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MÖSSBAUER STUDY OF THE THERMAL DECOMPOSITION OF SOME IRON(III) MONOCARBOXYLATES

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ABSTRACT

The thermal decomposition of iron(III) propionate trihydrate, $Fe(C_3H_5O_2)_3 \cdot 3\ H_2O$, and iron(III) butyrate trihydrate, $Fe(C_4H_7O_2)_3 \cdot 3\ H_2O$, has been studied at various temperatures for different intervals of time in a static air atmosphere. The reduction of the iron(III) moiety to iron(II) species takes place at 493 and 513 K in the case of iron(III) propionate and iron(III) butyrate, respectively. At higher temperatures, α-Fe_2O_3 is formed as the ultimate product of thermal decomposition.

INTRODUCTION

The thermal decomposition of metal carboxylates has become a subject of recent interest due to their wide use as medicinal agents and antiseptics [1–5]. A systematic study of the thermal decomposition of iron(III) carboxylates has been started using Mössbauer spectroscopy, DTG, DTA and TG techniques. In our earlier communications, the thermal decomposition of iron(III) adipate pentahydrate and iron(III) succinate has been reported [6,7]. In these complexes, the reduction of the parent iron(III) moiety to iron(II) species has been observed at 523–573 K, followed by the formation of α-Fe_2O_3 as the end product at higher temperatures. The present investigation deals with the thermal decomposition of iron(III) propionate trihydrate and iron(III) butyrate trihydrate using Mössbauer spectroscopy and derivatographic techniques.

EXPERIMENTAL

Iron(III) propionate trihydrate, $Fe(C_3H_5O_2)_3 \cdot 3\ H_2O$, and iron(III) butyrate trihydrate, $Fe(C_4H_7O_2)_3 \cdot 3\ H_2O$, were prepared by the addition of

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equimolar proportions of ferric chloride (AR) solution to the aqueous solution of sodium propionate and sodium butyrate, respectively. Keeping the pH of these solutions at 5.5, the precipitates of these carboxylates were formed in the cold. These precipitates were separated by filtration and dried in air. The identity of these compounds was established by infrared spectroscopy and chemical analysis. The percentage of iron was determined gravimetrically [8]. The percentages of carbon and hydrogen as determined by microanalysis are given in Table 1.

The infrared spectra were recorded in nujol mulls on a spectroMoM-2000 spectrophotometer (Hungarian Optical Works, Hungary). The infrared spectrum of iron(III) propionate trihydrate shows a broad band at 3200 cm^{-1} due to OH stretching of water molecules, a strong band at 1560 cm^{-1} due to $\nu_{asy}(C{=}O)$ and bands at 1450 cm^{-1} and 1315 cm^{-1} due to $\nu_{sym}(C{=}O)$.

The infrared spectrum of iron(III) butyrate trihydrate shows a band at 3250 cm^{-1} due to $\nu(OH)$, an intense band at 1570 cm^{-1} due to $\nu_{asy}(C{=}O)$ and bands at 1470 cm^{-1} and 1335 cm^{-1} due to $\nu_{sym}(C{=}O)$. These values indicate the presence of coordinated carboxylate groups [9].

Non-isothermal analysis was carried out by means of a Paulik–Paulik–Erdey MOM derivatograph (Hungary) with 110 mg of iron(III) propionate trihydrate and 180 mg of iron(III) butyrate trihydrate at 200 mg sensitivity in a static air atmosphere and at a heating rate of 10° min^{-1}. For Mössbauer study, the samples were heated in a silica crucible at different temperatures for different intervals of time in a muffle furnace.

The Mössbauer spectrometer MBS-35 (ECIL, India) coupled with MCA-38B with constant acceleration drive was employed to record the spectra. A 5 mCi $^{57}Co(Rh)$ source was used. The values of isomer shift have been reported with respect to natural iron. All the spectra were recorded at 298 ± 2 K. A sample containing approximately 10 mg cm^{-2} of natural iron was taken for each measurement. The uncertainties in isomer shift, quadrupole splitting and internal magnetic field values are ± 0.04 mm s^{-1}, ± 0.04 mm s^{-1} and ± 5 kOe, respectively.

TABLE 1

Analysis of the compounds studied

Compound	Fe (%)		C (%)		H (%)	
	Found	Calcd.	Found	Calcd.	Found	Calcd.
$Fe(C_3H_5O_2)_3 \cdot 3\ H_2O$	17.4	17.0	32.6	32.8	6.4	6.4
$Fe(C_4H_7O_2)_3 \cdot 3\ H_2O$	15.2	15.1	38.9	38.8	7.3	7.3

RESULTS AND DISCUSSION

Mössbauer spectroscopic study

The Mössbauer spectra of iron(III) priopionate trihydrate and iron(III) butyrate trihydrate consist of a doublet at room temperature (Figs. 1a, 2a). The isomer shift and quadrupole splitting values for iron(III) propionate are 0.38 and 0.57 mm s^{-1}, respectively, while for iron(III) butyrate they are found to be 0.44 and 0.75 mm s^{-1}, respectively. The values of the isomer shift indicate these complexes to be high spin with (+3) oxidation state of iron, whereas the quadrupole splitting values show their distortion from the regular octahedral symmetry. The greater values of isomer shift and quadrupole splitting for iron(III) butyrate may be due to its greater chelation compared with iron(III) propionate [10].

The Mössbauer spectrum of iron(III) propionate trihydrate after heating at 493 K for 5 min exhibits two quadrupole doublets (Fig. 1b), one with isomer shift and quadrupole splitting values of 1.06 and 2.09 mm s^{-1}, respectively, indicating the formation of iron(II) species [6,7,11], and the other due to the parent complex. The Mössbauer spectrum of this sample

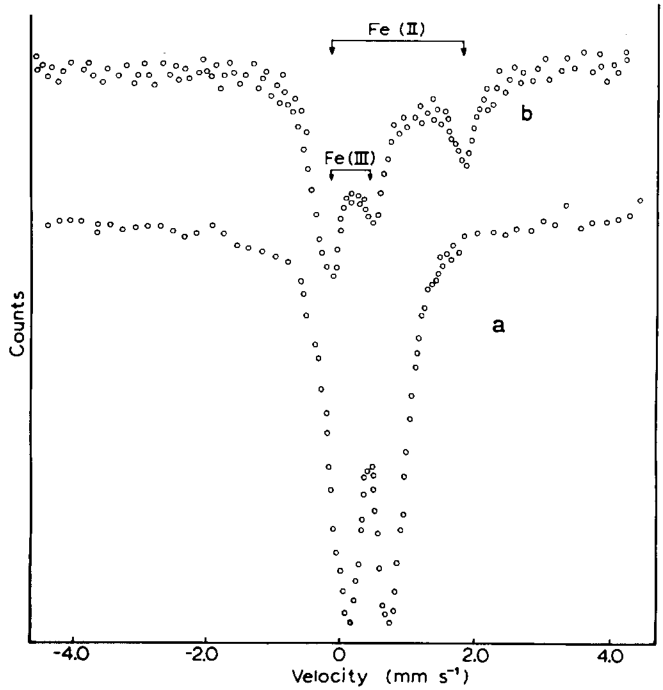

Fig. 1. Mössbauer spectra of iron(III) propionate trihydrate (a) at room temperature (298 ± 2 K) and (b) heated at 493 K for 5 min.

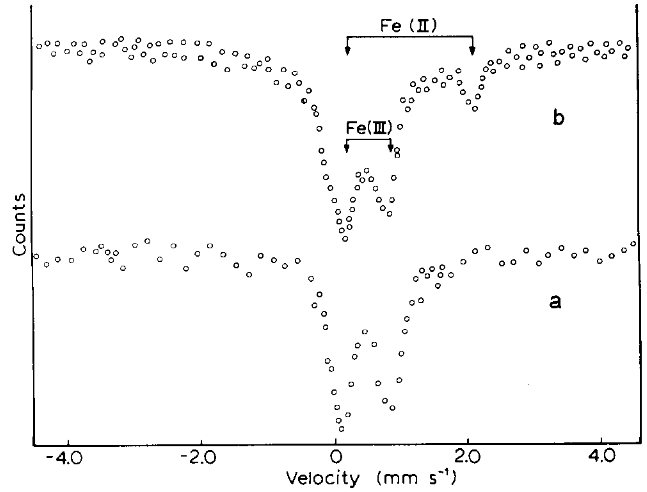

Fig. 2. Mössbauer spectra of iron(III) butyrate trihydrate (a) at room temperature (298 ± 2 K) and (b) heated at 513 K for 8 min.

heated at 573 K for 8 min consists of a six line pattern along with a central doublet (Fig. 3a) due to magnetic hyperfine interaction. The six-line pattern shows isomer shift, quadrupole splitting and internal magnetic field values of 0.40 mm s^{-1}, 0.10 mm s^{-1} and 502 kOe, respectively. These values are in good agreement with the reported values for α-Fe_2O_3 [12–15]. The central doublet has isomer shift and quadrupole splitting values of 0.30 and 0.80 mm s^{-1}, respectively, indicating the formation of α-Fe_2O_3 with particle size $<$ 10 nm [13]. Thus a mixture of iron(III) oxides with different particle sizes is formed at 573 K. The Mössbauer spectrum of the final residue of the sample, obtained by heating at 873 K for one hour, represents a six-line pattern associated with magnetic hyperfine interaction (Fig. 3b) with isomer shift, quadrupole splitting and internal magnetic field values of 0.31 mm s^{-1}, 0.15 mm s^{-1} and 510 kOe, respectively. These values are in close agreement with the values reported in the literature for α-Fe_2O_3 [12–15]. The formation of α-Fe_2O_3 as the final thermolysis product has also been reported in the case of iron(III) oxalate, iron(III) adipate [6] and iron(III) succinate [7] using Mössbauer and thermogravimetric techniques.

The Mössbauer spectrum of iron(III) butyrate heated at 513 K for 8 min consists of two quadrupole doublets (Fig. 2b), one with isomer shift and quadrupole splitting values of 1.11 and 1.98 mm s^{-1}, respectively, indicating the formation of iron(II) moiety [6,7,11], and the other doublet being due to the parent complex. For the sample heated at 573 K for 5–8 min the Mössbauer spectrum represents a six-line pattern due to magnetic hyperfine interaction (Fig. 4a) with isomer shift, quadrupole splitting and internal magnetic field values of 0.35 mm s^{-1}, 0.20 mm s^{-1} and 504 kOe, respec-

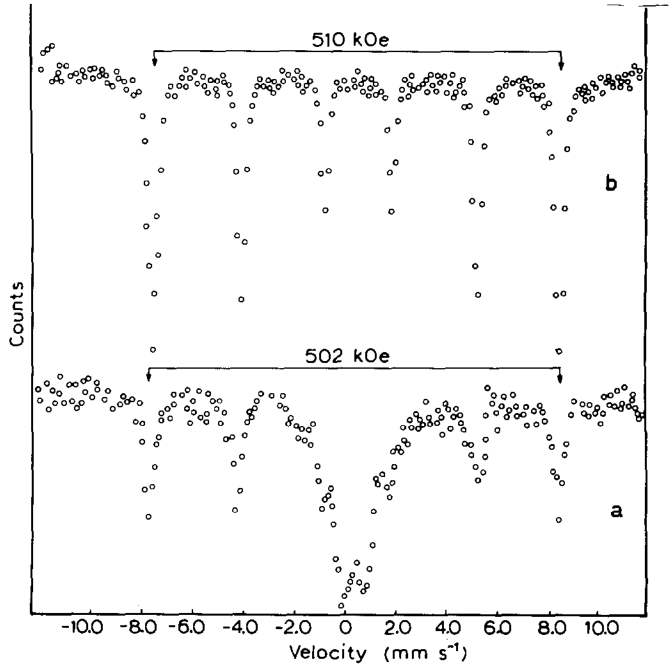

Fig. 3. Mössbauer spectra of iron(III) propionate trihydrate heated at (a) 573 K for 8 min and (b) 873 K for 1 h.

tively, indicating the formation of α-Fe_2O_3 [12–15]. No significant change in the Mössbauer parameters has been observed for the sample heated to 633 K for 10 min. The Mössbauer spectrum of the residue obtained by heating the sample at 873 K for one hour exhibits a six-line pattern along with a central doublet associated with magnetic hyperfine interaction (Fig. 4b). The six-line pattern shows isomer shift, quadrupole splitting and internal magnetic field values of 0.40 mm s^{-1}, 0.10 mm s^{-1} and 512 kOe, respectively. These values are in good agreement with the reported values for α-Fe_2O_3 [12–15]. The central doublet has isomer shift and quadrupole splitting values of 0.35 and 0.41 mm s^{-1}, respectively, which indicates the formation of α-Fe_2O_3 with particle size < 10 nm [13]. Thus a mixture of iron(III) oxides, α-Fe_2O_3, with different particle sizes is formed as the final thermolysis product.

Thermoanalytical study

Figure 5 shows the simultaneous DTG–DTA–TG plot of iron(III) propionate trihydrate. The DTA curve shows one endothermic peak at 378 K (with T_i at 373 K and T_f at 443 K). The first peak in DTG plot is at 376 K. There is one exothermic peak in the DTA curve at 603 K.

The TG plot at 443 K shows a loss of 15.5%, indicating the elimination of three water molecules of crystallisation (calcd. loss = 16.4%). Also the TG

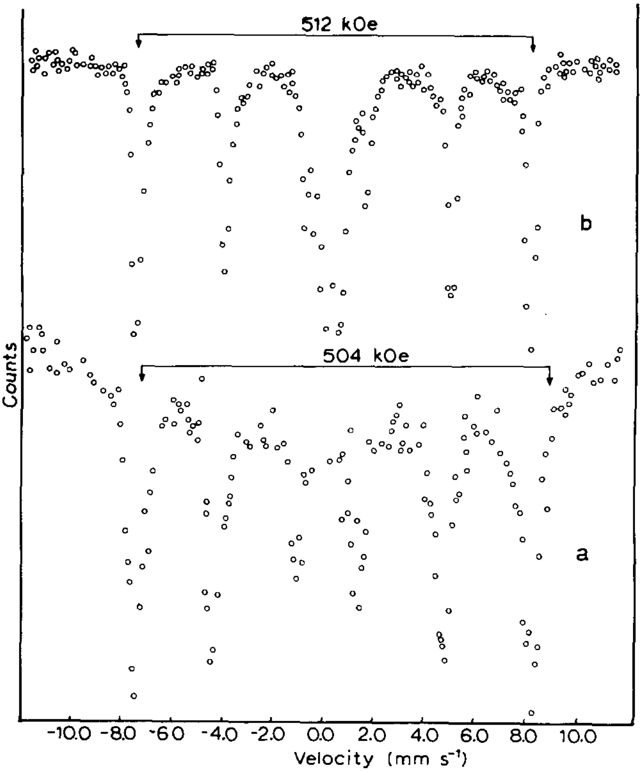

Fig. 4. Mössbauer spectra of iron(III) butyrate trihydrate heated at (a) 573 K for 5–8 min and (b) 873 K for 1 h.

curve shows a loss of 37.3% at 503 K, indicating the formation of iron(II) propionate (calcd. loss = 38.6%). The iron(II) species has also been detected by Mössbauer spectroscopy (Fig. 1b). Thereafter, the decomposition is very rapid. The TG plot shows a loss of 74.6% at 843 K, corresponding to the formation of Fe_2O_3 (calcd. loss = 75.7%). The end product has been confirmed to be α-Fe_2O_3 by Mössbauer spectroscopic technique (Fig. 3b).

The mechanism proposed for decomposition of this complex is

$$\mathrm{Fe(CH_3CH_2COO)_3 \cdot 3\,H_2O} \xrightarrow[-3\,\mathrm{H_2O}]{443\ \mathrm{K}} \mathrm{Fe(CH_3CH_2COO)_3}$$

$$\xrightarrow{503\ \mathrm{K}} \mathrm{Fe^{II}(CH_3CH_2COO)_2} \xrightarrow{843\ \mathrm{K}} \alpha\text{-}\mathrm{Fe_2O_3}.$$

Figure 6 shows the simultaneous DTG–DTA–TG curves of iron(III) butyrate trihydrate. There are two endothermic peaks in the DTA plot at 383 and 643 K and two exothermic peaks at 583 and 773 K. There are corresponding peaks in the DTG plot, indicating that the thermal effects are accompanied by weight losses.

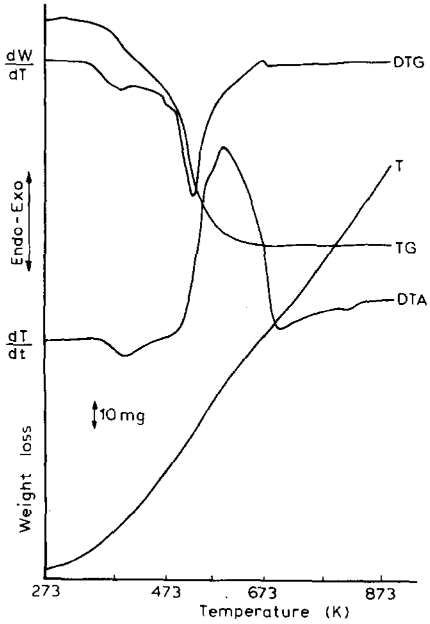

Fig. 5. Simultaneous DTG–DTA–TG curves of iron(III) propionate trihydrate at a heating rate of 10°min^{-1}.

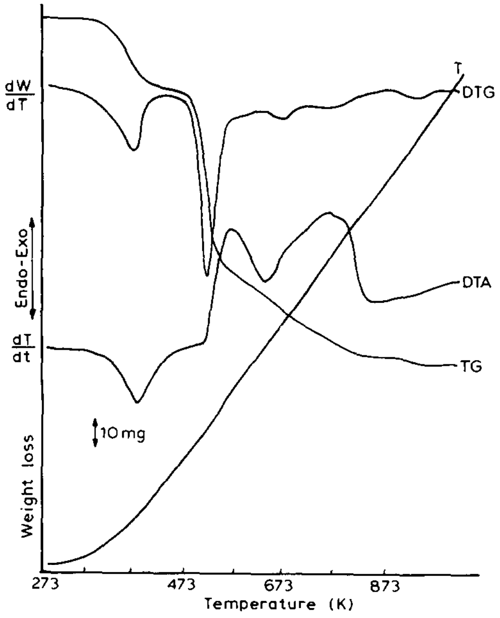

Fig. 6. Simultaneous DTG–DTA–TG curves of iron(III) butyrate trihydrate at a heating rate of 10°min^{-1}.

The first endothermic peak is at 383 K (with T_i at 365 K and T_f at 433 K). The TG curve at 433 K shows a loss of 15.0% corresponding to the elimination of three water molecules of crystallisation (calcd. loss = 14.6%). The TG curve at 523 K shows a loss of 37.5% indicating the formation of iron(II) butyrate, $Fe(C_4H_7O_2)_2$, (calcd. loss = 38.0%). The existence of iron(II) species has also been confirmed by Mössbauer spectroscopic technique as shown in Fig. 2b.

The TG curve corresponding to the DTA peak at 643 K shows a loss of 61.3% indicating the formation of $Fe_2(CO_3)_3$ [16] which is not as stable as indicated by the TG curve. This ultimately decomposes to form Fe_2O_3 at 843 K showing a loss of 76.9% (calcd. loss = 77.4%). The ultimate thermolysis product is α-Fe_2O_3 as confirmed by Mössbauer spectroscopic technique and chemical analysis.

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