

KINETICS OF THE NON-ISOTHERMAL DECOMPOSITION OF Cu- AND Co-ITACONATO COMPLEXES

A.A. El-Bellihi

Department of Chemistry, Faculty of Science, Benha, Egypt

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Abstract

The kinetics of the thermal decomposition of Cu- and Co-itaconato complexes were studied using dynamic thermogravimetric techniques. The dehydration process was found to proceed in a one-stage reaction, while the thermal decomposition of the anhydrous salts was followed a two-stage reaction. The first stage is the decomposition of the complex to metal carbonate, whereas the second stage is the decomposition of the formed carbonate to the oxide. Kinetic analysis of the dynamic TG curves were discussed with reference to a composite integral method on comparison with the integral methods of Coats and Redfern and Ozawa. The activation parameters were calculated and discussed for each decomposition step.

Keywords: complexes, Cu- and Co-itaconato complexes, kinetics, TG

Introduction

Thermal decomposition studies on solid metal complexes have shown some correlation of decomposition temperature with changing metal ion or ligand [1-3]. These studies led to the identification of products and interesting decomposition intermediates [4, 5], and, hence suitable decomposition schemes have been suggested [1, 3]. Some investigators have, also, used thermogravimetry as a means of synthesizing new compounds [1, 6]. Dynamic thermogravimetric analysis (TG) has been widely used as a tool to investigate the thermal stability of complexes and synthetic materials. Thermograms obtained, provide some information concerning the sample composition, thermal stability as well as the kinetic data relating the chemical changes occur on heating [7].

Therefore, in the present study we have used thermogravimetry to study the kinetics of the thermal decomposition of Cu- and Co-itaconato complexes to shed some light on the various integral methods used for analysis the non-isothermal decomposition. The kinetics and mechanism of solid state thermal decomposition reactions of metal salts have attracted the interest of several investigators [8]. Relatively, few studies on the kinetics of thermal decomposition reactions of complexes [9,10] were carried out.

Experimental

The metal itaconato complexes were prepared by reacting pure Cu- and Co-carbonate in 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 complexes 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 $M(C_5H_5O_4)_2 \cdot H_2O$ ($M = Cu, Co$).

The kinetics of thermal decomposition was investigated by means of dynamic TG technique using Shimadzu DT 40 Thermal Analyzer. The sample weights were about 6–8 mg to ensure linear heating and accurate temperature measurements.

Results and discussion

Figures 1 and 2 show the DTA and TG curves obtained for Cu- and Co-itaconato complexes, respectively. The DTA peaks are closely corresponding to the weight changes observed on the TG curve. The DTA and TG curves showed that the thermal decomposition of Cu- and Co-itaconato complexes at temperature below 600°C occurs in three steps. The first step starts at about 70°C for Cu- and about 100°C for Co-complex; it is characterised by a broad endothermic peak at 90 and 115°C accompanied with a weight loss of 10.0% and 8.0%, for these complexes, respectively. This step can be attributed to the loss of water of crystallization forming the anhydrous salts. Dehydration of the Cu- and Co-salts was found to be completed at about 130 and 150°C, and the anhydrous salts were stable up to about 210 and 270°C, respectively. The second decomposition step shows an exothermic process with peaks at about 230 and 310°C for the Cu- and Co- complexes respectively indicating a weight loss of 33% and 34%. It completes at about 250 and 330 °C which can be explained by the decomposition of the anhydrous salts to the carbonate. The third decomposition

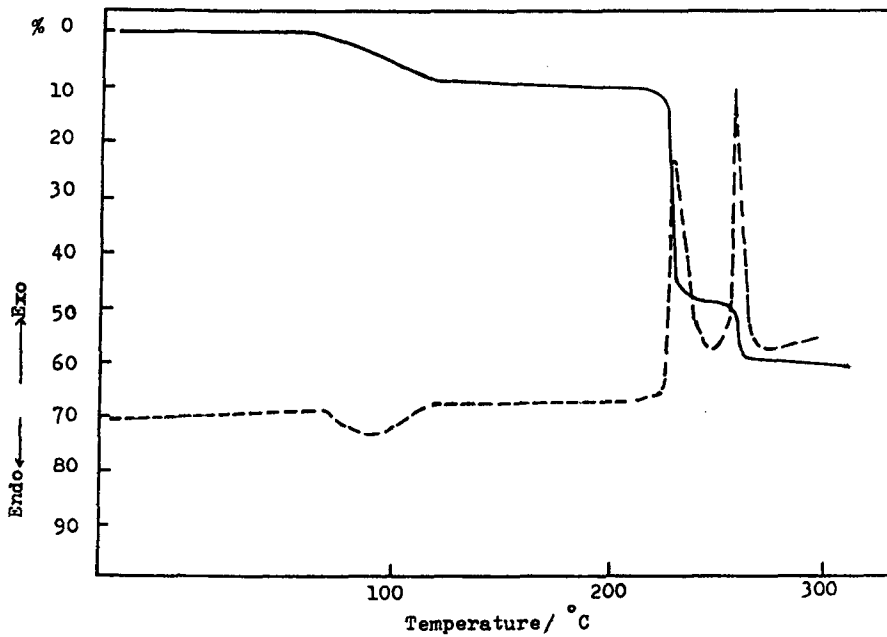


Fig. 1 DTA (----) and TG (—) curves of Cu-itaconato complex in air and heating rate $15 \text{ deg}\cdot\text{min}^{-1}$

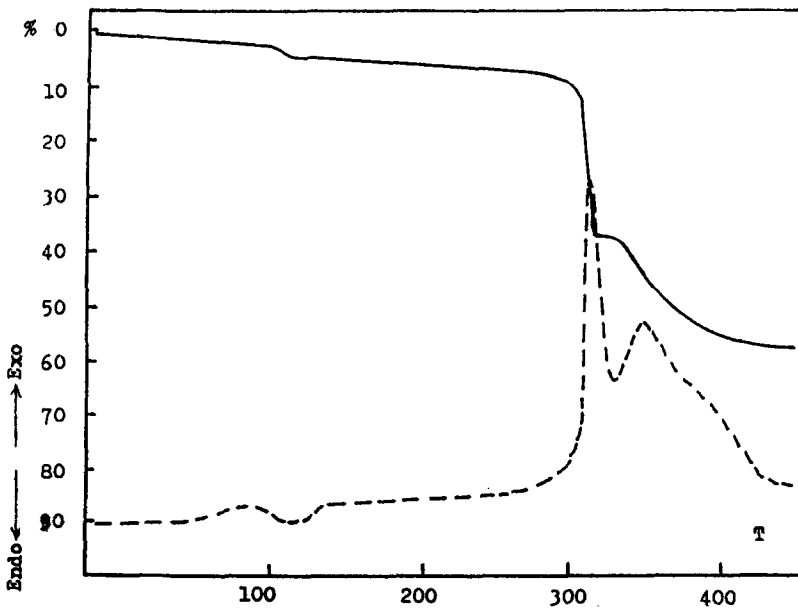


Fig. 2 DTA (----) and TG (—) curves of Co-itaconato complex in air and heating rate $15 \text{ deg}\cdot\text{min}^{-1}$

step is, also, exothermic with peaks at about 260 and 360°C, accompanied by a loss of 19% and 18% and may due to the decomposition of the carbonate to oxides.

The results of DTA and DTG curves showed that the DTA and DTG peak temperature lie in the order Co(II)itaconate > Cu(II)itaconate. This trend is similar to that obtained by Saha *et al.* [11] for oxalato, malonato and succinato complexes.

The kinetics of the three decomposition steps for the investigated complexes have been studied under dynamic conditions at heating rates 5, 10, 15 and 20 deg·min⁻¹. The kinetic analysis of the dynamic TG curves were carried out using three integral methods: Ozawa method [12], Coats and Redfern method [13] and Diefallah's composite methods [14, 15]. These methods were based on either Doyle's equation [16] (composite method I) or the modified Coats-Redfern equation [17] (composite method II).

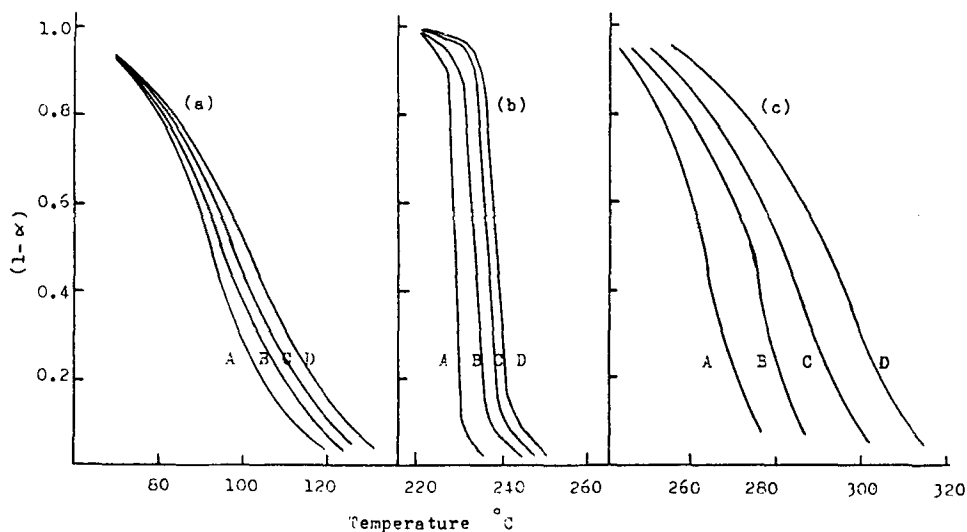


Fig. 3 Dynamic measurements for Cu-itaconato complex thermal decomposition. Heating rate: (A) 5, (B) 10, (C) 15 and (D) 20 deg·min⁻¹; (a) dehydration, (b) decomposition to carbonate and (c) decomposition to oxide

Figures 3 and 4 show representative weight changes as a function of temperature obtained from the dynamic measurements of copper and cobalt thermal decomposition, respectively. The kinetic analyses of the three decomposition steps for each complex were performed with reference to the different models of heterogeneous solid state reactions [14, 15] based on the two composite methods [14, 15]. According to composite method (I) [14] and (II) [15], the function $g(\alpha)$ may be written in the following forms respectively;

$$\log g(\alpha)\beta = (\log AE/R - 2.315) - 0.4567 E/RT$$

$$\ln [\beta g(\alpha)/T^2] = \ln (AR/E) - E/RT$$

where $g(\alpha)$ is the kinetic model function, β is the heating rate ($\text{deg}\cdot\text{min}^{-1}$), α is the fraction of the complexes decomposed, A is the frequency factor and E is the activation energy of the reaction. The plot of either $\log g(\alpha)\beta$ or $\ln [\beta g(\alpha)/T^2]$, for different values of " α " at their respective " β " values vs. $1/T$ must give rise to single master straight line, and, hence both E and $\log A$ can be calculated. The activation energy E and the frequency factor $\log A$ of the solid decomposition reaction were calculated by a computer program. Figures 5 and 6 show the results of the decomposition of Cu-itaconate to carbonate obtained by the composite methods [14, 15]. Figures 5a and 6a show that the phase boundary (R_3) gives best fit for the decomposition step to carbonate for the two anhydrous salts. Random nucleation (A_2) and other models gave less satisfactory fit data as shown in Figs 5b and 6b.

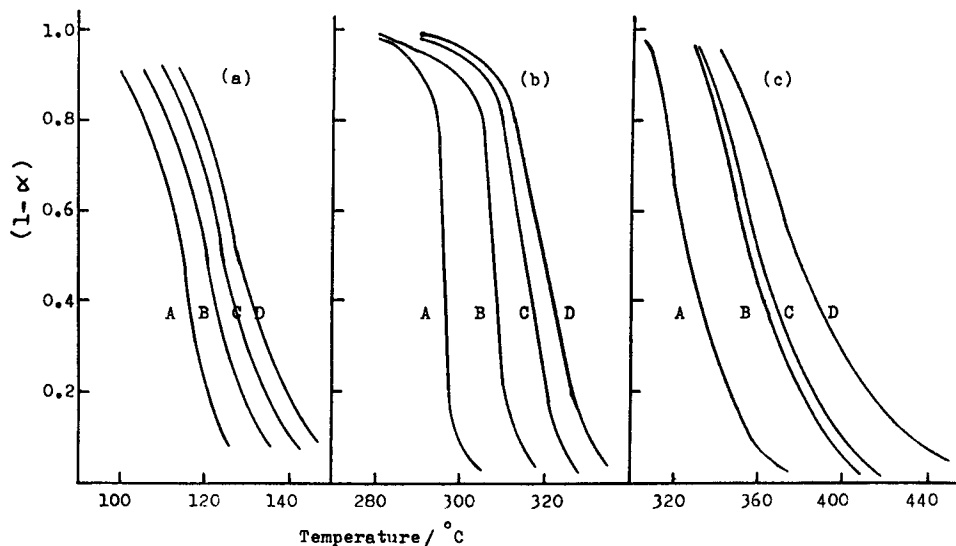


Fig. 4 Dynamic measurements for Co-itaconato complex thermal decomposition. Heating rate: (A) 5, (B) 10, (C) 15 and (D) 20 $\text{deg}\cdot\text{min}^{-1}$; (a) dehydration, (b) decomposition to carbonate and (c) decomposition to oxide

The results showed that phase boundary (R_3) and first order (F_1) are best fit data for the dehydration and decomposition steps of each samples. Tables 1 and 2 show the values of the activation parameters of the non-isothermal decomposition and dehydration steps of Cu- and Co-itaconato complexes based on the

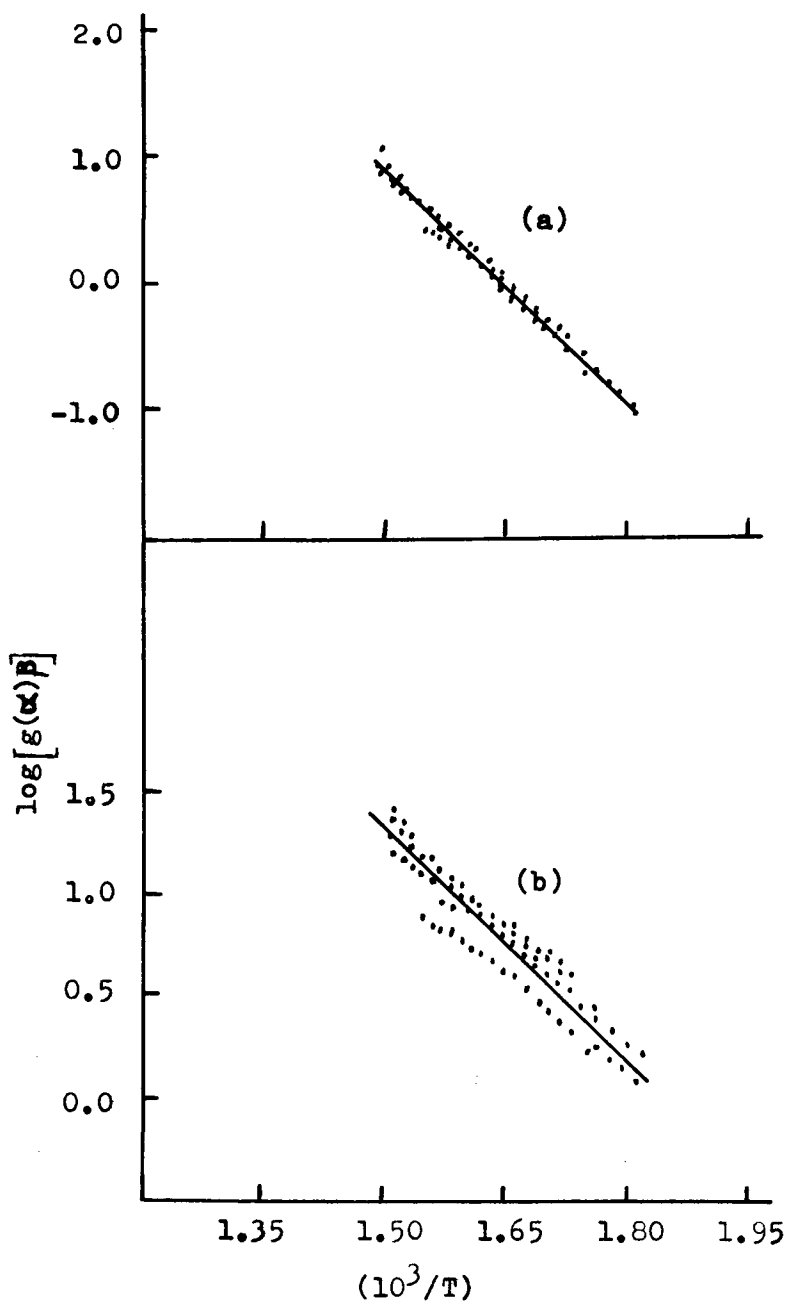


Fig. 5 Composite method I of dynamic TG data of the decomposition of Cu-itaconato complex to carbonate based on Doyle's equation. (a) R_3 ; (b) A_2

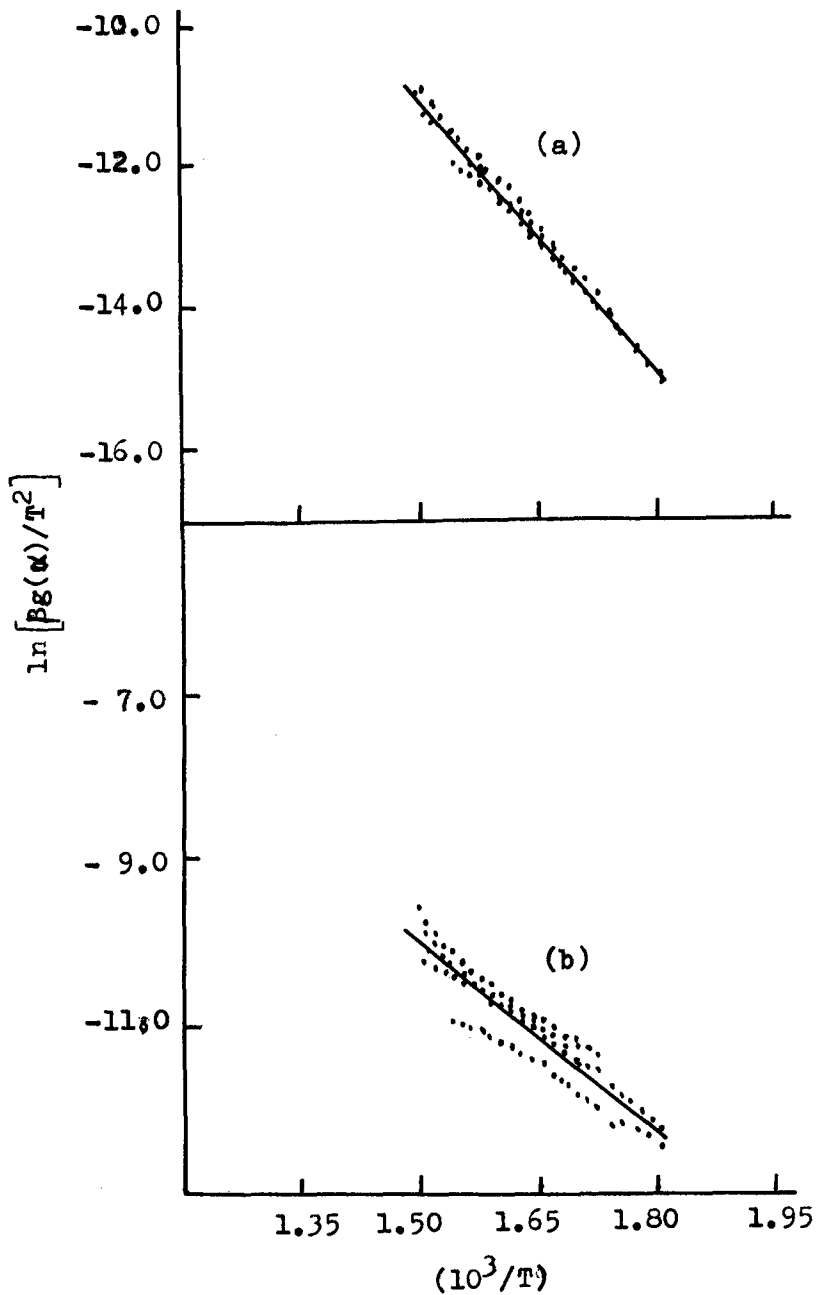


Fig. 6 Composite method II of dynamic TG data of the decomposition of Cu-itaconato complex to carbonate based on Coats-Redfern equation. (a) R_3 ; (b) A_2

two composite methods of analyses, and according to the (R_3) and (F_1) model functions. The values of the activation parameters were, also, calculated according to Coats-Redfern and Ozawa methods and the results are summarized in Tables 1 and 2. However, there is an agreement between the two composite methods and Coats-Redfern method, Ozawa method gives much less satisfactory results. Moreover, the results of E and $\log A$ calculated according to Coats and Redfern method reflect the well-known compensation effect, where $\log A$ decreases in the line with E as the experimental variables (in this case the heating rate) are changed.

The results show that the dehydration reaction has higher activation energy and frequency factor with Co-itaconate than Cu-itaconate. This fact was found

Table 1 The activation parameters of thermal dehydration and decomposition of Cu- and Co-itaconato complexes according to different integral methods and (R_3)

Method of analysis	Stage I (dehydration step)			
	Cu-		Co-	
	$E/\text{kJ}\cdot\text{mol}^{-1}$	$\log A/\text{min}^{-1}$	$E/\text{kJ}\cdot\text{mol}^{-1}$	$\log A/\text{min}^{-1}$
Composite I	67±4	8.6±1.3	117±4	14.7±1.2
Composite II	70±4	9.0±0.6	118±4	14.8±0.5
Coats-Redfern	61±6	7.7±0.8	116±10	14.7±1.3
Ozawa	178±37	26.4±5.9	115±13	14.2±1.7
Method of analysis	Stage II (decomposition to carbonate)			
	Cu-		Co-	
	$E/\text{kJ}\cdot\text{mol}^{-1}$	$\log A/\text{min}^{-1}$	$E/\text{kJ}\cdot\text{mol}^{-1}$	$\log A/\text{min}^{-1}$
Composite I	510±33	44.5±7.8	314±18	27.4±3.7
Composite II	493±31	43.1±3.4	308±17	26.9±1.6
Coats-Redfern	602±56	61.6±6.0	381±49	33.6±4.7
Ozawa	282±23	28.6±2.3	165±21	14.0±1.9
Method of analysis	Stage III (decomposition to oxide)			
	Cu-		Co-	
	$E/\text{kJ}\cdot\text{mol}^{-1}$	$\log A/\text{min}^{-1}$	$E/\text{kJ}\cdot\text{mol}^{-1}$	$\log A/\text{min}^{-1}$
Composite I	149±5	13.3±1.2	100±8	7.0±1.5
Composite II	151±5	13.4±0.5	106±8	7.6±0.7
Coats-Redfern	160±22	14.5±2.2	162±22	12.4±1.6
Ozawa	283±73	19.9±5.5	88±10	6.1±0.8

Table 2 The activation parameters of thermal dehydration and decomposition of Cu- and Co-itaconato complexes according to different integral methods and (F_1)

Method of analysis	Stage I (dehydration step)			
	Cu-		Co-	
	$E/\text{kJ}\cdot\text{mol}^{-1}$	$\log A/\text{min}^{-1}$	$E/\text{kJ}\cdot\text{mol}^{-1}$	$\log A/\text{min}^{-1}$
Composite I	76±4	10.4±1.2	128±4	16.8±1.2
Composite II	78±4	10.8±0.5	128±4	16.8±0.5
Coats-Redfern	69±6	9.5±0.8	129±12	17.0±1.6
Ozawa	178±37	26.3±6.7	115±13	14.2±2.4
Method of analysis	Stage II (decomposition to carbonate)			
	Cu-		Co-	
	$E/\text{kJ}\cdot\text{mol}^{-1}$	$\log A/\text{min}^{-1}$	$E/\text{kJ}\cdot\text{mol}^{-1}$	$\log A/\text{min}^{-1}$
Composite I	551±36	48.9±8.6	335±20	29.8±4.2
Composite II	532±34	48.8±3.7	328±19	29.4±1.9
Coats-Redfern	650±41	67.2±4.3	401±43	35.9±4.2
Ozawa	282±23	28.5±3.1	165±21	13.8±2.6
Method of analysis	Stage III (decomposition to oxide)			
	Cu-		Co-	
	$E/\text{kJ}\cdot\text{mol}^{-1}$	$\log A/\text{min}^{-1}$	$E/\text{kJ}\cdot\text{mol}^{-1}$	$\log A/\text{min}^{-1}$
Composite I	163±6	15.1±1.3	112±9	8.6±1.7
Composite II	164±6	15.2±0.6	117±8	9.1±0.7
Coats-Redfern	182±27	17.2±2.8	178±24	14.4±2.2
Ozawa	283±73	11.0±3.0	88±10	6.0±1.6

to be in good agreement with a previous study [11] for the dehydration steps of oxalato, malonato and succinato complexes. Nikolaev *et al.* [18] determined the activation energies of differently bound water molecules and concluded that the activation for losing crystal water lie in the range 60–80 $\text{kJ}\cdot\text{mol}^{-1}$, while for coordinately bounded water are within the range 130–160 $\text{kJ}\cdot\text{mol}^{-1}$. The activation energies of the dehydration step for the two complexes were attributed to losing crystal water and in good agreement with a previous results reported elsewhere [14].

For the two decomposition reactions the activation energy and frequency factor of Cu-itaconate are higher than that of Co-itaconate. The radius of Co^{2+}

(0.74 Å) is higher than that of Cu^{2+} (0.72 Å) and based on the Coulombic attractions, the Cu^{2+} will have a stronger bond to itaconate ion than that of Co^{2+} ion. Thus in turn should increase the energy needed to decompose the Cu-itaconate, and, hence the activation parameters for the decomposition reactions are increased.

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Zusammenfassung — Mittels DTG wurde die Kinetik der thermischen Zersetzung von Cu- und Co-Itakonato-Komplexen untersucht. Man fand, daß der Dehydratierungsprozeß eine Einschnitt-Reaktion ist, während die thermische Zersetzung der wasserfreien Salze in zwei Schritten verläuft. Der erste Teilschritt ist die Zersetzung des Komplexes in Metallcarbonat, der darauffolgende Schritt die Zersetzung des gebildeten Carbonates zu Oxid. Die kinetische Analyse der DTG-Kurven wurde bezüglich einer zusammengesetzten Integrationsmethode im Vergleich zu den Integrationsmethoden von Coats und Redfern und Ozawa ausgewertet. Für jeden Schritt der Zersetzung wurden die Aktivierungsparameter berechnet und diskutiert.