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MÖSSBAUER STUDY OF THE THERMAL DECOMPOSITION OF IRON(III) BENZOATE AND IRON(III) FUMARATE

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ABSTRACT

The thermal decomposition of iron(III) benzoate, $Fe(C_7H_5O_2)_3$, and iron(III) fumarate pentahydrate, $Fe_2(C_4H_2O_4)_3$ 5 H_2O, containing uni- and bidentate ligands, respectively, has been investigated at various temperatures for different intervals of time in a static air atmosphere. Thermolysis of these compounds leads directly to the formation of α-Fe_2O_3 in the case of iron(III) benzoate and Fe_3O_4 in the case of iron(III) fumarate as the ultimate products, thus without undergoing reduction to the iron(II) state.

INTRODUCTION

Mössbauer spectroscopy is an effective tool for detecting the changes in oxidation states, bonding and local environment of iron complexes during thermal decomposition. The combination of this technique with derivatographic methods (DTG–DTA–TG) provides very useful information concerning the structure of intermediates and products. In previous work on the thermal decomposition of iron(III) monocarboxylates [1], iron(III) dicarboxylates [2] and iron(III) tricarboxylate (citrate) [3], the formation of iron(II) species as an intermediate has been detected. To investigate whether the formation of iron(II) can be generalized or not, the thermal decomposition of more carboxylates is being studied. The present investigation deals with the thermolysis of iron(III) benzoate and iron(III) fumarate employing Mössbauer spectroscopy and non-isothermal techniques (DTG–DTA–TG).

EXPERIMENTAL

Iron(III) benzoate, $Fe(C_7H_5O_2)_3$, and iron(III) fumarate pentahydrate, $Fe_2(C_4H_2O_4)_3 \cdot 5\ H_2O$, were prepared by the addition of equimolar propor-

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TABLE 1

Microanalysis results for the iron(III) benzoate and iron(III) fumarate samples

Compound	Fe(%)		C(%)		H(%)	
	Found	Calcd.	Found	Calcd.	Found	Calcd.
$Fe(C_7H_5O_2)_3$	13.8	13.4	51.6	51.5	3.6	3.6
$Fe_2(C_4H_2O_4)_3 \cdot 5\ H_2O$	19.8	20.6	26.5	26.5	3.0	3.0

tions of ferric chloride (AR) solution to aqueous solutions of sodium benzoate and sodium fumarate, respectively, keeping the pH of the solutions at 5.5. The precipitates of these compounds formed in the cold were separated by filtration and dried in air. These compounds were identified by IR spectroscopy and chemical analysis. The percentage of iron was determined gravimetrically [4]. Microanalysis gave the percentages of iron, carbon and hydrogen shown in Table 1.

The IR spectra were recorded on a MOM-2000 spectrophotometer (Hungarian Optical Works, Hungary) in nujol mulls in the region 4000–700 cm^{-1}. The IR spectrum of iron(III) benzoate shows a band at 3100 cm^{-1} due to C–H stretching of the aromatic ring, two sharp bands at 1650 and 1610 cm^{-1} due to $\nu_{asym}(C{=}O)$ and a strong band at 1460 cm^{-1} due to $\nu_{sym}(C{=}O)$ of the coordinated carboxylate groups. The IR spectrum of iron(III) fumarate pentahydrate shows a band at 3200 cm^{-1} due to (OH) stretching of water molecules, and an intense band at 1600 cm^{-1} due to $\nu_{asym}(C{=}O)$ of the coordinated carboxylate ligands [5].

Non-isothermal analysis was performed on a Paulik–Paulik–Erdey MOM derivatograph (Hungary) with 160 mg of iron(III) benzoate and 200 mg of iron(III) fumarate pentahydrate at 200 mg sensitivity in a static air atmosphere and at a heating rate of 10°C min^{-1}. For the Mössbauer study the samples were heated in silica crucibles at different temperatures for different time intervals in a muffle furnace.

Experimental details of the Mössbauer investigation have been reported previously [1]. 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 spectroscopic study

The Mössbauer spectra of iron(III) benzoate and iron(III) fumarate pentahydrate exhibit a doublet at room temperature (Figs. 1a and 3). The isomer shift and quadrupole splitting values for iron(III) benzoate and iron(III) fumarate pentahydrate are 0.40 and 0.60 mm s^{-1}, respectively, the values are in agreement with the reported values for the high-spin octahedral iron(III) complexes [6].

The Mössbauer spectrum of iron(III) benzoate heated at 573 K for 10 min consists of a doublet (Fig. 1b) with isomer shift and quadrupole splitting values of 0.30 and 0.69 mm s^{-1}, respectively. These values are in close agreement with the reported values of isomer shift (0.30 mm s^{-1}) and quadrupole splitting (0.68 mm s^{-1}) for α-Fe_2O_3 with a particle size less than

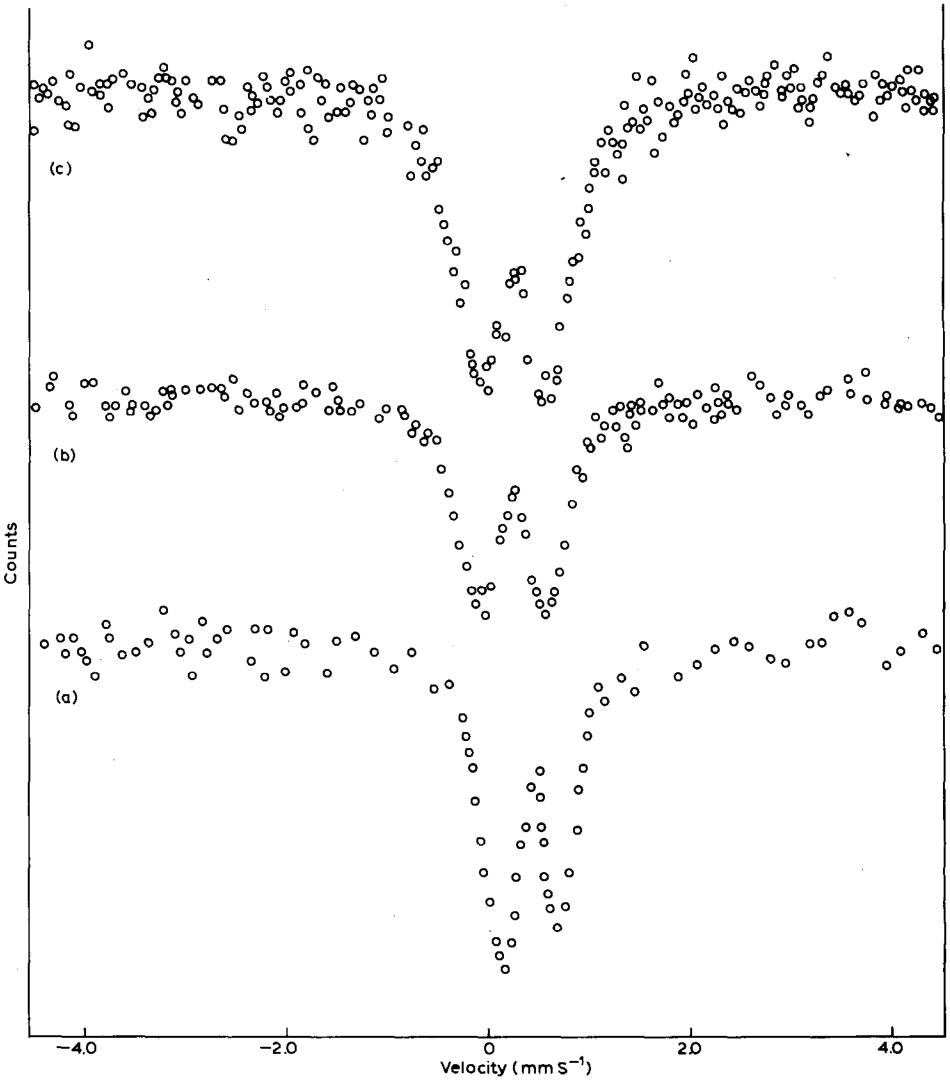

Fig. 1. Mössbauer spectra of iron(III) benzoate (a) at room temperature (298 ± 2 K); (b) heated at 573 K for 10 min; (c) heated at 663 K for 5 min.

10 nm [7]. No significant change in the Mössbauer parameters was observed for the sample heated at 663 K for 5 min (Fig. 1c). The Mössbauer spectrum of the final residue of the compound obtained on heating at 1073 K for 1 h exhibits a six-line pattern (Fig. 2) due to magnetic hyperfine interaction, with isomer shift and internal magnetic field values of 0.36 mm s^{-1} and 514 KOe, respectively. These values are comparable to the reported values for α-Fe_2O_3 with bulk size [8–10]. Thus the above results reveal that there is an increase in particle size of α-Fe_2O_3 on heating from 573 to 1073 K. Kundig et al. [7] have reported the room temperature Mössbauer spectra of α-Fe_2O_3 as a function of average particle size ranging from less than 10 nm to bulk. When the particle size approaches 10 nm, the magnetic hyperfine splitting is not observed and the spectrum exhibits only a doublet due to a decreasing relaxation time with decreasing particle size. As the particle size is gradually increased, a six-line hyperfine spectrum of increasing intensity appears, and for bulk oxide a symmetrical six-line pattern has been observed.

The Mössbauer spectrum of iron(III) fumarate pentahydrate at room temperature consists of a doublet (Fig. 3). The spectrum of the final residue of the sample obtained by heating at 873 K for 1 h shows two sets of six magnetic hyperfine resonance lines (Fig. 4) due to the formation of Fe_3O_4. The set of lines with the higher value of internal magnetic field (502 KOe) is attributed to the Fe^{3+} ions on tetrahedral sites, and the other set with the lower magnetic field value (471 KOe) is attributed to the Fe^{2+} and Fe^{3+} ions on octahedral sites [11]. The fact that the Mössbauer spectra of the Fe^{3+} and Fe^{2+} octahedral sites are indistinguishable is due to the rapid electron exchange between these ions above 120 K [12]. The central doublet observed in the Mössbauer spectrum with isomer shift and quadrupole splitting values

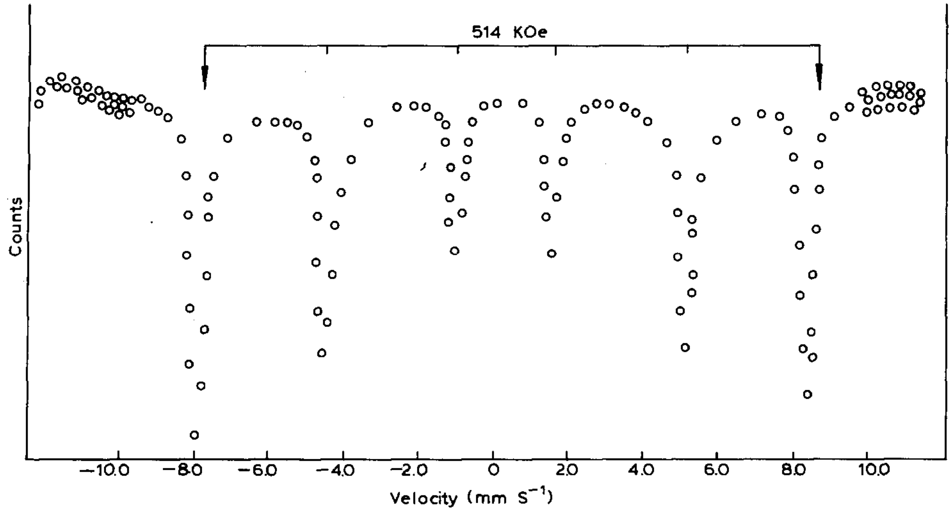

Fig. 2. Mössbauer spectrum of iron(III) benzoate heated at 1073 K for 1 h.

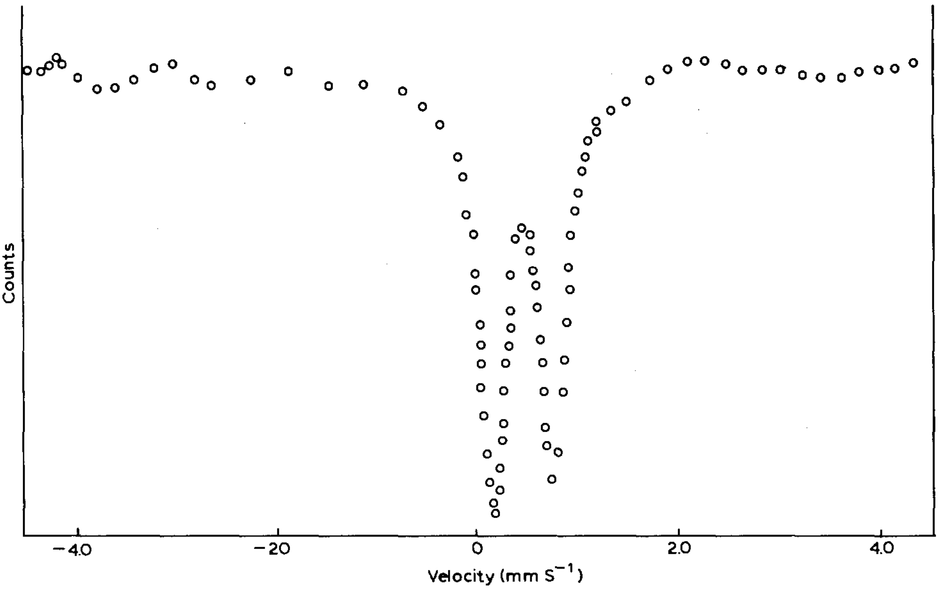

Fig. 3. Mössbauer spectrum of iron(III) fumarate pentahydrate at room temperature (298 ± 2 K).

of 0.30 and 0.51 mm s^{-1}, respectively, is also due to a small fraction of amorphous α-Fe_2O_3 [7]. Thus a mixture of iron(III) oxides with different particle sizes is formed at 873 K.

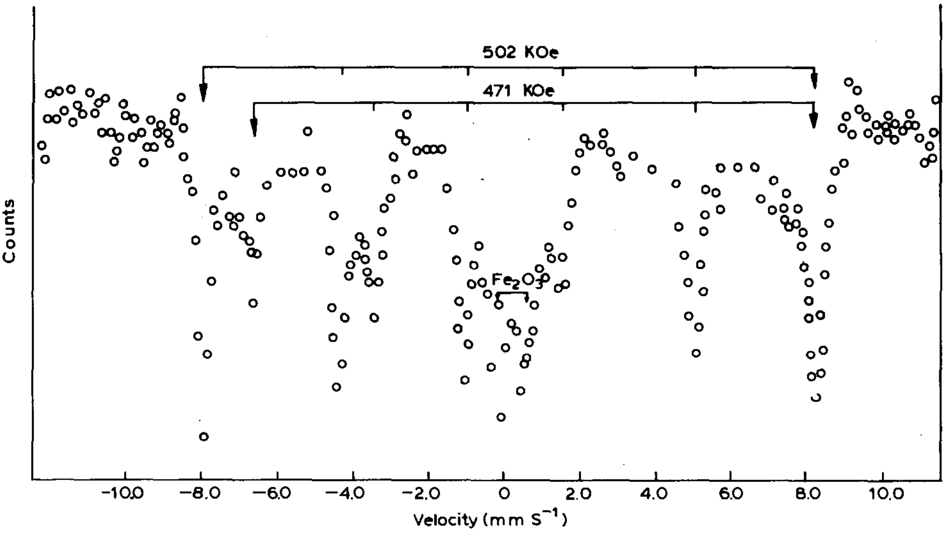

Fig. 4. Mössbauer spectrum of iron(III) fumarate pentahydrate heated at 873 K for 1 h.

Derivatographic study

Figure 5 shows the simultaneous DTA–TG plot of iron(III) benzoate. There are two endothermic peaks at 403 and 843 K and three exothermic peaks at 603, 673 and 743 K. The TG curve at 403 K shows a weight loss of 34.0% but the intermediate formed at this stage is very unstable and readily decomposes further, as shown by the arrest in the TG curve. Thus no stable intermediate has been detected even by the Mössbauer spectroscopic technique. The final weight loss of 80.0% above 843 K corresponds to the formation of Fe_2O_3 (calcd. loss = 80.9%). The oxide formed is α-Fe_2O_3, as confirmed by Mössbauer spectroscopy (Fig. 2) and chemical analysis.

Figure 6 shows the simultaneous DTG–DTA–TG curves of iron(III) fumarate pentahydrate. The DTG curve shows three distinct peaks at 398, 523 and 633 K. The DTA curve shows an endothermic peak at 413 K and a broad exothermic region between 503 and 778 K. The TG curve shows a

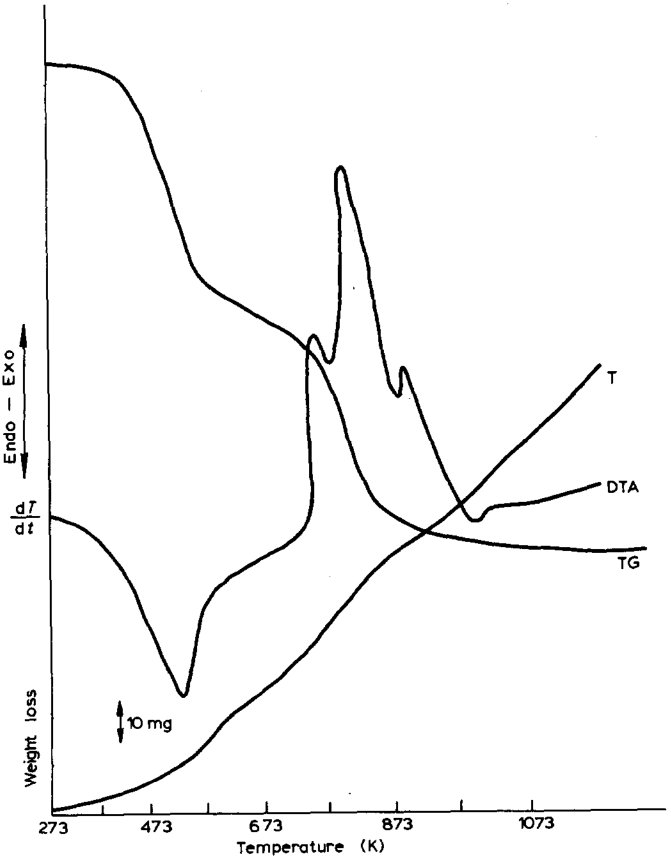

Fig. 5. Simultaneous DTA–TG curves of iron(III) benzoate at a heating rate of 10°C min^{-1}.

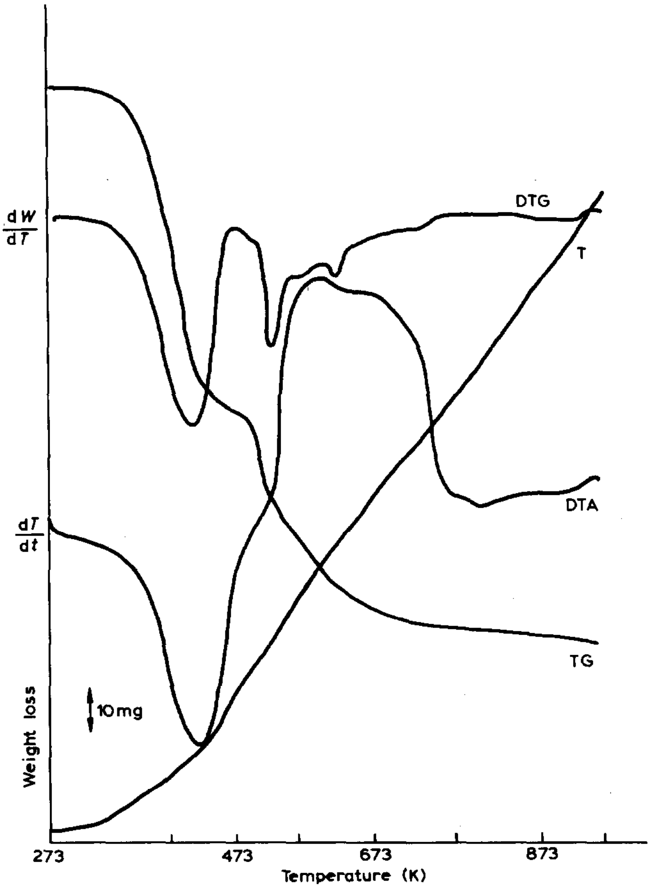

Fig. 6. Simultaneous DTG–DTA–TG curves of iron(III) fumarate pentahydrate at a heating rate of 10°C min^{-1}.

weight loss of 40.0% at 448 K, indicating the simultaneous removal of the five water molecules accompanied by one carboxylate group. Thus at this stage an unstable species of the type Fe(II)($C_4H_2O_4$) may be expected which could not be detected by Mössbauer spectroscopy. After this stage, the multi-step endothermic process starts, as shown by the DTA curve, and finally a weight loss of 72.0% at 963 K corresponding to the formation of Fe_3O_4 (calcd. loss = 71.6%) with a slight amount of α-Fe_2O_3 as confirmed by Mössbauer spectroscopy (Fig. 4) and chemical analysis.

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