

## **PHYSICO-CHEMICAL STUDIES ON THERMAL DECOMPOSITION OF ALKALI TRIS(MALEATO)FERRATES(III)**

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### **Abstract**

The thermal decomposition of alkali tris(maleato)ferrates(III),  $M_3[Fe(C_2H_2C_2O_4)_3]$  ( $M=Li, Na, K$ ) has been studied isothermally and non-isothermally employing simultaneous TG-DTG-DTA, XRD, Mössbauer and IR spectroscopic techniques. The anhydrous complexes decompose in the temperature range 215–300°C to yield Fe(II)maleate as an intermediate followed by demixing of the cations forming  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and alkali metal maleate/oxalate in successive stages. In the final stage of remixing of the cations (430–550°C) a solid state reaction occurs between  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and alkali metal carbonate leading to the formation of fine particles of respective ferrites. The thermal stabilities of the complexes have been compared with that of alkali tris(oxalato)ferrates(III).

**Keywords:** alkali Fe(III)maleates, DTA, ferrites, Mössbauer spectra, TG, thermal decomposition

### **Introduction**

The thermal analysis of the mixed Fe(III)carboxylates has become a fascinating subject of recent interest because of their complexing ability and ease of removal of non-toxic gases (CO/CO<sub>2</sub>), thus making them the pioneer precursors for the obtention of ferrites (the final thermolysis products). Ferrites are electroceramics which play a prominent role in a variety of applications and debated as an important class of magnetic materials [1]. The preparation of ferrites from thermal decomposition of Fe(III)carboxylate precursors (precursor technique) has two major advantages over the conventional ceramic method viz.

- (i) it does not involve milling of the starting material and
- (ii) ferrites are obtained in shorter time and at lower temperature.

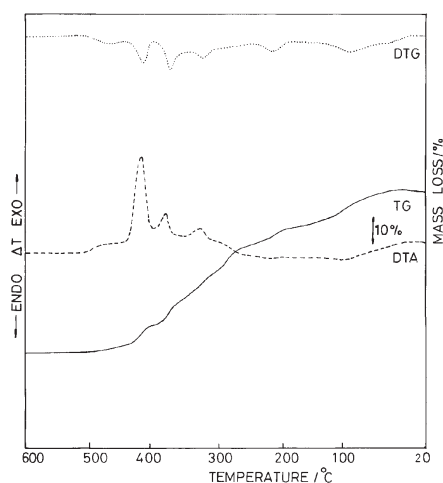
This technique has successfully been applied for the obtention of the alkali and alkaline earth metal ferrites from their respective Fe(III)carboxylates (oxalate/malonate) [2–4]. The present investigation is an extension of the decomposition studies earlier reported [5–7].

## Experimental

The methods of preparation and characterization of alkali metal Fe(III)maleates and the experimental details are reported elsewhere [8–9]. All the isomer shift values are quoted w.r.t. the pure iron absorber. XRD powder patterns were recorded at USIC, University of Roorkee, Roorkee using nickel filtered  $\text{CuK}_\alpha$  radiation. Non-isothermal curves (TG-DTG-DTA) were recorded on Stanton Red Craft Model (STA-780) at a heating rate of  $10^\circ\text{C min}^{-1}$ . For the identification of the intermediates/products, these complexes were calcined isothermally in silica crucibles in a muffle furnace at different temperatures for different time intervals. The variation in temperature was kept  $\pm 5^\circ\text{C}$ .

## Results and discussion

The infrared and Mössbauer spectra of alkali tris(maleato)ferrates(III) has already been reported [9]. Mössbauer parameters and magnetic susceptibility values have shown these complexes to be high spin iron(III) with octahedral geometry. The six coordination number of iron is satisfied by three maleate ligands which are bound through oxygen atoms. The alkali metal and water molecules seem to be responsible for linking together the complex ion,  $[\text{Fe}(\text{C}_2\text{H}_2\text{C}_2\text{O}_4)_3]^{3-}$ . Since various maleates differ in thermal behaviour a compound-wise discussion follows.



**Fig. 1** TG, DTA and DTG curves of lithium tris(maleato)ferrate(III) trihydrate

Figure 1 shows the simultaneous thermal analysis curves of lithium tris(maleato)ferrate(III) trihydrate at a heating rate of  $10^\circ\text{C min}^{-1}$ . TG curve shows a plateau at a mass loss of 11% at  $127^\circ\text{C}$  indicating the removal of three water molecules (calc. loss=11.4%), the corresponding broad DTG peak centered at about  $107^\circ\text{C}$  suggests a slow rate of dehydration. The enthalpy change for the dehydration step as calculated from DSC has been

found to be  $167.288 \text{ kJ mol}^{-1}$ . Another similar DTG peak at  $215^\circ\text{C}$  is associated with the gradual decomposition of the anhydrous complex into lithium maleate and Fe(II) maleate with a mass loss of 22% at  $270^\circ\text{C}$  (calc. loss 23.4%). Both these changes i.e. dehydration and subsequent decomposition are governed by an endothermic region from  $50$  to  $290^\circ\text{C}$  in DTA. Absence of any arrest in TG curve indicates that the Fe(II) intermediate is unstable and hence could not be detected by Mössbauer spectroscopic technique. It immediately starts decomposing until a mass of 42.1% is obtained at  $360^\circ\text{C}$  due to the formation of  $\text{Fe}_2\text{O}_3$  and lithium maleate (calc. loss=42.4%). The presence of  $\alpha\text{-Fe}_2\text{O}_3$  has been confirmed by the Mössbauer spectrum of the residue obtained by calcining isothermally the parent complex at  $350^\circ\text{C}$  for 2 h which shows a symmetrical sextet (Fig. 2) due to magnetic hyperfine interactions. The Mössbauer parameters of the sextet i.e. isomer shift and internal magnetic field values of  $0.38 \text{ mm s}^{-1}$  and 511 KOe respectively agree with those reported for  $\alpha\text{-Fe}_2\text{O}_3$  of bulk size [10].

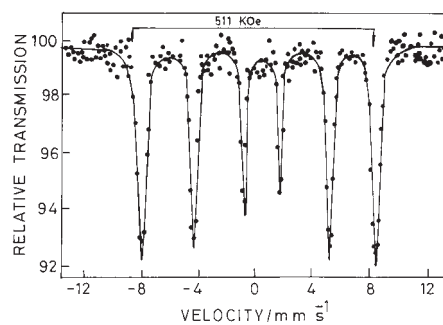


Fig. 2 Mössbauer spectrum of lithium Fe(III)maleate calcined at  $350^\circ\text{C}$

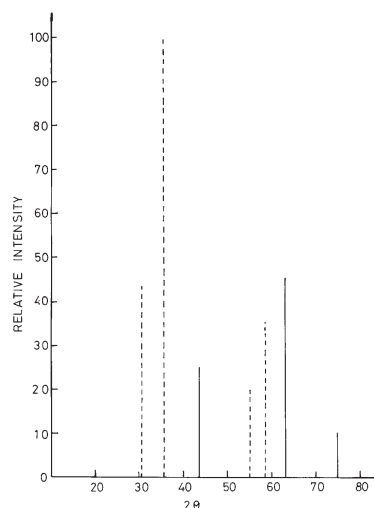


Fig. 3 XRD powder pattern of final thermolysis product of lithium Fe(III)maleate;  
 —  $\text{LiFeO}_2$ , ---  $\text{Li}_2\text{CO}_3$

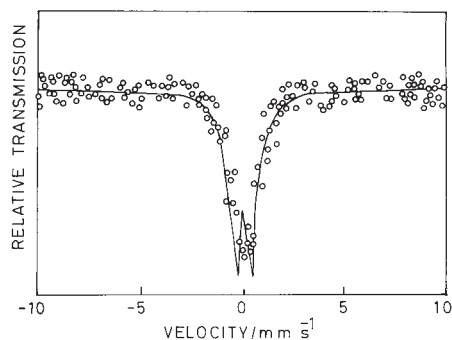
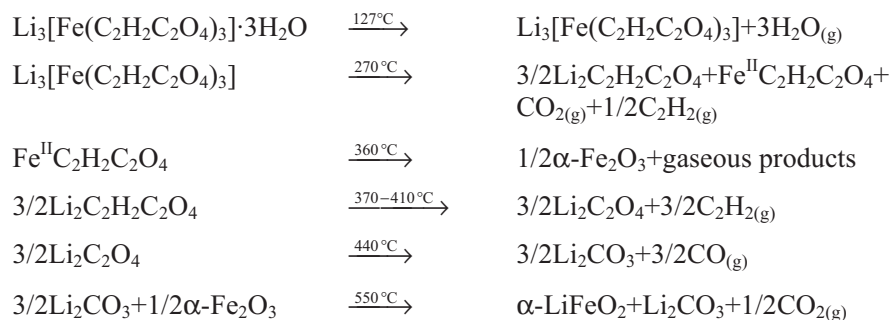


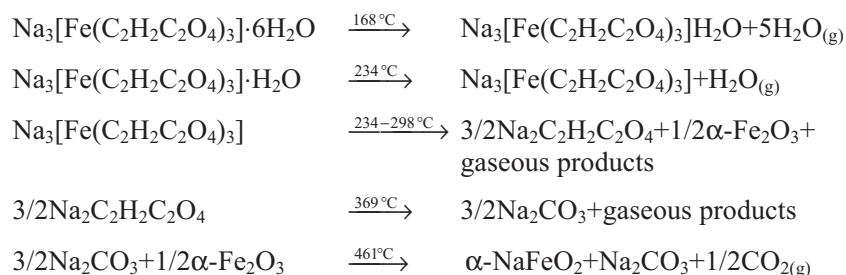
Fig. 4 Mössbauer spectrum of the final thermolysis product of lithium Fe(III)maleate

At higher temperature, lithium maleate loses an acetylene molecule, thereby giving lithium oxalate and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with a mass loss of 52% at 409°C (calc. loss=50.7%). The corresponding DTG peak exists at 390°C which is exo in DTA. The liberation of acetylene has been reported during 'Kolbe electrolysis' of potassium fumarate/maleate in solution phase [11, 12]. An arrest in TG at a mass loss of 59.0% at 440°C indicates the formation of lithium carbonate along with  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (calc. loss=59.6%). The respective DTG and DTA (exo) peaks exist at 419 and 418°C respectively. It has been observed that lithium maleate formed in the complex decomposes at a temperature (370°C) much lower than the decomposition temperature of its pure salt (420°C). This may be due to the metastable structure of the former and the catalytic effect of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> present. Further step in TG is the formation of lithium ferrite, LiFeO<sub>2</sub> and lithium carbonate at a mass loss of 63% at 550°C (calc. loss=64.2%) with DTG peak at 495°C and DTA (exo) at 500°C. The existence of lithium ferrite has been confirmed by X-ray diffractogram (Fig. 3) and Mössbauer spectrum (Fig. 4) of the residue obtained by calcining isothermally the parent complex at 550°C for 2 h. The central doublet in the Mössbauer spectrum, with the isomer shift and quadrupole splitting values of 0.38 and 0.58 mm s<sup>-1</sup>, is in agreement with the one reported for lithium ferrite,  $\alpha$ -LiFeO<sub>2</sub> [13]. The presence of quadrupole splitting value is due to the random distribution of Li<sup>+</sup> ions in the distorted cubic lattice of  $\alpha$ -LiFeO<sub>2</sub>. IR spectrum of the residue shows characteristic peaks of Li<sub>2</sub>CO<sub>3</sub> at 1440 and 1500 cm<sup>-1</sup>.

On the basis of above results, the following decomposition paths are proposed:



The thermolysis of sodium tris maleato ferrate(III)hexahydrate has been already reported elsewhere [8]. Various physico-chemical studies led to the following pathways of its decomposition:



Unlike its lithium counterpart, sodium ferrimaleate decomposes directly to  $\alpha\text{-Fe}_2\text{O}_3$  without undergoing reduction to iron(II) intermediate. A similar behaviour has also been reported during thermal decomposition of sodium ferrioxalate and ferrimalonate complexes [14].

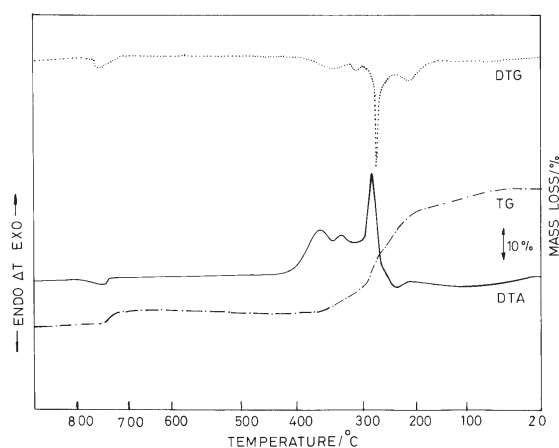
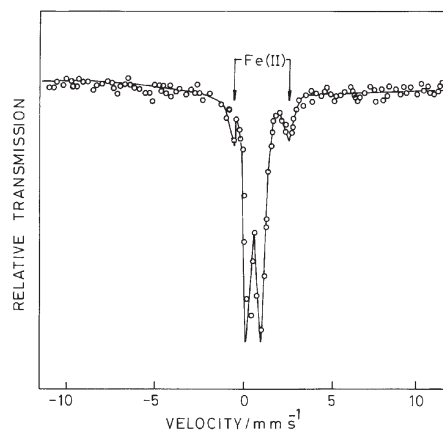


Fig. 5 DTA, TG and DTG curves of potassium tris(maleato)ferrate(III)tetrahydrate

Simultaneous TG-DTG-DTA curves of potassium tris(maleato)ferrate(III) tetrahydrate are shown in Fig. 5. The shape of the DTG and DTA (endo) curves shows that the dehydration is very slow process and completes at 185°C as shown by a mass loss of 9% (calc. loss=9.2%). The anhydrous complex, however, undergoes decomposition rapidly until a mass loss of 23% is reached at 245°C suggesting the formation of  $\text{K}_2[\text{Fe}^{\text{II}}(\text{C}_2\text{H}_2\text{C}_2\text{O}_4)_2]$  and potassium maleate. The respective DTG peak lies at 226°C and DTA shows an endotherm which subsequently changes into an exotherm. This decomposition step has been confirmed by the Mössbauer spectrum of the residue got after heating the parent complex isothermally for 15 min at 250°C. It displays two quadrupole doublets (Fig. 6) the outer one with isomer shift and



**Fig. 6** Mössbauer spectrum of potassium Fe(III)maleate calcined isothermally at 250°C

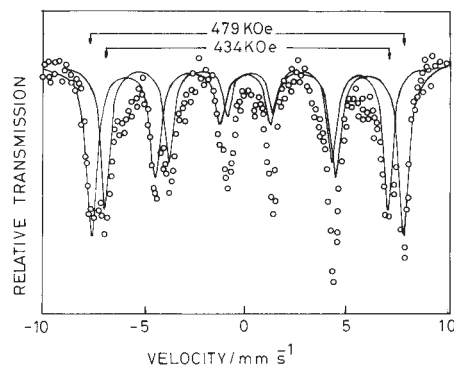
quadrupole splitting values 1.01 and 3.07  $\text{mm s}^{-1}$  respectively corresponding to the formation of iron(II) species while the inner doublet is due to the parent complex. The magnitude of the parameters of the outer doublet is comparable to those reported [15–17] for  $\text{K}_2[\text{Fe}^{\text{II}}(\text{ox})_2]$  formed during  $\gamma$ -radiolysis of potassium Fe(III)oxalate. The computer analysis of the spectrum shows the percentage of iron(II) species to be 18%. IR spectrum of this residue shows the presence of peaks due to carboxylate groups. A DTG peak consistent with the exotherm is present at 280°C and corresponding to this is a plateau in TG curve at a mass loss of 44%. This mass loss suggests the presence of  $\text{Fe}_2\text{O}_3$  formed due to the oxidation of Fe(II) species and potassium oxalate formed as a result of removal of an acetylene molecule from potassium maleate (calc. loss=43.9%). XRD data (listed in Table 1) and Mössbauer spectrum of the residue obtained by firing the parent complex isothermally at 300°C for 2 h confirms the presence of  $\alpha\text{-Fe}_2\text{O}_3$ . A six-finger pattern exhibited in Mössbauer spectrum with isomer shift and internal magnetic field values of 0.42  $\text{mm s}^{-1}$  and 513 KOe respectively agree with those reported for  $\alpha\text{-Fe}_2\text{O}_3$ . It has been observed that the pres-

**Table 1** Room temperature X-ray powder diffraction data of potassium Fe(III) maleate heated isothermally at 300°C for 2 h

$2\theta$	$d/\text{Å}$	Relative intensity	Assignment
24.26	3.66	71	$\alpha\text{-Fe}_2\text{O}_3$
33.28	2.69	100	$\alpha\text{-Fe}_2\text{O}_3$
35.70	2.51	75	$\alpha\text{-Fe}_2\text{O}_3$
40.94	2.20	35	$\alpha\text{-Fe}_2\text{O}_3$
49.53	1.84	31	$\alpha\text{-Fe}_2\text{O}_3$
54.11	1.69	37	$\alpha\text{-Fe}_2\text{O}_3$

Ref. ASTM Card No. 13–534

ence of free  $\alpha\text{-Fe}_2\text{O}_3$  has a profound effect on the thermal decomposition temperature of potassium maleate formed during the decomposition by lowering it to  $250^\circ\text{C}$  as compared to its pure salt which decomposes at much higher temperature ( $300^\circ\text{C}$ ). Further slackening in TG slope indicates the decomposition of potassium oxalate into carbonate at a mass loss of 52% (calc. loss=51.1%). IR spectrum shows peaks at  $1375$  and  $1435\text{ cm}^{-1}$  due to potassium carbonate [18].



**Fig. 7** Mössbauer spectrum of the final thermolysis product of potassium Fe(III) maleate at  $25\pm 2^\circ\text{C}$

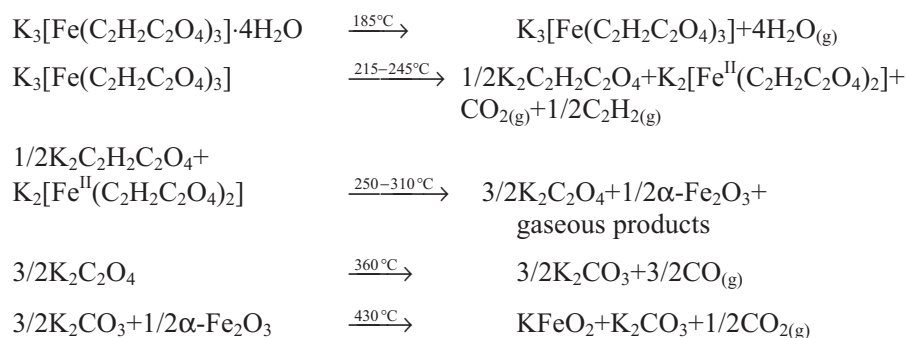
Next step in TG is the formation of potassium ferrite,  $\text{KFeO}_2$  and  $\text{K}_2\text{CO}_3$  at a mass loss of 55% (calc. loss=54.8%) due to the solid state reaction between  $\alpha\text{-Fe}_2\text{O}_3$  and a fraction of potassium carbonate with the corresponding exotherm in DTA at  $380^\circ\text{C}$ . Finally slow decomposition of remaining potassium carbonate above  $760^\circ\text{C}$  takes place as shown by a DTG peak at  $762^\circ\text{C}$  which is endo in DTA till a mass loss of 62.5% is reached indicating the formation of potassium oxide and potassium ferrite (calc. loss=62.3%). Mössbauer spectrum (Fig. 7) of the residue obtained after heating the parent complex isothermally at  $500^\circ\text{C}$  for 2 h displays two sextets revealing the presence of octahedral and tetrahedral sites, with cationic distribution of 56 and 44% respectively. Mössbauer parameters, listed in Table 2, confirm the existence of potassium ferrite,  $\text{KFeO}_2$  [19].

**Table 2** Mössbauer parameters of the thermolysis product of  $\text{K}_3[\text{Fe}(\text{C}_2\text{H}_2\text{C}_2\text{O}_4)_3]\cdot 4\text{H}_2\text{O}$  at  $300^\circ\text{C}$

$T_{\text{calc}}/^\circ\text{C}$	$\delta/\text{mm s}^{-1}$	$\Delta EQ/\text{mm s}^{-1}$	$H/\text{KOe}$	Cationic ( $\text{Fe}^{3+}$ ) distribution	Assignment
250	1.01	3.07	—	—	$\text{K}_2[\text{Fe}^{\text{II}}(\text{C}_2\text{H}_2\text{C}_2\text{O}_4)_2]$
	0.46	0.67	—	—	parent complex
300	0.42	—	513	—	$\alpha\text{-Fe}_2\text{O}_3$
500	0.34	0.10	479	56%	$\text{KFeO}_2$
	0.25	0.23	434	44%	

XRD pattern of the final residue shows only feeble lines due to the lack of crystallinity and formation of ultrafine particles of ferrite.

From the various physico-chemical studies adopted, the following mechanism for thermolysis is suggested:



## Conclusions

From the various physico-chemical studies adopted in the thermolysis of alkali tris(maleato)ferrates(III), following conclusions are drawn:

A. Decomposition occurs in four major consecutive steps:

- i. Dehydration of the original complex.
- ii. Reduction of anhydrous complex into iron[II] species by intramolecular charge transfer [ligand to iron(III)].
- iii. Reoxidation of iron(II) intermediate to  $\alpha\text{-Fe}_2\text{O}_3$ .
- iv. Solid state reaction between  $\alpha\text{-Fe}_2\text{O}_3$  and alkali metal carbonate at higher temperatures to form alkali metal ferrites.

B. Because of their different electrostatic properties (electronegativity, polarizability, cationic size etc.) the alkali metal cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) give rise to different intermediates and thermal decomposition temperatures. A comparison of initial decomposition temperature from DTG peak shows the following sequence of thermal stability:

sodium > potassium > lithium tris(maleato)ferrate(III)

A similar trend has been reported [13, 20] for thermal stability of alkali tris(oxalato)ferrates(III).

**Table 3** Decomposition temperature of  $\text{M}_3[\text{Fe}(\text{ox}/\text{mal})_3] \cdot n\text{H}_2\text{O}$

Metal	Oxalate/ $^\circ\text{C}$	Maleate/ $^\circ\text{C}$
Li	200	190
Na	280	234
K	260	215



From Table 3, it is evident that an oxalate complex, i.e. five membered chelate decomposes at a higher temperature than the respective seven-membered chelate i.e. maleate complex. It can be explained on the basis of high-temperature acid-base theory according to which, the weaker the anion base the higher the temperature of decomposition [21] and oxalate ion is a weaker anion base than maleate ion. Irving *et al.* [22] have also studied the influence of ring size upon the stability of metal chelates and have generalized that the stability of chelate complexes decreases with increasing ring size. Decrease in stability with increasing chain length of the ligand has been explained, to a large extent, on the basis of chelate/entropy factor.

C. An attracting feature of the precursor technique undertaken is the obtention of ferrite (end product) at a temperature much lower than that of conventional ceramic method ( $>1200^{\circ}\text{C}$ ). It is even lower in comparison to the temperature of ferrite formation ( $>800^{\circ}\text{C}$ ) from the thermolysis of respective oxalate precursors. These studies are important because of extensive application of ferrites as device materials in recording and microwave appliances.

D. Decrease in the decomposition temperature of alkali metal maleate when present in the complex as compared to its pure salt is due to the metastable structure of the former and catalyzing effect  $\alpha\text{-Fe}_2\text{O}_3$  present.

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