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MÖSSBAUER EFFECT STUDIES ON THERMAL DECOMPOSITION OF IRON(III) HYDROXY- AND AMINO-BENZOATES

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Abstract

The thermal decomposition of iron(III) aminobenzoates (*o*-, *m*-, *p*-) and iron(III) hydroxybenzoates (*o*-, *m*-, *p*-) have been investigated from ambient temperature to 873 K in air using derivatography DTG-DTA-TG, Mössbauer, IR spectroscopy and XRD. The importance of Mössbauer spectra recorded at various stages of heating, without separating the product mixture, in studying the mode of decomposition is highlighted. The intermediates (e.g., Fe(II)-species) were confirmed. The nature of water of hydration and the order of stability (*p*->*m*->*o*-) have been investigated from decomposition temperatures. The kinetic model and parameters have been investigated for dehydration.

Keywords: iron(III) hydroxy-benzoates, iron(III) aminobenzoates, IR, Mössbauer spectroscopy, thermal decomposition, XRD

Introduction

The thermal decomposition of iron carboxylates is a fascinating subject 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 [4–6]. The present investigation deals with the thermolysis of Fe(III) amino-benzoates (*o*-, *m*-, *p*-) and Fe(III) hydroxy-benzoates (*o*-, *m*-, *p*-) employing Mössbauer and infrared spectoscopy, derivatography (TG-DTG-DTA) and X-ray diffraction.

Experimental

Fe(III) *o*-, *m*- and *p*- aminobenzoates were prepared according to the method of Dinsel and Sweet [7] by the precipitation reaction between iron(III) chloride (AR, BDH) and the respective acid (all A.R.; E. Merck). Basic iron(III) hydroxy benzo-

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Table 1 Analytical data for the composition (%) of iron(III) aminobenzoates monohydrates and iron(III) hydroxybenzoates

Compound	C	H	N	Fe	Acid
Basic iron(III) *o*-amino-	46.18	4.16	7.69	15.34	
benzoate monohydrate	(45.91)	(4.29)	(7.71)	(15.74)	
Iron(III) *m*-amino	54.32	3.82	9.05	12.03	
benzoate monohydrate	(54.19)	(4.08)	(8.78)	(12.54)	
Iron(III) *p*-amino	54.62	3.82	9.05	12.03	
benzoate monohydrate	(53.96)	(4.14)	(9.55)	(12.30)	
Basic iron(III) *o*-hydroxy-				13.59	80.00
benzoate trihydrate				(13.79)	(79.50)
Basic iron(III) *m*-hydroxy-				13.80	78.50
benzoate tetrahydrate				(13.62)	(78.34)
Basic iron(III) *p*-hydroxy-				13.44	80.00
benzoate trihydrate				(13.79)	(79.50)

ates were prepared by a method similar to the one given by Takashima and Tateishi [8] for *o*-hyroxybenzoate. The analytical data for the compounds is given in Table 1. Iron and the hydroxy groups were estimated spectrophotometrically [9] and ion exchange method [10] respectively.

A MBS-35 Mössbauer spectrometer (ECIL, India) coupled with an MCA-38B constant acceleration drive was employed to record the spectrum. The Mössbauer parameters are w.r.t. natural iron. All the spectra were recorded at room temperature and fitted to Lorenzian line shape using program IBM/370/155 on ICL-2960 computer.

Paulik-Paulik-Erdey MOM derivatograph (Hungary) was used for thermal curves. IR spectra were recorded on a spectrophotometer SP3-300 (Pye-Unicam, Ltd., England) using KBr pellet.

Results and discussions

The thermal behaviour of aminobenzoates and hydroxy benzoates is described separately.

Iron(III) aminobenzoates

The three isomers on heating undergo dehydration and decomposition.

Isothermal dehydration

α *vs.* *t* plots show sigmoidal behaviour at 351–370 K for iron(III) aminobenzoates. The analysis of data for different mechanistic functions with very high correlation coefficient and very low error is found for the D_1, D_2, R_3, A_1 and $A_{3/2}$ mechanisms. Nucleation and growth controlled mechanism may be the correct mechanism for dehydration as seen from $F(\alpha)$ *vs.* t plot with values of activation energy E and frequency factor as 22.5 kcal mol^{-1} and 10^{10} s^{-1} respectively for *o*-isomer. Maximum correlation coefficient and the minimum error with the values of E and A as 8.5 kcal mol^{-1} and 1.5×10^4 s^{-1} respectively for the diffusion controlled dehydration mechanism in case of *m*-isomer; but corresponding values for D_3 are 16.6 kcal mol^{-1} and 1.53×10^{26} s^{-1} respectively for the *p*-isomer. The high values of frequency factor indicates that water is loosely bound to the metal.

Mössbauer study

Mössbauer spectra of iron(III) aminobenzoates show doublets at room temperature. The values of isomer shift and quadrupole splitting are 0.67 and 0.63, 0.42 and 0.57, 0.41 and 0.51 mm/s for basic iron(III) *o*-aminobenzoate monohydrate, iron(III)-*m*-aminobenzoate monodydrate (Fig. 1) and iron(III) *p*-aminobenzoate monohydrate respectively in agreement with those reported for high spin octahedral compounds.

When iron(III) *p*-aminobenzoate is heated to 473 K for 2 h, the resulting Mössbauer spectrum is a doublet with isomer shift and quardrupole splitting values of 0.37 mm/s and 0.85 mm/s showing an increase in quadrupole splitting. After heating at 573 K, the resulting spectrum is a doublet with isomer shift and quadrupole

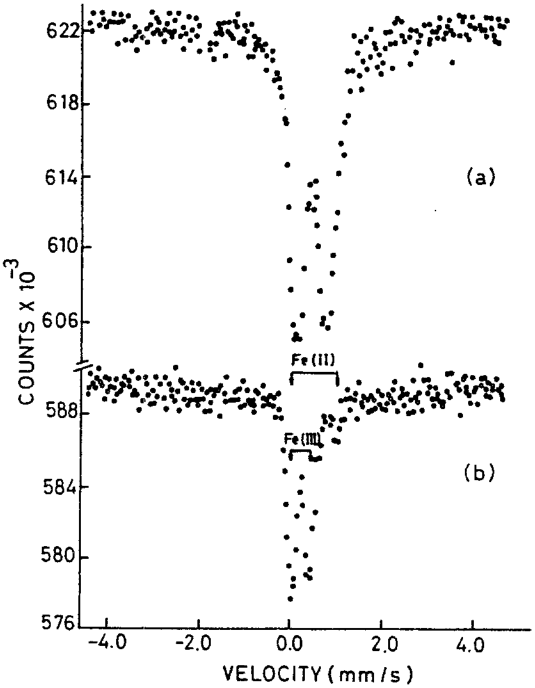

Fig. 1 Mössbauer spectra of Fe(III) *m*-aminobenzoate monohydrate (a) at 298 K and (b) heated for 2 h at 473 K

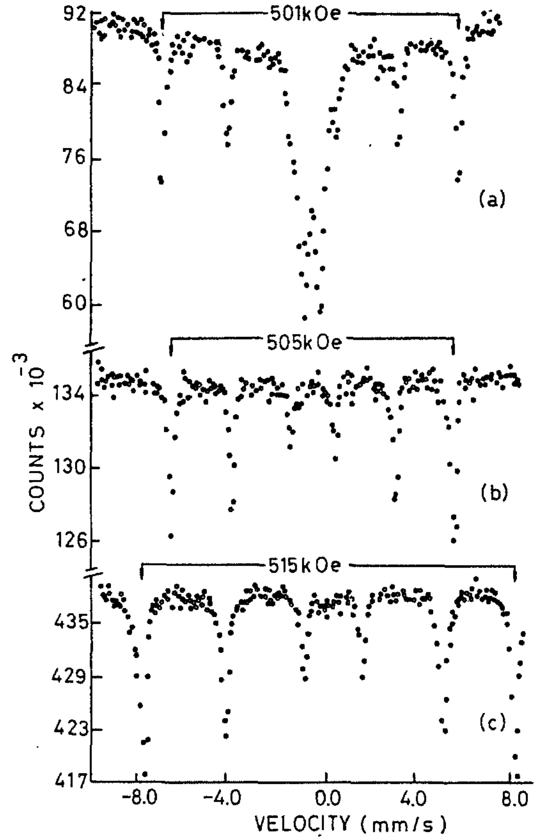

Fig. 2 Mössbauer spectra of basic Fe(III) *o*-aminobenzoate heated for 2 h at (a) 473 K, (b) 673 K and (c) 873 K

splitting values being 0.48 mm/s and 0.72 mm/s respectively for the salt due to α-Fe_2O_3 with particle size of 18±1 nm.

Basic Fe(III) *o*-aminobenzoate monohydrate when heated at 473 K for 2 h, gives a product whose Mössbauer spectrum shows a six-line pattern with the isomer shift, quadrupole splitting and internal magnetic field of 0.45 mm/s, 0.80 mm/s and 501 kOe respectively (Fig. 2). The product is identified as α-Fe_2O_3 with particle size 13.5±1 nm. Iron(III) *m*-aminobenzoate monohydrate when heated at 473 K gives a product the Mössbauer spectrum of which shows the presence of Fe(II) species (Fig. 1), though the percentage of Fe(II) species is very small. The values of isomer shift and quadrupole splitting are 0.55 mm/s and 1.00 mm/s for Fe(II) species, but 1.1 mm/s and 2.5 and for Fe(II) species.

At 874 K, a symmetrical six line pattern is observed, isomer shift and quadrupole splitting values (Fig. 2) are in good agreement with the reported values of α-Fe_2O_3 of bulk size. The value of magnetic field is found out to be 515 kOe.

Non-isothermal decomposition

The simultaneous DTA-TG-DTG curves of all the three salts are similar and hence only for iron(III) *m*-aminobenzoate monohydrate are shown in Fig. 3. DTA curve reveals an endothermic region in the temperature range 303–383 K while the DTG curve shows a peak in this temperature range and the corresponding TG curve shows a mass loss of 4.5% (cal. wt. loss 3.7%) due to the removal of one water molecule. The anhydrous product then undergoes decomposition which starts at

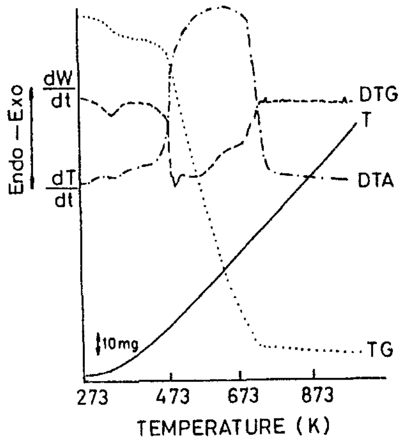

Fig. 3 Simultaneous TG-DTG-DTA curves for Fe(III) *m*-aminobenzoate monohydrate at a heating rate of 10°C min^{-1} in air

Table 2 T_m values (K) (DTA peaks) for non-isothermal dehydration and decomposition of iron(III) aminobenzoates and iron(III) aminohydroxybenzoates

Compound	Dehydration	Decomposition T_m	
	T_m	Step I	Step II
Basic iron(III) *o*-aminobenzoate monohydrate	343	478	
Iron(III) *m*-aminobenzoate monohydrate	333	498	
Iron(III) *p*-aminobenzoate monohydrate	338	523	
Basic iron(III) *o*-hydroxybenzoate trihydrate	403	448	533
Basic iron(III) *m*-hydroxyenzoate tetrahydrate	353	473	553
Basic iron(III) *p*-hydroxy-benzoate trihydrate	343	473	563

443 K and is completed at 778 K. The DTA curve which starts as an endo develops into a large exotherm in this temperature range because of the oxidation of organic products (ligands and others) formed during the reaction and the oxidation of Fe(II) species to Fe(III) species giving rise to Fe_2O_3. The DTG curve in the same region indicates that decomposition is a multistep process. The TG curve shows a continuous mass loss and ultimately the final mass loss is 83.2% (cal. wt. loss 83.4%) which corresponds to the formation of α-Fe_2O_3 confirmed by XRD and Mössbauer sepctrum. Very low T_m values (Table 2) for dehydration indicate that the bond between H_2O and metal ion is weak. T_m for decomposition suggest that the stability in the three aminobenzoates follows the order, *p*->*m*->*o*-. This can be explained on the basis of steric hindrance due to $-NH_2$ and $-COOH$ groups (follows the reverse order *o*->*m*->*p*-) and the formation of intra- and inter-molecular hydrogen bonding, the former being more pronounced in *o*-isomer in contrast to the predominance of the later in *m*- and *p*-isomers.

Iron(III) hydroxybenzoates

Isothermal dehydration

Kinetic data for dehydration at 335–354 K for the three hydroxybenzoates were taken for isothermal dehydration. Maximum correlation coefficient suggests diffusion as the rate determining step in *o*- and *m*-isomer with *E* and *A* values of 6.9 kcal mol^{-1} and 3.16×10^{24} s^{-1} and 19.76 kcal mol^{-1} and 4.4×10^{8} s^{-1} respectively. Nucleation and growth controlled process follows dehydration for *p*-isomer with 22.9 kcal mol^{-1} and 2.2×10^{11} s^{-1} for *E* and *A*.

Mössbauer spectroscopic study

The Mössbauer spectrum (Fig. 4) of basic iron(III) *o*-hydroxybenzoate trihydrate (a broad doublet) when computer fitted shows that it consists of two doublets with (mm/s) of 1.5 and Q.S. values as 0.57 and 0.66 for the inner doublet and 0.53 and 1.20 for the outer doublet in good agreement with reported ones [11]. The parameters arise from high spin and low spin states of iron respectively (the inner doublet shows a pronounced asymmetry). A trinuclear chain structure is assigned

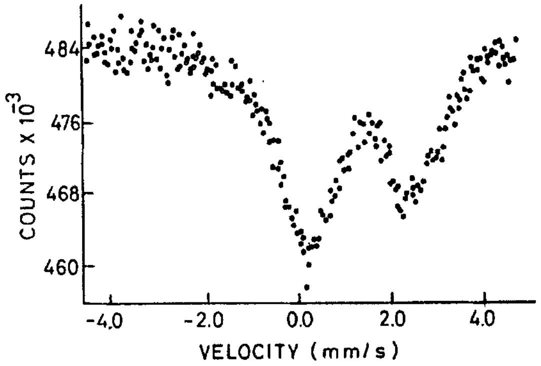

Fig. 4 Mössbauer spectrum of basic iron(III) *o*-salicylate trihydrate at room temperature

to the complex. The terminal iron atoms of the trinuclear chain have the tetrahedral ligand symmetry contrary to the octahedral symmetry [12] of central iron atom. The Mössbauer spectra for basic iron(III) *m*-hydroxybenzoate tetrahydrate and for basic iron(III) *p*-hydroxybenzoate trihydrate show a doublet at 298 K with the values (mm/s) of I.S. and Q.S. as 0.45 and 0.31, and 0.45 and 0.34 respectively and are for high spin octahedral compound [10]. The para isomer when heated at 473 K for 2 h shows the formation of Fe(II) species. The values (mm/s) of I.S. and Q.S. are 0.40 and 0.80 for Fe(III) species but 1.28 and 2.42 for Fe(II) species. Besides iron(II) species a white sublimate is also obtained which is identified as phenol. Fe(II) species are formed in *o*- and *m*-isomers also on isothermal heating at 473 K with I.S. and Q.S. values of 0.96 and 2.00 for *o*-isomer and 1.28 and 2.32 for the *m*-isomer. The respective values of Fe(III) species are 0.44 and 0.80 and 0.40 and 0.88 for *o*- and *m*-isomer.

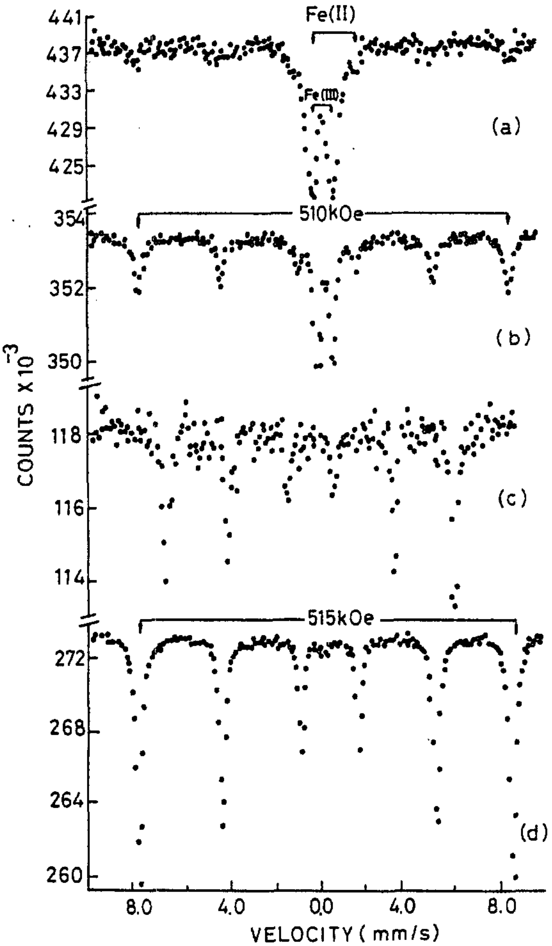

Fig. 5 Mössbauer spectra of basic iron(III) *m*-salicylate heated for 2 h at (a) 473 K, (b) 573 K, (c) 773 K and (d) 873 K

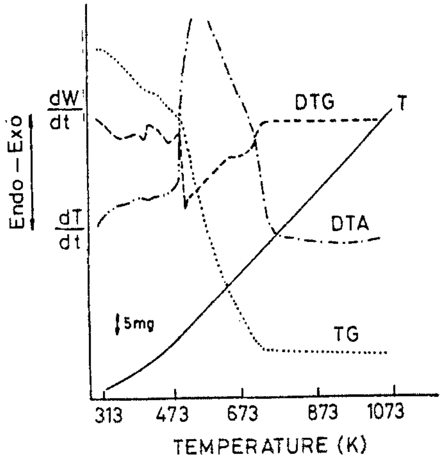

Fig. 6 Simultaneous TG-DTG-DTA curves for basic iron(III), *m*-salicylate tetrahydrate at a heating rate of 10°C min^{-1} in air

The spectrum of the compounds when heated at 573 K for 2 h shows a six-line pattern of α-Fe_2O_3 when the values (mm/s) for I.S. and Q.S. are 0.48 and 0.52 respectively for ortho salt and again at 773 K a six-line pattern with I.S. and Q.S. values (mm/s) of 0.82 and 0.31 characteristic of Fe_2O_3 with bulk size. The value of internal magnetic field is 505 kOe. Fe_2O_3 with bulk size is formed when the compound is heated at 873 K for 2 h. The value of internal magnetic field is 520 kOe i. e. increases as the particle size increases. Similar reports exist in the literature [11].

Non-isothermal study

Simultaneous DTA-TG-DTG curves of basic iron(III) *m*-hydroxybenzoate tetrahydrate are shown in Fig. 6. There is a shallow region in DTG but no thermal effect in DTA in the temperature range 313–373 K, suggesting there by that (i) all water molecules are not of same type and (ii) water is weakly held to metal ion. Subsequently, there are two endothermic peaks corresponding to the loss of 12 and 19.5%. The mass loss is in accordance with the formation of $Fe(C_6H_4COO.OH)_2$ complex (cal. wt. loss 19.7%). The residue obtained by isothermal heating of the complex at 473 K shows the formation of Fe(II) species Fig. 5. The IR spectrum and melting point studies of the sublimate deposited on the cooler sides of the tube show that it is phenol and can be formed by the decomposition of *m*-hydroxybenzoic acid. This study confirms the formation of $Fe(C_6H_4COO.OH)_2$ complex. Further decomposition shows an exotherm in the temperature range 483–773 K. DTG shows that at least two distinct decomposition stages occur in this region. First stage may be the loss of another acid molecule while second one is the oxidation of the remaining complex species to Fe_2O_3 as well as of organic material to CO_2 and other volatile products. However, the TG shows a continuous mass loss in the same temperature range. Ultimate product is α-Fe_2O_3 for the mass loss of 81.4% (cal. wt. loss 80.5%) confirmed by Mössbauer spectroscopy and XRD analysis.

Non-isothermal study demonstrates that the thermoanalytical curves of the three (*o*-, *m*-, *p*-) hydroxybenzoates are largely similar. Low T_m values for dehydration indicate that in all the complexes water is loosely held by the metal ion. The three complexes show three endotherms below 473 K and an exothermic region for decomposition between 473 and 773 K. First step of decomposition involving the loss of one salicylic acid molecule and the formation of Fe(II) species, is endothermic. Mössbauer spectrum of the three compounds on heating at 473 K confirms the formation of α-Fe_2O_3. But the second step of decomposition which involves the removal of another salicylic acid molecule, the fragmentation and oxidation of side products and formation of α-Fe_2O_3 as the final product, is exothermic. The comparison of T_m values for decomposition shows that the order of stability may be *p*->*m*->*o*- isomer.

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