Kinetics of Isothermal Decomposition of Copper (II) and Cobalt Salts of Itaconic Acid

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ABSTRACT. Differential thermal analysis-thermogravimetric techniques were used to study the thermal decomposition of the copper (II) and cobalt salts of itaconic acid. The kinetics of the isothermal decomposition were studied in air over the temperature ranges 60-120ºC, 200-310ºC and 250-370ºC for the three decomposition steps of dehydration, and decomposition to oxide (in two steps). Kinetic analysis of the isothermal data were discussed according to various theoretical kinetic models of heterogeneous reactions. The results showed that the phase boundary (R_3) and the first order (F_1) models give the best fit data. The isothermal activation parameters calculated according to (R_3) were compared and discussed with those obtained under non-isothermal techniques.

Introduction

Thermal analysis covers a series of techniques in which a property of a material or a system is measured as a function of temperature. Typical techniques were the measurements are made during programmed temperature programmes include, differential thermal analysis (DTA), thermogravimetry (TG) and differential scanning calorimetry (DSC)[1]. Thermal analysis (DTA-TG) analytical techniques are more widely used for the determination of thermodynamic and kinetic factors. In many cases the kinetics of thermal decomposition reactions are followed by thermogravimetry[2].

The shape and temperature-dependence of a curve of α (the fraction isothermally decomposed) against (time) in the thermal decomposition of solid materials offers information regarding the typical nature of the reacting solid and the nature of the chemical process[3].

Recently, unsaturated organic acid compounds are used in many industrial applications, *e.g.* adhesives, emulsions, optical fibers and polyester resins[4,5], but few studies[6-10] on the kinetics and mechanisms of the thermal decompositions of unsaturated organic acid chelates have been performed.

In the present study, the kinetics of the isothermal decompositions of Cu- and Co-itaconates were investigated in an air atmosphere and the results interpreted with reference to the different models of heterogeneous reactions[11-16]. The activation parameters were also calculated and compared with those obtained under non-isothermal thermogravimetric conditions[7].

Experimental

The metal itaconates salts were prepared by the method described previously[7]. Pure Cu- and Co-carbonate react with a hot aqueous solution of itaconic 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 characterized by elemental analysis, IR spectroscopy, DTA-TG analysis and X-ray powder diffraction patterns. Results showed that the products obtained have the chemical formula

$$M(C_5H_8O_4) \cdot H_2O) \text{ \{where M = Cu, Co\}}$$
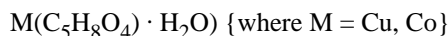
DTA-TG were performed under isothermal conditions on Shimadzu DT 40 Thermal Analyzer. The sample weights were 6-8 mg to ensure linear heating and accurate temperature measurements.

The kinetics of the thermal decomposition of Cu and Co-itaconato salts were investigated using isothermal TG technique and the temperature was varied between 60-120ºC, 200-310ºC and 250-370ºC for the three steps of decomposition.

Results and Discussion

Figures 1 and 2 show the DTA and TG curves obtained for Cu- and Co-itaconates monohydrate, respectively. The DTA and TG curves showed that the thermal decomposition of Cu- and Co-itaconate salts at temperatures below 600ºC occurs in three steps. The first step starts at about 70ºC for Cu- and about 100ºC for Co-complex; it is characterized by a broad endothermic peak at 90 and 115ºC accompanied with a weight loss of 10.0% and 8.0% for these salts, respectively. This step can be attributed to the loss of water of crystallization forming the anhydrous salts. Dehydration of the Cu- and Co-salts found to be completed at about 130 and 150ºC, and the anhydrous salts were stable up to about 210 and 270ºC, respectively. The second decomposition step shows an exothermic process with peaks at about 230 and 310ºC for Cu- and Co-salts, respectively accompanied with a weight loss of 33% and 34%. These are completed at about 250 and 330ºC. The third decomposition step is, also, exothermic with peaks at about 260 and 360ºC, accompanied by a weight loss of 19% and 18% and may due to the decomposition to the oxide[7].

X-ray diffraction patterns of the decomposition products of salts of Cu (II) and Co itaconates are shown in Fig. (3a and b) respectively. The patterns at room temperature are those characteristic of the monohydrate salts of Cu (II) and Co (II) itaconates. At 150ºC the XRD patterns showed low intensity lines of the anhydrous salts. Samples of
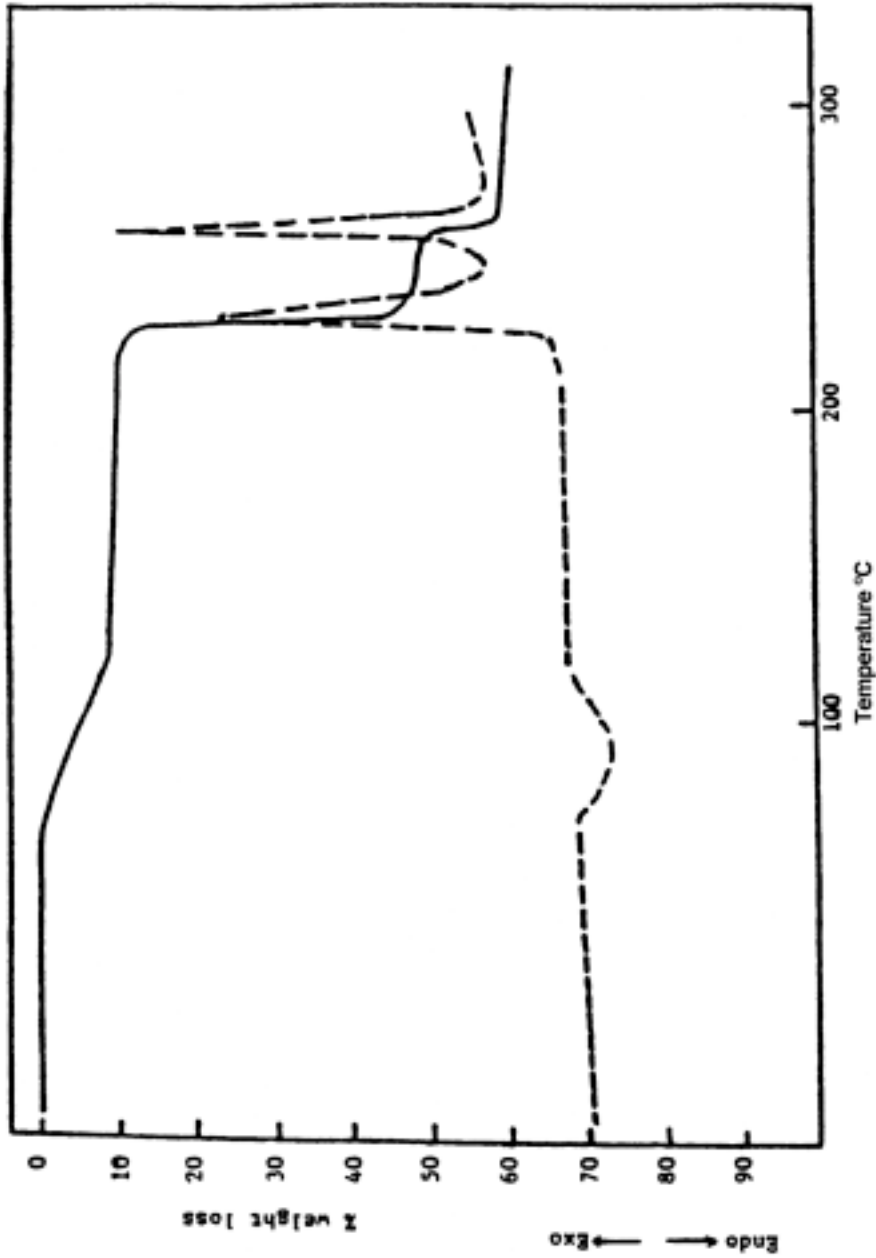
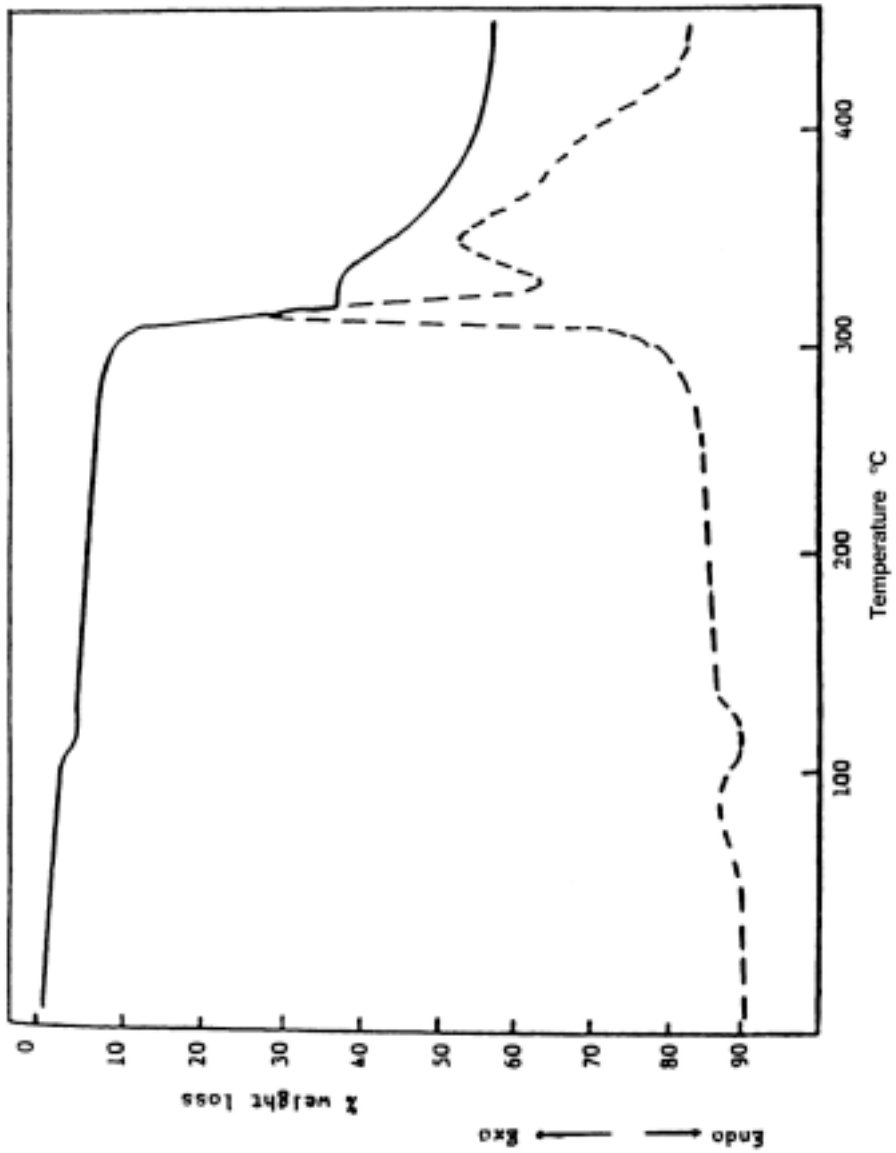FIG. 1. DTA ($-$ $-$ $-$) and TG (————) curves of Cu-itaconato complex in air and heating rate 15 deg. min^{-1}.

FIG. 2. DTA (– – –) and TG (———) curves of Co-itaconato complex in a air and heating rate 15 deg. min^{-1}.
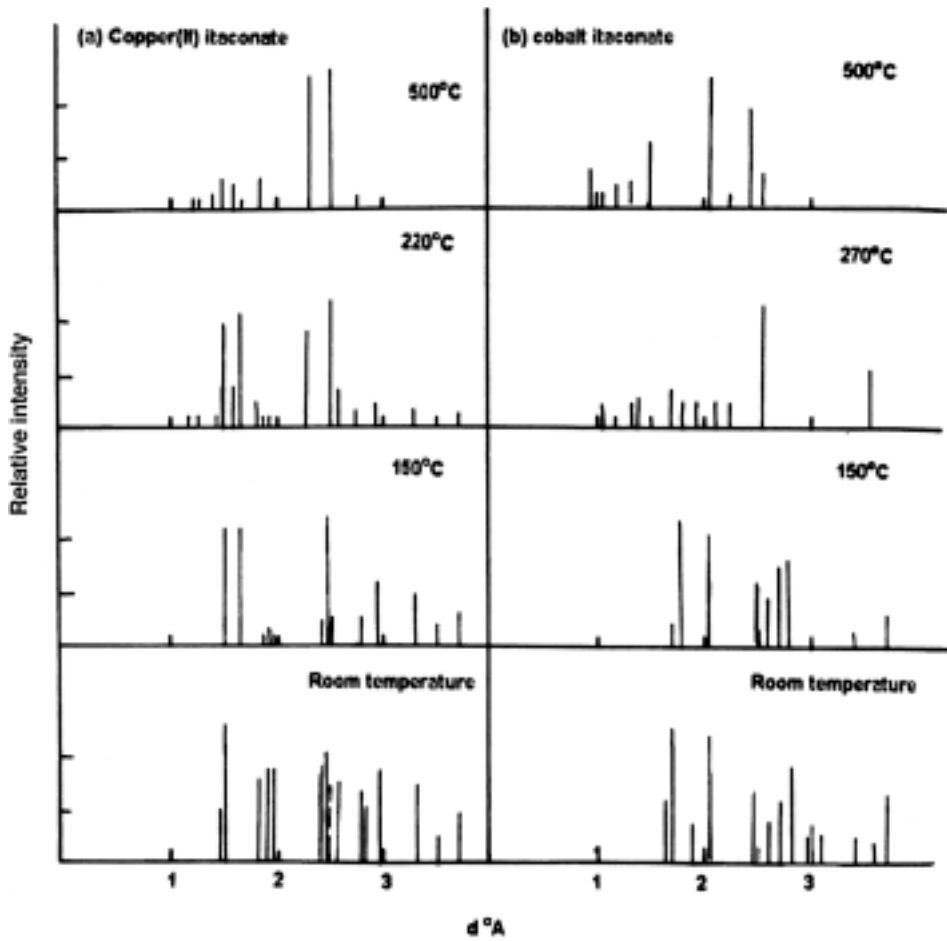
F<small>IG</small>. 3. X-ray diffraction patterns of: (a) Copper (II) itaconate and (b) Cobalt itaconate calcined at different specified temperature.

Cu (II) itaconate calcined at 220ºC showed the XRD patterns characteristic of a mixture products of Cu (II) itaconate and CuO. However, the thermal decomposition of Co (II) itaconate at 270ºC gave $CoCO_3$. At 500ºC and above, diffraction lines of CuO and CoO are the predominant products.

SEM micrographs of copper samples are shown in Fig. 4. The original samples consists of elongated crystals (Fig. 4a). The SEM micrographs after dehydration at 150ºC showed some roughning of crystal surfaces. After calcination at 220ºC for 15 min. the SEM micrographs showed a mixture of the elongated crystals and aggregates of the oxides particles (Fig. 4b). After calcination at 500ºC the whole sample has been transferred into very small crystallites forming porous and shapeless particles as shown in (Fig. 4c).

SEM micrographs for cobalt samples are shown in Fig. 5. The particles of the original samples (shown in Fig. 5a) have different sizes and shapes. After dehydration the SEM micrographs showed no remarkable changes. The SEM micrographs decomposition of samples calcined at 270ºC (Fig. 5b) showed trigonal crystals of different sizes (average diameter about 2 μm) indicating the formation of $CoCO_3$. After calcination at 500ºC for 30 min. the crystals degradation of the cobalt carbonate took place with the formation of cobalt oxide (Fig. 5c).

Under isothermal conditions, the fractional reaction-time (α - t) curves are expressed in the form $g(\alpha) = kt$, where k is the rate constant and the function $g(\alpha)$ depends on the mechanism controlling the reaction models[8-13] and on the size and the shape of the reacting particles. Figures (6 and 7) show typical plots α-t curves for isothermal decomposition of Cu- and Co-itaconates of the three decomposition reactions. The plot of $g(\alpha)$ versus time (t) should thus give a straight line if the correct form of $g(\alpha)$ function is used.

The results of the kinetic analysis of the isothermal data of the dehydration reaction and the two decomposition reactions of the anhydrous salt oxide, revealed that these reactions are best described by phase boundary (R_3) and the first order (F_1) models. Other models gave a less satisfactory fit to the experimental data. Typical plots of phase boundary (R_3) model vs. time of the three decomposition stages are shown in Fig. (8 and 9).

The activation parameters were calculated from the temperature dependence of the rate constants on the basis of the phase boundary controlled reactions of the three stages of decomposition calculated according to Arrhenius equation by linear regression (LR) analysis and the results are given Tables (1 and 2).

The results show that the activation parameters values of the dehydration step of Co-itaconate are higher than those of Cu-itaconate. These values are in agreement with the results obtained with previous study[17] for oxalato, malonato and succinate and the results were attributed to loss of the crystal water. Nikolaev *et al.*[18] determined the activation energies of differently bound water molecules and concluded that the activation for loosing crystal water lies in the range 60-80 kJ mol^{-1}, while for coordinating bounded water are within the range 130-160 kJ mol^{-1}. The activation energies of the de-
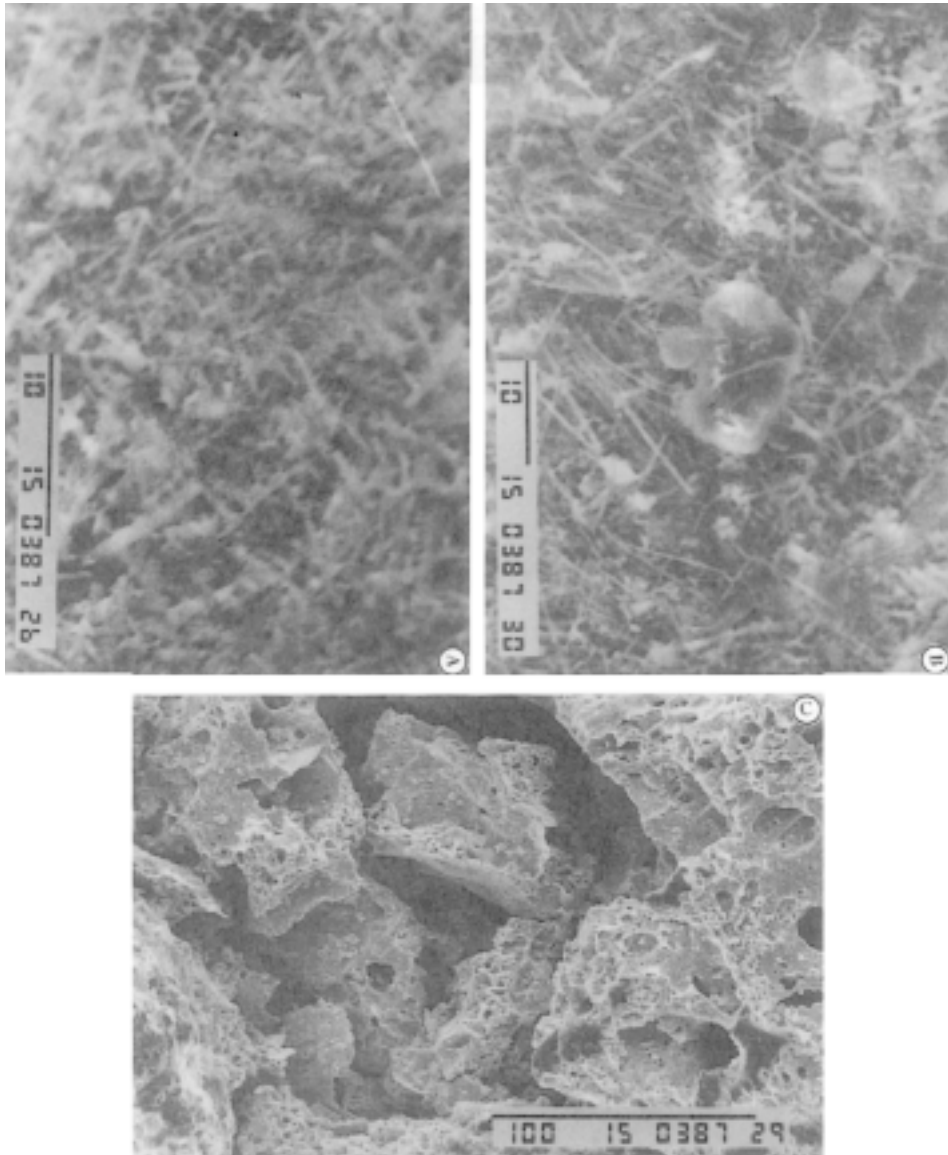
Fig. 4. Scanning electron micrographs: (a) hydrated crystals of copper (II) itaconate at room temperature; (b) samples after calcination at 220ºC and (c) samples after calcination at 500ºC.
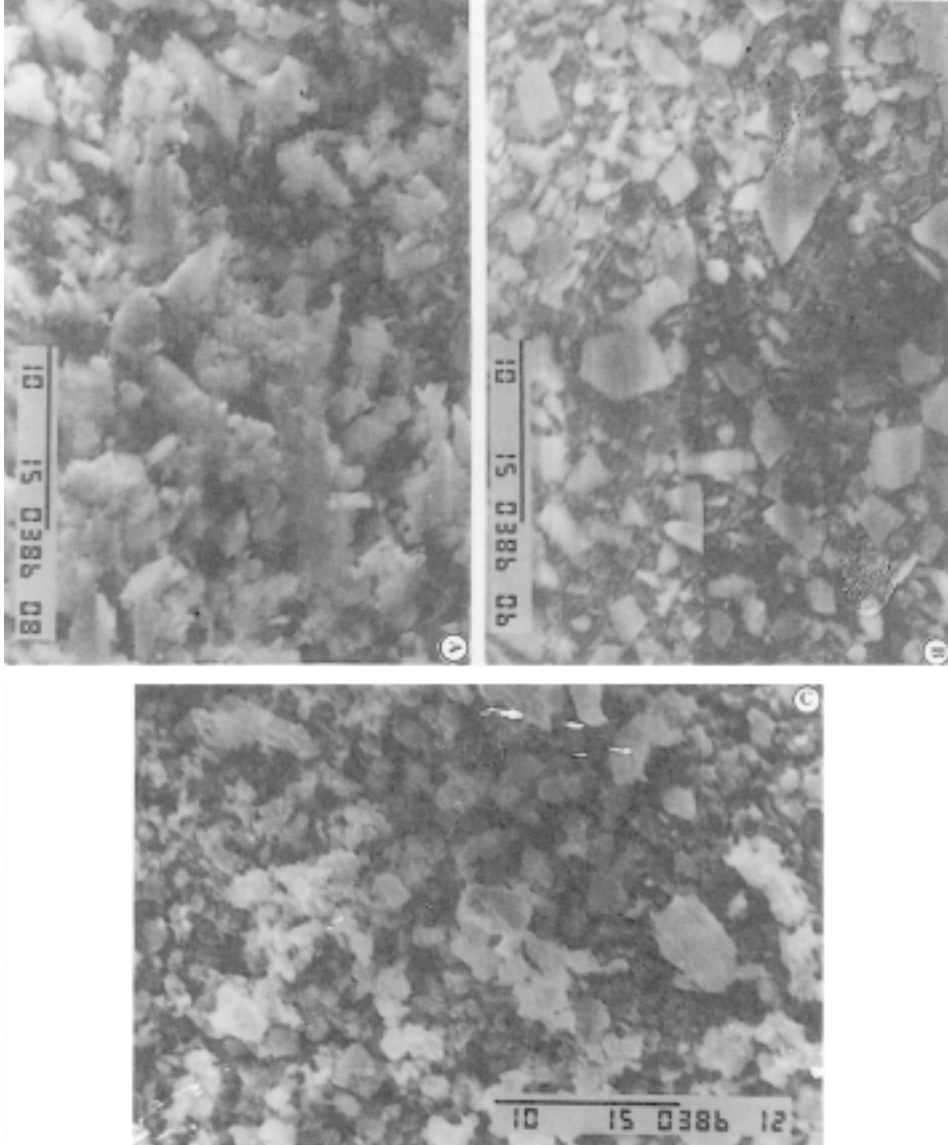
FIG. 5. Scanning electron micrographs: (a) hydrated crystals of cobalt itaconate at room temperature; (b) samples after calcination at 270ºC and (c) samples after calcination at 500ºC.
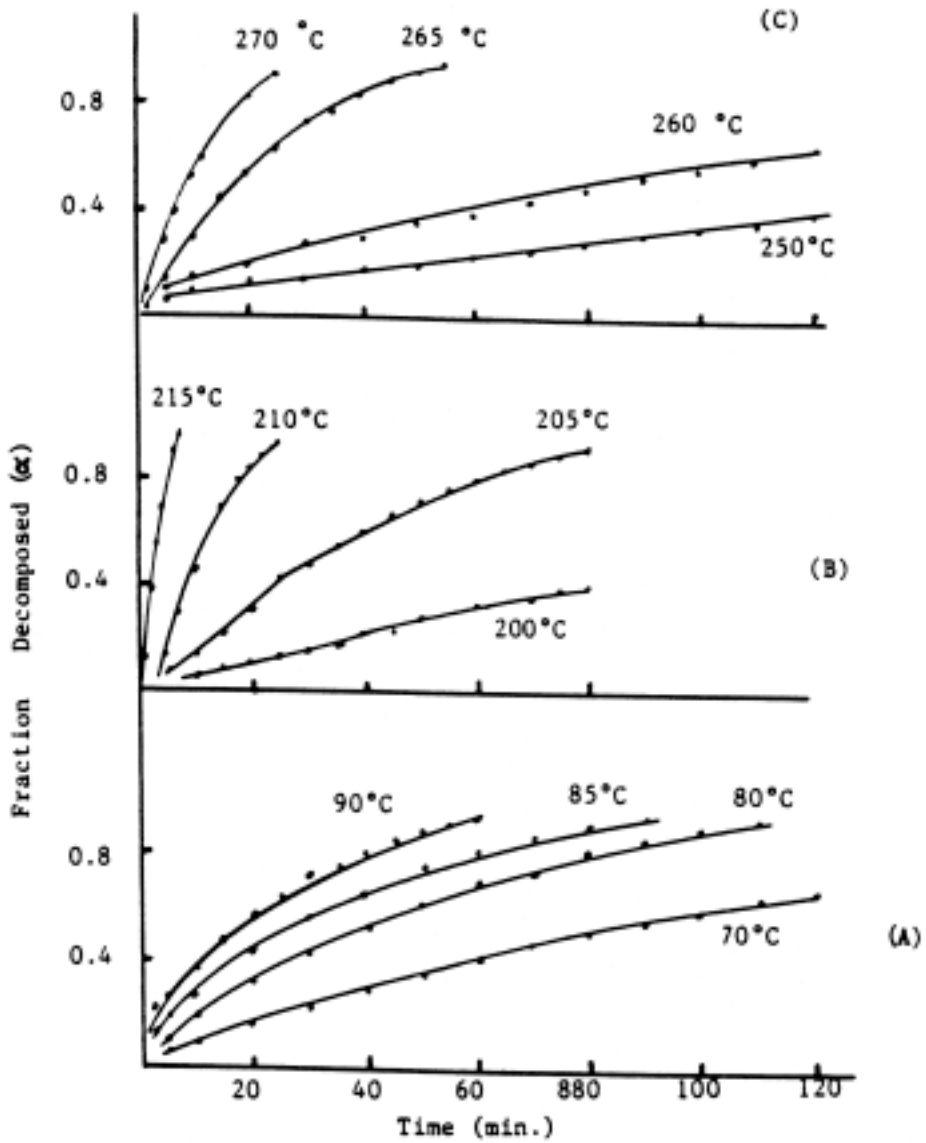
Fig. 6. Isothermal α–t curves of thermal decomposition of Cu-itaconato complex: (A) Dehydration step, (B) Decomposition to carbonate and (C) Decomposition to oxide.

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FIG. 7. Isothermal α-t curves for thermal decomposition of Co-itaconato complex: (A) Dehydration step, (B) Decomposition to carbonate and (c) Decomposition to oxide.
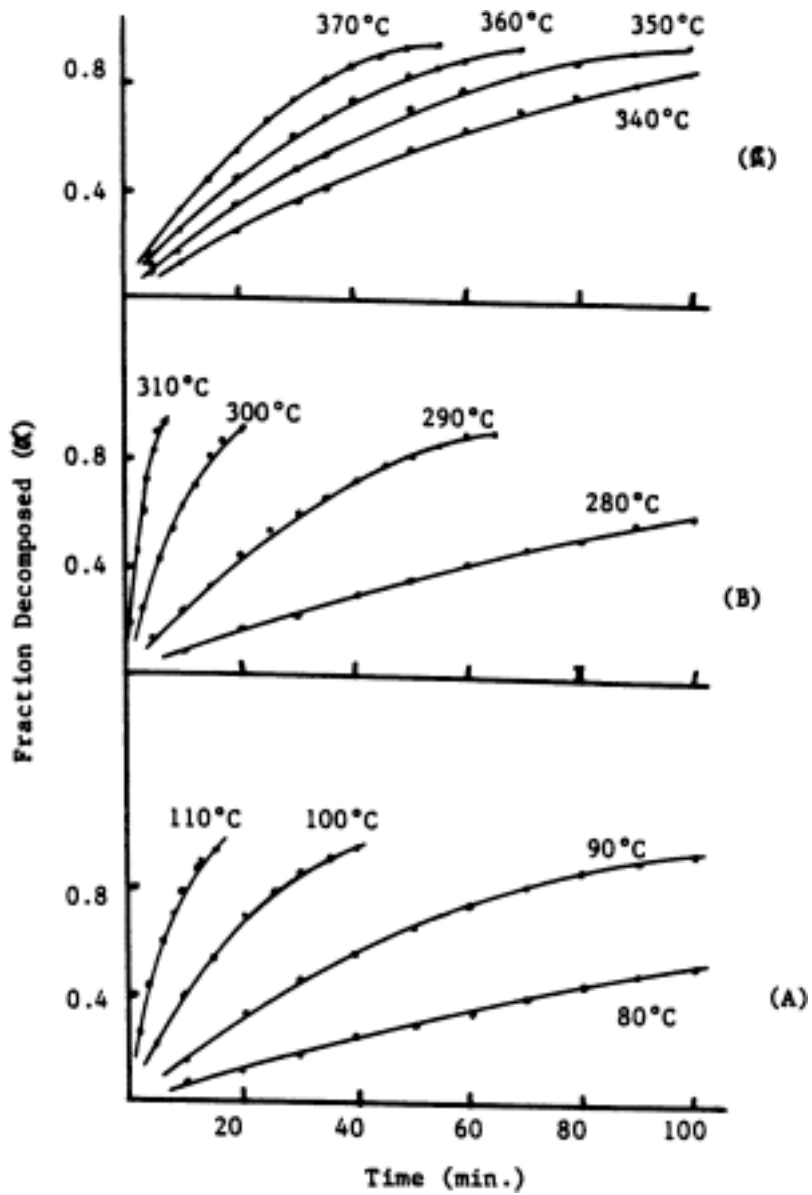
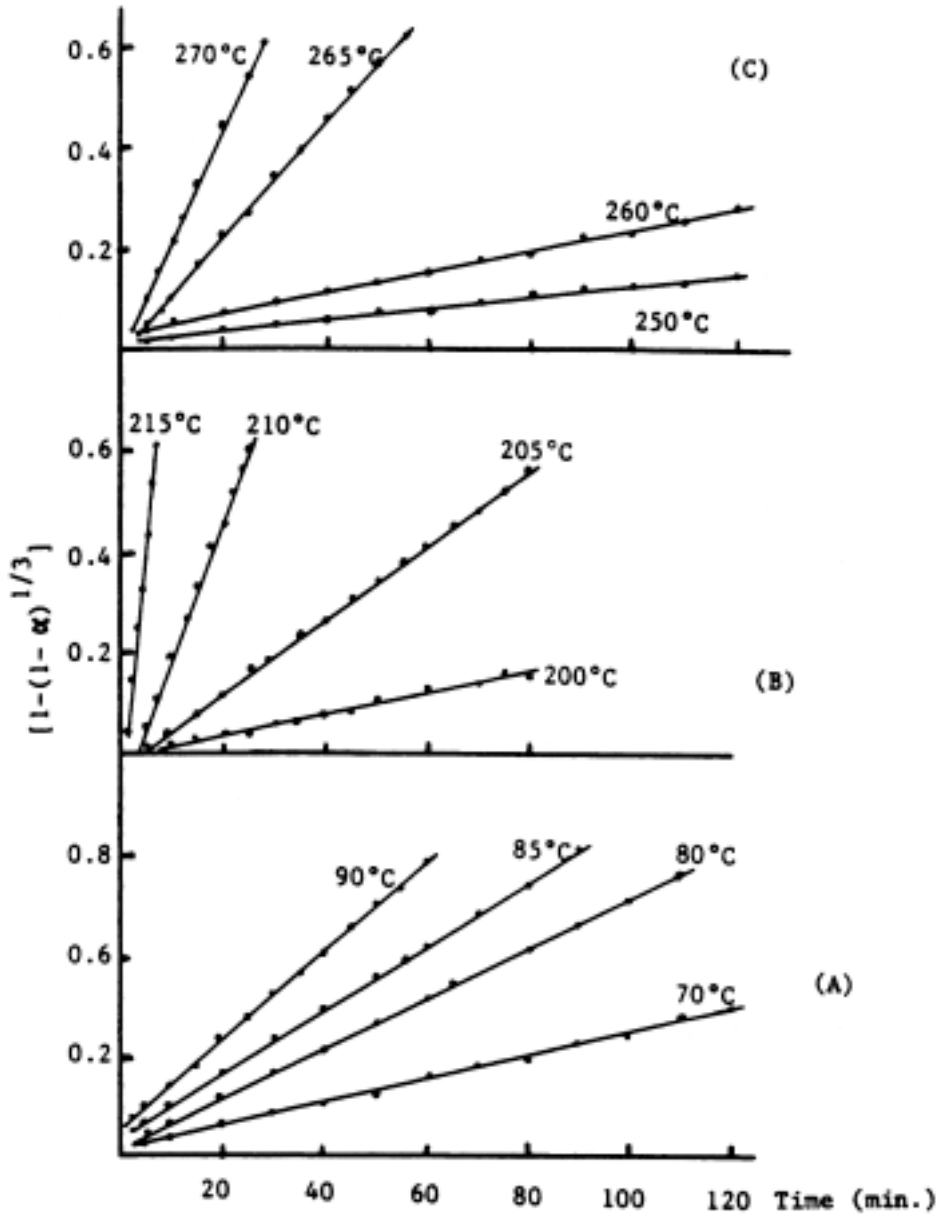FIG. 8. Isothermal decomposition of Cu-itaconato according to three dimensional phase boundary reaction model: (A) Dehydration step, (B) Decomposition to carbonate and (C) Decomposition to oxide.
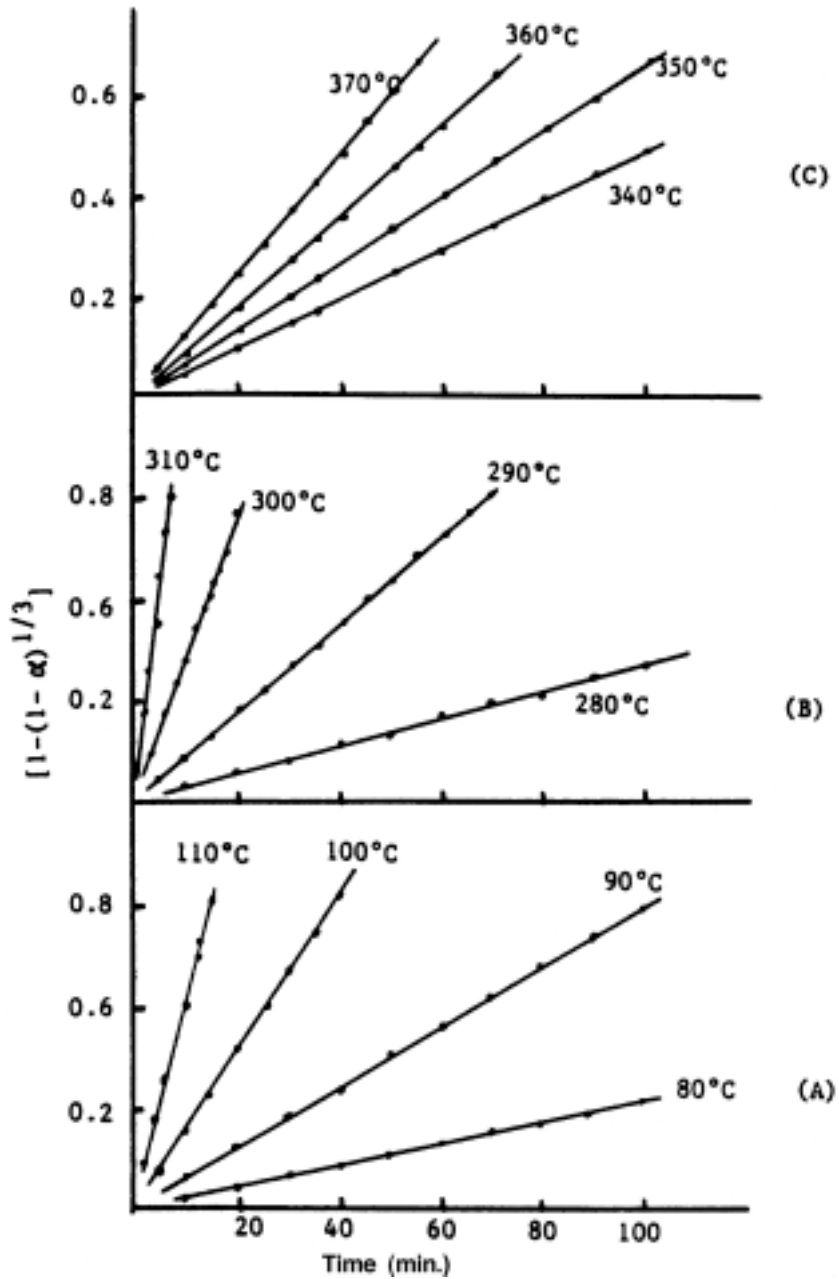
FIG. 9. Isothermal decomposition of Co-itaconato complex according to three dimensional phase boundary reaction model: (A) Dehydration step, (B) Decomposition to carbonate and (C) Decomposition to oxide.

hydration step for the two salts were attributed to loosing crystal water and is in good agreement with the previous results reported elsewhere[18].

TABLE 1. The activation parameters of thermal dehydration and decomposition of Cu and Co-itaconato complexes under isothermal conditions and (R_3).

Method of analysis	Cu-		Co-	
	E (kJ / mol)	log A (min^{-1})	E (kJ / mol)	log A (min^{-1})
Stage I (dehydration step)				
Isothermal	63 ± 3	7.9 ± 0.4	109 ± 6	14.4 ± 0.8
Dynamic*	69 ± 5	8.8 ± 1.3	117 ± 4	14.8 ± 1.2
Stage II (the first decomposition step)				
Isothermal	493 ± 40	53.0 ± 4.4	317 ± 25	28.6 ± 2.3
Dynamic*	500 ± 40	44.0 ± 8.0	311 ± 19	27.2 ± 4.0
Stage III (decomposition to oxide)				
Isothermal	163 ± 5	15.6 ± 0.5	99 ± 8	7.1 ± 0.6
Dynamic*	150 ± 6	13.4 ± 1.2	103 ± 11	7.3 ± 1.8

(*) Reference 9.

TABLE 2. The activation parameters of thermal dehydration and decomposition of Cu and Co-itaconato complexes under isothermal conditions and (F_1).

Method of analysis	Cu-		Co-	
	E (kJ / mol)	log A (min^{-1})	E (kJ / mol)	log A (min^{-1})
Stage I (dehydration step)				
Isothermal	69 ± 3	9.8 ± 0.4	109 ± 0.4	15.6 ± 0.7
Dynamic*	77 ± 5	8.8 ± 1.3	106 ± 1.4	16.8 ± 1.2
Stage II (the first decomposition step)				
Isothermal	500 ± 47	44.8 ± 4.2	310 ± 22	28.0 ± 2.0
Dynamic*	540 ± 45	48.9 ± 8.7	333 ± 25	29.6 ± 4.4
Stage III (decomposition to oxide)				
Isothermal	150 ± 6	14.3 ± 0.6	100 ± 6	8.2 ± 0.5
Dynamic*	164 ± 7	15.2 ± 1.4	115 ± 12	8.9 ± 1.9

(*) Reference 9.

The activation parameters for the decomposition reactions showed that the values are higher for Cu-itaconate than that of the Co-itaconate. The Pauling empirical ionic radii values are 0.74 Å and 0.72 Å for the Co^{2+} and Cu^{2+} ions respectively. The smaller radii of Cu^{2+} ions than that of Co^{2+} ions results in higher attraction for Cu^{2+} than Co^{2+}. This is reflected in the lower activation parameters in the dehydration step for Cu-itaconato and higher activation parameters in the decomposition reactions.

In view of the conclusions from non-isothermal study[7], the first order kinetics and phase boundary models should be used to analyze the results with reference to the composite integral method. This result is in agreement with the results obtained under isothermal conditions.

The activation parameters obtained under isothermal conditions are in agreement with those obtained under non-isothermal conditions[7]. For example, calculation on the basis of the boundary phase model (R_3) for the first decomposition step of anhydrous Cu-itaconate, gave under non-isothermal conditions[7], E_a = 500 + 42 kJ/mole and log A = 44 + 8 min^{-1}. These results are in agreement with those obtained under isothermal conditions E_a = 493 + 40 kJ/mole and log A = 53 + 5 min^{-1} as shown in Tables (1 and 2) and depending on Diefallah's Composite method of analysis for non-isothermal conditions[11].

In general, both composite methods gave equivalent values for the activation parameters, which are in good agreement with the results obtained under isothermal conditions. The values of the activation parameters calculated for Cu (II) and Co-salts are larger than normally found for most common decomposition reaction solids[19]. There is a small proportion of solid state decomposition reactions which has relatively large activation energy > 300 kJ mol^{-1}. This values of activation energies in the present study belong to this group and could possibly indicate that this high energy is associated with the breakage of the strong metal-chelate bonds.

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كينتيكيـة التحلـل الحـراري الأيـزوثـرمي لأمـلاح حمض إيتاكونك النحاس والكوبلت

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المستخلص .　يتضمن هذا البحث استخدام طرق التحليل الحراري التفاضلي والتـحليل الحراري الـوزني لدراسـة تحلل كل مـن أمـلاح إيتـاكونـاتو النحـاس والكوبلـت . تم دراسـة كينـاتيكيـة التحلـل الحراري الأيـزوثـرمي في المدى ٦٠- ١٢٠ْم و ٢٠٠-٣١٠ْم و ٢٥٠-٣٧٠ْم لخطوات التحلل الثلاث والتي تتضـمن إزالة الماء ثم خطوتي تحلل الملح اللامائي إلى أكـاسـيد الفلـز على التـوالي . تم تحليل نتائج كيناتيكية التحلل الأيزوثرمي في ضوء النماذج المختلفة للتفاعلات غير المتجانسة وأظهرت الحسابات أن نموذج حدود الطور (R_3-) ونموذج الرتبة الأولى (F_1-) تعطي أفـضل إرتبـاط للنتـائج . تم حسـاب مـعـامـلات التنشيط ومقارنة النتائج مع تلك التي تم الحصول عليها تحت ظروف غير أيزوثرمية .