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ON THE NON-ISOTHERMAL DETERMINATION OF ACTIVATION ENERGY FOR THERMAL DECOMPOSITION REACTIONS

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ABSTRACT

Attention is called to the frequently encountered linear sector in the isothermal course of the topochemical processes which is used in the kinetic treatment of the differential curves of thermal CoOOH decomposition. The effect of sample weight and heating rate on the values of the activation energy of this process under polythermal conditions has been investigated. Most of the values obtained are in good agreement among themselves as well as with those found isothermally. Existing differences have been explained satisfactorily.

INTRODUCTION

The study of the effect of various factors on the values of the kinetic parameters of chemical reactions is of major importance in non-isothermal kinetics. It helps to broaden our knowledge about the nature of these reactions as well as about the kinetic methods used. Sample weight and heating rate rank foremost among these factors. In some cases sample weight does not affect the value of the kinetic parameters [1,2], while in others it definitely does so [3]. Of particular interest is the case when sample weight in the same experiment affects a process at one stage but not at another [4–6]. Much the same can be said about heating rate: in some cases it does not affect the values of the kinetic parameters [1,7], while in others it modifies them [3,8–10].

Perplexed by these apparent irregularities, we set out to investigate the effect of sample weight and heating rate on the activation energy values of the reaction

$$12\ CoOOH = 4\ Co_3O_4 + 6\ H_2O + O_2 \qquad (1)$$

which proceeds kinetically in two stages with two activation energy values [11]. Besides its quantitative advantage, this is an additional feature for comparison. The differential kinetic curves (DTG and DTA) most sensitive to change in experimental conditions were kinetically analysed.

EXPERIMENTAL

The starting material, $CoOOH(H_2O)_{0.1}$ 0.025 $Co(OH)_2$, was investigated by means of a MOM OD 102 derivatograph in a flow of dry N_2. Sample weight experiments were made with 800 mg at 6°C min^{-1} (Fig. 1) and 3°C min^{-1} [12], as well as with 160 mg at 6°C min^{-1} [13]. Reaction (1) in Fig. 1 begins at point A [12] (the small DTG peak is due to the independent decomposition of $Co(OH)_2$ impurity).

RESULTS AND DISCUSSION

In order to determine the activation energy, we proceeded from the general equation for a topochemical reaction rate under polythermal conditions [14–17]

$$d\alpha/d\tau = f(\alpha)k(T) \qquad (2)$$

where α is the degree of completion of the process in time τ, $f(\alpha)$ is the function expressing the concentration dependence of the rate, and $k(T)$ is the rate constant expressing the temperature dependence of the rate. If the latter is subject to the

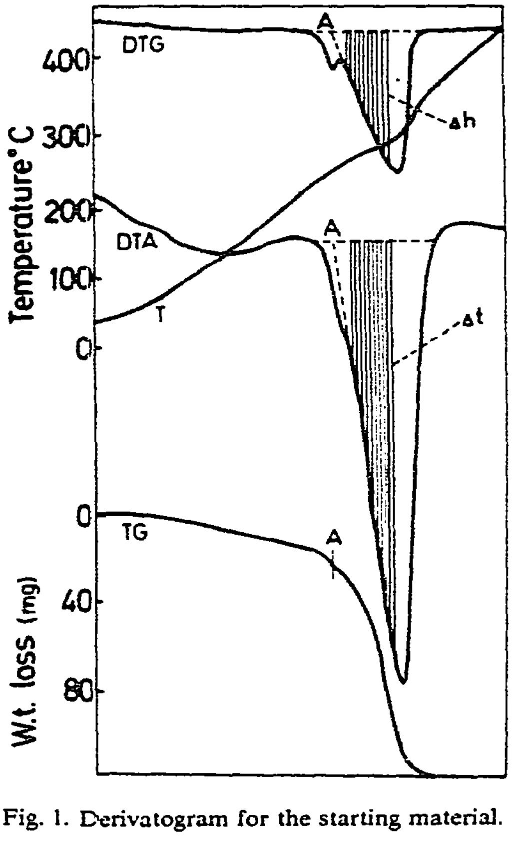

Fig. 1. Derivatogram for the starting material.

Arrhenius dependence, for which there are sufficient examples among topochemical processes, eqn. (2) assumes the form

$$d\alpha/d\tau = f(\alpha)A\exp(-E/RT) \tag{3}$$

where A is the frequency factor and E is the activation energy.

Relatively few methods apply directly to eqn. (3) without an exact knowledge of $f(\alpha)$. In those cases several differential curves at different heating rates [18] or only one curve admitting some approximations [19,20] are usually used. We shall try another way of solving this case, paying attention to an almost universal feature in the kinetics of topochemical processes: the presence of a linear sector on their experimental isothermal α–τ curves, i.e. a sector at a constant process rate, independent of α. Expressing this in eqn. (3), we obtain

$$d\alpha/d\tau = A'\exp(-E/RT) \tag{4}$$

with constant $A' = Af(\alpha)$. We thereby avoid quite correctly the necessity of a knowledge of $f(\alpha)$, even though only for part of the process. This restriction is the main shortcoming of the above argument which, we believe, has also certain advantages: (1) it requires no mathematical approximations; (2) it introduces a certain generalizing principle in the kinetics of the topochemical processes; and (3) it draws attention to the linear sector of the kinetic curves, which expresses a steady-state course of the process, relatively least encumbered by side phenomena (initial heating, diffusion, etc.) and is therefore closer to physicochemical processes in a solid state.

We made use of eqn. (4) in order to determine the activation energy of reaction (1), which is known to proceed isothermally at a constant rate up to about $\alpha = 0.4$ in the temperature range 260–310°C [11]. Application of eqn. (4) to the differential kinetic curves is a simple matter, insofar as Δh and Δt in mm (Fig. 1) for the initial period are proportional to $d\alpha/d\tau$ [19,20]. As base of the DTA peak we used a perpendicular to the Δt straight lines, and not the inclined line connecting the beginning and the end of that peak, as is generally accepted. Since the level at the end of the DTA peak is determined in principle by the heat characteristics of the solid product, and frequently also by accidental causes during the very recording, there is no justification for connecting them with the kinetics of the process.

The results of the application of eqn. (4) to the DTG and DTA curves are shown in Figs. 2 and 3, respectively. The corresponding values of the activation energy, statistically processed, are given in Table 1. The values for E_1 in Table 1 differ by a maximum of only ca. 20 kJ mole^{-1} with different sample weights for both differential curves. This difference is not great compared with the five-fold change in sample weight. It can easily be explained, most probably by the self-cooling of the sample because of the considerable endothermic effect of the process. The temperature in the sample itself during its decomposition always remains lower than that recorded by the instrument and used in Figs. 2 and 3. To a lower temperature in the sample there is corresponding lower rate of the process or correspondingly smaller values of Δh and Δt proportional to it. Consequently, the corresponding ordinates will lie lower and will trace a straight line with a smaller slope. This effect is obviously stronger with greater sample weight. It is no accident that it manifests itself chiefly at the first kinetic stage of reaction (1), when its rate increases most rapidly. From

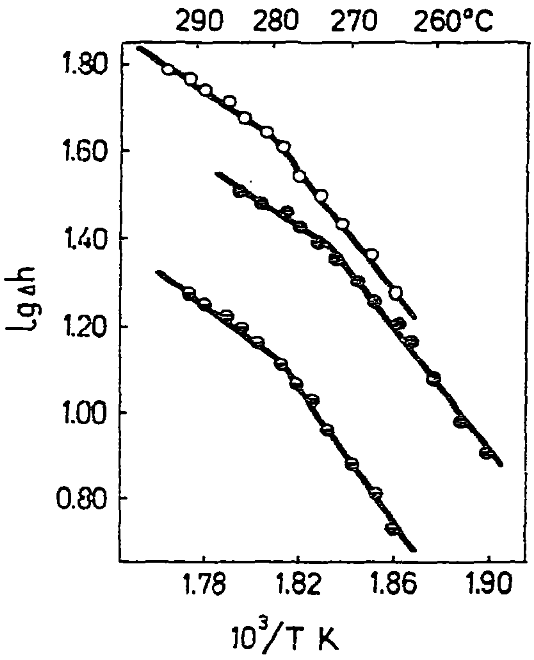

Fig. 2. Plots of the application of eqn. (4) to DTG. ○: 800 mg, 6°C min^{-1}; ◉: 800 mg, 3°C min^{-1}; ⊖: 160 mg, 6°C min^{-1}.

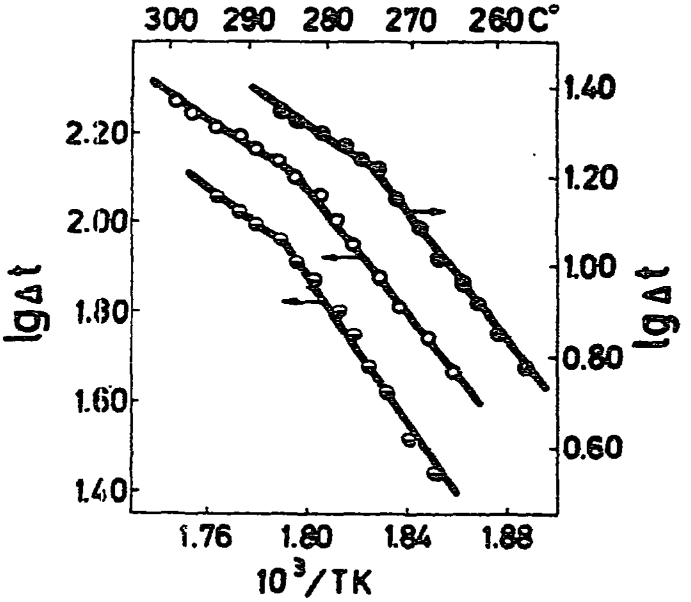

Fig. 3. Plots of the application of eqn. (4) to DTA. ◉: 800 mg, 3°C min^{-1}; ○: 800 mg, 6°C min^{-1}; ⊖: 160 mg, 6°C min^{-1}.

TABLE 1

Activation energy values of reaction (1)

Sample wt. (mg)	Heating rate (°C min^{-1})	DTG		DTA	
		E_1 (kJ mole^{-1})	E_2 (kJ mole^{-1})	E_1 (kJ mole^{-1})	E_2 (kJ mole^{-1})
160	6	150.35 (±5.53)	71.59 (±10.84)	151.44 (±7.75)	78.21 (±5.32)
800	6	130.92 (±7.62)	70.59 (±7.70)	132.93 (±6.36)	68.12 (±6.66)
800	3	137.87 (±5.90)	70.25 (±9.80)	132.51 (±6.28)	72.52 (±4.48)

this viewpoint the values of activation energy found with smaller sample weights are closer to the real ones. With equal sample weights the change in heating rate is weakly reflected on the values of E_1 and E_2.

It would be of interest to compare the data in Table 1 with those found isothermally. But such a comparison would call for other conditions to be as close as possible or else would have to be made in the case of the isothermal linear region ($E_1 = 126.88 \pm 3.60$ kJ mole^{-1}, $E_2 = 71.29 \pm 5.31$ kJ mole^{-1}, sample weight 1000 mg). The agreement is good when the sample weight values are close. In the latter case the differences in the E_1 and E_2 values are below the now admissible 10% limit [21,22].

The interpretation of the numerical results suggests that the changes introduced in the experimental conditions of reaction (1) affect not so much the real values of its activation energy as the conditions for their determination. This deduction, as well as the invariable manifestation of both kinetic stages of the process in all cases would seem to suggest that sample weight and heating rate in the not too widely applied limits do not modify the mechanism of the investigated process. On the other hand, the obtained results again showed an agreement between the isothermal and polythermal kinetic methods used in the study of reaction (1).

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