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# A NEW DIFFERENTIAL METHOD FOR DETERMINING ORDERS AND RATES OF REACTIONS AND ITS APPLICATION TO SOLID STATE REACTIONS. PART II. SOME EMPIRICAL OBSERVATIONS ON THE ISOTHERMAL DEHYDRATION OF CALCIUM OXALATE MONOHYDRATE

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## ABSTRACT

The recently described differential method of determining the order and rate of a reaction has been applied to the isothermal dehydration of calcium oxalate monohydrate. Literature data are compared with results obtained in this study, orders of reaction of ~0.2 and ~0.5 are found to describe the reaction well. No evidence could be found to support the often quoted orders of 0.666 or 1 for this process.

We have recently described [1] a differential method for determining both the rate and order of a process for which the concept of an order (or index) of reaction is appropriate. Calcium oxalate monohydrate is frequently used as a test material in thermal studies. We have undertaken a study of the dehydration of this compound both as a further test of our method and because of the general interest in this reaction.

The majority of kinetic studies of this dehydration have been carried out by thermogravimetric methods [2–8]; some of the available data are summarized in Table 1. There is a very wide range in reported values of the activation energy (84–264 kJ mole$^{-1}$). The reasons for this include the effects of sample size, heating rate and atmosphere. Indeed using this reaction Ninan and Nair [7–9] have shown that the variation in determined activation energy with reaction conditions is systematic. However, this system is further complicated by the "Smith Topeley Effect" (the anomalous dependence of rate and/or activation energy on the vapour pressure of the volatile component in a decomposition). Dollimore et al. [10] have shown a marked effect of water vapour pressure on both the rate and activation energy of this process. The build-up of water vapour pressure leads to the activation energy becoming higher, the most reliable method of studying this reaction is most probably in vacuo. Manche and Carroll [11] carried out an isothermal study to test a method suggested by Ng [12] for determining activation energies. In this paper we compare the fully published data of Manche and Carroll [11] with our results.

These many factors underlie the thermogravimetric behaviour of calcium oxalate

TABLE I

Summary of some kinetic studies of the dehydration of calcium oxalate monohydrate

| Order, $n$ | $A$ | $E_a$ (kJ mole$^{-1}$) | Ref. | Notes | Calculation method (ref.) |
|---|---|---|---|---|---|
| 0.71 | | 89.53 | 2 | 0.1 g, 3.45°C min$^{-1}$, static air | 2 |
| 0.97 | $7.22 \times 10^{-6}$ | 95.81 | 3 | non-linear $\Delta T$, static air | 3 |
| 0.9 | | 104.6 | 4 | 10°C min$^{-1}$, $N_2$ | 6 |
| | | 84.5 | 5 | 9°C min$^{-1}$, $N_2$ | 5 |
| 1.0 | | 92.05 | 6 | 423 mg, 10°C min$^{-1}$ | 6 |
| 0.66 | $8.34 \times 10^{15}$ | 264 | 7 | 5.1 mg, 5°C min$^{-1}$ $N_2$ | 2 |
| 0 | $\sim 10^{10}$ | $\sim$68 | 10 | Isothermal, 110–120°C, vacuum, 20 mg | |
| 0 | $\sim 10^{24}$ | $\sim$200 | 10 | Isothermal, 110–120°C, 1.3 K N m$^{-2}$ $H_2O$, 20 mg | |
| | | 56.76 | 11 | Isothermal, 120–170°C, $N_2$ | 12 |
| | | 70.71 | 11 | Isothermal, 120–170°C, $N_2$ | 11 |

monohydrate as for example studied by Simons and Newkirk [13]. All this must be appreciated when the substance is used as a "standard" or "test material" for thermogravimetry [14].

Finally the order of the reaction is most frequently reported as 0.666; this seems to owe its origin to the original work of Coats and Redfern [2]. The unreliability of non-isothermal methods in determining the order of reaction has frequently been commented on [15–18]; we are able to further investigate the concept of an order for this reaction using our differential method.

## EXPERIMENTAL

AnalaR calcium oxalate was dried in a vacuum desiccator and used (as a fine powder) with no further purification. The sample ($5 \mp 0.5$ mg) was introduced into the preheated furnace of a Stanton-Redcroft TG 750 thermobalance, dry $N_2$ (10 ml min$^{-1}$) was passed over the sample. The time for isothermal conditions to be established within the furnace was 45 s.

## CALCULATION PROCEDURE

Plots of $x^{-1}$ vs. time $[(1-\alpha)/\mathrm{d}(1-\alpha)/\mathrm{d}t$ vs. t] were constructed as previously described [1]. Such plots have been shown to have a gradient $(n-1)$ (where $n$ is the

TABLE 2

Summary of calculations for the isothermal decomposition of calcium oxalate monohydrate

| Temp. (°C) | Ref. | $m$ [a] | Intercept [b] | Slope [b] | $r$ [b] | $A$ | $E_a$ (kJ mole$^{-1}$) | $k$(s$^{-1}$) [c] | $A$ | $E_a$ (kJ mole$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| 120 | 10 | 1.02 | 111.6 | 0.84 | 0.99 | | | $7.25\times10^{-4}$ | | |
| 150 | 10 | 1.15 | 258.9 | 0.72 | 0.99 | $5\times10^{5}$ | 65.8 | $3.05\times10^{-3}$ | $1.21\times10^{6}$ | 69.5 |
| 170 | 10 | 1.17 | 115.2 | 0.80 | 0.99 | | | $8.08\times10^{-3}$ | | |
| 120 | [d] | 1.02 | 4,777 | 0.65 | 0.92 | | | $1.21\times10^{-4}$ | | |
| 131 | [d] | 1.03 | 1,311 | 0.52 | 0.99 | $4.8\times10^{8}$ | 91.7 | $3.88\times10^{-4}$ | $1.0\times10^{9}$ | 96.3 |
| 150 | [d] | 1.07 | 347.5 | 0.55 | 0.98 | | | $1.69\times10^{-3}$ | | |
| 161 | [d] | 1.08 | 171.7 | 0.56 | 0.98 | | | $3.24\times10^{-3}$ | | |
| 181 | [d] | 1.15 | 101.3 | 0.66 | 0.99 | | | $6.88\times10^{-3}$ | | |

[a] Slope of plot of ln−ln(1 −$\alpha$) vs. $t$ in the region $0.1<\alpha<0.5$.

[b] Intercept, slope and correlation coefficient of plots of $x^{-1}$ vs. time.

[c] Rate constant determined by use of most appropriate integrated rate law; data of Manche and Carroll [11] $(1-\alpha)^{0.78}$ vs. time, this work $(1-\alpha)^{0.5}$ vs. time.

[d] This work.

order of the reaction), and an intercept of $k^{-1}$ (where $k$ is the appropriate rate constant). For plots of ln–ln$(1-\alpha)$ vs. time and $\alpha$ vs. $t/t_{0.5}$ (reduced time plots) the time was corrected for any "zero time error" by extrapolating the initial nearly linear section of the $(1-\alpha)$ vs $t$ curve ($0.1<\alpha<0.3$) to the time axis. A 'corrected' time thus established was used for reduced time and ln–ln$(1-\alpha)$ plots only.

## RESULTS

Our calculations both on the data of Manche and our own results are summarized in Table 2. The gradients of plots of ln–ln$(1-\alpha)$ vs. ln time ($m$) are all close to unity. Hancock and Sharp [19] have pointed out that this is a good indication that the concept of an order of reaction is appropriate. When the two sets of data are processed by our differential method significant differences emerge; the order calculated from the data of Manche is ~0.2. Orders less than 0.5 are unusual but not unknown, their theoretical significance is uncertain. In marked contrast our data give an order of 0.4–0.5, close enough to 0.5 (the order required for phase boundary control in two dimensions) for us to suggest that a mechanism of this kind is operating.

The results of our method have been further checked by plotting integrated rate equations (Table 3; Figs. 1 and 2). For our results at 131°C we compare Fig. 1 orders of reaction 0.25, 0.5, 0.666 and 1, the order suggested by our method (~0.5) clearly gives the best straight line (Table 3; Fig. 1). For the results of Manche and Carroll [11] at 150°C we compare orders of reaction 0.28, 0.5, 0.666 and 1, again the best straight line (Table 3; Fig. 2) is given by the order suggested by our method (0.28). We have also constructed reduced time plots [20] for these orders of reaction; the

TABLE 3

Comparison of rate constants obtained from mechanisms based on the concept of an order of reaction

| Order of reaction | Integrated equation | $k$ (min$^{-1}$)×10$^{2}$ [a] | |
|---|---|---|---|
| | | 131°C (this work) | 150°C (ref. 11) |
| 2/3 | $1-(1-\alpha)^{1/3}$ | 1.89 (0.9981) | 11.0 (0.9755) |
| 0.5 | $1-(1-\alpha)^{1/2}$ | 2.33 (0.9999) | 15.1 (0.9972) |
| $(1-N)$ | $1-(1-\alpha)^{N}$ [b] | 2.78 (0.9973) | 17.8 (0.9999) |
| 1 | $-\ln(1-\alpha)$ | 7.71 (0.9900) | 35.0 (0.8283) |

[a] Rate constant (s$^{-1}$) and correlation coefficient obtained from plot of integrated rate vs. time.

[b] For 131°C $N=0.75$; for 150°C $N=0.72$ (from plot $x^{-1}$ vs. $t$).

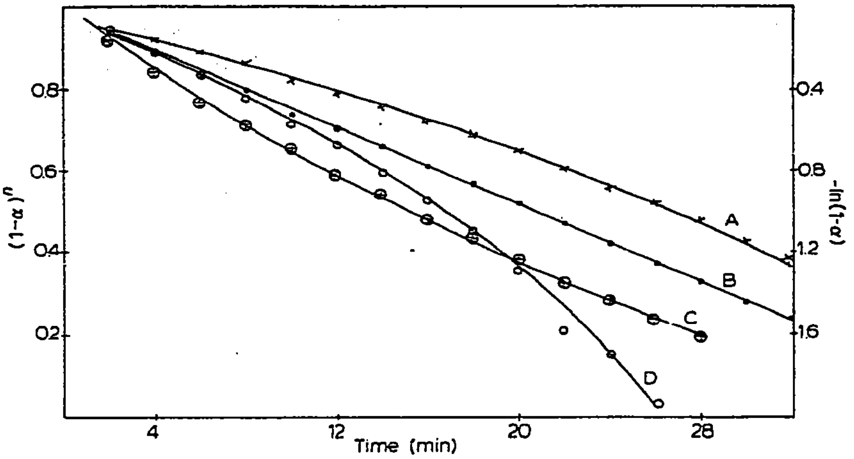

Fig. 1. Comparison of integrated rate law for results at 131°C obtained in this study. ×, $(1-\alpha)^{0.333}$; ●, $(1-\alpha)^{0.5}$; ○, $\ln(1-\alpha)$; ⊕, $(1-\alpha)^{0.75}$.

correlation of the experimental results with the theoretical plot for order 0.5 or 0.28, respectively, is excellent.

Activation energies have been calculated from the rate constants determined by the differential method (Table 2). The method essentially involves an extrapolation to zero time; as pointed out by Manche and Carroll [11] such methods will give a low result. Hence we have also calculated pre-exponential factors and activation energies using rate constants from plots of integrated rate equations against time, order = 0.5 (our result) and order = 0.22 (average from Table 2; Manche's data). The activation energy determined from Manche's data (69.5 kJ mole$^{-1}$) is in excellent

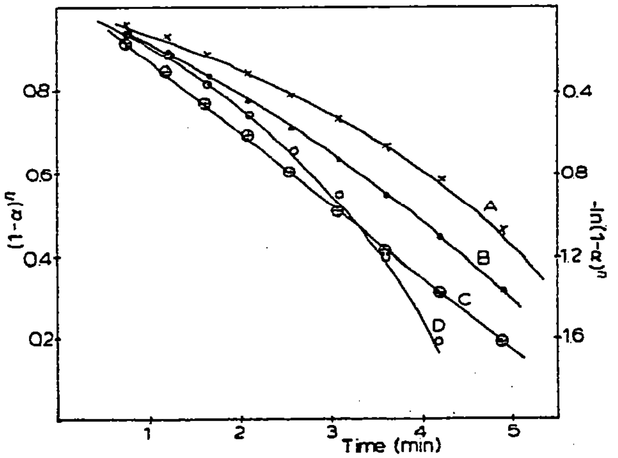

Fig. 2. Comparison of integrated rate laws for data of Manche and Carroll [11] at 150°C. ×, $(1-\alpha)^{0.333}$; ●, $(1-\alpha)^{0.5}$; ○, $\ln(1-\alpha)$; ⊕, $(1-\alpha)^{0.72}$.

agreement with the value obtained by his method (70.7 kJ mole$^{-1}$). Our results give a substantially higher value of 96.3 kJ mole$^{-1}$. The Arrhenius plots give good straight lines (Table 2; Fig. 3).

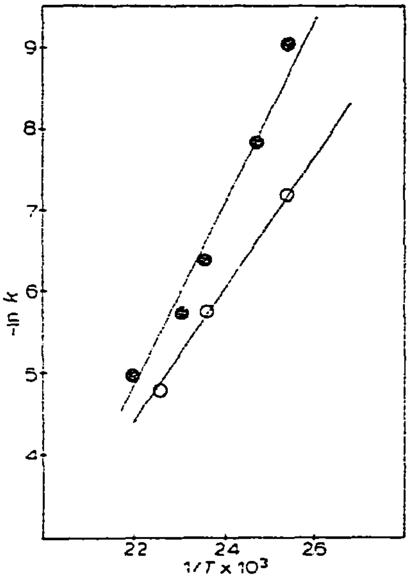

Fig. 3. Arrhenius plot of rate constants from integral equations. (○) Manche and Carroll [11], $n = 0.22$; (●) this work, $n = 0.5$.

DISCUSSION

The excellent modelling of this decomposition by the concept of an order has been shown for both sets of data considered. An explanation for this empirically observed behaviour must be sought in the theory of solid state processes. The data of Manche is modelled by an order of reaction of ~0.2. Zero order process have been observed for surface decompositions [12,21]. The main difference (judged from a reduced time plot) between orders of reaction zero and 0.2 lies at $t/t_{0.5} > 1.0$, the order of reaction 0.2 serves to decelerate the reaction in its later stages. The overlapping of nuclei could provide an explanation for this deceleration. Further evidence for a surface decomposition in this case is to be found in the work of Cordes [22]. Using a statistical approach Cordes was able to equate a pre-exponential factor of ~ $10^8$ ($10^6$ from the data of Manche) with a largely surface decomposition.

Our data gave a higher activation energy; the work of Dollimore et al. [10] would suggest this could be due to the build-up of water vapour on the sample during decomposition. In common with Dollimore we find this change to be accompanied by a change in mechanism. A somewhat higher pre-exponential factor is observed, and this can be equated with a bulk process in the crystal. Certainly the observed "order" is consistent with phase boundary control in two dimensions.

Another factor which can markedly affect solid state powder kinetics is particle size distribution [23,24], and this could also be of significance when the differences between the two sets of data are considered. Other factors which may affect the reaction include thermal flux and gross sample geometry. Gallagher and co-workers [25,26] have shown marked effects on the decomposition of $CaCO_3$ by such factors.

A number of points emerge from this study. Firstly, we find the reaction to be extremely well modelled by the concept of an order. The order observed is very sensitive to reaction conditions, in both cases an order of reaction $>0$ but $<0.5$ has been observed. We find no evidence for the often quoted orders of reaction of 0.666 or 1 (Table 1). There is little justification for the use of a zero order model, but for $\alpha < 0.3$ the fit is not unreasonable.

Secondly, the activation energy for the reaction is (as would be expected from the work of Dollimore) highly sensitive to reaction conditions. The "correct" value for the decomposition in the absence of water appears to be equal to or just greater than the heat of vaporization of water from $CaOX \cdot H_2O$. (70.70 kJ $mole^{-1}$) [27,28].

Finally, all these results indicate that the determination of kinetic parameters for this reaction by non-isothermal methods is likely to be unreliable. Indeed more work is needed for a full understanding of this "simple" and often studied decomposition.

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