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KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA. STUDY OF CALCIUM OXALATE MONOHYDRATE DEHYDRATION WITH A SEPARABLE-VARIABLES MODEL

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ABSTRACT

A study of the kinetic behavior of calcium oxalate dehydration using TG data is reported. Discrimination of integral kinetic models is carried out using a constant temperature and constant conversion analysis. The necessity of using no-separable-variables models to describe the reaction course is illustrated.

INTRODUCTION

The kinetic behavior of solid decompositions has been widely studied and even for presumably simple reactions, such as the dehydration of calcium oxalate monohydrate, there is an enormous diversity of results. The dehydration of this compound is a convenient reaction for studying the decomposition process both under isothermal and constant heating rate conditions. O'Brien and Ross [1] and Gadalla [2] have studied many kinetic models proposed to explain the dehydration of calcium oxalate. A glance over their results shows the difficulty of assigning a model to this reaction. Moreover, with the proposed kinetic equations we get different values for the reaction rates, as it is shown in Table 1.

The existence of these discrepancies may be explained by the complex phenomenon of the decomposition reaction of solids, since it is difficult to separate the macro- and microkinetics elements and the possible junction of phenomena.

This work shows the results obtained when an analysis of the data at constant conversion and constant temperature [4] is applied to three groups of non-isothermal experiments, namely, experiments of Ninan and Nair [5],

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TABLE 1

Summary of some reaction rates of thermal dehydration of calcium oxalate monohydrate (min^{-1})

Ref.	Notes	T(K) = 403			423			443		
		α = 0.2	0.5	0.8	0.2	0.5	0.8	0.2	0.5	0.8
2	7 K min^{-1}	0.003	0.002	0.001	0.016	0.012	0.006	0.071	0.052	0.028
3		0.010	0.008	0.005	0.091	0.072	0.046	0.673	0.532	0.336
5	5.0 mg, 1 K min^{-1}	0.025	0.019	0.010	0.696	0.509	0.276	14.156	10.355	5.621
6	1.16 K min^{-1}	0.007	0.008	0.005	0.023	0.026	0.016	0.072	0.079	0.048

Tanaka et al. [6] and this work. Our objetive is to prove the validity of the kinetic model of separable variables or, on the contrary, to show the necessity of using a more complex model.

GENERATION OF α–T CURVES

From the work of Ninan and Nair [5] we have chosen experiments carried out at seven heating rates (1, 2, 5, 10, 20, 50 and 100°C min^{-1}) and with initial samples of 5 mg. The best model in the authors opinion was the boundary surface reaction with spherical symmetry. By using this model and the kinetic parameters, E and A, found by these authors for each heating rate, and the Coats–Redfern method to solve the exponential integral, conversion–temperature curves have been obtained for each of the seven experiments.

The same procedure has been used in order to obtain α–T curves from the results of Tanaka et al. [6]. In this case, six heating rates (0.55, 1.16, 2.36, 4.71, 9.33 and 18.95°C min^{-1}), the kinetic model $[-\ln(1-\alpha)]^{1/2} = kt$, and the parameters proposed by the authors were used.

Our own experiments were carried out using a Model 990 DuPont thermogravimetric analyzer. Five diferent heating rates (0.5, 1, 2, 5 and 10°C min^{-1}) were used. The initial sample, calcium oxalate monohydrate (Carlo Erba RPE), was 10 ± 0.05 mg, the nitrogen flow (N49) was 2 $\text{cm}^3\ \text{s}^{-1}$ and a random distribution of the solid on the sample pan was used. Experiments were duplicated and the conversion difference was always $< 5\%$.

ANALYSIS OF THE NON-ISOTHERMAL CURVES AT CONSTANT TEMPERATURE

From the non-isothermal curves obtained at different heating rates, it is possible to obtain the conversion–time data at the same temperature. Assuming a kinetic model of separable variables, these values should adjust to the following equation [4]

$$g(\alpha) = K_{T'}t \tag{1}$$

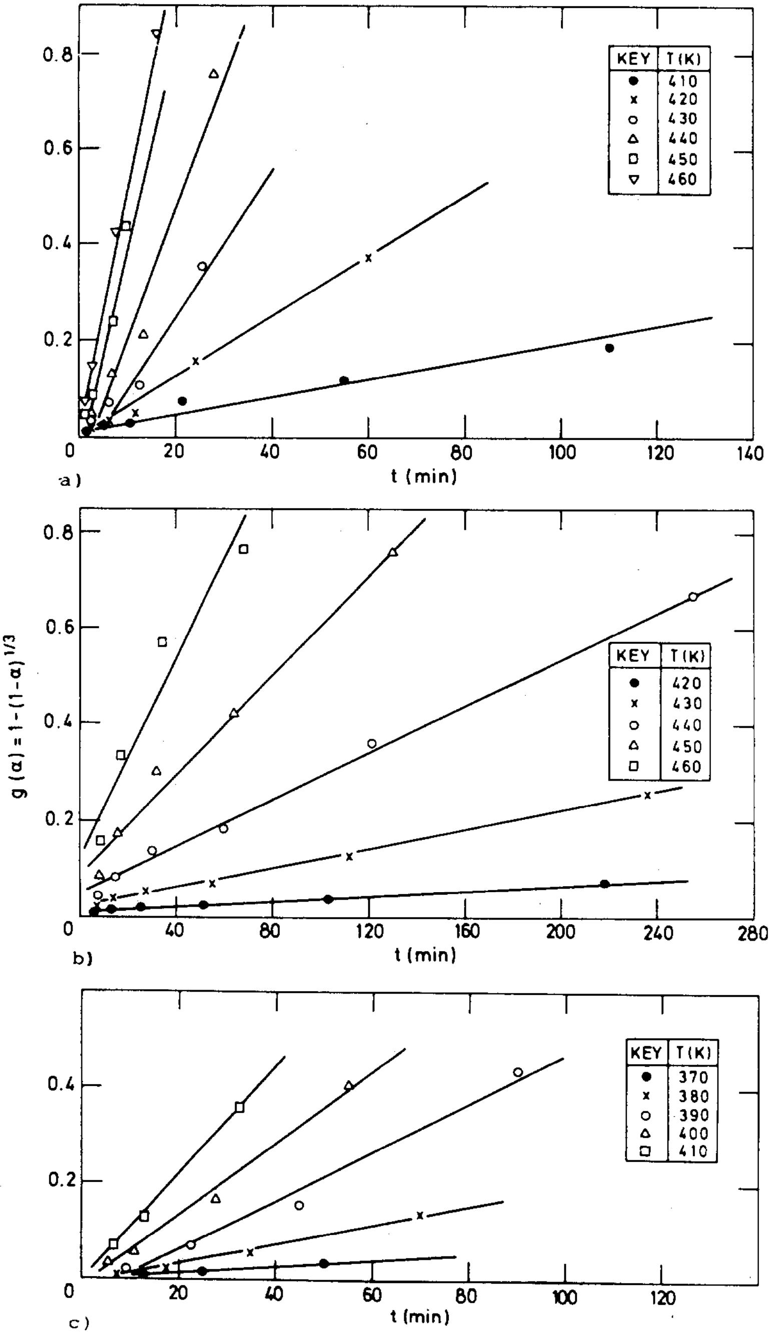

Fig. 1. Analysis at constant temperature: (a) Ninan and Nair [5]; (b) Tanaka et al. [6]; (c) this work.

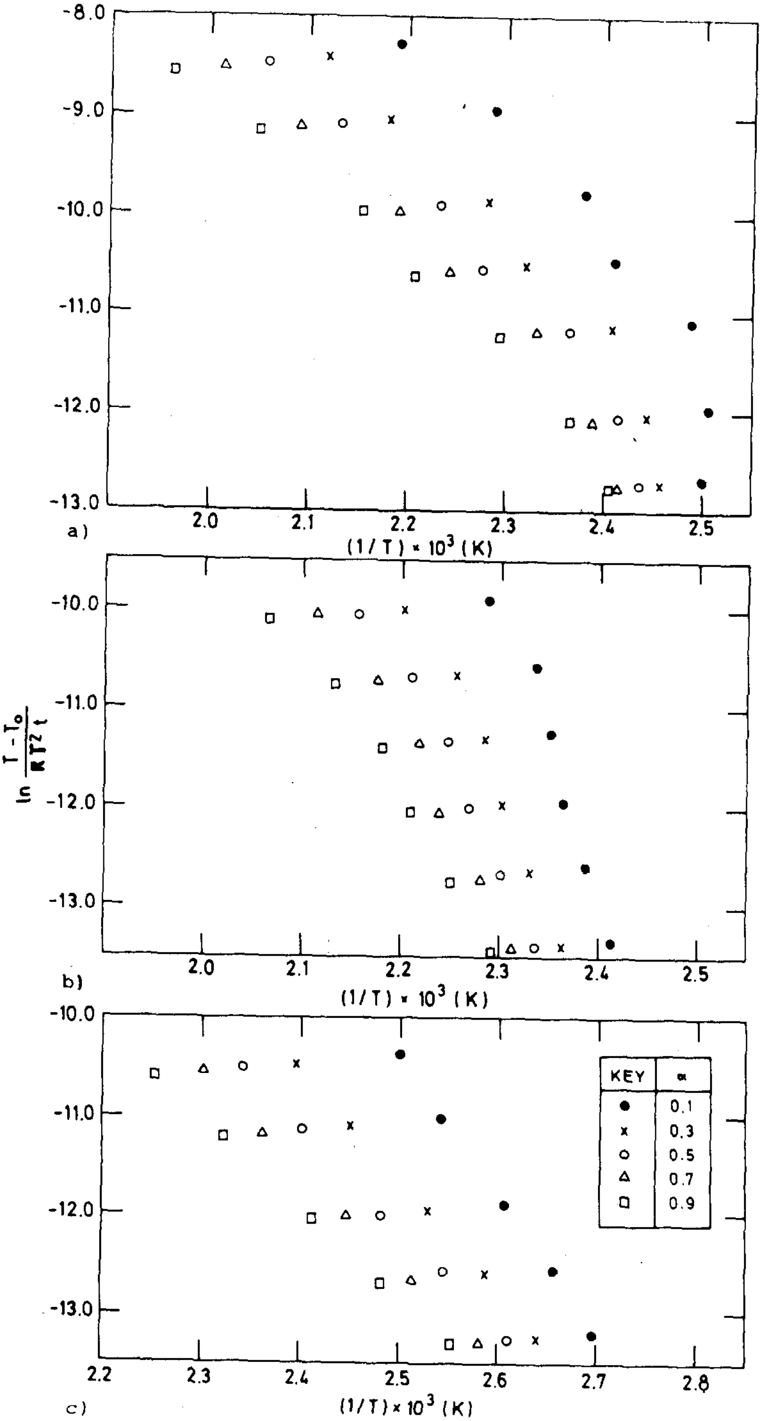

Fig. 2. Analysis at constant conversion: (a) Ninan and Nair [5]; (b) Tanaka et al. [6]; (c) this work.

TABLE 2

Analysis at constant temperature

	E (kcal mol^{-1})	A (min^{-1})	r
Ninan and Nair [5]	24.6	3.1×10^{11}	0.9581
Tanaka et al. [6]	34.9	6.4×10^{15}	0.9925
This work	26.0	5.2×10^{12}	0.9847

where

$$K_{T'} = \frac{\int_{T_0}^{T} A \exp(-E/RT)\mathrm{d}T}{T - T_0} \tag{2}$$

Figure 1 shows g(α), corresponding to the boundary surface reaction control with spherical symmetry, versus time, evaluated at different temperatures (T), for the three groups of experiments. Other kinetic models were tested but none improves this model. The E and A values obtained from the slopes of the straight lines are listed in Table 2.

ANALYSIS OF THE NON-ISOTHERMAL CURVES AT CONSTANT CONVERSION

The T–t pair obtained from the TG curves for each α-value are related by the following equation [4]

$$\frac{T-T_0}{RT^2t} = \frac{A}{Eg(\alpha)}\exp\left(\frac{-E}{RT}\right) \tag{3}$$

Figure 2 shows the experimental values, adjusted by the linear expression of eqn. (3), at different α-values. The slope of the straight lines decreases as the conversion level increases. Table 3 shows the values of E (slope) obtained when the points of Fig. 2 were adjusted to one straight line.

The E values obtained in this work are similar to those of Ninan and Nair [5] but very different to those of Tanaka et al. [6].

TABLE 3

E values in analysis at constant conversion (kcal mol^{-1})

$\alpha =$	0.1	0.3	0.5	0.7	0.9
Ninan and Nair [5]	28.6	23.3	21.2	20.0	18.5
Tanaka et al. [6]	57.8	44.0	38.4	34.6	30.2
This work	28.3	22.6	20.5	19.4	18.2

DISCUSSION

The most important remarks of this study are:

(1) The initial and interval of reaction temperatures are different for the three groups of experiments.

(2) When the analysis at constant temperature is applied, the experimental results for low conversion levels deviate appreciably from the model. Due to both the experimental characteristics and the interpretation methods it is not possible to prove if these deviations are produced at high conversion levels.

(3) In a constant-α analysis, E decreases considerably when the conversion increases. Many causes may explain this observation and the discrepancies described in the literature with respect to the kinetic model and the kinetic parameters of this reaction. Among these reasons are the following:

(a) Calcium oxalate samples may have different crystallographic forms and/or different physical structure. In both cases the reactivity would be different.

(b) The relative rate of different stages of decomposition can be modified while solid transformation occurs. In such a case, the kinetic equation should follow a no separable variables model, therefore, the different dependency of reaction rate on temperature for each stage of the reaction should be taken into account.

(c) Some experimental factors may affect the evolution of a reaction that are not included in an adequate form in the kinetic model, for example, thermobalance model, sample weight, particle size, the way the sample is introduced, etc. These factors may affect the temperature level at different regions of the sample.

Adequate experimental conditions may eliminate some of the last causes due to macrokinetic character, other causes need to be considered with more complex kinetic models.

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