

THERMAL DECOMPOSITION OF $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. DETERMINATION OF KINETIC PARAMETERS BY DTG AND DTA

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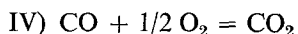
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The thermal decomposition of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ is studied in air and in a nitrogen atmosphere. The influence of the environment on the DTA curves is discussed. The activation energies and the frequency factors of the three reactions occurring in this decomposition have been determined by application of Kissinger's equations to the DTG curves and, for comparison, to the simultaneous DTA curves. DTG, unlike DTA, may be applied to a reaction: solid A = solid B + gas C when another transformation involving only enthalpy change is also occurring at the same time.

It is known that during the thermal decomposition of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ the following reactions occur:

- I) $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} = \text{CaC}_2\text{O}_4 + \text{H}_2\text{O}$
- II) $\text{CaC}_2\text{O}_4 = \text{CaCO}_3 + \text{CO}$
- III) $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$

Several authors have studied the kinetics of reactions I and III [1–8] and II [6–8] by means of TG and DTA techniques. Nearly all of them worked with a static air atmosphere. Under these conditions the endothermic reaction II is immediately followed by the exothermic reaction:



The DTA curve, being due to the thermal effects of the two reactions, therefore exhibits one or two exothermic peaks, depending upon the experimental conditions as will be discussed later. Most kinetic studies of thermal decompositions are in effects based on DTA which, in similar cases, does not permit the determination of the kinetic parameters.

The derivative thermogravimetric curve gives the course of a reaction: solid A = solid B + gas, and is therefore suitable for kinetic evaluations. A DTG curve, unlike a DTA curve, affords the advantage that the base-line is independent of the several variable parameters connected with heat conduction through the sample.

In evaluating the activation energy E_a and frequency factor A by DTA, Kissinger [9] assumes that the area under the DTA curve (at constant Φ heating rate) is proportional to the reacted matter (x). A DTG, unlike a DTA curve, always gives the value of dx/dt directly.

From the general kinetic equation:

$$\ln dx/dt = \ln A + \ln (1-x)^n - E_a/RT \quad (1)$$

Kissinger obtained the expressions:

$$-E_a/R = d \ln (\Phi/T_m^2)/d(1/T_m) \quad (2)$$

$$\ln A = \ln (E_a/R) + \ln (\Phi/T_m^2) + E_a/RT_m \quad (3)$$

where T_m is the absolute temperature of the highest reaction rate, and corresponds generally, to a good approximation, to the peak temperature of the DTA curve, and exactly to that of the DTG curve.

In the present work we have determined the activation energy and frequency factor values of the three reactions that occur in the decomposition of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, by means of DTG and DTA under different experimental conditions. We have found that the equations proposed by Kissinger for calculating the activation energy and frequency factor by means of DTA curves may also be applied to derivative thermogravimetric curves.

Experimental

$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (C. Erba RP) was used. Thermal analysis curves (DTG and DTA) were obtained simultaneously with a Mettler thermoanalyzer, at heating rates of 2, 4, 6, 8, 10, 15, 25°/min, in static and flowing (10 l/h) air atmospheres and in a flowing (10 l/h) nitrogen atmosphere. A Mettler sample holder, model

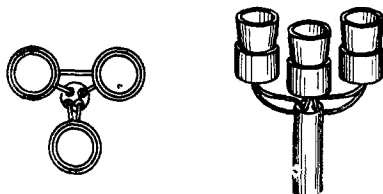


Fig. 1. Mettler sample holder model T-TD3

T-TD3 (Fig. 1) was used, with 0.3 ml platinum crucibles, 10% Rh-Pt/Pt thermocouples with a cold junction at 25° and, as reference material, Al_2O_3 (C. Erba RP) previously ignited at 1500°. The crucibles containing 30–50 mg of powdered sample were shaken for one minute on electric vibrator for regular packing.

The calculations were performed using a Hewlett-Packard calculator, model 9100 B. To calculate the activation energy from Eq. (2) $1/T_m$ and $\ln \Phi/T_m^2$ values obtained for each curve by entering data Φ and t_m (°C) were correlated; from the slope $-E_a/R$ of the straight line E_a was obtained. The best fit was determined by minimizing the sum of the squares of the deviation of the data points from the line.

The $\ln A$ values, for each Φ , were obtained by means of Eq. (3). The average of these values and the uncertainty interval, as twice the standard deviation [11], were calculated.

Results and discussion

The value of the activation energy E_a (kcal/mole) for each reaction under different conditions are given in Table 1.

The average of seven $\ln A$ values at different Φ values, and the relative uncertainty interval obtained for the reactions considered, are listed in Table 2.

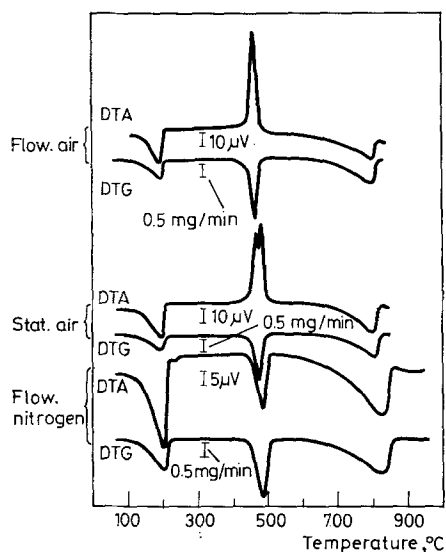


Fig. 2. DTG and DTA curves of thermal decomposition of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ at $\Phi = 8^\circ/\text{min}$ in different atmospheres

Every transformation gives DTA and DTG peaks at the same temperature, except for reaction II if it is carried in a static air atmosphere at $\Phi \geq 8^\circ/\text{min}$. The temperature corresponding to the maximum reaction rate depends upon the atmosphere and increases in the order: flowing air, static air, flowing nitrogen. This temperature increase is small in reaction I, but more for reactions II and III.

The DTA curves of the second transformation in a static air atmosphere, unlike the simultaneous DTG curves, do not permit the "a priori" determination of the kinetic parameters. In this atmosphere the endothermic reaction II is immediately followed by the exothermic reaction IV; at low heating rates the DTA curve exhibits one exothermic peak, and at $\Phi \geq 8^\circ/\text{min}$, two exothermic peaks. By placing the sample in a thin layer in a static air atmosphere, Paulik

Table 1
Values of activation energy E_a (kcal/mole) for the thermal decomposition of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$

Ref.	Technique	Apparatus	ϕ ($^{\circ}\text{C}/\text{min}$)	E_a		
				reaction I	reaction II	reaction III
This work*	DTG (stat. air)	Mettler	2, 4, 6, 8, 10, 15, 25	21.2	74.3	41.0
This work*	DTG (flow. air)	Mettler	2, 4, 6, 8, 10, 15, 25	21.1	73.6	40.9
This work*	DTG (flow. N_2)	Mettler	2, 4, 6, 8, 10, 15, 25	21.3	76.3	42.0
This work*	DTA (stat. air)	Mettler	2, 4, 6, 8, 10, 15, 25	21.2	74.3**	41.0
This work*	DTA (flow. air)	Mettler	2, 4, 6, 8, 10, 15, 25	21.1	73.6	40.9
This work*	DTA (flow. N_2)	Mettler	2, 4, 6, 8, 10, 15, 25	21.3	76.3	42.0
[1]	DTA (air)	Netzsch	5, 10, 20	$21.5 \pm 15\%$		$43.2 \pm 15\%$
[1]	DTA (air)	Netzsch	5, 10, 20	$21.6 \pm 20\%$		$43.3 \pm 15\%$
[1]	DTA (air)	Netzsch	10	$21.8 \pm 15\%$		43
[2]	DTA (air)	MOM	10	21.2		45
[2]	DTA (air)	MOM	5.3	21.8		
[3]	DTA (air)	MOM	10	$21.0 \pm 20\%$		
[4]	TG (vacuum)	his own	10-40	20.6		
[5]	TG (N_2)	Aminco	1-8.3	20.2		
[5]	TG (N_2)	Aminco	9	21.4		
[6]	TG (air)	Stanton (HT-D)	3.45		62.0	
[6]	TG (air)	Stanton (HT-D)	3.14			
[6]	TG (air)	Stanton (HT-D)	2.99			
[7]	DTA (He)	his own	10	27	85	51.7
[8]	TG (air)	Testut	10	22	74	39

* The linear correlation coefficient values were always better than 0.998.

** This value has been obtained by taking T_m as the temperature corresponding to the maximum of the curves at $\phi < 8^{\circ}/\text{min}$, and to the minimum of the curves at $\phi \geq 8^{\circ}/\text{min}$.

Table 2

Averages of the values of $\ln A$ (A = frequency factor)
at $\Phi = 2, 4, 6, 8, 10, 15$ and $25^\circ/\text{min}$

Reaction	Static air	Flowing air	Flowing nitrogen
(I)	21.13 ± 0.04	21.04 ± 0.04	21.21 ± 0.04
(II)	48.93 ± 0.02	48.69 ± 0.02	49.61 ± 0.02
(III)	17.55 ± 0.01	17.52 ± 0.01	17.82 ± 0.01

and co-workers [10] also obtained one peak at high rates of heating. We have obtained the same result by working in a flowing air atmosphere and using usual crucibles.

Simultaneous DTG and DTA curves at $\Phi = 8^\circ/\text{min}$ in different atmospheres are reported in Fig. 2.

The thermal effects of reactions II and IV are proportional to each other; in a static air atmosphere they appear to be fully recorded by the thermocouple only at low heating rates and, since the absolute enthalpy value of reaction IV is greater than that of reaction II, under these conditions the DTA curve shows only one exothermic peak. If the heating rate is increased, in the time lag when the reaction rate is high the CO oxidation front shifts toward the outside of the crucible; consequently, the exothermic effect of reaction IV is not fully recorded and the DTA curve exhibits two peaks. The minimum between the two peaks corresponds to the highest reaction rate, as shown also by the simultaneous DTG curve (Fig. 2), and the related temperature value, once its curve shape has been interpreted, can be introduced into Kissinger's equations.

In a flowing air atmosphere CO may be oxidized in the immediate surroundings of the thermocouple, the exothermic effect is fully recorded, and the DTA curve shows only one peak the temperature of which corresponds to the highest reaction rate.

The kinetic parameters obtained by solving Kissinger's equations (2) and (3) by means of DTG and DTA are reported in Tables 1 and 2 with the relevant data from the literature. Each value was obtained by evaluating seven curves at different Φ values. DTG and DTA techniques gave the same activation energy values in each atmosphere; the linear correlation coefficient values were always better than 0.998. The values for reaction I vary a little according to the atmospheres. The variation increases in reaction III and is even greater in reaction II.

Literature values [6-8] for reaction II (see Table 1) disagree; our values are close to one another and to the value found by Freeman and Carroll [8].

The $\ln A$ values (see Table 2) are practically independent of the atmosphere.

All the data show that DTG is suitable for the calculation of the kinetic parameters of a reaction: solid A = solid B + gas; it is particularly helpful when this reaction proceeds simultaneously with another transformation involving enthalpy changes that do not permit the use of the DTA technique.

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RÉSUMÉ — On a étudié la décomposition thermique de $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ dans l'air et dans l'azote et l'on discute le rôle de l'atmosphère sur les courbes ATD.

On détermine l'énergie d'activation et le facteur de fréquence des trois réactions successives de la décomposition à l'aide des équations de Kissinger appliquées aux courbes TGD ainsi qu'aux courbes ATD obtenues simultanément.

La TGD, contrairement à l'ATD, peut s'appliquer à une réaction du type solide A = solide B + gaz C, même lorsqu'une autre réaction, ne mettant en jeu que des variations d'enthalpie, s'effectue simultanément.

ZUSAMMENFASSUNG — Die thermische Zersetzung von $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ wurde in Luft und in Stickstoffatmosphäre untersucht. Der Einfluß der Umgebung auf die DTA-Kurven wird erörtert. Die Aktivierungsenergie und der Frequenzfaktor der drei Reaktionen, welche bei dieser Zersetzung einen entsprechenden Einfluß haben, wurden an Hand der für DTG-Kurven angewandten Kissinger Gleichungen ermittelt und, für Vergleichszwecke, auch für die simultan erhaltenen DTA-Kurven berechnet. Im Gegensatz zu DTA kann DTG für Reaktionen der Form A Feststoff = B Feststoff + C Gas angewandt werden, selbst wenn sich gleichzeitig eine andere, nur Enthalpieänderungen erfordernde Umwandlung abspielt.

Резюме — Изучен термораспад $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ в атмосфере воздуха и азота. Рассмотрено влияние окружающей среды на кривые ДТА. С помощью уравнений Киссингера, примененных для кривых ДТГ и, с целью сравнения, для кривых ДТА, определены энергия активации и фактор частоты трех реакций, происходящих при этом распаде. Кривые ДТГ, в отличие от кривых ДТА, можно использовать при изучении реакции: А твердый = В твердый + С газ, и в том случае, если происходит одновременно другое превращение, сопровождающееся только изменением энтальпии.