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APPLICATION OF PROGRAMMED TEMPERATURE DECOMPOSITION TO THE STUDY OF SOLID DECOMPOSITION REACTIONS TAKING PLACE THROUGH THE PROUT AND TOMPKINS MECHANISM

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ABSTRACT

A method has been developed to allow kinetic analysis of the Prout and Tompkins mechanism of solid decomposition reactions using a single TG diagram obtained in a linear heating program. On the other hand, provided that the nickel formate decomposition follows such a mechanism, this reaction has been used for checking the kinetic equation obtained.

INTRODUCTION

Thermogravimetric analysis at programmed temperature has been widely used in the calculation of kinetic parameters of solid thermal decomposition reactions[1–3].

The TG methods described in the literature[1] usually consider that the decomposition rate of a solid holds the general equation:

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

where α is the decomposed fraction of solid after a time t, k the rate constant, expressed by the Arrhenius equation, and n the reaction order.

Sharp et al.[4] have pointed out the weakness of this "order of reaction equation" because the thermal decomposition of a solid is a heterogeneous reaction and cannot be kinetically analysed in the same way as a homogeneous reaction like eqn (1) assumes. Bearing in mind what the literature establishes about heterogeneous reactions, these authors show that eqn (1) can only have theoretical meaning when the values of n are 0, 1/2, 2/3 or 1.

On the other hand, it is well known[5] that solid state reactions occur through many other mechanisms and, therefore, it seems necessary to develop new equations which take into account these different solid thermal decompositions in order to spread the use of non-isothermal methods to the kinetic analysis of such reactions.

Equations for obtaining kinetic parameters from non-isothermal TG data of reaction following the Avrami-Erofeev mechanism[6] have been deduced by us in a previous paper[7].

In the present work, a procedure of kinetic analysis of reactions which take place through the Prout and Tompkins mechanism[8] is developed and it is applied to determine the kinetic parameters of the thermal decomposition of nickel formate:

$$\mathrm{Ni(HCOO)_2 \rightarrow Ni + H_2 + 2CO_2} \tag{2}$$

This reaction was studied by us in a previous paper[9] by classical isothermal methods, and the kinetic data only hold the Prout and Tompkins mechanism, in good agreement with Bircumshaw and Edwards'results[10].

Owing to the possible influence of the preparation method on the decomposition mechanism of salts[5], the same $Ni(HCOO)_2$ sample as in a previous reference[9] has been employed in the present work, in order to compare these kinetic data with those obtained by isothermal TG[9]. In this way, we are sure that the same reaction mechanism is followed in both cases.

In summary, the aim of this paper is, first of all, to develop equations for performing the kinetic analysis of the Prout and Tompkins mechanism from non-isothermal TG data, and secondly, provided that nickel formate decomposition proceeds through such a mechanism, using this reaction for checking the equations deduced.

EXPERIMENTAL

Materials

The same sample of $(HCOO)_2Ni \cdot 2H_2O$ D'Hemio a.r., dehydrated at 130°C, used in an early work[9] has been employed.

Thermogravimetric analysis

A Cahn electrobalance, model RG, was used. Decomposition was always carried out in N_2 atmosphere to avoid nickel oxidation. Previous papers[9,11] have shown that the kinetic data of nickel formate decomposition are not affected by the pressure of the inert gas. However, all the experiments were performed at 150 torr in order to minimize the electrobalance noise.

Heating rates between 4 and 25°C min^{-1} were selected.

RESULTS AND DISCUSSION

The Prout and Tompkins equation can be written in differential form:

$$\frac{d\alpha}{\alpha(1-\alpha)} = k\,dt \tag{3}$$

or, taking into account the Arrhenius equation:

$$\frac{\mathrm{d}\alpha}{\alpha(1-\alpha)} = A \cdot \mathrm{e}^{-E/RT}\mathrm{d}t \tag{4}$$

where E and A are the activation energy and the Arrhenius preexponential factor, respectively.

The right-hand side of eqn (4) can be integrated[12] making the substitution $u = E/RT$ in the expression:

$$\int_{u}^{\infty} \mathrm{e}^{-u} u^{-b} \mathrm{d}u \simeq u^{1-b} \mathrm{e}^{-u} \sum_{n=0}^{\infty} \frac{(-1)^n b^n}{u^{n+1}} \tag{5}$$

when the temperature and the time are related by:

$$\beta = \frac{\mathrm{d}T}{\mathrm{d}t} \tag{6}$$

the heating rate being β.

Bearing this in mind, eqn (4) can be integrated and transformed into:

$$\left[\ln \frac{\alpha}{1-\alpha}\right]_{\alpha_0}^{\alpha} = \left[\frac{ART^2}{E\beta}\left(1 - \frac{2RT}{E}\right)\mathrm{e}^{-E/RT}\right]_{T_0}^{T} \tag{7}$$

The integration lower limit of temperature, T_0, can be arbitrarily selected on the TG diagram. The value of decomposed fraction of solid, α_0, at this temperature will be the other integration lower limit. If the value of T_0 at which $\alpha_0 = 1/2$ is selected, the more simplified equation is obtained:

$$\ln\left[\ln \frac{\alpha}{1-\alpha} + C\right] - 2 \ln T + \ln \beta = \ln \frac{AR}{E} - \frac{E}{RT} \tag{8}$$

where C is:

$$C = \frac{ART_{c}^{2}}{E\beta} \cdot \mathrm{e}^{-E/RT} \tag{9}$$

The plot of the left-hand side of eqn (8) versus $10^3/T$ would give a straight line from which the reaction kinetic parameters can be calculated. However, as it is not possible to know "a priori" the value of C, it will be necessary to assign it arbitrarily and follow an iterative method until kinetic parameters are obtained which, substituted in eqn (9), give the value of C assumed.

The procedure described might have the difficulty in that it is possible to adjust both eqns (8) and (9) with several values of C.

An empirical procedure to give limits to eqn (7) could consist of partially decomposing the solid until reaching any particular value of the reacted fraction, α_0, before performing the programmed temperature experiment. In this way, if a lower limit of temperature, T_0, is taken at which the reaction has not begun (i.e., $\exp(-E/RT_0) = 0$), the lower limit of α will be the value α_0 previously set. Thus, eqn (7) becomes:

$$\ln\left[\ln\frac{\alpha}{1-\alpha} - \ln\frac{\alpha_0}{1-\alpha_0}\right] = \ln\frac{ART^2}{E\beta} - \frac{E}{RT} \qquad (10)$$

and the kinetic analysis is notably simplified. This method has been used in the present work.

Figure 1 shows the TG diagrams of $Ni(HCOO)_2$ recorded at different heating rates and after previous decomposed fractions of 0.12;0.45 and 0.75, respectively.

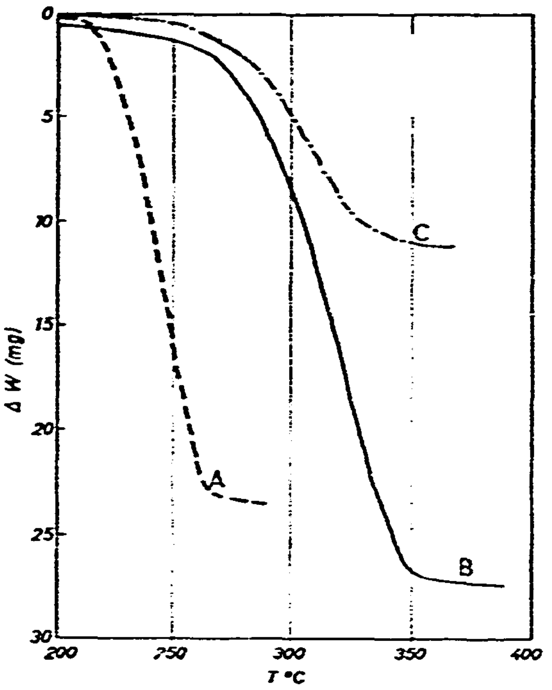

Fig. 1. TG diagrams for nickel formate. A: $\alpha_0 = 0.122$ and $\beta = 5\,°C\ min^{-1}$; B: $\alpha_0 = 0.45$ and $\beta = 23\,°C\ min^{-1}$; C: $\alpha_0 = 0.75$ and $\beta = 23\,°C\ min^{-1}$.

In the above diagrams, values of α were taken and the corresponding values of $\ln[\ln \alpha/(1-\alpha) - \ln \alpha_0/(1-\alpha_0)] - 2\ln T + \ln\beta$ were calculated and represented in Fig. 2 against $10^3/T$, according to eqn (10).

The kinetic parameters calculated from Fig. 2 are included in Table 1 together with those obtained[9] by isothermal TG.

The agreement between the kinetic parameters obtained by both procedures, whatever the previous decomposed fraction or heating rate may be, supports the validity of the method developed for performing the kinetic analysis of the Prout and Tompkins mechanism.

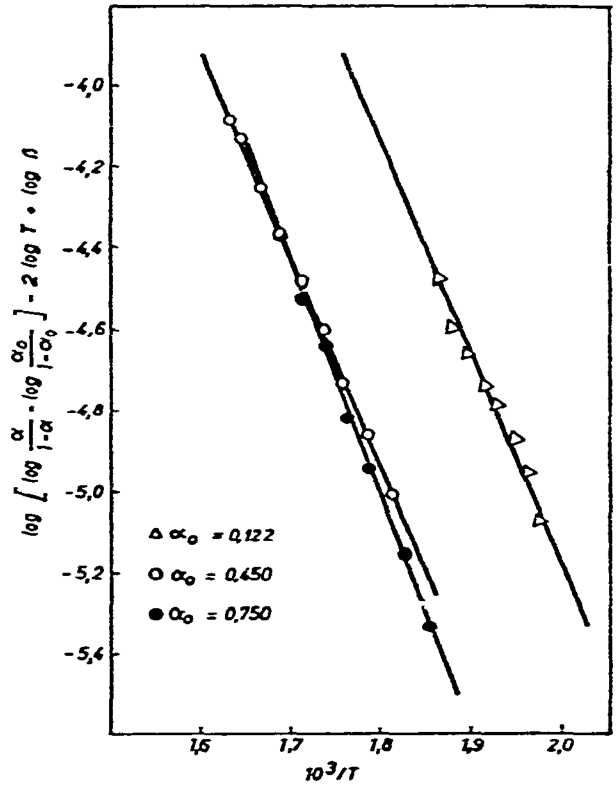

Fig. 2. Calculation of the kinetic parameters of the thermal decomposition of nickel formate by means of eqn (9).

TABLE 1

KINETIC PARAMETERS OF THE THERMAL DECOMPOSITION OF Ni $(HCOO)_2$

The kinetic analysis has been performed in a range of reacted fraction from α_0 to $\alpha \cong 0.95$.

α_0 *Previously reacted*	β (°C min^{-1})	*E* (*kcal* mol^{-1})	*A* (*seg*$^{-1}$)
0.12	5	24	8.10^{7}
0.45	23	23	8.10^{6}
0.75	23	25	6.10^{7}
0.00[a]	Isothermal	23	7.10^{6}

[a] Ref. (9).

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