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KINETIC PARAMETERS OF THE THERMAL DECOMPOSITION OF Cu(II) AND Zn(II) SALTS OF CARBOXYLIC ACIDS*

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The kinetic parameters of thermal decomposition of Cu(II) and Zn(II) salts of carboxylic acids were investigated on the basis of the respective thermal curves. The values of the activation energy (E_a) of thermal decomposition, reaction order (n), frequency factor (A) and velocity constant (k) (in the Arrhenius kinetic equation), established from thermal data, were compared. Based on the initial decomposition temperature, the following sequences of stabilities of the studied compounds have been proposed:

1. $Cu(CH_3COO)_2$ (235°) > $Cu(C_6H_5O_7)_2$ (220°) > $Cu(HCOO)_2$ (150°) > > $Cu(OH)_2 \cdot Cu(CO_3)$ (50°)
2. $Zn(C_{18}H_{35}O_2)_2$ (305°) > $ZnCO_3$ (210°) > $Zn(CH_3COO)_2$ (170°)

A knowledge of the thermal decomposition stages and mechanisms involved in the heating of salts of metals with carboxylic acids is useful in many branches of the chemical industry and in food chemistry [1–5]. In the latter branch the transition metal ions are very important as microelements [3, 6, 7]. The carboxylic acids are among of the basic components of food [3, 6].

The salts which have been investigated, anhydrous and hydrated, are listed in Table 1. The methods used to obtain them, and their properties, were described earlier [7]. In this paper we present the mechanism of their decomposition and calculations of the kinetic parameters of this decomposition.

Experimental

The thermal curves were recorded on a MOM (Budapest) derivatograph, equipped with a four-channel recorder and TGT and DTGT adapters for titration of gases. Samples of the Cu(II) or Zn(II) salts were heated in corundum crucibles, using α-Al_2O_3 (corundum) as reference. In the gaseous products of decomposition of the

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sample, the acid components were determined by means of adsorption in the TGT and DTGT adapter, and then by titration with 0.1 *M* KOH at pH 9.2. In the solid products obtained in crucibles, the total metal contents were determined by complexometric methods [8]. The diffractograms of these solid products were made on a DRON (USSR) apparatus using $Cu_K\alpha_1$ radiation.

Results and discussion

Figure 1 shows the thermal curves of the Cu(II) and Zn(II) salts in a dynamic argon atmosphere, and Fig. 2 those of the Cu(II) salts in static air atmosphere. We have found that the thermal decompositions of the studied compounds display one or two stages. These stages are accompanied by endothermic effects. The weight losses and consumptions of the 0.1 *M* KOH for the titration of acid gases from the decomposition in dynamic argon are given in Table 1. The hydrated salts decompose in two stages. The first stage of weight loss is connected with dehydration and the second with pyrolysis. We have found that the hydrated Cu(II) salts lose their crystallization water at the following temperatures:

$$Cu(CH_3COO)_2 \cdot H_2O\ (90°) > Cu(C_6H_5O_7)_2 \cdot 2.5\ H_2O\ (80°) >$$
$$> Cu(HCOO)_2 \cdot 2\ H_2O\ (50°)$$

The weight losses and diffractograms show that the final products in the decomposition of the Cu(II) salts are free copper, CuO or Cu_2O, or a mixture of these components. In the case of Cu(II) citrate, $Cu(C_6H_5O_7)_2$, free carbon has also been in the solid-state products. Table 2 presents examples of d/n and I/I_0 values from powder diffractograms of solid-state products obtained from $Cu(HCOO)_2 \cdot 2\ H_2O$ and $Cu(CH_3COO)_2 \cdot H_2O$.

The thermal decomposition of the Zn(II) compounds is simpler than that of the Cu(II) salts. This is connected with the difference in redoxy properties. As the final decomposition product of the Zn(II) salts, ZnO has been found. The weight losses suggest that during the thermal decomposition acid anhydrides are formed. This has been confirmed by the consumption of 0.1 *M* KOH for the titration of the gas products.

The thermal decomposition of $Zn(CH_3COO)_2 \cdot 2\ H_2O$ may be described by Eqs (1) and (2):

$$Zn(CH_3COO)_2 \cdot 2\ H_2O \longrightarrow Zn(CH_3COO)_2 + 2\ H_2O \quad (1)$$

$$Zn(CH_3COO)_2 \longrightarrow ZnO + (CH_3CO)_2O \quad (2)$$

With the initial decomposition temperature as criterion of thermal stability, the following series of thermal stabilities of the studied compounds may be proposed:

$$Cu(CH_3COO)_2\ (235°) > Cu(C_6H_5O_7)_2\ (220°) > Cu(HCOO)_2\ (150°) >$$
$$> Cu_2(OH)_2CO_3\ (50°)$$

and

$$Zn(C_{18}H_{35}O_2)_2\ (305°) > ZnCO_3\ (210°) > Zn(CH_3COO)_2\ (170°)$$

Table 3 gives values of the activation energy E_a, the reaction order n, frequency factor A and velocity constant k for the thermal decomposition of the compounds under test. The calculation technique and equations used were given earlier [2, 7].

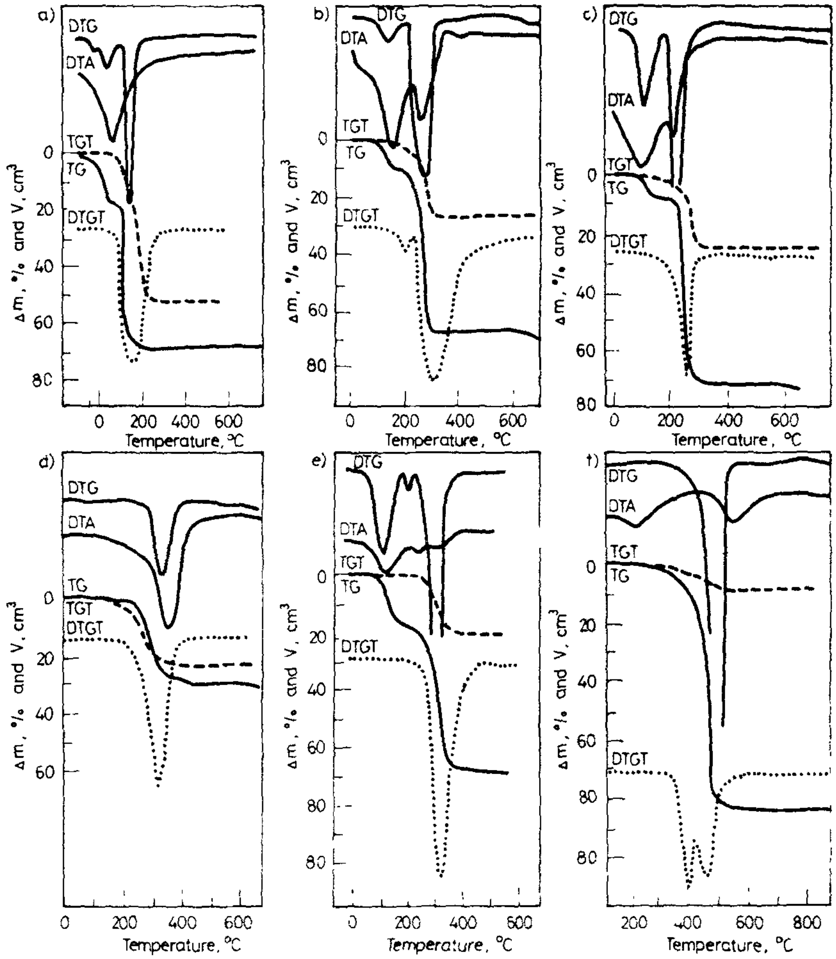

Fig. 1 Thermal curves obtained in the dynamic argon atmosphere ($V = 20\ dm^3/h$). Heating rate 5 deg min^{-1}. a) $Cu(HCOO)_2 \cdot 2H_2O$; b) $Cu(CH_3COO)_2 \cdot H_2O$; c) $Cu_3(C_6H_5O_7)_2 \cdot 2.5H_2O$; d) $Cu(OH)_2 \cdot CuCO_3$; e) $Zn(CH_3COO)_2 \cdot 2H_2O$; f) $Zn(C_{18}H_{35}O_2)_2$. Sensitivity: DTA 1/5; DTG 1/10; DTGT 1/10

Table 1 Data based on thermograms and additional investigations the dynamic argon atmospheres

Studied compound	Mass of the sample, mg	Temperature ranges, °C	Weight loss, %	Consumption of 0.1 M KOH, cm^3	Metal contents in the sintered products, %	Decomposition reactions
$Zn(CH_3COO)_2 \cdot 2\,H_2O$	200	50–150	17	0	80.4	$Zn(CH_3COO)_2 \cdot 2\,H_2O \rightarrow Zn(CH_3COO)_2 + H_2O$
		170–360	47	17.8		$Zn(CH_3COO)_2 \rightarrow ZnO + (CH_3CO)_2O$
$Zn(C_{18}H_{35}O_2)_2$	200	305–510	86	6.3	79.6	$Zn(C_{18}H_{35}O_2)_2 \rightarrow ZnO + (C_{18}H_{35}O)_2O$
$ZnCO_3$	200	210–400	33	16.4	79.4	$ZnCO_3 \rightarrow ZnO + CO_2$
$Cu(CH_3COO)_2 \cdot H_2O$	500	90–180	11	0		$Cu(CH_3COO)_2 \cdot H_2O \rightarrow Cu(CH_3COO)_2 + H_2O$
		235–325	58	24.0	82.4	$Cu(CH_3COO)_2 \rightarrow CuO + CH_3CHO + H_2O + CO + C$ $CuO + CH_3CHO \rightarrow Cu_2O + CO_2$ $CuO + CO \rightarrow Cu + CO_2$ $C + 2\,CuO \rightarrow Cu + CO_2$
$C(C_6H_5O_7)_2 \cdot 2.5\,H_2O$	500	80–220	8	0	83.2	$Cu(C_6H_5O_7)_2 \cdot 2.5\,H_2O \rightarrow Cu(C_6H_5O_7)_2 + 2.5\,H_2O$
		220–340	63	21.5		$Cu(C_6H_5O_7)_2 \rightarrow Cu + CuO + Cu_2O$ + gas products
$Cu(HCOO)_2 \cdot 2\,H_2O$	500	50–150	17	0	84.3	$Cu(HCOO)_2 \cdot 2\,H_2O \rightarrow Cu(HCOO)_2 + 2\,H_2O$
		150–240	48	54.0		$Cu(HCOO)_2 \rightarrow Cu + H_2 + 2\,CO_2$

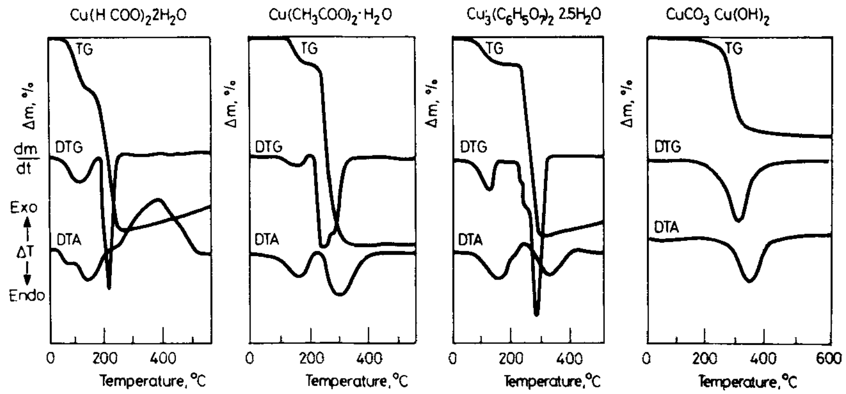

Fig. 2 Thermal curves obtained in the static air atmosphere. Heating rate 10 deg/min, $m_0 = 500$ mg

The thermogravimetric data on $Cu(CH_3COO)_2 \cdot H_2O$ were used to calculate the relationship between $\log dm/dt$ and $1/T$ (Fig. 3) or $1/T\ \mathrm{tg} + \log dm/dt$ and $\log c$ (Fig. 4), where

$$c = \frac{\Delta m_\infty - \Delta m}{\Delta m_\infty}$$

The value of the error in the determination of E_a in this way is ±3.5% while for A it is ±5.2%.

The value of the velocity constant k was calculated at 290 K.

Table 2 Comparison of identify numbers of powder diffractograms of sintered products

Sintered products				Literature data [9, 10]							
$Cu(HCOO)_2 \cdot 2H_2O$		$Cu(CH_3COO)_2 \cdot H_2O$		Cu		Cu_2O		CuO		CuO (teneryt)	
d/n	I/I_0	*d/n*	I/I_0	*d/n*	I/I_0	*d/n*	I/I_0	*d/n*	I/I_0	*d/n*	I/I_0
										2.72	20
		2.60	32					2.51	100	2.52	100
		2.43	6			2.46	100				
		2.23	12								
2.16	100	2.16		2.08	100	2.13	80				
1.88	45	1.85	48	1.81	53			1.85	20		
						1.74	20	1.70	8	1.70	20
										1.58	30
		1.51	9			1.51	80	1.50	15		
								1.41	20		
						1.34	40				
		1.20	6							1.30	20
1.28	18	1.28	24	1.28	33	1.28	80				
								1.26	10	1.26	40

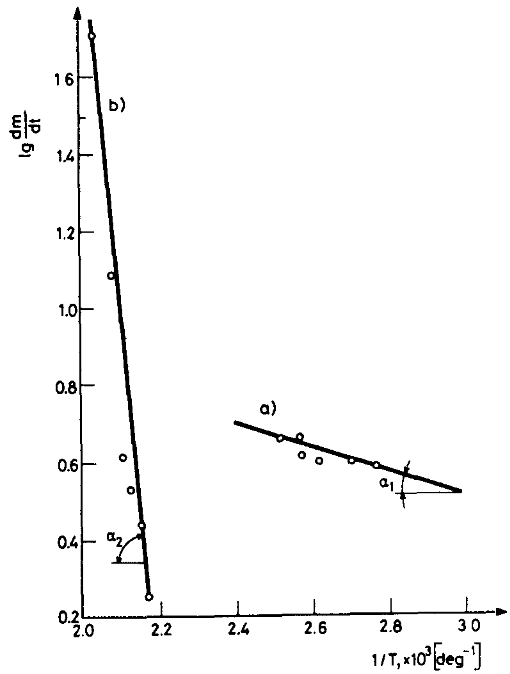

Fig. 3 Graphic determination of activation energy E_a of reaction ($E_a = 2.303 \cdot R \cdot \mathrm{tg}\,\alpha$ for the $Cu(CH_3COO)_2 \cdot H_2O$): a) the dehydration of reaction $Cu(CH_3COO)_2 \cdot H_2O \rightarrow Cu(CH_3COO)_2 + H_2O$; tg $\alpha = 3 \cdot 10^3$, $E_a = 57.4$ kJ/mol; b) the thermal decomposition of reaction: $Cu(CH_3COO)_2 \rightarrow Cu$ + gas products; tg $\alpha = 1 \cdot 10^4$, $E_a = 191.5$ kJ/mol

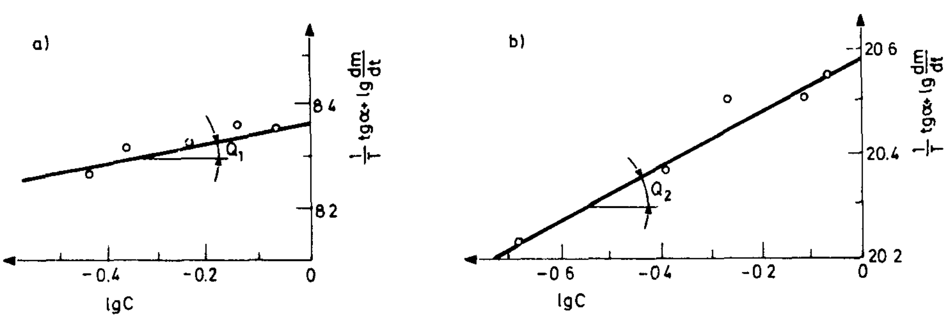

Fig. 4 Graphic determination of the velocity constant k of reaction ($\lg k = \lg A - E_a/2.303\ RT$) for the $Cu(CH_3COO)_2 \cdot H_2O$: a) the dehydration of reaction: $n = \mathrm{tg}\,\theta = 0.2$, $A = 2.3 \cdot 10^8$, $k = 7.1 \cdot 10^{-3}$; b) the thermal decomposition of reaction: $n = 0.5$, $A = 3.8 \cdot 10^{20}$, $k = 9.5 \cdot 10^{-13}$

Table 3 Kinetic parameters of the thermal decompositions of Cu(II) and Zn(II) salts with carboxylic acids

No.	Compound formula	Temperature range, K	Activation energy E_a, kJ/mol	Order of reaction n	Value of A	Valocity constant k in temp. 290 K, s^{-1}
			Dehydration reactions			
1.	$Zn(CH_3COO)_2 \cdot 2\,H_2O$	323–423	45.0	0.2	$1.2 \cdot 10^8$	$8.6 \cdot 10^{-1}$
2.	$Cu(HCOO)_2 \cdot 2\,H_2O$	323–423	74.7	0.5	$8{,}7 \cdot 10^{11}$	$4.3 \cdot 10^{-2}$
3.	$Cu(CH_3COO)_2 \cdot H_2O$	263–453	57.4	0.2	$2.3 \cdot 10^8$	$7.1 \cdot 10^{-3}$
4.	$Cu(C_6H_5O_7)_2 \cdot 2.5\,H_2O$	353–493	63.2	0.3	$3.9 \cdot 10^9$	$2.1 \cdot 10^{-2}$
			Thermal decomposition reactions			
5.	$Zn(CH_3COO)_2$	443–633	109.0	0.2	$2.8 \cdot 10^{12}$	$1.7 \cdot 10^{-7}$
6.	$Zn(C_{18}H_{35}O_2)_2$	578–783	97.7	0.2	$1.7 \cdot 10^9$	$7.9 \cdot 10^{-9}$
7.	$ZnCO_3$	483–673	172.3	0.1	$2.3 \cdot 10^{18}$	$2.4 \cdot 10^{-13}$
8.	$Cu(HCOO)_2$	423–613	159.4	1.1	$3.7 \cdot 10^{19}$	$4.0 \cdot 10^{-10}$
9.	$Cu(CH_3COO)_2$	508–598	191.5	0.5	$3.8 \cdot 10^{20}$	$9.5 \cdot 10^{-13}$
10.	$Cu(C_6H_5O_7)_2$	493–613	226.0	1.0	$1.0 \cdot 10^{24}$	$9.4 \cdot 10^{-18}$
11.	$Cu_2CO_3(OH)_2$	323–603	181.9	0.9	$5.7 \cdot 10^{18}$	$3.2 \cdot 10^{-14}$

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Zusammenfassung — Die kinetischen Parameter der thermischen Zersetzung von Verbindungen der Formeln $M(HCOO)_2 \cdot n\,H_2O$, $M(CH_3COO)_2 \cdot n\,H_2O$, $M(C_6H_5O_7) \cdot n\,H_2O$, $M(C_{18}H_{35}O_2)_2$ und $M(OH)_2 \cdot MCO_3$ ($M = Cu^{2+}$ oder Zn^{2+}; $n = 1, 2, \ldots$) wurden mittels TG und DTG untersucht. Die Reaktionsordnung (n) und die Aktivierungsenergie (E_a) wurden nach der graphischen Methode ermittelt.

Резюме — Исследованы кинетические параметры термического разложения карбоксилатов двухвалентных меди и цинка, исходя из их соответствующих термических кривых. Установлены и сопоставлены значения энергии активации (E_a) термического разложения, порядок реакции, частотный множитель (A) и константа скорости (k) в уравнения Аррениуса. На основе начальных температур разложения выведен следующий порядок устойчивости изученных соединений:

1. $Cu(CH_3COO)_2$ (235°) > $Cu(C_6H_5O_7)_2$ (220°) > $Cu(HCOO)_2$ (150°) > > $Cu(OH)_2 \cdot CuCO_3$ (50°).
2. $Zn(C_{18}H_{35}O_2)_2$ (305°) > $ZnCO_3$ (210°) > $Zn(CH_3COO)_2$ (170°).