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COMPARATIVE STUDY OF THE THERMAL ANALYSES OF SOME TRANSITION METAL(II) MALEATES AND FUMARATES

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The thermal decompositions of maleates and fumarates of Cu(II) and Zn(II) have been studied by employing simultaneous non-isothermal techniques (DTG, DTA and TG). The end-products are the corresponding metal oxides, as characterized by chemical analysis and X-ray diffraction. Comparison of the Tm values led to the stability sequences Cu(F) > Cu(M); Zn(F) > Zn(M) and Cu(M) ≈ Cu(F); Zn(F) > Zn(M) for dehydration and decomposition, respectively.

The importance of comparative studies of thermal decompositions has been amply brought out in references [1–3]. The effects on the thermal stability of systematically varying the cation while the carboxylate anion is kept the same have been determined by means of isothermal and non-isothermal techniques [2]. Bassi et al. [3] recently studied the thermal stabilities of M(II) propionates (M = Co. Ni, Cu and Zn). The stability sequence established by thermogravimetry is different from that expected on the basis of the stability constants [3]. Subsequently, the thermal decompositions of copper and zinc carboxylates in which the anion permits two different positional isomeric structures, i.e. the iso- and terephthalates of copper and zinc, were described [4]. A comparison of non-isothermal analyses for the same cation with the anion in two different conformations has not been published, although the isothermal decompositions of Ni(II) and Cu(II) maleates and fumarates have been reported [5–7]. The relatively high activation energy (208 ± 8 kJ/mole) for the decomposition of nickel fumarate compared to that for nickel maleate (188 ± 12 kJ/mole) has been attributed to steric factors, which preclude the approach of two carboxyl groups to a single nickel atom [5, 6]. Only preliminary isothermal decomposition measurements [7] have been made on Cu(II) maleate and Cu(II) fumarate. These show the occurrence of an initial acceleratory process, followed by a diminition in the rate, ascribed to the deposition of C on the active surface of decomposition. A comparison of non-isothermal studies of zinc

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and copper salts, however, has not been reported. Accordingly, in this paper simultaneous DTG, DTA and TG results are presented on the maleates and fumarates of Cu(II) and Zn(II).

Experimental

Copper(II) maleate monohydrate was prepared by adding basic copper carbonate in small amounts during constant stirring to a saturated solution of maleic acid. After removal of the excess solid by filtration, the pH of the resulting solution was adjusted so that it was less than 3.0. The solid copper maleate crystallized out after concentration of the solution. It was filtered off, washed several times with water, recrystallized and finally air-dried. The fumarate of copper(II) was prepared similarly, a saturated solution of fumaric acid being used.

Zinc(II) maleate dihydrate was prepared by the addition of zinc oxide in small instalments during constant stirring to a hot aqueous solution of maleic acid. Zinc oxide, which easily settled out in the form of excess powder, was removed by filtration and the resulting clear solution was concentrated on a water bath. The solid zinc maleate that crystallized out was washed several times with water, recrystallized and air-dried. Zinc(II) fumarate monohydrate was prepared in an analogous way.

The identities of these compounds were established by chemical analysis and infrared spectroscopy. The percentages of copper and zinc were determined gravimetrically [8]. The percentages of carbon and hydrogen were determined by microanalysis. Analytical data showing the percentages of metals, carbon and hydrogen are listed in Table 1.

Table 1 Analytical data on metal(II) carboxylates

Compound		Metal, %	C, %	H, %
^{a}Cu(CHCOO)$_2\cdot$H$_2$O	Found.	32.2	24.8	2.5
	Calcd.	32.5	24.5	2.0
^{b}Cu(CHCOO)$_2\cdot$2H$_2$O	Found.	29.5	22.5	2.5
	Calcd.	29.7	22.5	2.8
^{a}Zn(CHCOO)$_2\cdot$2H$_2$O	Found	30.3	22.3	2.6
	Calcd.	30.4	22.3	2.8
^{b}Zn(CHCOO)$_2\cdot$H$_2$O	Found.	33.0	24.2	2.0
	Calcd.	33.2	24.3	2.0

^{a} = maleate, ^{b} = fumarate

These carboxylates were studied with a Paulik–Paulik–Erdey MOM derivatograph (Hungary), using 200 mg of the sample at 2 mg sensitivity for the Cu(II) carboxylates, and 85 and 80 mg of the sample at 1 mg sensitivity for zinc(II) maleate and fumarate, respectively. The heating rate was kept at 5 deg/min in a static air atmosphere. The X-ray powder diffraction patterns of the end-products were recorded using CuK$_\alpha$ radiation. The TG, DTG and DTA patterns found are shown in Figs 1 to 4.

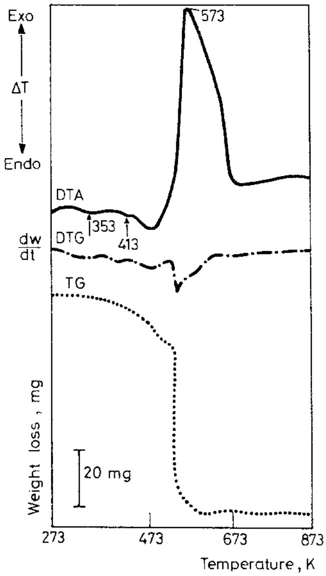

Fig. 1 Simultaneous DTG–DTA–TG curves of copper(II) maleate hydrate at the heating rate of 5 deg/minute

Results and discussion

Non-isothermal derivatographic study

Copper(II) maleate monohydrate

Figure 1 presents the simultaneous DTG, DTA and TG curves of copper(II) maleate monohydrate. The DTA curve exhibits two small endotherms, with maxima at 353 and 413 K, respectively, and one broad endotherm between 433 and 523 K, followed immediately by a large exothermic region (533 to 663 K). Comparison of the DTA and DTG curves shows that all the stages of thermal decomposition are accompanied by weight change. The TG curve corresponding to the first DTA peak, at 353 K, indicates only a small fraction of the total loss, which does not account for any prominent change and is due to the loss of adsorbed gases.

The second DTA peak, at 413 K, corresponds to a loss of 8 mg due to the removal of 0.5 water molecule (calc. loss = 9.2 mg). The loss corresponding to the third endothermic DTA peak is in accordance with the formation of anhydrous copper(II) maleate. A slightly higher loss than that required indicates that decomposition of the anhydrous compound starts immediately, as is clear from the nature of the DTA and DTG curves. The anhydrous sample then undergoes decomposition without the formation of any intermediate. The broad exotherm is attributed to the oxidation of hydrocarbons, H_2, etc. released on decomposition. The TG curve reveals a weight loss of 121 mg at 623 K, indicating the formation of CuO (calc. loss = 119 mg). Finally, the TG curve points to a slight increase in weight, a mixture of Cu, CuO and Cu_2O being formed, as indicated by the X-ray powder diffraction pattern of the end-product (Table 2) [9–11].

Table 2 X-ray powder diffraction data for the final thermolysis product of copper(II) maleate monohydrate

Experimental		ASTM data file		Product
d, Å	Intensities	d, Å	Intensities	Assignment
3.078	95	3.020	100	Cu_2O
2.557	100	2.530	49	CuO
2.483	80	2.465	100	Cu_2O
2.307	30	2.312	30	CuO
2.156	20	2.135	37	Cu_2O
2.104	40	2.090	100	Cu
1.994	20	1.959	3	CuO
1.856	20	1.866	25	CuO
1.819	20	1.810	50	Cu

Copper(II) fumarate dihydrate

Figure 2 depicts the simultaneous DTG, DTA and TG curves of copper(II) fumarate dihydrate. The DTA curve shows an endothermic peak at 463 K and an endothermic dent at 488 K, followed immediately by a broad exothermic region with peaks at 573 and 613 K. There are corresponding peaks in the DTG curve, indicating that the thermal effects are accompanied by weight loss. The TG curve corresponding to the first DTA step reveals a loss in weight equivalent to the loss of one water molecule. The TG curve corresponding to the endothermic dent in the DTA and the second peak in the DTG indicates a weight loss amounting to 32.5 mg, which means the complete removal of both water molecules. The anhydrous compound then undergoes decomposition without suggesting the

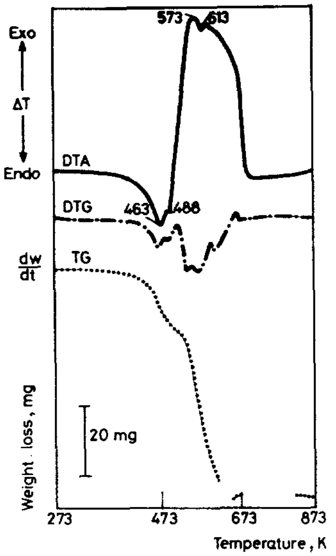

Fig. 2 Simultaneous DTG–DTA–TG curves of copper(II) fumarate dihydrate at the heating rate of 5 deg/minute

formation of a stable intermediate. This is shown by a broad exotherm, again due to the oxidation of Cu, hydrocarbons and H_2 obtained during decomposition of the fumarate. At 663 K, a weight loss of 122 mg is observed, indicating the formation of CuO (calc. loss = 122 mg). Finally, the TG curve points to a slight increase in weight, suggesting the formation of a mixture of CuO and Cu_2O, as verified by the X-ray powder diffraction pattern of the residue at 683 K.

Zinc(II) maleate dihydrate

Figure 3 shows the simultaneous DTG, DTA and TG curves of zinc(II) maleate dihydrate. In DTG the reaction proceeds with a triplet peak, with maxima at 423, 433 and 463 K, respectively. Another double DTG peak starts at 653 K, with maxima et 703 and 738 K, respectively. Before the completion of the decomposition reaction at nearly 883 K, there is a flat region from 773 to 873 K in the DTG. This flat region indicates that the rate of decomposition does not increase with temperature and there is therefore no maximum in this region. The DTA curve shows an initial endothermic transition at 428 K, followed by a major endothermic peak at 453 K. The next process is exothermic over the range of temperature 688–913 K, with a sharp exothermic curvature, an exothermic peak and finally exothermic transitions at 703, 758 and 868 K, respectively. The TG curve reveals a weight loss of 6.0 mg corresponding to the initial endothermic transition, indicating the formation of zinc(II) maleate monohydrate (calc. loss = 7.1 mg). The major

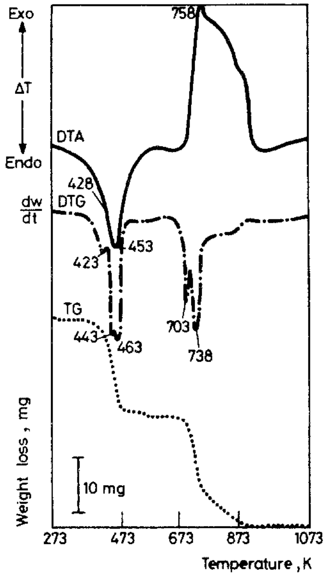

Fig. 3 Simultaneous DTG–DTA–TG curves of zinc(II) maleate dihydrate at the heating rate of 10 deg/minute^{-1}

endothermic peak and the corresponding DTG peak are associated with a weight loss of 25.0 mg in the TG curve for the complete dehydration. Along with dehydration, decomposition of the anhydrous salt also occurs in this stage, as seen from the higher mass loss than anticipated for the complete removal of water. The subsequent step of decomposition is accompanied by a broad exotherm and is due to the burning of ligand and evolved gases such as CO, H_2, etc. in air. The TG curve shows a weight loss of 46.0 mg between 713 and 768 K. The final residue has been found to be ZnO (calc. loss = 45.6 mg), as confirmed by chemical analysis and the X-ray powder diffraction pattern (Table 3) [12].

Table 3 X-ray powder diffraction data for the final thermolysis product of zinc(II) maleate dihydrate

Experimental		ASTM data file for Zno	
d, Å	Intensities	d, Å	Intensities
2.829	66	2.816	71
2.612	54	2.602	56
2.475	100	2.476	100

Zinc(II) fumarate monohydrate

Figure 4 presents the simultaneous DTG, DTA and TG curves of zinc(II) fumarate monohydrate. The DTG curve exhibits two sharp peaks, at 573 and 783 K. In the DTA curve, initially there is a shallow endothermic region, followed by a small endothermic peak at 583 K. This peak is then followed by an exothermic peak commencing from 683 K, giving a maximum at 793 K and an exothermic effect at 873 K. The first stage in the TG curve indicates a loss of 7.5 mg, corresponding to the formation of anhydrous zinc(II) fumarate (calc. loss = 7.3 mg). The exothermic peak at 793 K in the DTA, associated with a weight loss of 38 mg, accounts for the elimination of the carbonaceous material from the compound and its burning in air. The ultimate formation of ZnO has been varified by chemical analysis and the X-ray diffraction pattern.

Comparative study of the thermal analyses

In general, the T_i (temperature of initial weight loss) values provide more accurate information than T_m (maximum temperature of DTG) regarding the thermal stabilities of metal carboxylates. However, when the T_i values are somewhat difficult to measure with sufficient accuracy, the T_m values should be preferred, provided the latter are sharp. Comparison of the T_m values for dehydration leads to the stability sequences: Cu (F) > Cu (M) and Zn (F) > Zn (M).

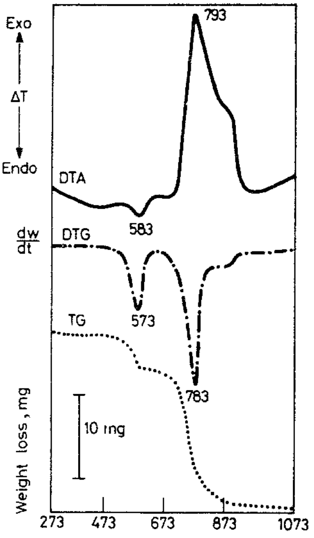

Fig. 4 Simultaneous DTG–DTA–TG curves of zinc(II) fumarate monohydrate at the heating rate of 10 deg/minute⁻

This result indicates that the fumarate derivatives are more stable than the corresponding maleate salts. This is due to the structures of these carboxylates. The fumarate is a trans isomer and can crystallize either as a three-dimensional or as a linear polymer, whereas a dimeric structure is expected for the cis isomer (maleate).

A common feature of the decompositions of copper(II) maleate and copper(II) fumarate is the occurrence of an exothermic region at 533–663 K for the maleate and at 528–683 K for the fumarate. The shapes of the DTA curves of the maleate and fumarate of copper(II) are similar, and even the decomposition temperatures such as T_i and T_m do not differ much. This shows that in these thermal decompositions the rate-controlling step is the same. However, for zinc(II) maleate and zinc(II) fumarate the exothermic region is located at 713–883 K for the maleate and at 773–893 K for the fumarate, which indicates that the maleate and fumarate of zinc(II) are thermally much stabler than the corresponding copper(II) salts. This is in accordance with the strengths of the M—O bonds, the Zn—O bond being stronger than the Cu—O bond, as seen from the square of the differences in the electronegativities [13].

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Zusammenfassung — Die thermische Zersetzung von Maleaten und Fumaraten von Cu(II) und Zn(II) wurde mittels simultan angewandter nicht-isothermer Techniken (DTG, DTA und TG) untersucht. Die Endprodukte sind die entsprechenden Metalloxide, wie durch chemische Analyse und Röntgendiffraktometrie nachgewiesen wurde. Ein Vergleich der T_m-Werte ergab für die Stabilität in der Dehydratisierungs- bzw. Zersetzungsreaktion die Reihenfolgen Cu (F) > Cu (M); Zn (F) > Zn (M) bzw. Cu (M) $\approx$ Cu (F); Zn (F) > Zn (M).

Резюме — Совмещенным неизотермическим методом ДТГ, ДТА и ТГ изучено термическое разложение малеатов и фумаратов меди и цинка. Конечными продуктами реакции разложения являлись окиси соответствующих металлов, идентифицированных химическим анализом и рентгенофазовым анализом. Согласно значениям T_m, устойчивость комплексов располагается в ряд Cu (F) > Cu (M); Zn (F) > Zn (M) и Cu (M) $\approx$ Cu (F); Zn (F) > Zn (M), соответственно, для реакций дегидратации и разложения.