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A COMPARATIVE STUDY ON THE THERMAL DECOMPOSITION OF SOME TRANSITION METAL MALEATES AND FUMARATES

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Thermal decomposition of M(mal/fum)·xH$_2$O (M=Mn, Co, Ni) has been studied in static air atmosphere from ambient to 500°C employing TG-DTG-DTA, XRD and IR spectroscopic techniques. After dehydration the anhydrous maleate salts decompose to metal oxalate in the temperature range of 320–360°C, which at higher temperature undergo an abrupt oxidative pyrolysis to oxides. The anhydrous fumarate salts have been found to decompose directly to oxide phase. A comparison of thermal analysis reveals that fumarates are thermally more stable than maleates.

Keywords: *metal fumarates, metal maleates, TG-DTG-DTA, thermal decomposition, XRD*

Introduction

Thermal decomposition of transition metal carboxylates has become a fascinating subject of recent interest due to the technological importance of these studies. The final thermolysis products (metal oxides) find extensive applications as catalysts, ceramic colorants, photoconductors, etc. [1–5]. Although the thermolysis of transition metal oxalates [6–8] has been extensively studied, a similar interest on transition metal maleates and fumarates that are geometrical isomers is lacking. The thermal analysis of copper and zinc maleates/fumarates has already been reported [9]. In continuation of that work the present investigation on thermolysis of other transition metal (M=Mn, Co, Ni) maleates and fumarates has been undertaken, with a view to study the effect of geometry (*cis*, *trans*) on their thermal stabilities and mode of decomposition.

Experimental

Transition metal maleates and fumerates were prepared by mixing vigorously the equimolar solutions of respective transition metal carbonate and carboxylic acid (maleic, fumaric). The resultant solution was concentrated on a water bath after filtering off the excess unreacted carboxylic acid. The precipitates of transition metal maleate and fumarate were obtained by the addition of acetone (in excess). The precipitates were filtered, dried and stored in a vacuum desiccator. The identity of these compounds was established by elemental analysis (Table 1). The manganese content was determined titrimetrically using Eriochrome Black-T as indicator whereas cobalt and nickel contents were determined electrogravimetrically [10].

Simultaneous TG-DTG-DTA curves were recorded on a Stanton Red Craft Model (STA-780) in static air atmosphere at a heating rate of 10°C min^{-1}. For isothermal decomposition, transition metal maleates and fumarates were calcined isothermally at 450°C in static air atmosphere for a duration of 2 h to obtain the final thermolysis residue for its characterization. IR spectra of parent carboxylates and their thermolysis products were recorded in the range 4000–200 cm^{-1} on PYE-UNICAM SP3-300 IR spectrophotometer using KBr matrix. The room temperature XRD powder patterns (using CuK$_\alpha$ radiation) were recorded at USIC, IIT Roorkee.

Table 1 Microanalytical data of transition metal maleates and fumarates

Salt		C/%	H/%	M/%
Mn(mal)·3H$_2$O	obs.	20.90	3.42	24.63
	cal.	21.52	3.58	24.66
Mn(fum)	obs.	28.22	1.09	32.48
	cal.	28.40	1.18	32.54
Co(mal)·7H$_2$O	obs.	15.80	5.26	19.56
	cal.	16.05	5.35	19.73
Co(fum)·4H$_2$O	obs.	18.90	4.81	23.88
	cal.	19.59	4.08	24.08
Ni(mal)·4H$_2$O	obs.	19.09	4.01	23.95
	cal.	19.59	4.08	24.08
Ni(fum)·4H$_2$O	obs.	19.21	4.02	23.75
	cal.	19.59	4.08	24.08

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Results and discussion

IR spectrum of manganese maleate trihydrate exhibits a broad band centered at about 3400 cm^{-1} marking the presence of ν_{O-H} of lattice water. A small shoulder lies at 2960 cm^{-1} due to ν_{C-H} of the ligand. An overlapping of bands due to $\nu_{C=C}$ and $\nu_{asym(C=O)}$ exist in the range 1570–1600 cm^{-1}, whereas a strong band at 1390 cm^{-1} is assigned to $\nu_{sym(C=O)}$ of the coordinated carboxylate group. Bands in the range 1210–985 cm^{-1} are attributed to the (O–H) bending modes. A sharp and distinct band at 815 cm^{-1} is due to *cis*(C–H) wagging and bands at 585 and 330 cm^{-1} indicate the presence of Mn–O bonding [11, 12]. The infrared spectra of manganese fumarate and other transition metal carboxylates are almost similar to that of manganese maleate. The compound-wise discussion on thermal decomposition studies follows.

Manganese maleate trihydrate, $Mn(C_2H_2C_2O_4)\cdot 3H_2O$

Figure 1 shows the simultaneous thermal curves (TG-DTG-DTA) of manganese maleate trihydrate at a heating rate of 10°C min^{-1}. The compound undergoes decomposition in three steps. The first step is the dehydration which commences at 95°C and is completed at 187°C as indicated by a mass loss of 24% (calc. loss=24.2%), DTA and DTG show corresponding peaks at 157°C (endothermic) and 155°C, respectively. In the second step, the anhydrous compound undergoes a gradual decomposition process until a mass loss of 32% is reached at 320°C suggesting the formation of manganese oxalate from manganese maleate after the removal of an acetylene molecule. The respective DTG peak lies at 290°C which is endo in DTA. The liberation of acetylene has been reported during ‘Kolbe electrolysis’ of metal maleate in solution phase [13, 14]. The presence of manganese oxalate, MnC_2O_4 as an intermediate has been confirmed from XRD powder data of the residue (Table 2) obtained by isothermal calcination of parent compound at 320°C for 15 min. Manganese oxalate undergoes an abrupt oxidative decomposition accompanied by a steep mass loss i.e. 68% at 410°C revealing the formation of manganese oxide, MnO (calc. loss=68.2%). The respective DTA (strong exotherm) and DTG peaks lie at 360 and 355°C, respectively. The identity of the final thermolysis product has been confirmed from XRD data which agree to that reported for MnO [15]. IR spectrum of the residue, obtained by calcining the parent complex at 450°C for 2 h shows characteristic bands at 589 and 290 cm^{-1} due to ν_{Mn-O} bonding [16]. Manganese oxalate is reported to decompose directly to MnO [6].

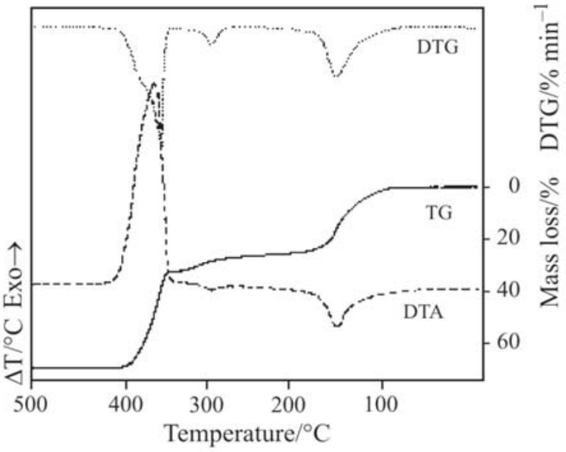


Fig. 1 DTA, TG and DTG curves of manganese maleate trihydrate

Manganese fumarate, $Mn(C_2H_2C_2O_4)$

Figure 2 shows the simultaneous (TG, DTG, DTA) curves of manganese fumarate at a heating rate of 10°C min^{-1}. The compound is anhydrous and undergoes a single step decomposition. The anhydrous compound remains stable up to 380°C and then undergoes an oxidative decomposition. A large exother-

Table 2 XRD powder data of the intermediate obtained at 320°C by isothermal calcination of $Mn(mal)\cdot 3H_2O$

Experimental			ASTM* data		
d/Å	I_{rel}	*h k l*	*d*/Å	I_{rel}	Assignment
5.826	100	0 1 0	5.830	100	MnC_2O_4
5.575	58	0 1 1	5.570	60	MnC_2O_4
4.886	23	0 1 1	4.890	25	MnC_2O_4
3.539	47	2 0 0	3.550	50	MnC_2O_4
2.921	14	0 2 0	2.928	17	MnC_2O_4
2.753	28	1 0 3	2.761	30	MnC_2O_4
2.286	17	3 0 1	2.297	20	MnC_2O_4
2.011	10	1 2 3	2.015	12	MnC_2O_4

*ASTM Card No. 32-646

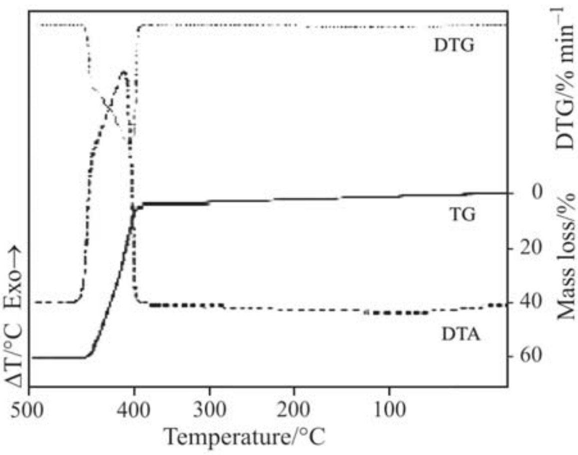


Fig. 2 DTA, TG and DTG curves of manganese fumarate

mic peak at 400°C is associated with the decomposition process. The corresponding DTG peak lies at 395°C. A mass loss of 58% (calc. loss=58%) at 440°C suggests the presence of manganese oxide (MnO). The formation of manganese oxalate intermediate, as observed in manganese maleate, has not been detected in fumarate salt. This is due to the fact that the carboxylate groups of fumarate present at *trans* position, do not facilitate the formation of oxalate. Formation of manganese oxide, MnO as the end product has been confirmed by IR spectrum and XRD powder diffraction pattern of the final thermolysis residue.

Cobalt maleate heptahydrate, $Co(C_2H_2C_2O_4)\cdot 7H_2O$

The mode of decomposition of this compound is similar to that of manganese maleate trihydrate. The compound undergoes decomposition in two steps (Fig. 3). The first step is dehydration which commences at 107 and is completed at 225°C as indicated by a mass loss of 42% (calc. loss=42%). DTA and DTG show corresponding peaks at 147 (endothermic) and 145°C, respectively. In the second step the anhydrous salt undergoes a rapid oxidative decomposition as shown by a steep mass loss i.e. 74% at 400°C revealing the formation of cobalt oxide, CoO. The accompanying DTG and DTA (exothermic) peaks lie at 375 and 365°C, respectively. The presence of CoO has been confirmed by XRD powder pattern of the final thermolysis product [17]. IR spectrum also shows characteristic bands at 570 and 280 cm^{-1} due to ν_{Co-O} bonding.

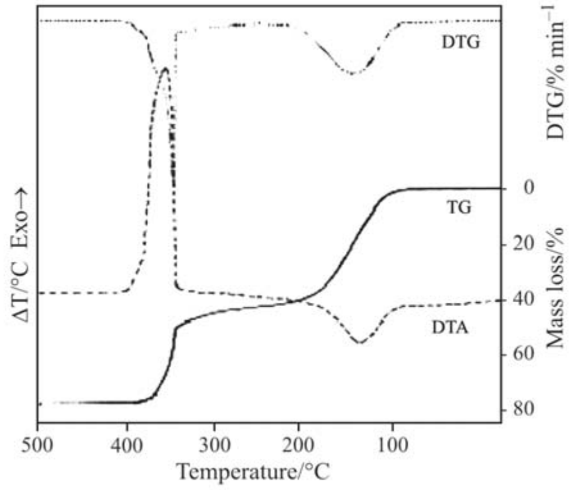


Fig. 3 DTA, TG and DTG curves of cobalt maleate heptahydrate

Cobalt fumarate tetrahydrate: $Co(C_2H_2C_2O_4)\cdot 4H_2O$

Figure 4 shows the STA curves (TG-DTG-DTA) of cobalt fumarate tetrahydrate at a heating rate of 10°C min^{-1}. The compound undergoes decomposition in two steps as shown by TG curve. The first step is the dehydration, which starts at 110°C and completes at 180°C as indicated by a mass loss of 29% (calc. loss=29.4%). DTG shows corresponding peak at 145°C which is endo in DTA. The anhydrous compound remains stable up to 330°C and then undergoes rapid oxidative decomposition process until a mass loss of 69% is attained at 380°C suggesting the formation of CoO (calc. loss=69.4%). The respective DTG peak lies at 350°C which is exothermic in DTA.

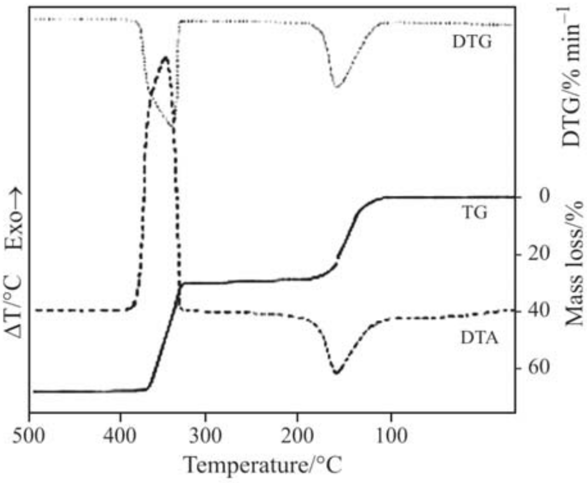


Fig. 4 DTA, TG and DTG curves of cobalt fumarate tetrahydrate

Nickel maleate tetrahydrate: $Ni(C_2H_2C_2O_4)\cdot 4H_2O$

The compound undergoes a multistep dehydration process as shown by the DTG curve (Fig. 5) and there is a corresponding endothermic region in DTA from 70 to 210°C. TG shows a plateau at a mass loss of 22% suggesting the removal of three water molecules (calc. loss=22.2%). A further slackening of TG curve at a mass loss of 29% suggests the removal of fourth water molecule at 210°C (calc. loss=29.4%). The anhydrous compound undergoes a gradual decomposition until a mass loss of 40% is reached at 360°C indicating the for-

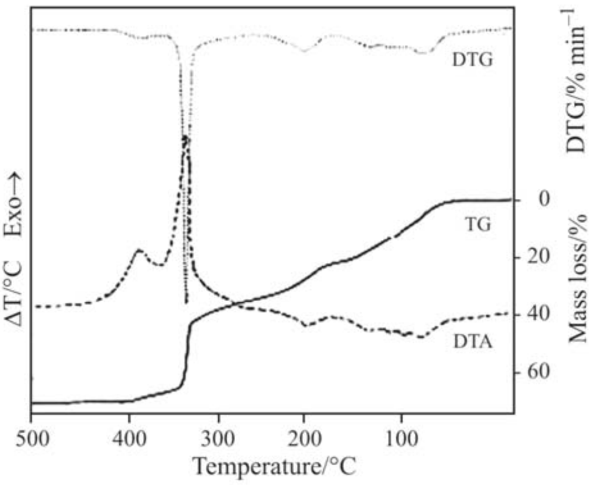


Fig. 5 DTA, TG and DTG curves of nickel maleate tetrahydrate

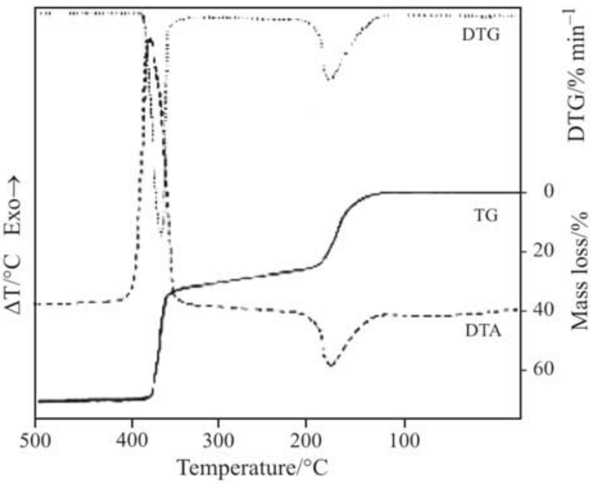


Fig. 6 DTA, TG and DTG curves of nickel fumarate tetrahydrate

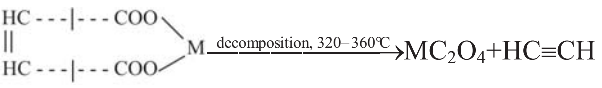
mation of nickel oxalate (calc. loss=40.3%). The respective DTG peak exists at 340°C which is exo in DTA. The identity of nickel oxalate, NiC_2O_4 formed has been revealed by recording XRD powder data of the residue obtained by isothermal heating of the parent salt at 360°C for 15 min (Table 3). Being unstable, nickel oxalate immediately undergoes an oxidative decomposition until a mass loss of 69.5% is reached at 420°C revealing the formation of NiO (calc. loss= 69.4%). There are corresponding DTA and DTG peaks at 395 (exo) and 400°C, respectively. The presence of NiO has been confirmed by XRD powder data of the final thermolysis residue [18]. IR spectrum shows characteristic bands at 565 and 282 cm^{-1} due to $\nu_{Ni–O}$ bonding.

Nickel fumarate tetrahydrate: $Ni(C_2H_2C_2O_4)\cdot 4H_2O$

Figure 6 displays the simultaneous thermal curves (TG-DTG-DTA) of nickel fumarate tetrahydrate at a heating rate of 10°C min^{-1}. The compound decomposes in two steps as shown by TG curve. The first step is dehydration which commences at 130 and completes at 225°C as shown by a plateau at a mass loss of 29% (calc. loss=29.4%). The corresponding DTG peak lies at 175°C which is endo in DTA. In the second step the anhydrous compound undergoes rapid oxidative decomposition as shown by an abrupt mass loss i.e. 69% up to 390°C indicating the formation of nickel oxide (NiO) directly from nickel fumarate. DTA shows an exotherm at 370°C for this oxidative decomposition step and the corresponding DTG peak lies at 365°C. XRD powder data of the final thermolysis product confirms the existence of nickel oxide, NiO.

On the basis of various thermoanalytical studies, the following mechanism may be proposed for the aerial decomposition of transition metal maleates:

$$M(C_2H_2C_2O_4)\cdot xH_2O \xrightarrow{\text{dehydration, 187–225℃}} M(C_2H_2C_2O_4)+xH_2O$$



$$\begin{matrix} HC---|---COO \\ \| \\ HC---|---COO \end{matrix} M \xrightarrow{\text{decomposition, 320–360℃}} MC_2O_4+HC\equiv CH$$

$$MC_2O_4 \xrightarrow{\text{decomposition, 390–440℃}} MO+CO+CO_2$$

Table 3 XRD powder data of the intermediate obtained at 360°C by isothermal calcination of Ni(mal)·$4H_2O$

Experimental			ASTM* data		
d/Å	I_{rel}	*h k l*	*d*/Å	I_{rel}	Assignment
4.765	100	2 0 2	4.770	100	NiC_2O_4
3.932	15	0 0 4	3.940	16	NiC_2O_4
3.045	12	1 1 4	3.080	14	NiC_2O_4
2.938	37	4 0 0	2.959	40	NiC_2O_4
2.615	10	1 1 5	2.642	11	NiC_2O_4
2.510	26	0 2 2	2.528	25	NiC_2O_4
1.575	28	3 3 2	1.589	30	NiC_2O_4
1.512	20	2 0 0	1.518	18	NiC_2O_4
1.470	20	1 3 6	1.480	20	NiC_2O_4

*ASTM Card No. 25-0582

However, anhydrous fumarate salts decompose directly to the oxide phase. The formation of oxalate intermediate from fumarate is not possible due to the '*trans*' location of carboxylate groups in the latter.

Conclusions

A comparison of thermal analysis shows that the fumarate compounds are more stable than the corresponding maleate salts. A similar trend has also been observed [7] for copper and zinc carboxylates (maleates, fumarates). This is attributed to the structure of these carboxylates. The fumarate, being a *trans* isomer, can crystallize either as a three dimensional or as linear polymer whereas only dimeric structure is expected for the *cis*-isomer (maleate).

The highest thermal stability of manganese fumarate (395°C) is attributed to its existence as anhydrous salt whereas all other carboxylates are hydrated. Being anhydrous, it does not have to undergo any reorganization/restructuring prior to decomposition.

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