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# NON-ISOTHERMAL KINETICS OF CoOOH DECOMPOSITION

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## ABSTRACT

The non-isothermal kinetics of the decomposition of CoOOH powder has been studied derivatographically in a temperature range of 20–450°C in air. The reaction proceeds in two stages: up to about 280°C with an activation energy $E_1 = 38$–$50$ kcal mol$^{-1}$ and above that temperature with $E_2 = 20$–$25$ kcal mol$^{-1}$, depending on the kinetic equations which are employed. The results have been critically discussed on the basis of certain current concepts.

## INTRODUCTION

In a previous paper[1] we investigated isothermally the kinetics of the reaction

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

and proposed a model of its mechanism based on the movement of a reaction interface through disc-shaped particles. The reaction proceeded in two stages: in a temperature range of 260–280°C and 280–310°C with activation energies of $E_1 = 34.75$ kcal mol$^{-1}$ and $E_2 = 18.91$ kcal mol$^{-1}$, respectively.

In this paper we investigate the same process under non-isothermal conditions, which represents a necessary step in its further study. This is of interest for the following reasons: First, some thermoanalytical curves of reaction (1) mentioned in the literature[2,3] have not been subjected to kinetic analysis, i.e., there are no values of the kinetic parameters under dynamic conditions for this reaction. Second, a comparison of the results of the isothermal kinetics and of those obtained non-isothermally is of considerable importance, both as a first check of the adopted mechanism and because the use of a dynamic heating-curve technique for kinetic purposes in topochemistry is still a moot question[4–6].

## EXPERIMENTAL

### *Materials and methods*

The characteristics of the material with an approximate composition $CoOOH \cdot 0.1\,H_2O \cdot 0.025\,Co(OH)_2$ were described in ref. 1. The derivatography was performed in the manner and with apparatus described elsewhere[7].

## RESULTS

Figure 1 shows a derivatogram of reaction (1) in air obtained under conditions conductive to kinetic analysis. The relatively small sample weight (160 mg) decreased the self-cooling of the sample due to the reaction's considerable endoeffect, so that the linear course of the T-curve in the peak region is maintained. The other conditions were: heating rate 6°C $\text{min}^{-1}$; DTG, DTA and TG sensitivities, 1/20, 1/2 and 50 mg, respectively. As start of reaction (1) point A was taken at $t = 253$°C, up to which the slight weight decrease is due to the separation of the non-stoichiometric bound water in the initial material, whose detailed derivatographic investigation is the subject of another publication of ours.

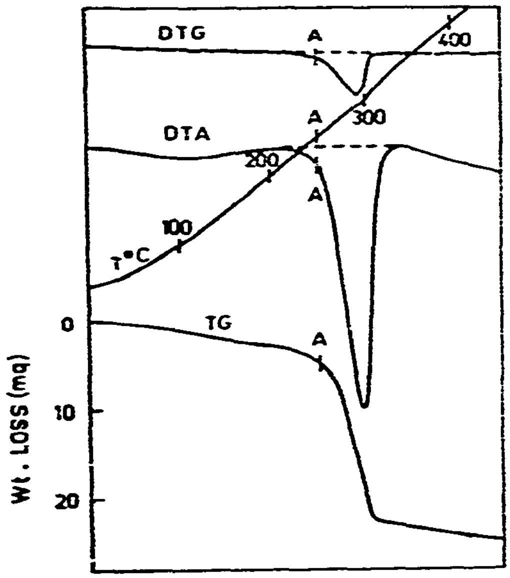

Fig. 1. Derivatogram for CoOOH decomposition.

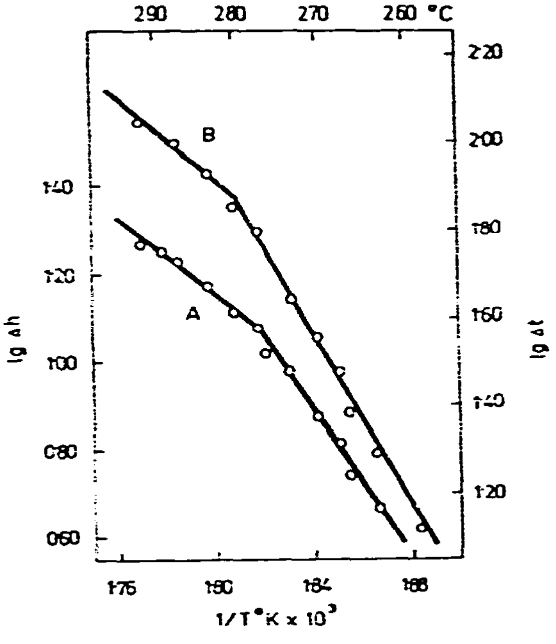

Fig. 2. Plots of eqn(3) with $\Delta h$(A) and $\Delta t$(B).

Well-known kinetic methods of a different type were applied, including an independent or combined use of all the thermoanalytical curves. Eight kinetic equations were tried out, four of which are submitted as the most typical in this case. The first two require no preliminary information about the mechanism of the process, while the last two are based on the following previously[1] used isothermic dependence:

$$1-(1-\alpha)^{1/2} = K\tau \tag{2}$$

where $\alpha$ is the degree of decomposition, $K$ is a constant and $\tau$ is the time.

*Method 1*

Fotiev and Mochalov's[8] treatment (Fig. 2A) using only the DTG curve applying the equation

$$\ln \Delta h = B - \frac{E}{RT} \tag{3}$$

where $\Delta h$ is the deviation of the DTG curve from the baseline in unit of length (mm), $B$ is a constant, and $E$ is the reaction's activation energy. This equation can be applied to the DTG peak down to the lowest point (Fig. 1).

*Method 2*

Piloyan and Ale's[9] treatment (Fig. 2B) using only the DTA curve applying eqn (3), where $\Delta h = \Delta t$ against the DTA curve.

*Method 3*

Škarin and Zhabrowa's[10] treatment (Fig. 3A) using the differential form of eqn (2) and two curves: TG and DTG

$$\ln \left[\frac{1}{(1-\alpha)^{1/2}} \cdot \frac{d\alpha}{dT}\right] = C - \frac{E}{RT} \tag{4}$$

where $C$ is a constant. The values of $d\alpha/dT$ were found by the DTG curve (mm).

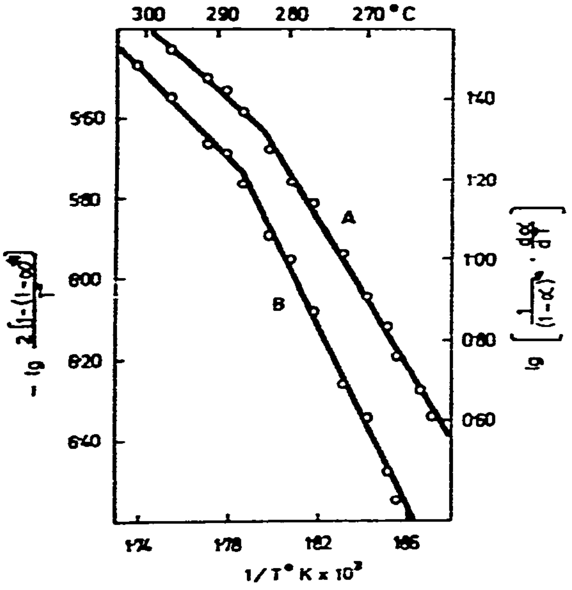

Fig. 3. Plots of eqn(4)—A; and eqn(5)—B.

*Method 4*

Coats and Redfern's[11] treatment using eqn (2) and the TG and T curves

$$\ln \frac{2[1-(1-\alpha)^{1/2}]}{T^2} = D - \frac{E}{RT} \tag{5}$$

where $D$ is a constant.

The values obtained for the activation energy using the four methods are shown in Table 1.

TABLE 1

ACTIVATION ENERGIES FOUND USING FOUR METHODS

| *Method No.* | *Range of $\alpha$ %*[a] | *Activation energy (kcal mol$^{-1}$)* | |
|---|---|---|---|
| | | $E_1$ | $E_2$ |
| 1 | 4.9–57.3 | 38 | 20 |
| 2 | 1.7–57.3 | 44 | 22 |
| 3 | 3.9–70.7 | 41 | 23 |
| 4 | 8.0–81.0 | 50 | 25 |

[a] These values were found by the TG curve.

## DISCUSSION

Our kinetic investigations of reaction (1) under dynamic conditions (Figs. 2 and 3 as well as the other eqns used) clearly show that it proceeds in two stages as regards the value of the activation energy: up to ca. 280°C with a greater value and above 280°C with a smaller value. The results of the dynamic kinetics thus confirm the most characteristic feature of reaction (1) which was established earlier isothermally[1]. Moreover, this confirmation was obtained by the use of the four thermoanalytical curves, either separately (methods 1 and 2) or combined (methods 3 and 4), the first two methods being based directly only on data on the respective curves. On the other hand, the possibility of applying methods 3 and 4, which call for a previous knowledge of the $\alpha$–$\tau$ function, indirectly confirms the contrasting disc model adopted in the isothermal investigation[1].

Still, the values obtained for the activation energy (Table 1), especially for the reaction's first stage, considerably differ from each other and from those found isothermally. The values obtained by method 1 are closest to the latter within the limits of the conventionally adopted error up to about 10 per cent[12]. The differences are most pronounced with method 4. Similar differences in the values of the activation energy, obtained dynamically in other processes again for a single sample, are known[13,14], even in the much simpler and better known case of a homogeneous reaction[15]. We shall try to explain this on the basis of some now current concepts.

The values of kinetic parameters in topochemical reactions are known to be more or less influenced by some at first sight 'external' factors, such as sample weight, container shape, thickness of sample layer, and the like. In dynamic conditions their number increases by some parameters inherent to this method, such as heating rate and sensitivity of recording. In order to compare the values of the kinetic parameters obtained under different conditions and with different methods, it is therefore necessary to select for every particular case the optimal conditions under which all these factors least affect the essential values of these parameters and to be able to express this effect quantitatively. The values obtained under these conditions will be determined to the utmost by the characteı of the chemical process in a solid. Unfortunately these are as yet still airy castles. The selection of optimal conditions in the above sense and the assessment of the values obtained are made more or less empirically. Still, the upward trend in the activation energy values obtained dynamically in our case is in agreement with some theoretical considerations based on crystal anisotropy[16].

The results submitted here show in the final count that, regardless of the differences in the values of the activation energy, the dynamic kinetics reflect the profound essence of the investigated process manifesting itself in this case in its two stages, which we earlier[1] attempted to associate with some basic chemical processes in a solid. It follows from this that in general the numerical value of the activation energy should not be the only criterion determining the value of the dynamic method kinetically.

The different values of the activation energy of reaction (1), obtained by us so far, naturally give rise to the question as to which of them should be considered as most suitable for its adopted mechanism. If, like other authors[17,18], we turn our attention to the linear region of the isothermal dehydration curges[1] extending to about $\alpha = 0.4$ on the average and since this region corresponds to the early growth of a completely developed interface, its slope can be taken as directly proportional to the rate constant for interfacial reaction. The activation energy derived from Arrhenius plots will then represent the true energy ($E_1 = 30$ kcal mol$^{-1}$ and $E_2 = 16$ kcal mol$^{-1}$) for this reaction. This idea can be more broadly justified from the viewpoint of the conception of a steady or quasi steady state[19] in topochemical reactions, viewed as a series of consecutive reactions. In this respect the linear part of an isothermal TG curve shows a steady state course determined by a pronounced rate-determining step, which we assumed to be the reaction interface. The values of the kinetic parameters, calculated in this region, reflect to the utmost the nature of this rate-determining step. But with the progress of the decomposition (owing, say, to diffusion processes) the latter gradually loses its dominant position so that the linearity is upset and the kinetic parameter values now found will be more or less overall. Applying from these positions mathematically simple equations comprising the largest possible region of decomposition and finding through them the overall values of the kinetic parameters is only the first task of a kinetic investigation which must be followed up by a study of the ratio of the elementary stages throughout the course of the process.

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