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Note

Kinetics of thermal decomposition of copper basic carbonate

Part 2. The analysis of differential thermal data

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The activation energy (ΔE^{*}) and the order of the reaction (n) may be estimated from differential thermal analysis (DTA) curves using three general procedures: (a) trial and error[1]; (b) direct method[2]; (c) a semidirect method[3–5]. The authors adopted a semidirect procedure to determine ΔE^{*} from the induction period data and used the Murray and White equation[6] and Kissinger plot[7]. The Kissinger semidirect method of determining the reaction order n from the endothermic DTA peaks was used in this paper to determine the reaction order from the endothermic DTA peak of copper basic carbonate heated at a rate of 1°C min^{-1} in air.

EXPERIMENTAL

A Netzsch differential thermoanalyzer, Model 409, was used for the DTA measurements with thermocouples of Pt–Pt–Rh. The holders of the crucibles as well as the crucibles themselves are made from calcinated alumina. The differential thermocouple peaks are positioned in such a manner that during the heating period they take position right above the sample. Heating rates of 1, 2, 5 and 10°C min^{-1} were used to determine the temperature gradient, T, between the sample and the calcinated alumina reference.

Kinetic method

The reaction rate constant K is directly proportional to the specific rate constant K' and inversely proportional to the induction period τ[9]. Therefore by the Arrhenius equation as

$$K' = A \exp\left(\frac{-\Delta E^{\ddagger}}{RT}\right) \tag{2}$$

where A, $\Delta E^{\ddagger}$, R and T are frequency factor, activation energy, universal gas constant and absolute temperature, respectively. Relating eqn (2) with eqn (1), followed by rearrangement yields in the logarithmic form

$$\log\left(\frac{1}{\tau}\right) = \lambda - \frac{\Delta E^{\ddagger}}{2.3\,RT} \tag{3}$$

where λ is a constant equal to $\log(A/c)$. The value of K' is also given by the Eyring absolute reaction rate theory[10] as

$$K' = \frac{\mathrm{k}kT}{h} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right) \exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right) \tag{4}$$

where k, k, T, h, $\Delta S^{\ddagger}$, R, and $\Delta H^{\ddagger}$ are transmission coefficient (normally assumed as 1), Boltzmann constant, absolute temperature, Planck's constant, activation entropy, molar gas constant, and activation enthalpy, respectively. Combining eqns (4) and (1), rearranging, and taking the logarithm we obtain

$$\log\left(\frac{1}{\tau T}\right) = \left[\log\left(\frac{\mathrm{k}k}{ch}\right) + \frac{\Delta S^{\ddagger}}{2.3\,R}\right] - \frac{\Delta H^{\ddagger}}{2.3\,RT} \tag{5}$$

Similar equations can be derived for $\Delta E^{\ddagger}$ and $\Delta H^{\ddagger}$ by using the time, t_p, at which the DTA temperature peak appears instead of τ.

The activation energy ($\Delta E^{\ddagger}$) can also be calculated from the Murray and White equation[6]

$$\log\left(\frac{\Phi}{T_s^2}\right) = I - \frac{\Delta E^{\ddagger}}{2.3\,RT_s} \tag{6}$$

where Φ, T_s, and I are heating rate, absolute temperature of the sample at maximum deflection on DTA curve, and a constant which also contains the conversion factor. The term T_s is defined by $T_s = T_f + \Delta T$, where T_f is the furnace temperature at the time of the maximum decrease in the temperature of the sample due to the endothermic reaction and ΔT is the sample temperature decrease due to self-cooling.

Equation (6) indicates that the reaction rate constant K is proportional to

If we insert eqn (4) and (7) into eqn (1), rearrange and take the logarithm we obtain

$$\log \frac{\Phi}{T_s^3} = I' - \frac{\Delta H^*}{2.3RT_s} \tag{8}$$

where the constant I' is given by

$$I' = \log \left[\frac{a}{\beta} \frac{kk'}{h} e^{\Delta S^*/R} \right]$$

The reaction order, n, can be related to the shape of the DTA peaks. Kissinger[8] defined a shape index S for endothermic DTA peaks of various minerals, as the ratio of the slope of the tangent at the inflection point on the left side of the peak to that at the inflection point on the right side. The shape index, S, and the reaction order, n, are related by[8]

$$n = 1.26 S^{1/2} \tag{9}$$

RESULTS AND DISCUSSION

The experimental results obtained from DTA investigations by heating the same quantity of the sample of 225.9 mg in air with different heating rates are shown in Fig. 1. The shift in the position of the DTA peak is due to the change in heating rate.

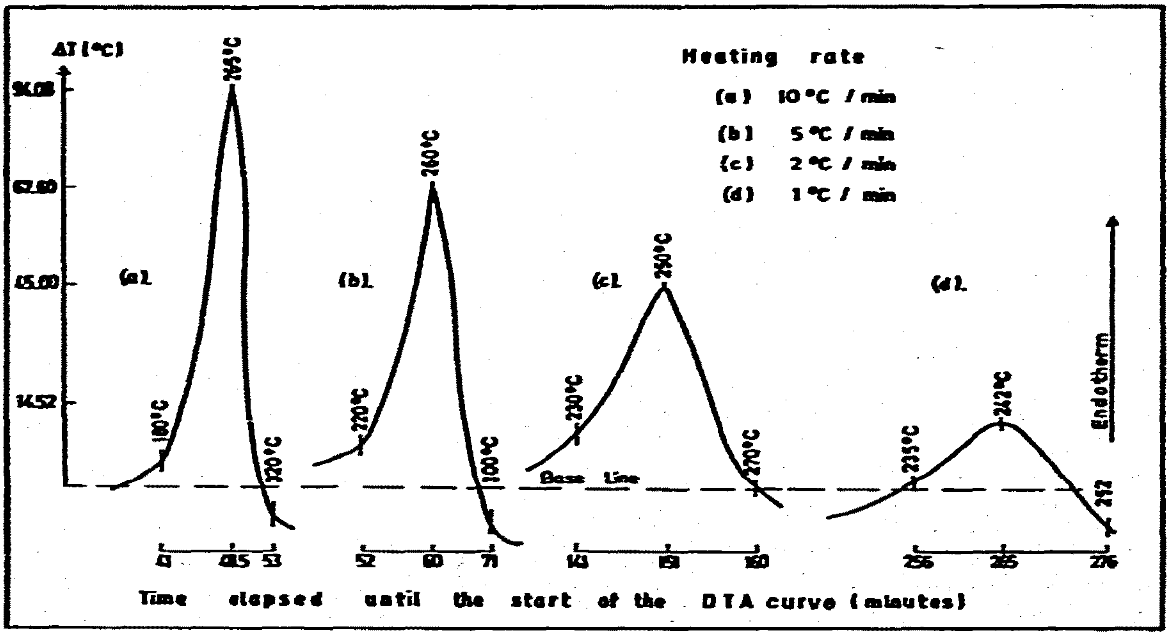

Fig. 1. DTA curves for $CuCO_3Cu(OH)_2$ at different heating rates in air.

The necessary data for the calculation of kinetic parameters of the thermal decomposition of copper basic carbonate are given in Table 1.

TABLE 1

DATA FOR CALCULATION OF KINETIC PARAMETERS OF THERMAL DECOMPOSITION OF $CuCO_3Cu(OH)_2$ IN AIR

Φ = Heating rate; W_0 = sample weight (mg); τ = induction time (min); T_i = temperature of furnace at the end of the induction period; T_f = temperature of the furnace at the time of maximum deflection on the DTA curve; ΔT = the maximum decrease in the temperature of the sample; T_s = temperature of the sample at the time of maximum deflection on the DTA curve, i.e., $T_s = T_f - \Delta T$; t_p = time (min) taken to reach maximum deflection on DTA curve.

Φ (°C min^{-1})	W_0 (mg)	τ (min)	T_i (K)	T_f (K)	ΔT (°C)	T_s (K)	t_p (min)
1	225.9	256	508	515	14.52	500.48	265
2	225.9	141	503	523	45	478	151
5	225.9	52	473	533	67.60	465.40	60
10	225.9	41	453	538	94.08	433.92	48.5

Table 2 summarizes the various ways of calculating $\Delta E^{\ddagger}$ and $\Delta H^{\ddagger}$ using the method of least squares at 95% confidence range.

TABLE 2

ESTIMATIONS OF $\Delta E^{\ddagger}$ AND $\Delta H^{\ddagger}$

NUMBER	From of plot used to find $\Delta E^{\ddagger}$	$\Delta E^{\ddagger}$ (Kcal/mole)	From of plot used to find $\Delta H^{\ddagger}$	$\Delta H^{\ddagger}$ (Kcal/mole)
1	Induction period; Log $\frac{1}{\tau}$ VS. $\frac{1}{T_i}$	15.22 ± 4.13	log $\frac{1}{\tau T_i}$ VS. $\frac{1}{T_i}$	16.17 ± 3.57
2	Induction period; Log $\frac{\Phi}{T_i^2}$ VS. $\frac{1}{T_i}$	16.48 ± 7.80	log $\frac{\Phi}{T_i}$ VS. $\frac{1}{T_i}$	18.20 ± 10.10
3	Considering ΔT: log $\frac{1}{t_p}$ VS. $\frac{1}{T_s}$	10.93 ± 6.86	log $\frac{1}{t_p T_s}$ VS. $\frac{1}{T_s}$	11.83 ± 6.86
4	Considering ΔT; Log $\frac{\Phi}{T_s^2}$ VS. $\frac{1}{T_s}$	16.65 ± 7.90	log $\frac{\Phi}{T_s}$ VS. $\frac{1}{T_s}$	17.46 ± 7.85
AVERAGE BASED ON PLOT (1), (2), (3) AND (4)		14.82 ± 6.67	—	15.92 ± 7.10
THERMOGRAVIMETRIC RESULTS		17.08 ± 6.50	—	—

All the calculations are based on the data presented in Table 1. The values of $\Delta E^{\ddagger}$ and $\Delta H^{\ddagger}$ based on thermogravimetric measurements[11] are calculated and included for comparison.

The following conclusions may be drawn from the results presented in Table 2.

(1) Plots (1), (2) and (4) produced approximately the same values of ΔE^* and ΔH^*, while eqn (3) gave somewhat smaller values. This difference could be attributed to experimental error, method of calculation and sample weight.

(2) The values of ΔE^* and ΔH^* differ by an average of 1.10 kcal mol^{-1}. This small difference could not be differentiated experimentally and in our present study we could safely say that ΔE^* and ΔH^* are equivalent.

The lower values from DTA results have been calculated in compared to the thermogravimetric results. This was also approved by the authors of this article speaking of this kind of comparison[4,9].

By means of the Kissinger's method the reaction order is determined from the shape of DTA curve for the heating rate of 1 °C min^{-1}. The shape index S of the endothermic peak presented in Fig. 1 was calculated to be 0.312. According to eqn (9), a value of $n = 0.70$ was calculated.

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