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THE TECHNIQUE OF STEP HEATING APPLIED TO THERMAL ANALYSIS

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ABSTRACT

By use of the technique of step heating and a new type of sample holder, the undesirable effects caused by a number of external and internal factors in thermal analysis are eliminated. To point out the thermal effects appearing during sample decomposition, the thermograms were carried out without inert reference material. In function of the decomposition temperatures, thermal effects and the factors of the Arrhenius equation, the behaviour to decomposition of compounds was classified in five classes.

By means of this classification is explained ideal and abnormal behaviour of the calcium oxalate monohydrate and respective of the ferrous oxalate dihydrate at the thermal decomposition in dynamic heating.

This technique is applied to the study of the decomposition mechanism of the ferrous oxalate dihydrate and the decomposition temperatures and the activation energies were determined.

INTRODUCTION

Numerous studies have been carried out on various compounds to elucidate the mechanism of the thermal decomposition by the dynamic thermogravimetric technique. An appreciable number of studies have been obtained with erroneous results due to the superposition of certain external and internal factors. These factors have already been mentioned by different authors[1–4].

If thermal investigations are taken from the same material under different experimental conditions, they may differ so much that it is very difficult to identify them.

Jacobs and Tompkins[5] have shown that all solid substances thermally decompose according to the four typical curves, representing the plot of the fraction decomposed, α, as a function of the time, t. In general they are sigmoid, indicating the "nature" of reaction.

By using the dynamic method of heating for studying a compound which decomposes according to the general reaction:

$$\begin{array}{ll} A_{solid}(T_1,\theta_1) \rightarrow & B_{solid}(T_2,\theta_2)+C_{gas} \\ & \downarrow \\ & D_{solid}(T_3,\theta_3)+E_{gas} \\ & \downarrow \\ & F_{solid}(T_4,\theta_4)+G_{gas} \\ & \vdots \end{array} \tag{1}$$

where $T_1, T_2, T_3, \ldots$ are the decomposition temperatures of successively formed products, $\theta_1, \theta_2. \theta_3, \ldots$ are the differences of temperature between sample temperature and furnace temperature. Some typical curves of successive reactions may be superposed due to the resistance of the sample to heat transmission and by interaction of other factors.

It is known that all decomposition reactions are accompanied by elimination or absorption of heat, and the radial distribution of the temperature in a crucible is shown in Fig. 1. The sample temperatures during thermal decomposition with exothermic (θ_{ex}) and endothermic (θ_{en}) effects are dependent on the amount, compactness, layer thickness, thermal conductivity and heat capacity of the sample, on the secondary reaction between gaseous substances of the surrounding atmosphere and gaseous evolved products or with a newly formed solid product, and on the shape and size of the sample holder and heating rate.

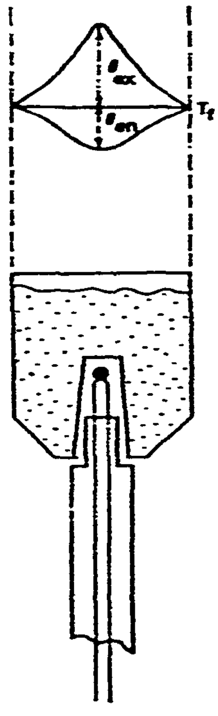


Fig. 1. Radial distribution of the temperature in a crucible during dynamic heating. T_f, furnace temperature; θ_{ex}, increase of the temperature for exothermic reactions; θ_{en}, decrease of the temperature for endothermic reactions.

Though several attempts have been made to remove the undesirable effects appearing during dynamic heating by application of stepwise heating, the results obtained[6,7] are not satisfactory. More recently Paulik and Paulik[3] obtained rather promising results.

This paper attempts to remove a number of factors contributing to the masking of real decomposition mechanisms by using a new type of sample holder and the technique of step heating. This technique is applied to the study of thermal decomposition of ferrous oxalate dihydrate.

EXPERIMENTAL

High purity commercial ferrous oxalate dihydrate from Reactivul was used for all experiments and its composition was determined by titration against potassium permanganate, followed by estimation of the resulting ferric ion with mercurous nitrate solution in the presence of excess ammonium thiocyanate[8]. Found: Fe 31.05, oxalate 48.91% (calculated: Fe 31.04%, oxalate 48.93%).

The decomposition temperatures of $Fe(COO)_2 \cdot 2H_2O$ were obtained by extrapolation to zero heating rate, from two thermograms made at two heating rates of 2.5 and 5.0°C/min using a platinum crucible with a capacity of 0.25 cm^3 and the same quantity and volume density of oxalate (Fig. 2).

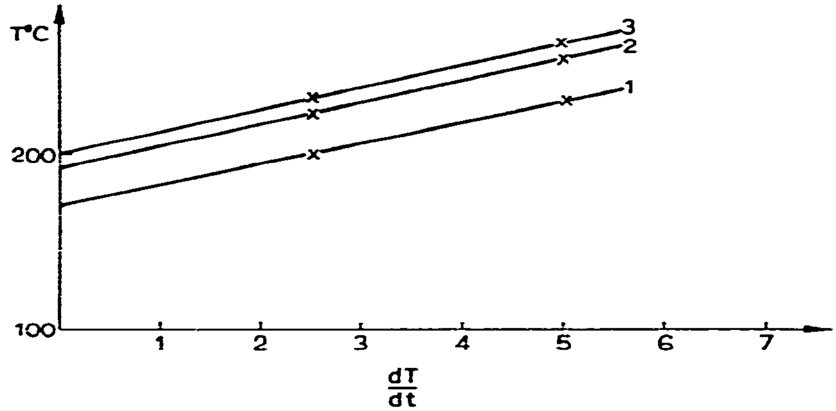
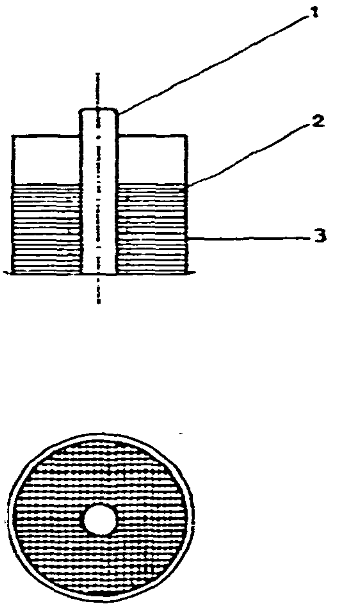


Fig. 2. Determination by extrapolation of the decomposition temperature of ferrous oxalate dihydrate for the zero heating rate. 1, $Fe(COO)_2 \cdot 2H_2O \rightarrow Fe(COO)_2$; 2, $Fe(COO)_2 \rightarrow FeCO_3$; 3, $FeCO_3 \rightarrow Fe_2O_3$.

A fine suspension of ferrous oxalate dihydrate in carbon tetrachloride saturated with water was deposited in a thin layer on the disks from platinum gauze [(2) from Fig. 3], followed by drying at 110°C for 1 hour, and the disks were mounted on the platinum holder (1).

An analytical balance, AB (Fig. 4), of sensitivity 10^{-4} g, modified by the suspension of a platinum wire (Pt) at the bottom of one scalepan, was used. To this wire a sample holder (SH) is attached. The sample holder is suspended in a copper tube (CT) which is plunged into the glycerine bath (GB) of the ultrathermostat (UT).



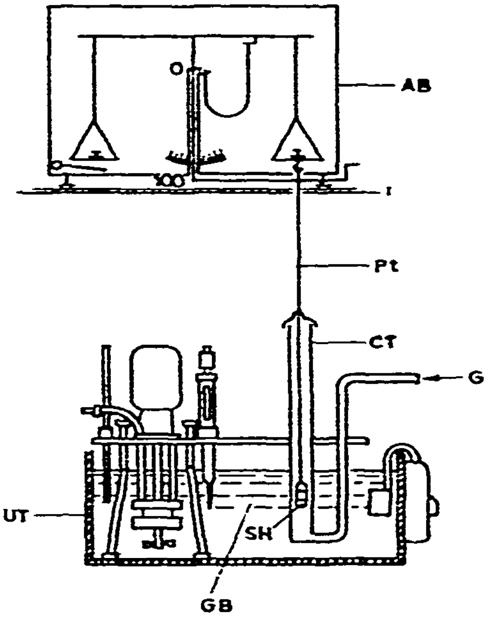


Fig. 3 (left). Sample holder. 1, platinum holder for disks; 2, disks from platinum gauze; 3, protector cylinder from platinum gauze.

Fig. 4 (right). Experimental device. AB, analytical balance; I, support for balance; Pt, platinum wire; CT, copper tube; SH, sample holder; G, air stream (or the other gas with reduced content of oxygen); UT, ultrathermostat; GB, glycerine bath.

The temperature of the glycerine bath is raised up to the first chosen temperature, and is kept constant (±0.1 °C) until the weight of the sample remains constant; a similar procedure is followed for the other temperatures.

RESULTS AND DISCUSSION

A reference crucible filled with inert material is used for studying the decomposition mechanisms by dynamic heating. However, due to the fact that the thermal conductivities of the inert material and of the sample are different, the quantity of inert material remains constant during heating, while the quantity of sample varies with temperature. These differences can mask certain thermal effects in the sample studied. During the decomposition of ferrous oxalate dihydrate we obtained thermograms without using an inert reference material, and one of these is given in Fig. 5.

In Fig. 5 the decomposition of ferrous oxalate dihydrate is accompanied by a pronounced decrease and increase of the temperature. If the decomposition of the $Fe(COO)_2 \cdot 2H_2O$ in $Fe(COO_2)$ takes place at T_1, while the furnace temperature increases linearly, at the end of decomposition the difference between the furnace temperature (dotted line) and that of the crucible centre is θ_1, 20°C. Due to the

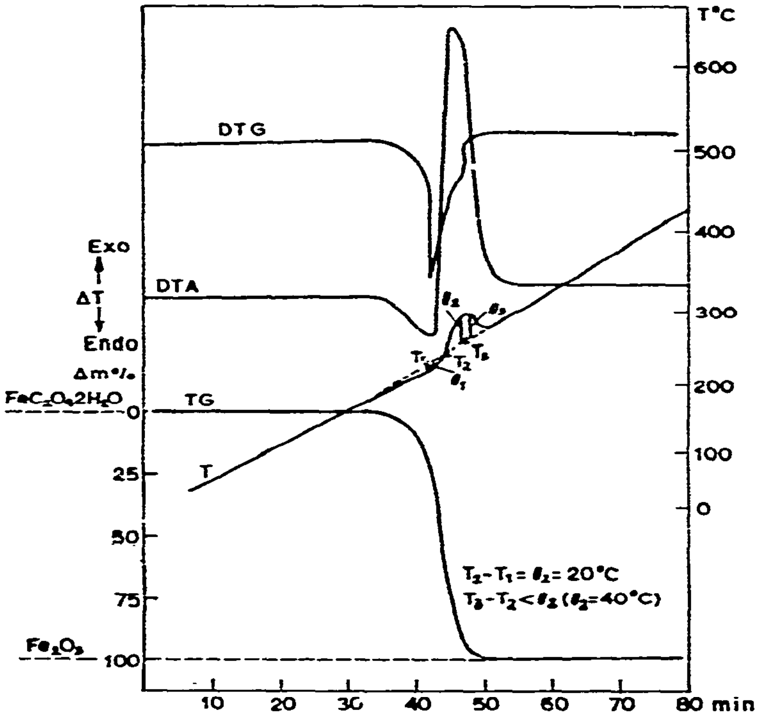


Fig. 5. A thermogram obtained by means of the derivatograph without reference inert material at a heating rate of 5°C/min and with the crucibles of 0.25 cm³. T_1, T_2, T_3 are the decomposition temperatures of the ferrous oxalate dihydrate to Fe_2O_3; θ_1, θ_2, θ_3, are the differences between sample temperature and furnace temperature (dotted line) due to the thermal effects of the respective reactions.

resistance of the sample to heat transmission and by dynamic heating the temperature of the exterior part of the crucible reaches T_2 while the centre remains at T_1, but at the temperature T_2 it begins to decompose $Fe(COO)_2$ into $FeCO_3$, so there is a superposition of reactions. Due to the fact that the last reaction is exothermic the temperature of the sample may increase up to 40–60°C (θ_2) and produce simultaneous transformation of $FeCO_3$ to Fe_2O_3 because the decomposition temperature of this reaction is T_3 and the difference between the last two successive reactions is $T_3-T_2<\theta_2$.

Thus, by applying the dynamic technique of heating currently described to the study of the compounds which decompose according to the general reaction (1) and working with the crucible given in Fig. 1, the results will be influenced in the following manner:

1) When $T_2-T_1 \gg \theta_1$, $T_3-T_2 \gg \theta_2$, ..., we obtain thermograms with plateaus, irrespective of the values of the activation energies and the pre-exponential factors.

2) When $T_2-T_1 \ll \theta_1$, $T_3-T_2 \ll \theta_2$, ..., we do not obtain thermograms with plateaus, irrespective of the values of the activation energies, of the pre-exponential factors and of other factors.

3) When $T_2-T_1=\theta_1$, $T_3-T_2=\theta_2$, ..., the shapes of the thermograms depend

on the values of the activation energies, of the pre-exponential factors and of the other critical factors.

4) When $T_n - T_1 < \theta_1$, all preceding reactions will be masked, irrespective of the values of the activation energies and of the pre-exponential factors.

5) Various combinations of the above-mentioned cases.

By applying the technique of step heating we prevent an accelerated rise of temperature in the crucible, and by using a new type of the sample holder (Fig. 3) we facilitate both the heat exchange between sample holder and the surrounding atmosphere and the diffusion of the gaseous products in both directions.

Thus, by studying the thermal decomposition of $Fe(COO)_2 \cdot 2H_2O$ by the step heating technique we can establish the real mechanism of decomposition and also calculate the activation energies for each reaction from the equation for the isothermal conditions[9]. The decomposition thermogram of ferrous oxalate dihydrate is given in Fig. 6. Figure 6 shows the curves of the temperature change (T) and weight change (TG) of the 0.12 g sample as functions of time. The thermal decomposition of ferrous oxalate dihydrate began at 170 °C by loss of water, then at 190 °C carbon monoxide is expelled and at 200 °C elimination of carbon dioxide takes place with simultaneous oxidation of FeO to Fe_2O_3. This process takes place very slowly, over a period of about 300 minutes.

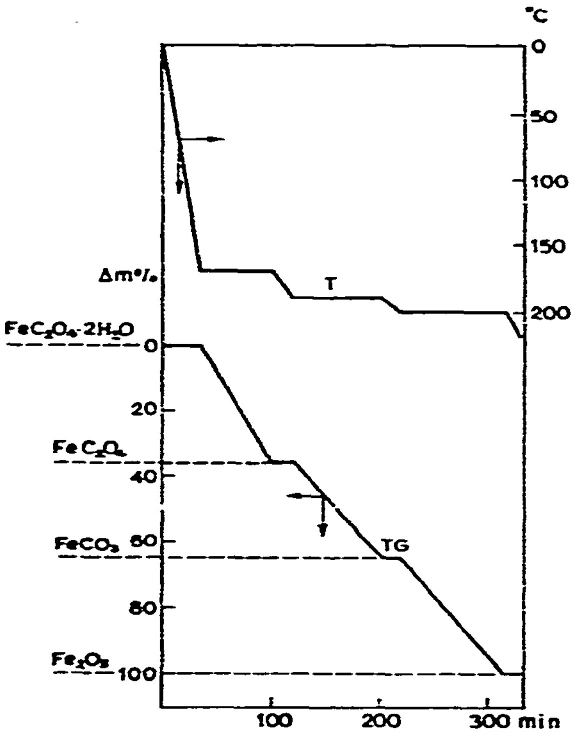
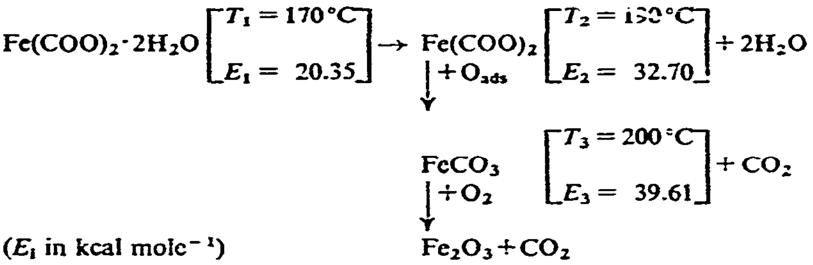


Fig. 6. Change in weight (curve TG) and change in temperature (curve T) plotted as functions of time for the thermal decomposition of ferrous oxalate dihydrate.

The real mechanism of decomposition of $Fe(COO)_2 \cdot 2H_2O$ in air may be represented by the following scheme:



$$\begin{array}{lll} Fe(COO)_2 \cdot 2H_2O \begin{bmatrix} T_1 = 170\,^{\circ}C \\ E_1 = 20.35 \end{bmatrix} \rightarrow & Fe(COO)_2 \begin{bmatrix} T_2 = 190\,^{\circ}C \\ E_2 = 32.70 \end{bmatrix} + 2H_2O & \\ & \downarrow + O_{ads} & \\ & FeCO_3 \begin{bmatrix} T_3 = 200\,^{\circ}C \\ E_3 = 39.61 \end{bmatrix} + CO_2 & (2) \\ & \downarrow + O_2 & \\ (E_i \text{ in kcal mole}^{-1}) & Fe_2O_3 + CO_2 & \end{array}$$

During of the dehydration reaction the specific surface of the ferrous oxalate grows and the oxygen from the surrounding atmosphere diffuses through the newly formed space and adsorbs onto the active centres of the oxalate. When the ferrous oxalate molecules are heated to decomposition temperature, simultaneously is produced the separation of CO from oxalate and combination of this with adsorbed oxygen which is a highly exothermic process.

Various authors[10-15] have described the thermal decomposition of ferrous oxalate dihydrate, but they failed to separate the dehydration and dissociation stages during thermogravimetric analysis in air. Brown and Bevan[14] and Nicholson[15] have isolated anhydrous ferrous oxalate in vacuum and in nitrogen. The failure of the investigations made by the above-mentioned authors may be explained by the fact that $T_2 - T_1 = \theta_1$ (20°C) and $T_3 - T_2 < \theta_2$ (40–60°C).

During the dynamic heating the temperature of the sample in the crucible has been raised up to 40–60°C as a function of the shape and size of the crucible (Fig. 5). This means that the temperature at certain points of the sample can be higher, and the thermal decomposition of anhydrous ferrous oxalate can be explained by means of the hot spot theory[16]. By using the hot spot theory the presence of carbon and iron in the decomposition products can be explained, which were identified by Gunther and Rehaag[17] and Lihl[18].

The ideal thermal decomposition behaviour by dynamic heating of the calcium oxalate monohydrate may be explained by the fact that the decomposition reactions took place: dehydration at $T_1 = 247\,^{\circ}C$ and $\theta_1 = 24\,^{\circ}C$, decomposition of oxalate to carbonate at $T_2 = 480\,^{\circ}C$ and $\theta_2 = 48\,^{\circ}C$, and the decomposition of carbonate to calcium oxide at $T_3 = 880\,^{\circ}C$ and $\theta_3 = 14\,^{\circ}C$, i.e. $T_2 - T_1 \gg \theta_1$, $T_3 - T_2 \gg \theta_2$, is an example of case one from the above-mentioned classification.

Thus, by application of the technique of step heating and a use of a new type of sample holder the superposition of the above-mentioned factors which masks the real mechanisms of decomposition could be removed.

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