Journal of Thermal Analysis, Vol. 31 (1986) 1083–1090

MÖSSBAUER STUDY OF THE THERMAL DECOMPOSITIONS OF ALKALINE EARTH TRIS(OXALATO)FERRATES(III)

A. S. Brar, S. Brar* and *S. S. Sandhu***

CHEMISTRY DEPARTMENT, INDIAN INSTITUTE OF TECHNOLOGY, DELHI
HAUZ KHAS, NEW DELHI-16;
**CHEMISTRY DEPARTMENT, G.N.D. UNIVERSITY, AMRITSAR, INDIA

(Received September 3, 1985)

The thermal decompositions of alkaline earth tris(oxalato)ferrates(III) (Mg, Ca, Sr and Ba) have been studied by Mössbauer spectroscopy and other techniques. During the thermal decomposition, dehydration occurs first, followed by reduction to iron(II) species, and oxides and ferrites ($MFe^{III}O_4$) are then formed at higher temperature. In the case of strontium tris(oxalato)ferrate(III), strontium ferrite ($SrFe^{IV}O_4$) is formed at 700°.

Because of the interest in the unusual +4 valence state of iron, investigations on alkaline earth ferrates(III) offer one of the best documented examples of the use of Mössbauer spectroscopy [12]. The thermal decompositions of alkaline earth metal tris(oxalato)ferrates(III) are interesting to chemists, due to the presence of iron(IV) in their ferrites [3]. The effects of change of the cation (Li^+, Na^+, K^+, Cs^+ and NH_4^+) on the thermal decompositions of the alkali metal tris(oxalato)ferrates (III) have been reported in our earlier work [4]. The thermolyses and photolyses of alkali metal bis citrato-ferrates(III) [5–6] and the solid-state photolyses of strontium and barium tris(oxalato)ferrates(III) have also been reported [7]. Perusal of the literature reveals no systematic study of the thermal decompositions of alkaline earth tris oxalato ferrates(III). In a continuation of our earlier work, the effects of the cations (Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) on the thermal decompositions of alkaline earth tris(oxalato)ferrates(III) in the solid state are now reported. Thermogravimetric techniques and Mössbauer and infrared spectroscopy were employed.

---

* To whom correspondence may be addressed.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Experimental

For the preparation of magnesium, calcium, strontium and barium tris(oxalato)ferrates(III), equimolar quantities of alkaline earth oxalate (barium and strontium oxalates were prepared from an aqueous solution of barium or strontium chloride with oxalic acid and were made free from chloride ions) and oxalic acid were dissolved in an aqueous solution of iron(III) chloride with vigorous stirring. The reaction mixture was heated to about 80° and was allowed to cool slowly with constant stirring. At approximately 55°, yellow-green crystals began to appear. The precipitates were filtered off and washed with acetone. The precipitation was performed in the dark and the product was stored in the dark over anhydrous calcium chloride. Elemental analyses of the magnesium, calcium, strontium and barium tris(oxalato)ferrates(III) were performed and the numbers of water molecules were also calculated via TG. The thermal decomposition technique and the details of the recording of the Mössbauer spectra have already been reported [5, 7]. All spectra were fitted to Lorentzian curves using an ICL–2960 computer (IIT, Delhi). The uncertainty in the Mössbauer parameters was ± 0.03 mm s^{-1} and the chi square values were less than 2 in all cases.

Results and discussion

The Mössbauer spectra of all of these alkaline earth metal tris(oxalato)ferrates(III) exhibit a similar pattern; Lorentzian curve fitting to the absorption spectra shows that the broadening of the spectra is due to a spin lattice relaxation effect [8]. The values of the isomer shifts for magnesium, calcium, strontium and barium tris(oxalato)ferrates(III) are 0.24, 0.26, 0.25 and 0.31 mm s^{-1}, respectively. The values of the isomer shifts for strontium and barium tris(oxalato)ferrates(III) are close to the values reported in the literature [9]. The isomer shift values indicate that these complexes involve high spin, with the +3 oxidation state of iron, and are octahedral in symmetry.

The infrared spectra of all these complexes show the presence of coordinated oxalate ligand, as reported in the literature [10]. The reflectance spectra of all these complexes exhibit a continuous absorption band from 200 to 550 nm, which is presumably due to ligand to metal charge transfer (LMCT) transitions and a very weak (*d-d* spin-forbidden) band in the range 650 to 690 nm. These values tally with values reported in the literature [11, 12].

The magnetic moment values calculated using the spin-only formula $\mu = \sqrt{n(n+2)}$ for magnesium, calcium, strontium and barium tris(oxalato)ferrates(III) are 5.65, 5.64, 5.78 and 5.76 B.M., respectively. The values are in good agreement with the reported value of 5.92 BM for the high-spin $Fe^{3+}(d^5)$ system.

The Mössbauer spectra of the alkaline earth tris(oxalato)ferrates(III) heated at 200° for 3 hours reveal decomposition. For magnesium tris(oxalato)ferrates(III), the isomer shift and quadrupole splitting of the product are 1.22 and 1.90 mm s^{-1}, respectively. The isomer shift and quadruple splitting for the product of calcium tris(oxalato)ferrates(III) are 1.20 and 1.96 mm s^{-1}, respectively. These values indicate the formation of iron(II) oxalate. The Mössbauer spectrum of strontium tris(oxalato)ferrates(III) shows an isomer shift of 1.22 mm s^{-1} and a quadrupole splitting of 2.24 mm s^{-1} (Fig. 1). The isomer shift and quadruple splitting for the barium complex heated at 200° are 1.24 and 2.19 mm s^{-1}, respectively. The value of the isomer shift shows that the iron(III) has been reduced to iron(II). Sato and Tominaga [16] reported an isomer shift of 1.22 mm s^{-1} and a quadrupole splitting of 2.20 mm s^{-1} for $[Fe(C_2O_4)_2(H_2O)_2]^{2-}$. Here, the quadrupole splitting values are slightly higher than that for iron(II) oxalate dihydrate (1.80 mm s^{-1}), due to the electric field gradient created by the two types of ligands in an octahedral environment. From these investigations, it can be concluded that $[Fe(C_2O_4)(H_2O)_2]^{2-}$ is formed during the thermal decompositions of strontium and barium tris(oxalato)ferrates(III), while in the cases of magnesium and calcium,

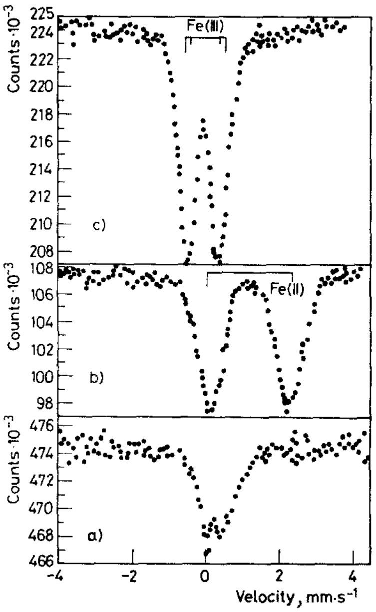

Fig. 1 Mössbauer spectra of strontium tris(oxalato)ferrate(III); (a) at room temp. (b) heated at 200° (c) heated at 300° for three h

iron(II) oxalate is formed as an intermediate, as the isomer shifts and quadrupole splitting tally with the values reported in the literature for these compounds. The infrared spectra exhibit absorption bands due to oxalate at 1640, 1435 and 1285 cm^{-1} in all the complexes, and also due to water at 3300 cm^{-1} in the barium and strontium complexes. The presence of bands due to both oxalate and water at this temperature accords with the results of the Mössbauer studies.

The Mössbauer spectra of the alkaline earth metal tris(oxalato)ferrates(III) heated at 300° reveal complete decomposition. In the case of magnesium tris(oxalato)ferrates(III) heated at 300°, the isomer shift is 0.28 mm s^{-1} and the quadrupole splitting is 0.78 mm s^{-1}, which indicate the formation of α-Fe_2O_3 (<15 nm) [13]. The Mössbauer spectrum of calcium tris(oxalato)ferrates(III) heated at 300° shows an isomer shift of 1.20 mm s^{-1} and a quadrupole splitting of 1.80 mm s^{-1} due to iron(II) oxalate, which was formed at lower temperature, and another doublet having an isomer shift and a quadrupole splitting of 0.34 and 0.62 mm s^{-1}, respectively, due to α-Fe_2O_3. In the case of strontium tris(oxalato)ferrates(III) heated at 300°, two doublets are observed (Fig. 1). One doublet, with an isomer shift of 0.29 mm s^{-1} and a quadrupole splitting of 0.60 mm s^{-1}, is due to an iron(III) species. The other doublet, with an isomer shift of 0.29 mm s^{-1} and a higher quadrupole splitting, may be due to interactions with strontium ions. Similar Mössbauer parameters were observed in the case of the barium complex heated at 300°. The IR frequencies at 1600, 1290 and 1480 cm^{-1} show the presence of oxalate and carbonate groups in the intermediates. TG studies support the above results, and weight losses are given along with the suggested mechanism of decomposition (Table 1).

The Mössbauer spectrum of magnesium tris(oxalato)ferrates(III) heated at 500° shows a doublet with an isomer shift of 0.30 mm s^{-1} and a quadrupole splitting of 0.60 mm s^{-1}, which reveals the presence of iron(III) species. It has been reported that in $MgFe_2^{III}O_4$ prepared at 1185°, there are tetrahedral and octahedral sites around Fe^{2+} [14]. Lorentzian fitting of the spectrum of calcium tris(oxalato)ferrates(III) shows two sextets. The isomer shift, quadrupole splitting and magnetic field at the nucleus are 0.15 mm s^{-1}, 0.70 mm s^{-1} and 506 kOe, respectively, for one sextet, and 0.26 mm s^{-1}, 0.55 mm s^{-1} and 485 kOe, respectively, for the other; these results are due to the octahedral and tetrahedral environments of the nuclei. In the case of strontium tris(oxalato)ferrates(III) heated at 500°, two sextets were observed. One has an isomer shift, a quadrupole splitting and a magnetic field at the nucleus of 0.16 mm s^{-1}, −0.22 mm s^{-1} and 495 kOe, respectively, while the other sextet has corresponding values of 0.28 mm s^{-1}, 0.37 mm s^{-1} and 484 kOe, respectively (Fig. 2). The Mössbauer spectrum of barium tris(oxalato)ferrates(III) shows the presence of ferrite with iron in oxidation state +3. The isomer shift, quadrupole splitting and magnetic field at the nucleus

Table 1

				Percentage weight loss	
				from TG	Calculated
I)	$Mg_2[Fe(C_2O_4)_3]_2 \cdot \cdot 6H_2O$	*140°*	$Mg_3[Fe(C_2O_4)_3]_2$ $6H_2O$	13.0	13.2
	$Mg_3[Fe(C_2O_4)_3]_2$	*200°*	$2MgFe(C_2O_4)_2 + + MgCO_3 + 3CO_2$	26.0	27.3
	$2MgFe(C_2O_4)_2$	*300°*	$Fe_2O_3 + 2MgCO_3 + + 6CO_2$	45.0	49.8
	$3MgCO_3 + Fe_2O_3$	*700°*	$MgFe^{III}_2O_4 + 3CO_2 + + 2MgO$	66.0	69.8
II)	$Ca_3[Fe(C_2O_4)_3]_2 \cdot 8H_2O$	*140°*	$Ca_3[Fe(C_2O_4)_3]_2 + 8H_2O$	14.0	15.9
	$Ca_3[Fe(C_2O_4)_3]_2$	*200°*	$2CaFe(C_2O_4)_2 + + CaCO_3 + 3CO_2$	26.5	28.8
	$2CaFe(C_2O_4)_2$	*300°*	$Fe_2O_3 + 2CaCO_3 + + 6CO_2$	47.8	49.1
	$3CaCO_3 + Fe_2O_3$	*700°*	$CaFe^{II}_2O_4 + 3CO_2$ $+ 2CaO$	63.2	63.7
III)	$Sr_3[Fe(C_2O_4)_3]_2 \cdot \cdot 12H_2O$	*120°*	$Sr_3[Fe(C_2O_4)_3]_2 \cdot \cdot 4H_2O + 8H_2O$	10.0	12.8
	$Sr_3[Fe(C_2O_4)_3]_2 \cdot \cdot 4H_2O$	*200°*	$2SrFe(C_2O_4)_2(H_2O)_2 + + SrCO_3 + 3CO_2$	18.5	23.3
	$2SrFe(C_2O_4)_2(H_2O)_2$	*300–400°*	$Fe_2O_3 + 2SrCO_3 + + 2H_2O + 6CO_2$	46.0	42.5
	$SrCO_3 + Fe_2O_3$	*500°*	$SrFe^{III}_2O_4 + CO_2$	—	46.5
	$2SrCO_3 + SrFe^{III}_2O_4$	*700°*	$2SrFe^{IV}O_3 + 2CO_2$ $+ SrO$	53.0	53.3
IV)	$Ba_3[Fe(C_2O_4)_3]_2 \cdot \cdot 10H_2O$	*140°*	$Be_3[Fe(C_2O_4)_3]_2 \cdot \cdot 4H_2O + 6H_2O$	9.1	8.75
	$Ba_3[Fe(C_2O_4)_3]_2 \cdot \cdot 4H_2O$	*200°*	$2BaFe(C_2O_4)_2(H_2O)_2 + + BaCO_3 + 3CO_2$	15.0	18.2
	$2BaFe(C_2O_4)_2(H_2O)_2$	*300–450°*	$Fe_2O_3 + 2BaCO_3 + + 2H_2O + 6CO_2$	39.5	34.4
	$3BaCO_3 + Fe_2O_3$	*700°*	$BaFe_2O_4 + 2BaO + + 3CO_2$	43.0	45.1

for one sextet are 0.20 mm s^{-1}, 0.30 mm s^{-1} and 435 kOe, respectively, and for the other sextet 0.23 mm s^{-1}, 0.36 mm s^{-1} and 410 kOe, respectively, which are due to barium ferrite formed during thermolysis. The above investigations show that iron(III) oxide formed at 300° reacts with alkali metal carbonates to form ferrites.

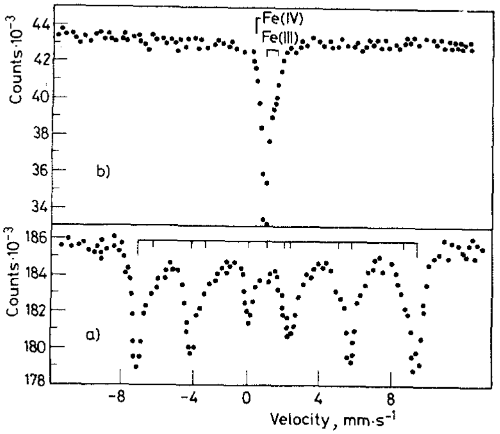

Fig. 2 Mössbauer spectra of strontium tris(oxalato)ferrate(III); (a) heated at 500° (b) heated at 700° for three h

The IR spectra show bands at 1470–85 cm^{-1}, due to the presence of carbonate in the products.

The Mössbauer spectrum of magnesium tris(oxalato)ferrate(III) heated at 700° does not reveal any change as compared to the spectrum of the sample heated at 500°, whereas in the case of calcium tris(oxalato)ferrate(III) at 700°, the intensity of the doublet increases and the intensity of the six-line pattern decreases. Lorentzian fitting demonstrates two doublets, one with an isomer shift of 0.10 mm s^{-1} and a quadrupole splitting of 0.76 mm s^{-1} and the other with an isomer shift of 0.26 mm s^{-1} and a quadrupole splitting of 0.70 mm s^{-1} which are due to the Fe^{3+} high-spin state in octahedral and tetrahedral environments, respectively [14]. The Mössbauer spectrum of strontium tris(oxalato)ferrate(III) heated at 700° (Fig. 2) gives an isomer shift of -0.12 mm s^{-1}, which is due to an Fe(IV) species [9, 15]. The outer doublet with an isomer shift of 0.18 mm s^{-1}, is due to ferrite containing iron in oxidation state $+3$. Fractional intensities obtained by computer fitting show the presence of 72% Fe(IV) species and 28% iron(III) species. The Mössbauer spectrum of barium tris(oxalato)ferrate(III) heated at 700° contains two sextets. indicating tetrahedral and octahedral environments. The isomer shift, quadrupole splitting and magnetic field at the nucleus for one sextet are 0.21 mm s^{-1}, 0.31 mm s^{-1} and 416 kOe, respectively and for the other are 0.21 mm s^{-1}, 0.61 mm s^{-1} and 439 kOe, respectively, which shows the presence of ferrites. Alkaline earth carbonates formed at lower temperature decompose at 700° and react with iron oxide to form ferrites. In the case of strontium tris(oxalato)ferrate(III), $SrFe^{IV}O_3$ is formed at 700°. Fe(IV) species are not formed at 700° from the magnesium, calcium and barium complexes. The IR spectra do not contain an absorption band at 1470 cm^{-1}, which shows the complete decomposition of carbonates at this temperature.

There are two possible explanations for the different intermediates and products formed during the thermal decompositions of these complexes. One is the difference in size of the cations, and other relates to the quenching efficiency. The kinetics of oxygen uptake may be very different for these complexes. All these samples were heated at 700° and cooled in the same environment. The kinetic factors are due to the incorporation of increased imperfection and growth of the particle size, which affects the uptake of oxygen in the M_3FeO_{7-x} system.

During the thermal decompositions of alkaline earth tris(oxalato)ferrates(III), the oxidation state of iron undergoes several changes. At 200°, it is reduced to Fe(II) species, while at 300° it is oxidized to Fe(III) with the formation of metal carbonate, and a solid-solid reaction then takes place to yield ferrites at higher temperature. As the decomposition takes place both the particle size and the magnetic properties of the products change. The formation of Fe(IV) species was observed at 700° in the case of strontium, but not in the other cases. However, at higher temperature and under different conditions, the formation of ferrites containing Fe(IV) has been reported for calcium and barium [3, 15]. On the basis of Mössbauer results, Maddock and co-workers [17] reported the formation of intermediate $K_6Fe^{II}(OX)_5$ in the decomposition of potassium tris(oxalato)ferrate(III). No such intermediate has been observed for these alkaline earth metal complexes. From the above studies, it can be concluded that the outer cation (Mg, Ca, Sr or Ba), and the conditions under which thermal decomposition is taking place, affect the nature of the intermediates formed. Gallagher and Kurkijan [9] have reported the formation of $[Fe_2^{II}(C_2O_4)_5]^{6-}$ as an intermediate, having an isomer shift and a quadrupole splitting of 1.44 and 2.30 mm s^{-1}, respectively, during the thermal decomposition of strontium or barium tris(oxalato)ferrate(III), while Sato and Tominaga [16] and Bencroft and co-workers [17] have reported an isomer shift and a quadrupole splitting of 1.18 and 3.89 mm s^{-1} for the similar intermediate $[Fe_2^{II}(C_2O_4)_5]^{6-}$ from alkali metal tris(oxalato)ferrates(III). We confirmed these latter values of the Mössbauer parameters for this intermediate in an earlier publication [4]. Thus, in the solid-state thermal decomposition of strontium or barium tris(oxalato)ferrate(III), the intermediate $[Fe(C_2O_4)_2(H_2O)_2]^{2-}$ is formed instead of $[Fe_2^{II}(C_2O_4)_5]^{2-}$, contradicting the conclusion of Gallagher and Kurkijan. Our results are confirmed both by the Mössbauer parameters and by the inferences drawn from infrared spectroscopy. Gallagher and Kurkijan did not record the IR spectra of their samples.

The solid-state decomposition of the alkaline earth tris(oxalato)ferrates(III) may be complex, but, on the basis of the Mössbauer, infrared spectroscopic and thermal results, the above paths of decomposition may be suggested (Table 1). The percentage weight losses calculated from the equations, together with the weight losses from TG, are also given.

References

1 P. K. Gallagher, Inorg. Chem., 4 (1965) 965.

2 R. L. Cohen (Editor). Applications of Mössbauer Spectroscopy, Academic Press, 1976, p. 199.

3 T. Skimgo, N. Hosoito, T. Pakada, M. Takano and V. Takada, Proc. III Int. Cont. Ferrates (III), Japan, 1980, p. 392.

4 A. S. Brar and B. S. Randhawa, J. Solid State Chem. (In press).

5 A. S. Brar and B. S. Randhawa, 7th International Conference on 'Thermal Analysis', Plenum Press, 1983, p. 476.

6 A. S. Brar and B. S. Randhawa, Polyhedron, 3 (1984) 169.

7 A. S. Brar, S. Brar and S. S. Sandhu, Polyhedron, 2 (1983) 45.

8 M. Blume, Phys. Rev. Letts., 14 (1965) 96.

9 P. K. Gallagher and C. R. Kurkijan, Inorg. Chem., 5 (1966) 314.

10 K. Nakamoto, Infrared Spectra of Inorganic and Co-ordination Compounds, 2nd Edition, Whiley Interscience, New York, 1970, p. 245.

11 C. A. Parkar, Trans. Faraday Soc., 50 (1954) 1213.

12 C. A. Parkar, Proc. Roy. Soc. London, 220A (1953) 104.

13 W. Kundig, H. Bommel, G. Canstablis and R. H. Lindquist, Phys. Rev., 142 (1966) 327.

14 E. Degeeve,ÜC. Baudde, J. Desitter and A. Gouaert, J. Phys. Paris, 37, C-6 (1976) 497.

15 M. Takano, N. Nakamishi and Y. Takeda, Heter. Rev. Bull., 12 (1977) 923.

16 H. Sato and T. Tominaga, Bull. Chem. Soc. Japan, 52 (1979) 1302.

17 G. M. Bancroft, K. G. Dharmavardena and A. G. Maddock, Inorg. Chem., 9 (1970) 223.

Zusammenfassung — Die thermische Zersetzung von Tris(oxalato)ferraten(III) der Erdalkalimetalle (Mg, Ca, Sr, Ba) wurde durch Mössbauer-Spektroskopie und andere Techniken untersucht. Im Verlaufe der thermischen Zersetzung verläuft zunächst die Dehydratisierung, gefolgt von der Reduktion zu Eisen(II)-Species. Oxide und Ferrite ($MFe^{III}O_4$) werden danach bei höheren Temperaturen gebildet. Strontium-tris(oxalato)-ferrat(III) geht bei 700 °C in Strontiumferrit ($SrFe^{IV}O_4$) über.

Резюме — Термическое разложение трис(оксалато)ферратов(III) магния, кальция, стронция и бария было изучено мёссбауэровской спектроскопией и другими методами. Во время термического разложения сначала происходит дегидратация, за которой следует восстановление железа до двухвалентного, а затем при более высокой температуре образуются окислы и ферриты $MFe^{III}O_4$. В случае стронциевой соли при 700° образуется феррит стронция $SrFe^{IV}O_4$.