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

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ABSTRACT

The thermal decomposition of iron(III) succinate, $Fe_2(C_4H_4O_4)_2(OH)_2$ and iron(III) adipate pentahydrate, $Fe_2(C_6H_8O_4)_3 \cdot 5\ H_2O$, has been investigated at different temperatures for different time intervals in static air atmosphere using Mössbauer spectroscopy and nonisothermal techniques (DTG–DTA–TG). The reduction of iron(III) to iron(II) species has been observed at 533 K and 563 K in the case of iron(III) succinate and iron(III) adipate, respectively. At higher temperatures, α-Fe_2O_3 is formed as the final thermolysis product.

INTRODUCTION

Derivative and simultaneous thermoanalytical methods of analysis [1] in combination with other techniques [2] have provided extremely useful information. Thus Mössbauer spectroscopy is currently employed to supplement studies from the thermal analysis of solids containing iron metal [3]. Recently the presence of iron(II) has been revealed from Mössbauer spectra which was only inferred from thermoanalytical studies [4]. In a previous study [5] it was shown that Fe(II) is formed as an intermediate during the thermal decomposition of iron(III) monocarboxylates. The present study deals with the decomposition of iron(III) dicarboxylates(succinate and adipate) where Fe(II), which could not be even inferred from thermal analysis, has been found.

EXPERIMENTAL

Iron(III) succinate and iron(III) adipate were prepared using the methods described previously [6,7]. The complexes were identified by chemical analysis and IR spectra. The percentage of iron determined gravimetrically [8] and the percentages of carbon and hydrogen determined by microanalysis are

Compound	Observed value	Calculated value
$Fe_2(C_4H_4O_4)_2(OH)_2$	Fe = 29.7, C = 25.4, H = 2.6	Fe = 29.6, C = 25.4, H = 2.7
$Fe_2(C_6H_8O_4)_3 \cdot 5\ H_2O$	Fe = 17.6, C = 34.7, H = 6.0	Fe = 17.7, C = 34.1, H = 5.4

The IR spectra of these complexes were recorded on a spectro MOM-2000 spectrophotometer (Hungarian Optical Works, Hungary) in nujol mulls. The IR spectrum of iron(III) succinate showed a broad band at 3100 cm^{-1} due to coordinated (OH) stretching, a strong band at 1580 cm^{-1} due to $\nu_{asy}(C{=}O)$, and bands at 1430 and 1310 cm^{-1} due to $\nu_{sym}(C{=}O)$ of the coordinated carboxylate groups. In the case of iron(III) adipate pentahedrate, the IR spectrum exhibited a broad band at 3250 cm^{-1} due to ν(OH) of water molecules, an intense band at 1560 cm^{-1} due to $\nu_{asy}(C{=}O)$, and bands at 1430 and 1315 cm^{-1} due to $\nu_{sym}(C{=}O)$ of the coordinated carboxylate ligands [9].

Nonisothermal analysis was performed by means of a Paulik–Paulik–Erdey MOM derivatograph (Hungary). Two-hundred mg of iron(III) succinate and 170 mg of iron(III) adipate were taken for non-isothermal runs at 200 mg sensitivity with a heating rate of 10°C min^{-1} in static air atmosphere.

For the Mössbauer study, the samples were heated isothermally in silica crucibles at different temperatures for different intervals of time in a muffle furnace under an atmosphere of static air. Experimental details of the Mössbauer investigation have been reported previously [5]. The values of isomer shift have been reported with respect to natural iron. All the spectra were recorded at 298 ± 2 K. 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.

RESULTS AND DISCUSSION

Mössbauer study

The Mössbauer spectra of iron(III) succinate and iron(III) adipate pentahydrate at room temperature consist of a doublet [Figs. 1(a) and 3(a)] with isomer shift and quadrupole splitting values of 0.40 and 0.53 mm s^{-1} respectively in the case of iron(III) succinate, and 0.42 and 0.64 mm s^{-1}, respectively, in the case of iron(III) adipate. The higher value of quadrupole splitting for iron(III) adipate compared to iron(III) succinate may be due to its more complicated chemical structure [10].

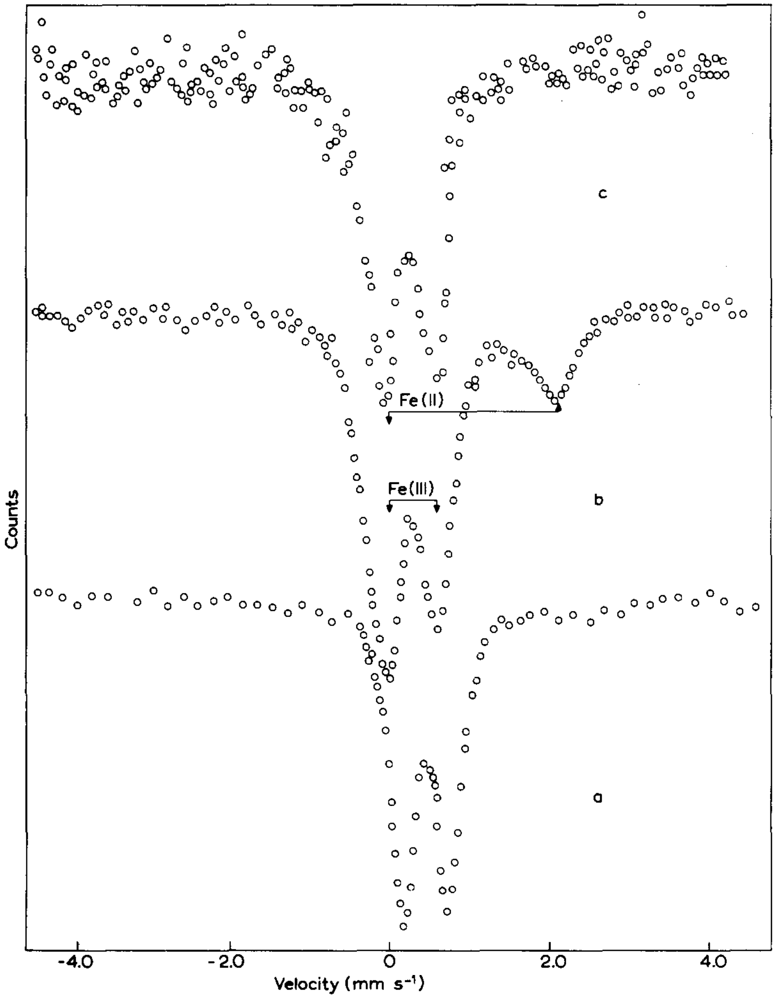

Fig. 1. Mössbauer spectra of iron(III) succinate (a) at room temperature (298 ± 2 K); (b) heated at 533 K for 8 min; (c) heated at 623 K for 10 min.

The Mössbauer spectrum of iron(III) succinate heated at 533 K for 8 min represents two quadrupole doublets (Fig. 1b), one with isomer shift and quadrupole splitting values of 1.11 and 2.08 mm s^{-1}, respectively, indicating the formation of iron(II) species [3,5], and the other doublet due to the parent complex. The Mössbauer spectrum of the sample heated at 623 K for 10 min consists of a doublet [Fig. 1(c)] with isomer shift and quadrupole splitting values of 0.30 and 0.67 mm s^{-1}, respectively. The values are in good agreement with the reported values for α-Fe_2O_3 with a particle size less than 10 nm [11]. No significant change in Mössbauer parameters was observed for the sample heated at 673 K for 5 min. In the case of the sample heated at 883 K for 1 h the Mössbauer spectrum showed a six-line pattern due to magnetic hyperfine splitting (Fig. 2) with isomer shift, quadrupole splitting

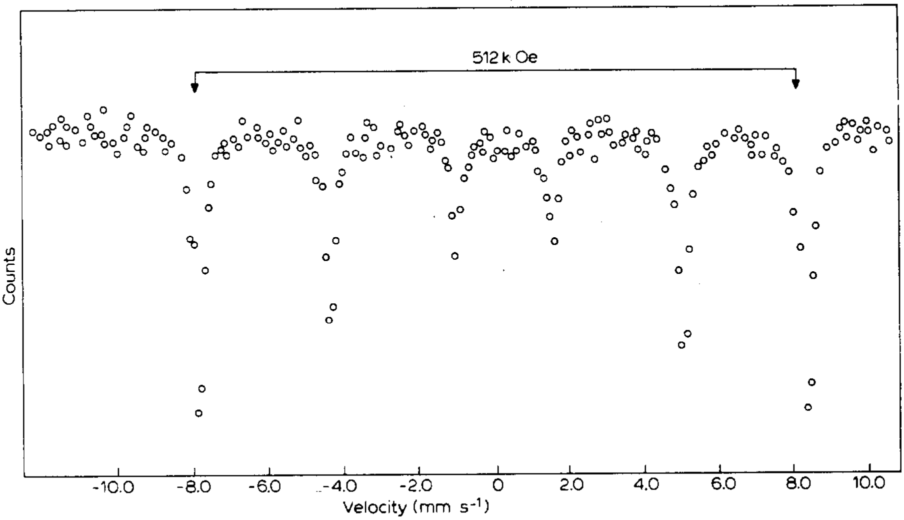

Fig. 2. Mössbauer spectrum of iron(III) succinate heated at 883 K for 1 h.

and internal magnetic field values of 0.31 mm s^{-1}, 0.20 mm s^{-1} and 512 kOe, respectively. These values are in close agreement with the formation of α-Fe_2O_3 [12–14]. No noticeable change was observed in Mössbauer parameters on further heating the sample.

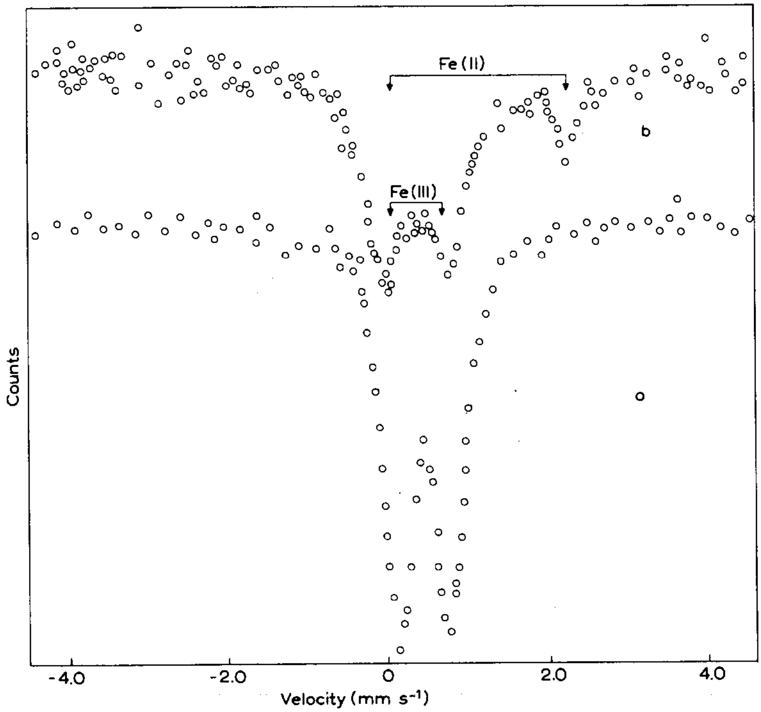

Fig. 3. Mössbauer spectra of iron(III) adipate pentahydrate (a) at room temperature (298 ± 2 K); (b) heated at 563 K for 7 min.

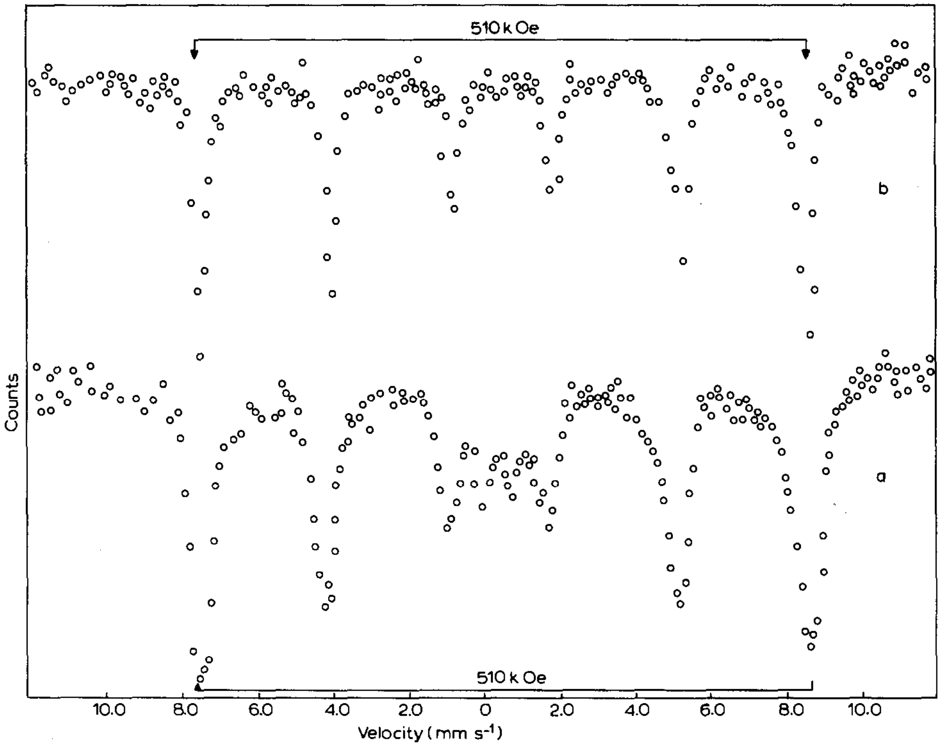

Fig. 4. Mössbauer spectra of iron(III) adipate pentahydrate heated at (a) 633 K for 5 min; (b) 793 K for 5 min.

The Mössbauer spectrum of iron(III) adipate pentahydrate heated at 563 K for 7 min exhibits two quadrupole doublets [Fig. 3(b)], one with isomer shift and quadrupole splitting values of 1.20 and 2.36 mm s^{-1} respectively, indicating the formation of iron(II) species [3,5], and the other doublet due to the parent compound. A similar reduction of iron(III) oxalate to iron(II) during thermal decomposition using Mössbauer spectroscopy has been reported in the literature [3]. The Mössbauer spectrum of the sample heated at 633 K for 5 min represents a six-line pattern along with a central doublet [Fig. 4(a)] with isomer shift, quadrupole splitting and internal magnetic field values of 0.40 mm s^{-1}, 0.10 mm s^{-1} and 510 kOe, respectively, indicating the formation of α-Fe_2O_3 [12–14]. The central doublet shows isomer shift and quadrupole splitting values of 0.40 and 0.70 mm s^{-1}, respectively, which is also due to α-Fe_2O_3 with a particle size less than 10 nm [11]. For the sample heated at 793 K for 5 min, the Mössbauer spectrum exhibits a six-line pattern [Fig. 4(b)] associated with magnetic hyperfine interaction with isomer shift, quadrupole splitting and internal magnetic field values of 0.35 mm s^{-1}, 0.20 mm s^{-1} and 510 kOe, respectively. These values are in good agreement with the reported values for α-Fe_2O_3 [12–14]. No significant change was observed in the Mössbauer parameters on further heating. Thus, the ultimate product of thermolysis of iron(III) adipate pentahydrate is α-Fe_2O_3, similar to that observed for iron(III) propionate and iron(III) butyrate [5].

Derivatographic study

Figure 5 shows the simultaneous DTA–TG plot of iron(III) succinate. The DTA shows one endothermic peak at 393 K and exothermic peaks at 583, 693, 793 and 883 K. The TG plot at 523 K shows a weight loss of 31.0%, indicating the reduction of iron(III) to iron(II) succinate (calculated loss 30.7%). It is proposed that $Fe_2(II)\ (C_4H_4O_4)(OH)_2$ is formed as an intermediate during the decomposition of $Fe_2(C_4H_4O_4)_2(OH)_2$. The formation of iron(II) species is supported by the Mössbauer spectroscopic technique [Fig. 1(b)]. Further decomposition of the sample is a complicated multistep process. TG shows a weight loss of 57.0% at 883 K corresponding to the formation of Fe_2O_3 (calculated loss 57.8%). The oxide formed at this temperature is α-Fe_2O_3, as confirmed by Mössbauer spectroscopy (Fig. 2).

Figure 6 shows the simultaneous DTG–DTA–TG curves of iron(III)

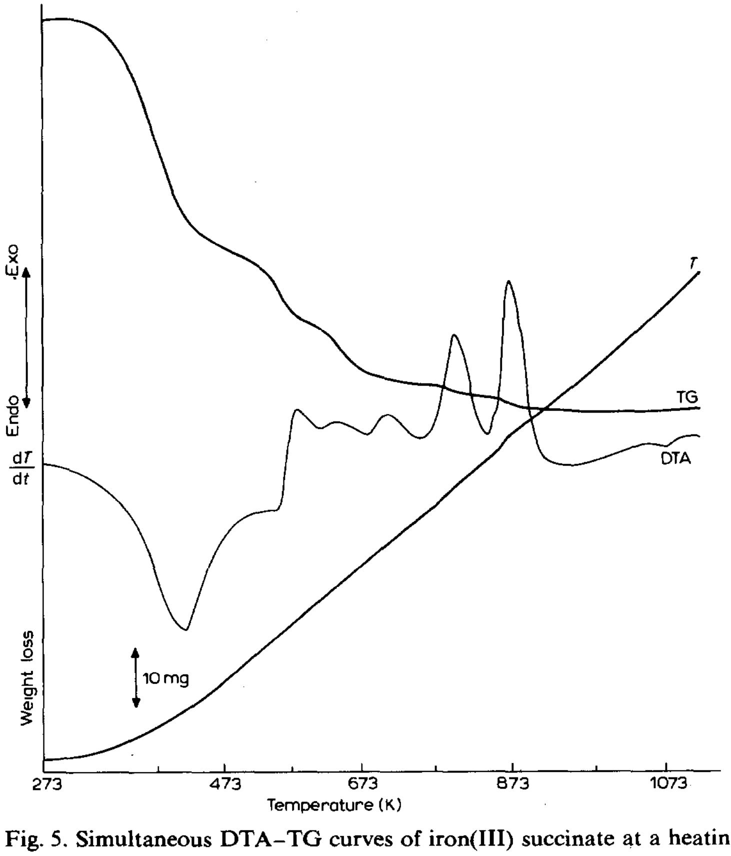

Fig. 5. Simultaneous DTA–TG curves of iron(III) succinate at a heating rate of 10°C min^{-1}.

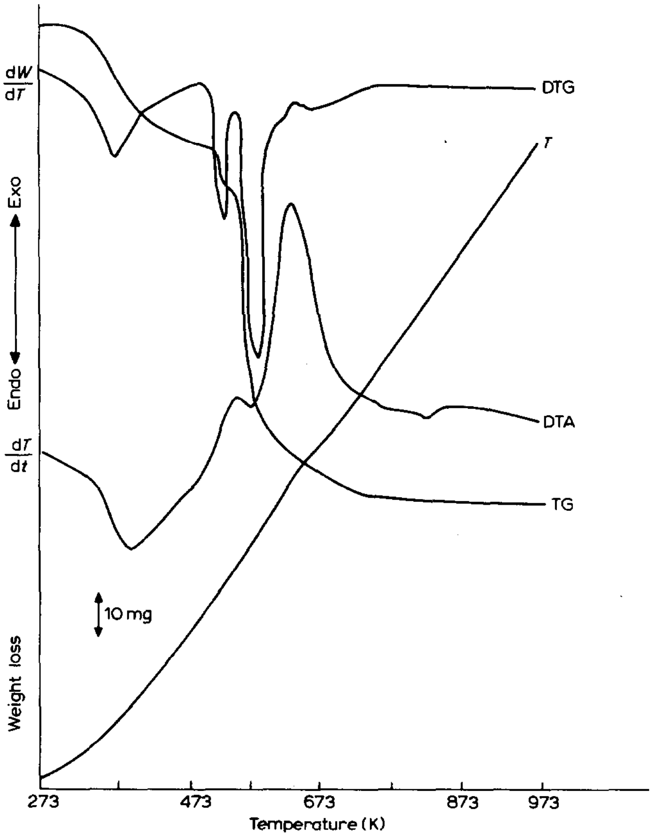

Fig. 6. Simultaneous DTG–DTA–TG curves of iron(III) adipate pentahydrate at a heating rate of 10°C min^{-1}.

adipate pentahydrate. The DTA curve shows endothermic peaks at 383 and 583 K and an exothermic peak at 643 K. There are peaks in the DTG curve corresponding to the peaks in the DTA curve, showing that the thermal changes are accompanied by weight losses. Dehydration of the sample starts at 333 K and is complete at 443 K. The TG curve at 443 K shows a loss of 14.1%, indicating the elimination of five molecules of water of crystallization (calculated loss 14.2%). TG could not show the formation of Fe(II) but it was confirmed from the Mössbauer spectrum [Fig. 3(b)]. The TG plot at 793 K shows a weight loss of 74.1%, indicating the formation of Fe_2O_3 (calculated loss 74.8%). The end product is α-Fe_2O_3, as confirmed by Mössbauer spectroscopy [Fig. 4(b)].

A comparison of the above thermal decomposition pattern with that of iron(III) monocarboxylates (propionate and butyrate) [5] shows that iron(III) dicarboxylates decompose at a higher temperature. This may be due to stronger covalent bonding, i.e. the bidentate nature of the dicarboxylates compared to the monodentate nature of the monocarboxylates.

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