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PHYSICO-CHEMICAL STUDIES ON THE THERMAL DECOMPOSITIONS OF IRON(III) PHTHALATES

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The thermal decompositions of basic salts of iron(III) *o*-phthalate sesquihydrate, $Fe(C_8H_4O_4)(OH)\cdot 1.5H_2O$, iron(III) *m*-phthalate trihydrate, $Fe(C_8H_4O_4)(OH)\cdot 3H_2O$, and iron(III) *p*-phthalate monhydrate, $Fe(C_8H_4O_4)(OH)\cdot H_2O$, have been investigated from ambient temperature up to 973 K in air using Mössbauer and infrared spectroscopy, derivatography (DTG-DTA-TG) and X-ray diffraction. The thermal decomposition proceeds without reduction to Iron(II) species in the cases of iron(III) *o*-phthalate and iron(III) *p*-phthalate, whereas iron(II) species have been detected in the case of basic iron(III) *m*-phthalate. α-Fe_2O_3 is formed as the end-product. Increase in the particle size of the α-Fe_2O_3 with increasing decomposition temperature has also been observed.

The thermal decomposition of iron carboxylates has become a fascinating subject of recent interest, due to their wide use as medicinal agents and as antiseptics [1, 2]. Mössbauer spectroscopy is an effective tool for detecting the changes in oxidation state, bonding and local environment of iron atoms during thermal decomposition [3]. In combination with other methods (derivatography, X-ray diffraction, etc.) this technique provides useful information about the nature of the intermediates formed during thermal decomposition. Since Mössbauer parameters are very sensitive to the size of iron oxide particles, it is possible to select a catalyst from particle size studies. With the above facts in mind, a systematic study of the thermal decomposition of iron carboxylates has been started [4, 5]. The present investigation deals with the thermolysis of hydrated basic iron(III) *o*-, *m*- and *p*-phthalates, employing Mössbauer and infrared spectroscopy, derivatography (DTG-TGA- TG) and X-ray diffraction.

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Experimental

Iron(III) *o*-phthalate was prepared by the method reported elsewhere [6]. For the preparation of iron(III) *m*- and *p*-phthalates, equimolar aqueous solutions of iron(III) chloride (AR) and sodium *m*-phthalate or sodium *p*-phthalate were mixed. The precipitates formed were washed with distilled water several times to remove chloride ions, and dried in air. The identities of the compounds were established by infrared spectroscopy and chemical analysis. The percentage of iron was determined spectrophotometrically, using the 1,10-phenanthroline method [7]. The percentages of carbon, hydrogen and iron are listed in Table 1.

Table 1 Analytical data on iron(III) phthalates

Compound		%C	%H	%Fe
o-phthalate	calcd.	36.30	2.95	21.20
	obsd.	36.50	2.48	21.00
m-phthalate	calcd.	32.99	3.78	19.24
	obsd.	32.96	3.65	18.92
p-phthalate	calcd.	37.60	2.73	21.96
	obsd.	37.82	2.75	21.80

The infrared spectra were recorded on a spectrophotometer (Pye Unicam Ltd., England) in the range 4000–200 cm^{-1}, using the KBr pellet technique.

Non-isothermal analysis was performed on a Paulik–Paulik–Erdey MOM derivatograph (Hungary) with 102 mg of iron(III) *o*-phthalate, 110 mg of iron(III) *m*-phthalate or 160 mg of iron(III) *p*-phthalate in a static air atmosphere at a heating rate of 10 deg min^{-1}. For Mössbauer study, the samples were heated in a silica crucible at different temperatures, i.e. 473, 573, 673 and 973 K, for 2 hours in a muffle furnace.

The experimental details of the Mössbauer investigation have been reported previously [4, 5]. The isomer shift values are reported with respect to natural iron. All the spectra were recorded at 298 ± 2 K.

The X-ray diffraction analyse of the final thermal decomposition products were done using CuK_α radiation.

Results and discussion

(i) Mössbauer and infrared spectroscopic study

The Mössbauer spectra of the iron(III) phthalates consist of a doublet (Figs 1 and 3A). The isomer shift and quadrupole splitting values for iron(III) *o*-phthalate are 0.32 and 0.77 mm/s; for iron(III) *m*-phthalate 0.38 and 0.74 mm/s; and for iron(III) *p*-phthalate 0.34 and 0.97 mm/s, respectively. These values are in agreement with the values reported for high-spin iron(III) octahedral complexes [8].

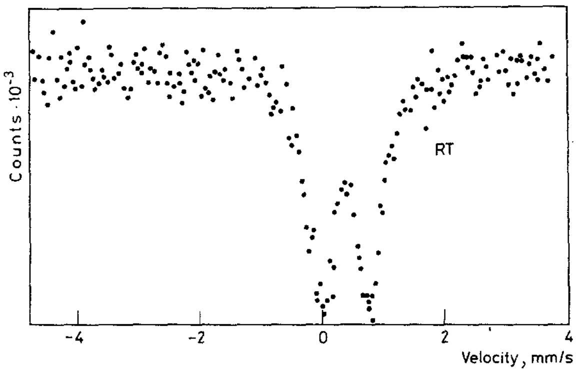

Fig. 1 Mössbauer spectrum of iron(III) *o*-phthalate sesqui-hydrate at 298 K

For iron(III) *o*-phthalate, a very broad band is observed in the region 2700–3700 cm^{-1}; with a shoulder at about 3420 cm^{-1}, which is attributed to the presence of the coordinated OH group. This broad region also includes the ν(OH) due to lattice water and the ν(C—H) of the aromatic ring [9]. The presence of a coordinated OH group is also confirmed by the presence of a weak band (bending) at 1150 cm^{-1}. The strong bands at 1565 cm^{-1} and 1420 cm^{-1} are due to the presence of the $\nu_{asym}(C=O)$ and $\nu_{sym}(C=O)$ of the coordinated carboxylate group [10]. A sharp band at 495 cm^{-1} indicates the presence of ν(M—O) bonding. The infrared spectra of iron(III) *m*-phthalate and iron(III) *p*-phthalate are comparable to that of iron(III) *o*-phthalate.

For the samples heated at 473 K, increases in the Mössbauer parameters are observed, due to the dehydration of the compounds. A similar observation has been reported in the literature [11, 12].

The Mössbauer spectrum of iron(III) *o*-phthalate heated at 573 K exhibits a six-line pattern along with a central doublet (Fig. 2A), due to magnetic hyperfine interaction, with isomer shift and quadrupole splitting values of 0.31 and 0.78 mm/s, respectively. These values are in good agreement with the reported values for α-Fe_2O_3 with an average particle size of $13.5+1$ nm [13]. In addition to the brown α-Fe_2O_3, another needle-shaped white product is obtained on the walls of a the silica crucible. The identity of this compound has been confirmed by infrared spectroscopy and melting point determination; it is phthalic anhydride [14].

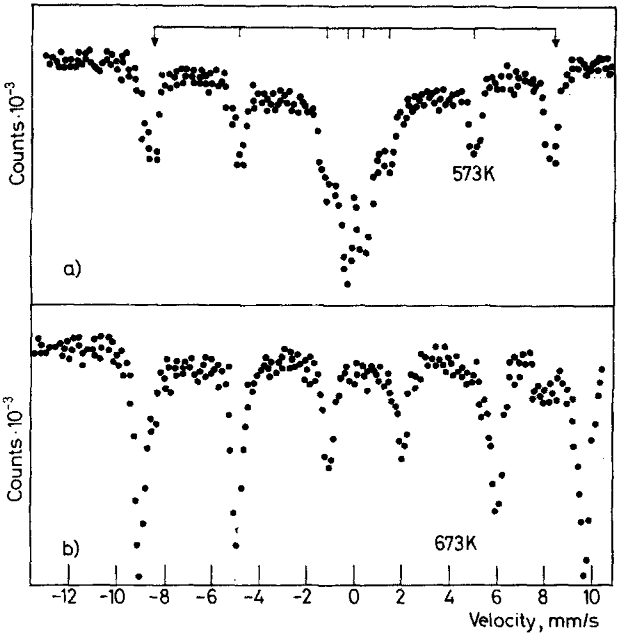

Fig. 2 Mössbauer spectra of iron(III) *o*-phthalate sesqui-hydrate heated at: (a) 573 K; (b) 673 K

The Mössbauer spectrum of iron(III) *m*-phthalate heated at 573 K for 2 hours exhibits two quadrupole doublets (Fig. 3B), one with isomer shift and quadrupole splitting values of 1.32 and 2.60 mm/s, indicating the formation of iron(II) species, and the other doublet due to the presence of the parent compound.

In the case of iron(III) *p*-phthalate heated at 573 K, a six-line pattern along with a central doublet is observed in the Mössbauer spectrum. The Mössbauer parameters are in agreement with the values reported for α-Fe_2O_3 with an average particle size of 15 ± 1 nm [13]. The formation of a white product besides α-Fe_2O_3 is also observed, the infrared parameters and melting point of which are in good agreement with those reported for terephthalic acid [14].

The Mössbauer spectra of all three compounds heated at 673 K consist of a symmetrical six-line pattern (Fig. 2B), due to magnetic hyperfine interaction. The values of the Mössbauer parameters are in close agreement with the values reported

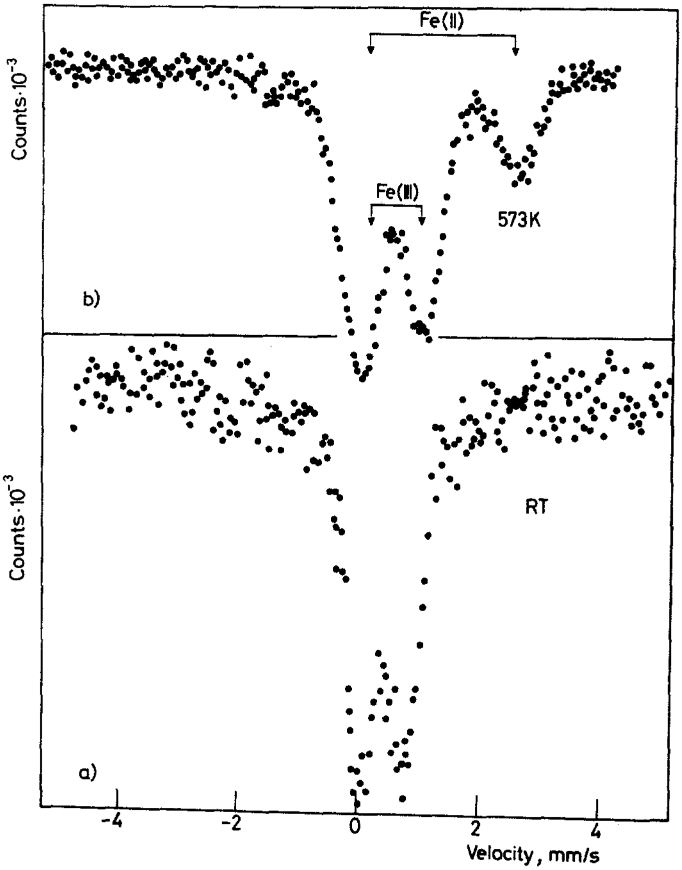

Fig. 3 Mössbauer spectra of iron(III) *m*-phthalate trihydrate. (a) at 298 K; (b) heated at 573 K

for α-Fe_2O_3 of bulk size [15–17]. No further change in the Mössbauer parameters is observed on heating up to 973 K.

For all three compounds, an increase in particle size is observed on going from 573 K to 673 K, which is due to the fact that the heat treatment results in the growth of small particles to large crystallites of α-Fe_2O_3, and the microstructural variations involved in this growth cause slight changes in the bonding and site symmetry of the iron, as indicated by shifts in the Mössbauer parameters.

(ii) Derivatographic study

Figure 4 shows the simultaneous DTG, DTA and TG plots of iron(III) *o*-phthalate. The DTG curve exhibits two peaks, at 353 K and 573 K. The DTA curve reveals two broad regions, due to endo and exothermic changes in the ranges 333 to

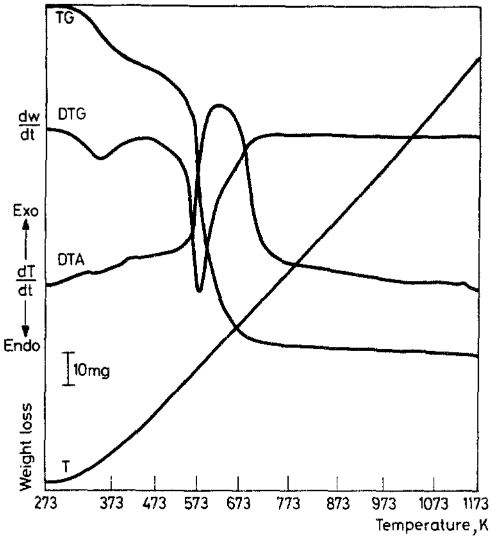

Fig. 4 Simultaneous DTG, DTA and TG curves of iron(III) *o*-phthalate sesqui-hydrate at a heating rate of 10 deg min^{-1}

433 K and 513 to 763 K, respectively. The TG curve shows a weight loss of 10.5% at 400 K, indicating the removal of 1.5 lattice water molecules (calcd. loss 10.2%). After dehydration, the TG curve displays a continuous loss of mass and finally a weight loss of 70.0% is observed at 1073 K, which is in close agreement with the loss of 70.0% calculated for the formation of Fe_2O_3. These results may be compared with the thermal analysis curves for *o*-phthalic acid and its anhydride, which are reported elsewhere [18]. The acid melts and dehydrates at 468 K to give the anhydride, which boils at 553 K. It is seen that the exothermic region in Fig. 4 is in the boiling (also condensation) range of *o*-phthalic anhydride. The anhydride was also obtained under isothermal heating. The endothermic process of boiling is superimposed by a large exothermic effect in the same region, due to the oxidation of Fe(II) to Fe_2O_3. The oxide formed is α-Fe_2O_3, as confirmed by Mössbauer spectroscopy and the X-ray diffraction pattern (Table 2).

Figure 5 shows the simultaneous DTG, DTA and TG curves of iron(III) *m*-phthalate. The DTG curve contains two peaks, at 353 K and 513 K, in the endothermic region, and three peaks one after the other in the exothermic region. The corresponding DTA curve reveals two broad endotherms in this range and a broad exothermic region. The TG curve corresponding to the first endotherm gives a loss of 18.6%, indicating the removal of three water molecules (calcd. loss 18.5%). Another arrest (a change in slope) in the TG curve at a loss of 25.0%, at 573 K, is due to the elimination of OH, resulting in the formation of an iron(II) species, as

Table 2 X-ray data on the final products of thermal decomposition of iron(III) phthalates

Experimental		Literature	
d values, Å	Intensity	*d* values, Å	Intensity
3.67	20–25	3.66	25
2.69	100	2.69	100
2.51	47–52	2.51	50
2.20	20–30	2.20	30

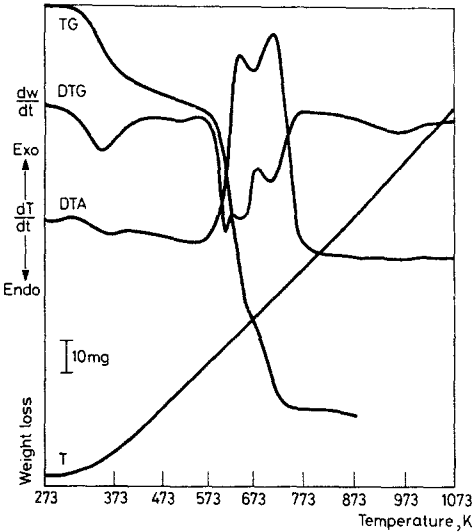

Fig. 5 Simultaneous DTG, DTA and TG curves of iron(III) *m*-phthalate trihydrate at a heating rate of 10 deg min^{-1}

confirmed by the Mössbauer spectrum (Fig. 3B). This occurs at a much lower temperature than the melting point of *m*-phthalic acid, i.e. 620.8 K. The further decomposition involves a two-step exothermic process where iron(II) is oxidized to iron(III) and gives Fe_2O_3 with a weight loss of 74.1% (calcd. loss 72%). The oxide formed is α-Fe_2O_3, as confirmed by X-ray diffraction and Mössbauer spectroscopy.

Figure 6 shows the simultaneous DTG, DTA and TG curves of iron(III) *p*-phthalate. The DTG curve has one peak at 393 K, due to dehydration, and peaks at 603, 653, 693 and 803 K due to decomposition. The corresponding DTA curve shows two broad endotherms at around 423 and 608 K, followed by a multistep decomposition, characterized by a very broad exotherm between 615 and 990 K. The TG curve reveals a weight loss of 6.3%, due to the removal of one water molecule (calcd. loss 7.0%). After dehydration, the decomposition is a multistep

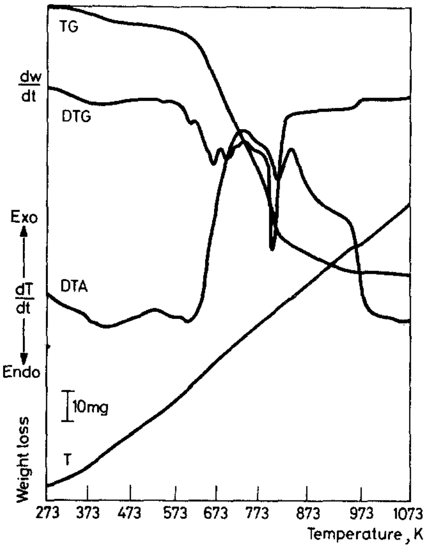

Fig. 6 Simultaneous DTG, DTA and TG curves of iron(III) *p*-phthalate monohydrate at a heating rate 10 deg min^{-1}

process and finally a weight loss of 68.8% is observed. The oxide formed is confirmed by X-ray diffraction (Table 2) and Mössbauer spectroscopy to be α-Fe_2O_3.

The isothermal heating of iron(III) terephthalate gives phthalic acid as a sublimate, and the thermal curves of terephthalic acid [19] show that it melts at 583–683 K and does not decompose till above 1073 K. From a comparison of these results with those in Fig. 6, it is concluded that anhydrous iron(III) terephthalate gives phthalic acid in an endothermic process in the region around 608 K, along with the oxidation of Fe(II) to Fe_2O_3 in the exothermic region.

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Zusammenfassung — Die thermische Zersetzung basischer Salze von Eisen(III)-*o*-phthalat-Sesquihydrat, $Fe(C_8H_4O_4)(OH)\cdot 1{,}5H_2O$, Eisen(III)-*m*-phthalat-Trihydrat, $Fe(C_8H_4O_4)(OH)\cdot 3H_2O$, und Eisen(III)-*p*-phthalat-Monohydrat, $Fe(C_8H_4O_4)(OH)\cdot H_2O$, wurden im Temperaturbereich von Raumtemperatur bis 973 K in Luft mittels Mössbauer- und IR-Spektroskopie, Derivatographie (DTG-DTA-TG) und Röntgendiffraktometrie untersucht. Im Gegensatz zu basischem Eisen(III)-*m*-phthalat erfolgt bei den entsprechenden *o*- und *p*-Phthalatverbindungen im Verlaufe der Zersetzung keine Reduktion zu Eisen(II)-Species. α-Fe_2O_3 wird als Endprodukt erhalten. Mit steigender Zersetzungstemperatur nimmt die Größe der α-Fe_2O_3-Partikel zu.

Резюме — Термическое разложение различных гидратов основных солей трехвалентного железа и фталевых кислот с общей формулой $Fe(C_8H_4O_4)(OH)\cdot xH_2O$, где $x = 1.5$, 3 и 1, соответственно, для *о*-, *м*- и *п*-фталатов, было изучено до температуры 973 К в атмосфере воздуха методами ДТГ, ДТА, ТГ, мёссбауэровской и инфракрасной спектроскопии и рентгенофазовым анализом. В случае *о*- и *п*-фталатов термическое разложение протекает без восстановления железа, тогда как разложение *м*-фталата сопровождается восстановлением железа до двухвалентного. В качестве конечного продукта разложения образуется α-Fe_2O_3. С увеличением температуры разложения наблюдалось увеличение размеров частиц образующегося α-Fe_2O_3.