

Thermal Decomposition of Copper Tartarate Trihydrate

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Abstract:

Differential thermal analysis - thermogravimetry (DTA-TG) techniques were used to study the thermal decomposition reaction of Copper tartarate trihydrate. The kinetics of the non-isothermal decomposition in air were studied using thermogravimetric techniques. Analysis of the kinetic data were performed using integral methods due to composite, Coats-Redfern and Ozawa methods. The results of the kinetic analysis of the non-isothermal data were discussed in view of various solid state reaction models. The results showed that the phase boundary (R_2) model gives the best fit of data. The activation parameters were calculated and discussed for each decomposition step.

Keywords: Decomposition, Thermal analysis, X-ray, Copper tartarate trihydrate.

Introduction:

Progress in an increasing number of areas of technology and hence industry is being recognized as directly related to understanding the factors influencing reactivity of solids and how they react (10). Thermoanalytical methods have been used extensively for studying the kinetics of solid powder decomposition reactions. The kinetics of thermal decomposition of solids are affected by experimental factors (12,20,25), such as heating rate, particle size, sample mass and holder design.

Several studies have been published on the thermal properties of metal carboxylates (4,15,16,18,20,23,24) and, relatively little has been done on the kinetics of the decomposition (8,21). In the thermal decomposition of Cu(II) carboxylates, Cu^+ salts have been identified as intermediates, and the reaction of Cu(II) proceeds in two steps ($Cu^{2+} \rightarrow Cu^+ \rightarrow Cu^0$), with possibly appreciable overlap of the consecutive rate processes(13). Emphasis has been made on the identification of both products and the intermediate solid phases appearing during the decomposition process.

The study of the thermal decomposition of Copper acetate (4) leads to the formation of CuO as an end product.

In the present study, the kinetics of thermal decomposition of copper tartarate trihydrate were studied using dynamic thermogravimetric techniques. Kinetic analysis of data were performed and considered with reference to the various theoretical models of solid-state reactions. The results of the different methods of data analysis were compared and discussed.

Materials and Methods:

The copper tartarate trihydrate samples were prepared by reacting pure copper(II) carbonate with a hot aqueous solution of tartaric acid. The solution was then filtered and concentrated on a water bath until a solid product was obtained on cooling. The product was filtered off and kept over anhydrous calcium chloride. The products were studied by elemental analysis, IR spectroscopy, DTA-TG analysis and X-ray powder diffraction patterns.

The kinetics of thermal decomposition were investigated by means of non-isothermal TG technique using Perkin- Elmer 7 Thermal Analyzer. The sample weights were about 6-8 mg to ensure linear heating and accurate temperature measurements.

X-ray diffraction patterns for the calcined samples were recorded with a Philips PW 1710 X-ray diffraction unit using a Cu target and a Ni filter.

Results and Discussion

Figure (1) shows the DTA and TG curves obtained for copper tartarate trihydrate. The DTA and TG curves showed that the thermal decomposition occurs in three steps. The first step starts at 40°C. It is characterized by an endothermic peak at about 80°C accompanied with a weight loss of 20% (theor. 20.3%). This step can be attributed to the dehydration of the copper tartarate trihydrate to anhydrous salt. The second decomposition step shows an exothermic process with a peak at about 220°C accompanied with a loss of 52% (theor. 51.2%) which may be due to the decomposition of anhydrous salt to copper(II) oxide. In air, above 280°C, a slight mass increase was observed in the TG curve and a corresponding broad exothermic peak in the DTA curve, due to the partial oxidation of Cu to Cu(II)O. The third decomposition step shows an exothermic process with a peak at about 1050°C accompanied with a loss of 4% (theor. 3.8%) which may be due to the decomposition of copper(II) oxide and copper(I) oxide.

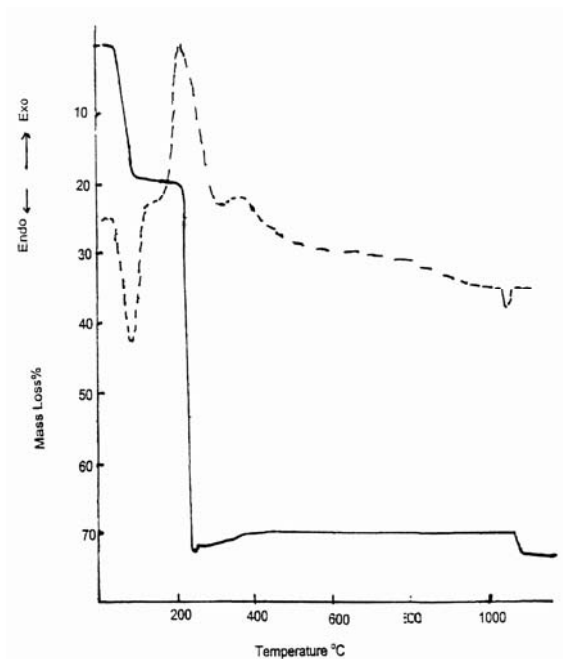


Fig. 1. DTA-TG of copper tartarate trihydrate in air and heating rate of 10deg/min.

X-ray diffraction (XRD) patterns of the decomposition products of copper tartarate trihydrate are shown in Figure (2). The patterns at room temperature are those characteristic of the Copper tartarate trihydrate. At 150oC the XRD patterns showed lines of the anhydrous copper tartarate. Samples calcined at 800oC showed the XRD patterns characteristic of the copper(II) oxide. Samples calcined at 1200oC showed the XRD patterns characteristic of the copper (I) oxide.

In general , the rate constant , k of a solid –state reaction is given by the formal kinetic equation:

$$\frac{d(\alpha)}{dt} = kf(\alpha) = A e^{-E/RT} f(\alpha) \quad (1)$$

Where α is the fractional reaction; t is the time; A is the pre-exponential factor; E is the activation energy ; R is the gas constant; T is the temperature in

Kelvin and $f(\alpha)$ is the kinetic function which takes different forms depending on the particular reaction rate equation(2,7,8,11,12). In isothermal kinetic studies, the rate equation used to calculate the rate constant has the form:

$$g(\alpha) = kt \quad (2)$$

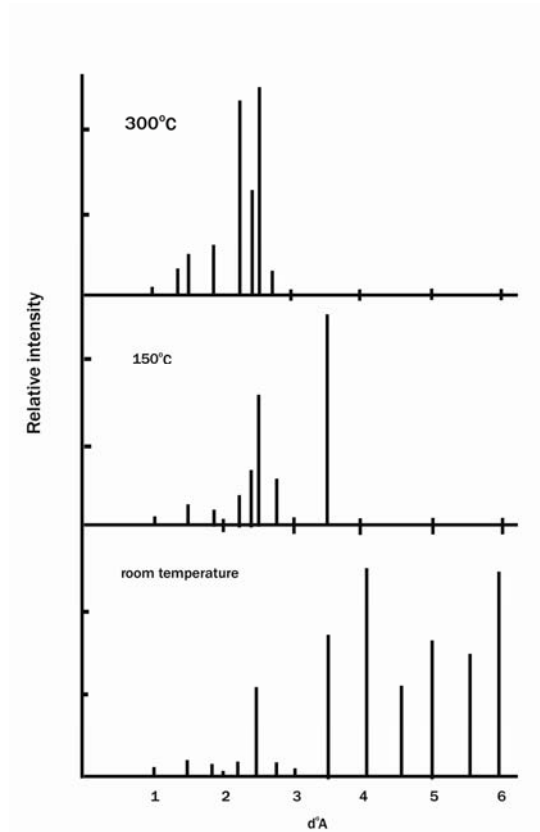


Fig. 2. X-ray diffraction patterns of copper tartarate trihydrate calcined at different specific temperature

where $g(\alpha) = \int_0^{\alpha} \frac{d(\alpha)}{f(\alpha)}$, are the integrated forms of $f(\alpha)$ (2,7,11,12).

However, non-isothermal methods are becoming more widely used because they are more convenient than the classical isothermal methods(5).

In non-isothermal kinetics the time dependence on the left side of equation [1], is eliminated using constant heating rate $\beta = \frac{dT}{dt}$, so that $T = T_0 + \beta t$,

where T_0 is the starting temperature and t is the time of heating. Using integral methods of analysis, equation [1] may be written as:

$$g(\alpha) = \frac{A}{\beta} \int_{T_0}^T e^{-E/Rt} dt \quad (3)$$

Because the reaction rate is negligible at low temperatures, hence:

$$g(\alpha) = \frac{A}{\beta} \int_0^T e^{-E/Rt} dt \quad (4)$$

Integration of this equation leads to Doyle's equation(9) :

$$g(\alpha) = \frac{AE}{R\beta} \left[\frac{e^{-x}}{x} - \int_0^{\infty} \frac{e^{-u}}{u} du \right] = \frac{AE}{R\beta} p(x) \quad (5)$$

$$T \rightarrow \infty \quad \text{where } T \text{ tends to } \infty$$

where $u = (E/RT)$ and x is the corresponding value of u at which a fraction of material has decomposed. This equation has been reformulated as:

$$\ln g(\alpha) - \ln P(x) = \ln \left(\frac{AE}{R\beta} \right) = B \quad (6)$$

where B is a constant for a particular reaction at a constant heating rate β . The integral function $P(x)$ is not definite and may be written in expanded form and estimated using procedure of trial – and error type involving iteration(3) .

In the present study, analysis of non-isothermal data were performed using approximate computational approaches due to (6,8,17,22).

Integral methods are often more reliable and generally preferred than differential methods of kinetic analysis.

In the Coats–Redfern method (6), the $g(\alpha)$ is approximated to the form:

$$g(\alpha) = \frac{ART^2}{\beta E} \left[1 - \frac{2RT}{E} \right] e^{-E/RT} \quad (7)$$

The equation has been written in the form:

$$-\ln \left[\frac{g(\alpha)}{T^2} \right] = -\ln \frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) + \frac{E}{RT} \quad (8)$$

The quantity $\ln \frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right)$ is reasonably constant for most values of E and in the temperature range over which most reactions occur. However, both E and A could vary with the experimental heating rate.

In the Ozawa method(1965), a master curve has been derived from the TG data obtained at different heating rates (β) using Doyle's equation and assuming that $\frac{AE}{\beta R} P\left(\frac{E}{RT}\right)$ is a constant for a given function of material

decomposed. The function $P\left(\frac{E}{RT}\right)$ was approximated by the equation:

$$\log P\left(\frac{E}{RT}\right) = -2.315 - 0.4567 \left(\frac{E}{RT}\right) \quad (9)$$

so that

$$-\log \beta = 0.4567 \left(\frac{E}{RT}\right) + \text{constant} \quad (10)$$

Hence, the activation energy is calculated from the thermo-gravimetric data obtained at different heating rates. The frequency factor is obtained from the equation:

$$\log A = \log g(\alpha) - \log \left[\frac{E}{\beta R} P\left(\frac{E}{RT}\right) \right] \quad (11)$$

Although the calculated activation energy is independent of the reaction model and the frequency factor depends on the determined form of $g(\alpha)$, both E and A could vary much with the fractional reaction.

In the composite method of analysis of dynamic data the results obtained, not only at different heating rates but also with different (α) values, are superimposed on one master curve.

This has been achieved by rewriting the approximate integral equations due to different factors in a form such that the kinetic function $g(\alpha)$ and the linear heating rate (β) lie on one side of the equation and $(1/T)$ on the other side. When use is made of the modified Coats and Redfern equation (1962), then in order to do the composite analysis the equation is written in the form:

$$\ln \left[\frac{\beta g(\alpha)}{T^2} \right] = \ln \left(\frac{AR}{E} \right) - \frac{E}{RT} \quad (12)$$

Hence, the dependence of $\ln \left[\frac{\beta g(\alpha)}{T^2} \right]$ calculated for different (α) values at their respective (β) values, on $(1/T)$ must give rise to a single master straight line for the correct form of $g(\alpha)$ and a single activation energy and frequency factor can readily be calculated.

When using Doyle's approximate equation (9) the equation for composite analysis has the form:

$$\log [g(\alpha) \beta] = \left[\log \frac{AE}{R} - 2.315 \right] - 0.4567 \left(\frac{E}{RT} \right) \quad (13)$$

Again, the dependence of the left side of equations [12] and [13] on $(1/T)$ should give rise to a single master straight line for the correct form of $g(\alpha)$

and hence the activation energy and the frequency factor can be readily calculated.

In general the use of the different approximate integral equations for the kinetic analysis of non-isothermal decomposition kinetic data according to the composite method of analysis, gave rise (within experimental error), to identical values of activation parameters and the correct form of $g(\alpha)$.

Figure (3) shows the results obtained from non-isothermal measurements for the dehydration and decomposition reactions, for the samples studied in air at different heating rates of 5, 10, 15 and 20 deg. min⁻¹.

The activation parameters were calculated and listed in Table 1.

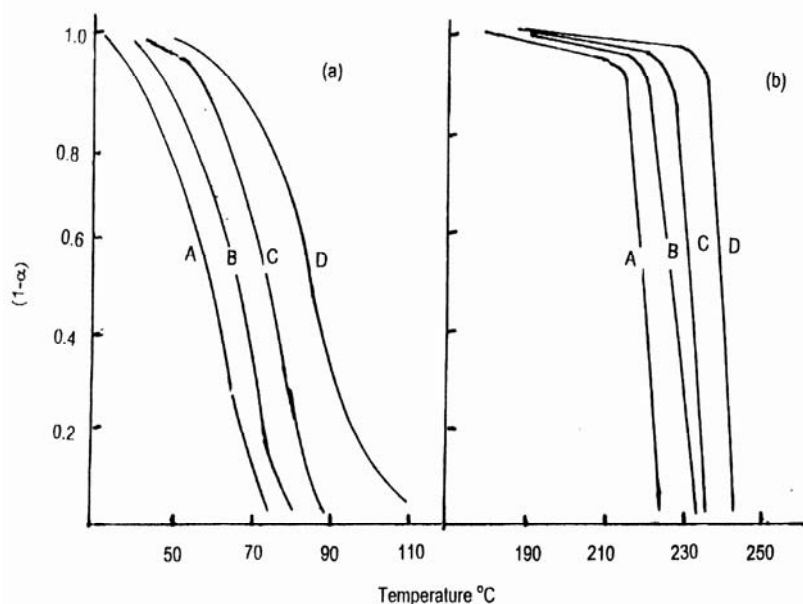


Fig. 3. Dynamic measurements for copper tartarate trihydrate thermal decomposition with heating rate A 5. B 10. C 15 and D 20 (a) first step and (b) second step

Table (1)

Activation parameters of the thermal dehydration and decomposition of copper tartarate trihydrate calculated according to R_2 models

Methods of Analysis		First decomposition step		Second decomposition step	
		E_a kJ mol ⁻¹	log A min ⁻¹	E_a kJ mol ⁻¹	log A min ⁻¹
Composite Method *		69.5±1.0	9.85±0.03	135.2±0.6	13.12±0.03
Coats-Redfern Method	$\beta=2$	59.7	6.3	160.5	17.1
	3	60.5	6.9	155.6	16.6
	5	69.8	7.8	145.3	13.5
	7	71.7	9.5	124.2	12.0
	Av.	65.43±5.725	7.625±1.325	146.4±14.1	14.8±2.4
Ozawa Method	$\alpha=0.1$	125.2	11.54	166.6	7.54
	0.2	149.7	11.66	181.8	11.20
	0.3	167.2	21.23	179.1	10.13
	0.4	180.3	19.28	172.2	10.58
	0.5	184.1	17.12	160.3	11.80
	0.6	191.6	18.55	159.9	10.65
	0.7	187.2	16.34	164.2	10.06
	0.8	170.8	13.79	166.0	9.32
	0.9	160.6	9.52	167.7	8.12
	av.	168.5±33.32	15.45±0.38	168.6±11.21	9.94±1.39

* Analysis according to this method were done using integral methods of Coats-Redfern, Madhunsanan, modified coats-Redfern, etc and the listed values represent average values of the results obtained using the different methods.

Figure (4) shows typical composite plots for the two decomposition steps according to the contracting surface (R2) which gives, better regression factors and less standard deviations in the calculated experimental parameters. The activation energy for the dehydration step is in agreement with that reported by Mu and Perlmutter (19) and indicates that the water of hydration is co-ordinated water. The activation energy for the decomposition of anhydrous salt is in agreement with the values of many thermal decomposition reactions. This supports the view that charge transfer is the rate – controlling step in the mechanism of carboxylate decomposition (14).

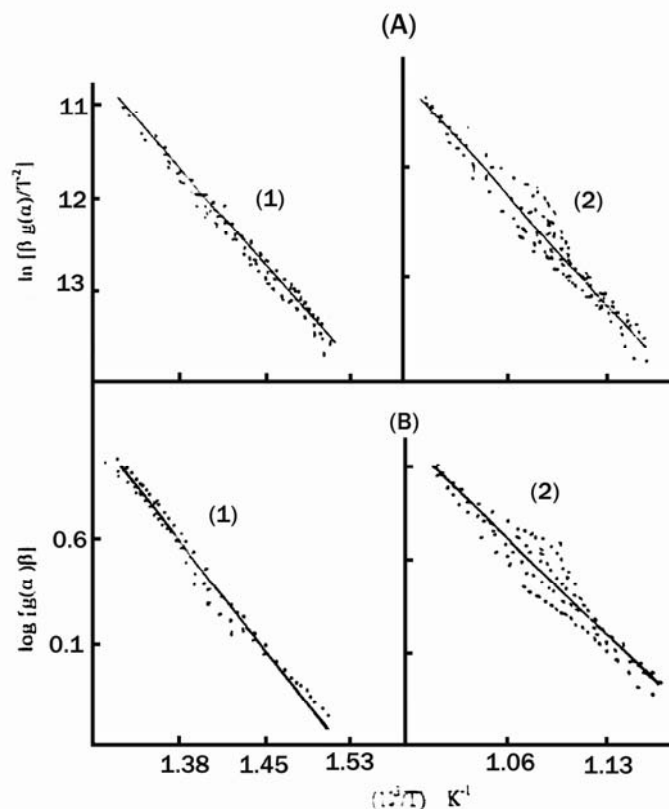


Fig. 4. Composite analysis of dynamic TG data based on the modified coats-Redfern equation (A) and Dole's equation (B), assuming contracting, R₂-model, (1) first decomposition step and (2) second decomposition step

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التكسير الحرارى لطرطرات النحاس المائية

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جدة - المملكة العربية السعودية

الملخص :

تم دراسة التكسير الحرارى لطرطرات النحاس المائية فى الهواء باستخدام تقنية التحليل الحرارى الوزنى والتحليل الحرارى التفاضلى. وقد تم دراسة حركية خطوات التكسير الحرارى باستخدام طرق التحليل الحرارى الوزنى بالطرق غير الأيزوثرمية. وقد نوقشت النتائج فى ضوء طرق التحليل التكاملى المختلفة لطريقة التراكم وطريقة كوتس- ريدفيرن وطريقة أوزاوا. وقد وجد أن تفاعل التحلل لخطوتى التكسير يتبع حد الطور (R_2). تم حساب معاملات التنشيط ومناقشتها وذلك لكل خطوة من خطوات التكسير.