0.9983	53.9	22.9	0.9996	47.6	19.6	0.9984
56.9	24.5	0.9959	49.8	20.9	0.9988	43.9	17.8	0.9960
23.7	8.97	0.9875	20.7	7.56	0.9933	18.0	6.34	0.9872
28.2	11.0	0.9965	24.6	9.30	0.9991	21.5	7.86	0.9965
29.9	11.8	0.9982	26.0	9.89	0.9998	22.9	8.37	0.9983
33.6	14.2	0.9997	29.3	12.0	0.9992	25.8	10.3	0.9998
21.8	8.27	0.9997	18.9	6.92	0.9992	16.6	5.86	0.9998
15.9	5.29	0.9997	13.7	4.33	0.9991	12.0	3.60	0.9998
10.0	2.25	0.9996	8.56	1.69	0.9990	7.38	1.29	0.9997
7.09	0.708	0.9996	5.98	0.355	0.9989	5.08	0.127	0.9997

A_m (m = 1.904)		
E (kcal mole^{-1})	log$A$ (s^{-1})	$-r$
24.10 ± 0.03	9.06 ± 0.03	0.9994
22.08 ± 0.07	8.13 ± 0.03	0.9973
18.97 ± 0.09	6.66 ± 0.05	0.9935
16.82 ± 0.02	5.74 ± 0.01	0.9997
14.52 ± 0.03	4.72 ± 0.01	0.9991
12.67 ± 0.01	3.94 ± 0.01	0.9998

as low a heating rate as possible; otherwise, the parameters may only be valid for a comparison of the values derived under the identical measurement conditions.

Although a number of methods have been reported so far on the determination of kinetic parameters by means of thermal analyses, no decisive method seems to have been found. It is not so easy, in general, to obtain reliable kinetic parameters uniquely from the dynamic method alone. It is interesting, however, that the dynamic method will have some advantages over the isothermal in determining the relative values, e.g. kinetic deuterium isotope effects [35].

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