

# **SPECTRAL AND THERMAL FEATURES OF SOME NOVEL IRON(III) CHELATES WITH SUBSTITUTED 2-HYDROXYARYLOXIMES**

## **Kinetic analysis of thermogravimetric data**

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### **Abstract**

The reaction products of five substituted 2-hydroxyaryloximes with Fe(III) ion were obtained and characterized by means of elemental analysis, conductometric measurements, magnetic moment determinations and spectroscopic data (IR and electronic absorption).

The thermal stability and mode of decomposition were studied in air atmosphere by using TG-DTA. Kinetic analysis of the TG data was performed with the Coats-Redfern method to determine the apparent activation energies and the pre-exponential factor of the Arrhenius equation. Mass spectrometry was also used, and possible fragmentation patterns are given and discussed.

**Keywords:** decomposition kinetics, 2-hydroxyaryloximes, iron(III) chelates, spectroscopy, TG-DTA

### **Introduction**

Hydroxyoximes have been extensively used as analytical reagents and as chelating extractants in large-scale solvent extraction processes. Although such applications are of continuing interest and industrial importance, most of the reported studies deal with kinetic and equilibrium extraction properties [1, 3] and relatively little work exists in the literature referring to structural and electronic features of the coordinated species [4, 5]. Few reports on isolated pure chelates of hydroxyoximes contain spectroscopic and analytical data, despite the necessity to understand the coordination behaviour and the chemical properties of the various classes of these compounds. Such information is relevant since hydroxyoximes are ambidentate with the possibility of a variety of coordination modes, depending among other factors upon hydrogen bonding, electron distribution and steric hindrance. In this respect

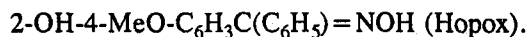
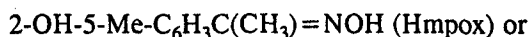
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we have already studied several transition metal complexes of aromatic hydroxyaryloximes to establish the chemical, electronic and redox properties of the various coordination geometries obtainable with the oxime systems [6, 7]. Our results were found to be in accordance with well-established X-ray structure determinations of the trans square-planar geometry of some salicylaldoximates [7-9].

References relating to iron(III) chelates of 2-hydroxyoximes suggest that two types of compounds are formed, the first with a metal-to-ligand ratio of 1:1, and the second with a ratio of 1:3. However, none of these chelates were isolated [5, 10]. Iron(III) chelates with aliphatic hydroxyoximes corresponding to the general formula  $\text{FeL}_3 \cdot 5 \text{H}_2\text{O}$  have been isolated and characterized [11, 12] and one report [13] deals with the chelate of salicylaldoxime having the formula  $\text{FeL}_2(\text{OH})$ . The isolation of an iron(III) complex with the ligand *o*-vanillinoxime (a derivative of salicylaldoxime), with the formula  $[\text{FeL}_2(\text{H}_2\text{O})_2]\text{Cl}$ , has recently been reported [14]. The rarity of reports on iron(III) chelates may be due to the difficulties encountered during the separation and isolation of these compounds.

Although the thermal behavior of several divalent metal salicylaldoximates has received considerable attention from some investigators ([15] and references therein), one paper on the thermal behavior of tris(orthovanillinoximate)chromium(III) [16] is the only report regarding the trivalent metal hydroxyaryloximates. Continuing our investigations, we report here results concerning the synthesis and characterization of iron(III) complexes with the general formula  $\text{FeL}_3$ , where *L* is the anion of the following 2-hydroxyaryloximes.



The mass spectra and the results of thermogravimetric measurements on three of the investigated complexes are included and discussed, since preliminary analysis of the thermal behaviour of the remaining two compounds indicated that their decompositions follow the same pattern. Kinetic parameters (activation energy  $E^*$ , pre-exponential factor *Z* and reaction order *n*) for the main decomposition stage, derived from the Coats-Redfern method [17], are also reported and discussed.

## Experimental

### *Preparation of the complexes*

The ligands were synthesized by literature methods [18]. The chelates were prepared by established solvent extraction procedures [19], i.e. by adding a buffered aqueous  $\text{FeCl}_3$  solution to a toluene solution of the hydroxyoxime in a ratio of 1:3. Better complexation was achieved when  $\text{H}_3\text{BO}_3$  (*pH*~3.5) was used in the cases of Hbpox and Hopox as ligands, while for the remaining hydroxyoximes (Hapox, Hppox and Hmpox) buffering of the iron solution to *pH*~5.5 was effected with  $\text{CH}_3\text{COOH-CH}_3\text{COONa}$ .

Extraction was accomplished by separation of the toluene layer from the aqueous one, the latter being repeatedly washed with small portions of toluene. A reddish-brown solid separated out when the toluene was removed from the organic layer by flash evaporation. The isolated complex was further purified by column chromatography on cellulose, with toluene or chloroform as eluent. The compounds prepared are stable in air, both in the solid state and in solution, rather soluble in common organic solvents, indicative of mononuclear species, and insoluble in petroleum ether, methanol and water. Their melting points, magnetic moments and elemental analyses are listed in Table 1.

### *Physical measurements*

Stoichiometric analyses (C, H, N) were performed on a Perkin-Elmer 240B elemental analyzer. Metal contents were determined by EDTA titration after decomposition of the chelates with sulfuric and nitric acids.

Molar conductivities were measured in acetonitrile solutions, employing a WTW conductivity bridge and a calibrated dip-type cell. The cell constant was determined at 25°C in a series of measurements on potassium chloride solutions of known concentration.

Magnetic susceptibility measurements on powdered samples were performed at 25°C, by means of the Faraday method, on a home-built balance, calibrated against  $\text{Hg}[\text{Co}(\text{SCN})_4]$ . Diamagnetic corrections were estimated from Pascal's constants.

Infrared spectra were recorded in the region 4000–300  $\text{cm}^{-1}$  on a Perkin-Elmer model 1430 spectrophotometer, using KBr pellets.

Electronic absorption spectra in chloroform solution were obtained on a Perkin-Elmer-Hitachi 200 spectrophotometer.

Mass spectra were run at 70 eV on an RMU-6L Hitachi Perkin-Elmer single focusing mass spectrometer, using direct probe insertion for the samples. The ionization source used was a T-2p model.

The TG-DTA curves were obtained on a Rigaku-Denki model 8076-D1 thermal analyzer. Samples were heated in platinum crucibles, with  $\alpha\text{-Al}_2\text{O}_3$  as reference compound, in a static air atmosphere, within the temperature range 25–800°C. The heating rate was 10°C  $\text{min}^{-1}$  and the samples ranged in mass from 13 to 17 mg. The TG range was 20 mg full scale, while the DTA range was 250  $\mu\text{V}$  full scale.

X-ray powder diffraction analyses of the final residues were made with a Philips PW 1130/00 X-ray diffractometer, using  $\text{CuK}_\alpha$  radiation.

## **Results and discussion**

The reactions of the iron(III) ion with 2-hydroxyaryloximes proceed smoothly. The results of elemental analyses of the isolated compounds are consistent with a metal-to-ligand ratio of 1:3, while the molar conductivities of their solutions in acetonitrile indicate the formation of neutral complexes, implying that the ligand molecules coordinate as anions by losing a hydrogen atom. At room temperature, the new Fe(III) complexes exhibit paramagnetism (2.06–2.55 BM, Table 1) arising from one unpaired electron, indicative of a low-spin octahedral configuration ( $t_{2g}^5$ ) [20].

Table 1 Analytical, physical and magnetic data for the iron(III) chelates

Compound	mp/ °C	Yield/ %	$\mu_{\text{eff}}$ BM	N/ %	C/ %	H/ %	Fe/ %
Fe(apox) <sub>3</sub>	207-209	26	2.28	8.0 (8.3) <sup>a</sup>	56.7 (56.6)	5.4 (5.3)	11.2 (11.1)
Fe(mpox) <sub>3</sub>	228-231	18	2.35	7.7 (7.6)	59.0 (58.8)	6.1 (6.0)	10.4 (10.2)
Fe(ppox) <sub>3</sub>	165-167	20	2.55	7.6 (7.6)	58.9 (58.8)	6.1 (6.0)	10.3 (10.2)
Fe(bpox) <sub>3</sub>	210-211	25	2.26	6.0 (6.0)	67.0 (67.3)	4.9 (4.8)	8.0 (8.1)
Fe(opox) <sub>3</sub>	185-186	15	2.06	5.7 (5.7)	68.8 (68.7)	5.0 (4.9)	7.0 (7.2)

<sup>a</sup> Calculated values in parentheses

### *Infrared spectra*

In the IR spectra of the ligands, the stretching mode of the oximino hydroxyl group was observed as an intense broad band at  $3360 \pm 30 \text{ cm}^{-1}$  [6, 7]. The variation in the position of this band reveals the influence of the substituents. Upon complexation, this band appeared at slightly lower energies ( $15 \text{ cm}^{-1}$  negative shift), indicative of coordination through the nitrogen atom [21].

Evidence for this coordination also arose from the small shift (about  $5 \text{ cm}^{-1}$ ) towards lower frequencies of the medium-intensity band at  $1610 \text{ cm}^{-1}$ , assigned to the C=N bond [22], and from the positive shift of  $\sim 5 \text{ cm}^{-1}$  in the stretching (N-O) mode observed in the region  $940\text{--}1030 \text{ cm}^{-1}$  for the complexes.

Coordination through the phenolic oxygen was indicated by the absence of the bands due to the stretching and to the in-plane O-H bending mode, found for the free ligands at  $3200\text{--}3050 \text{ cm}^{-1}$  and at  $1410\text{--}1360 \text{ cm}^{-1}$ , respectively [23]. This is also inferred from the positive shift of about  $10 \text{ cm}^{-1}$  in the  $\nu(\text{C-O})$  band, which for the studied complexes was found at  $1295 \text{ cm}^{-1}$  [24]. In the far-IR spectra of the iron complexes, the stretching vibration of the Fe-N bond was observed at  $565 \text{ cm}^{-1}$  while that of the Fe-O bond could not be assigned with certainty.

### *Electronic spectra*

The very intense bands observed at about 270 and 300 nm in the electronic spectra of the complexes in chloroform solution are due to the aryloxime ligands and should be assigned to  $\pi\text{--}\pi^*$  transitions. In the visible region, which is the most informative area of the spectra as concerns the geometry of a chromophore involving a transition metal, only one relatively intense broad band was observed, at 510 nm, which could be assigned as a charge-transfer band or  $d\text{--}d$  band.

The IR and magnetic data indicated that the studied Fe(III) complexes are six-coordinated, with the aryloxime ligands being strong enough to cause spin pairing leading to Fe(III) low-spin octahedral complexes. It is known that such iron  $d^5$  complexes give an intense charge-transfer band in the visible, obscuring the  $d\text{--}d$  bands [25]. Moreover, in the case of the low-spin  $[\text{Fe}(\text{en})_3]\text{Cl}_3$ , which is free of charge-transfer bands, the two spin-forbidden bands were observable only at 80 K, but not at room temperature [26].

Since we know that the 2-hydroxyaryloxime ligands give an intense charge-transfer band with transition metals [6, 7], it is reasonable to assign the band found at 510 nm as the charge-transfer band. This is in agreement with what was found for the Fe(III) low-spin octahedral complex  $[\text{Fe}(o\text{-vanillinoxime})_2(\text{H}_2\text{O})_2]\text{Cl}$  [14].

### *Mass spectra*

Mass spectra were obtained for three iron chelates under investigation and for five 2-hydroxyaryloximes. The most prominent mass spectral peaks of the studied compounds are given in Table 2.

In the mass spectra of the chelates, neither the molecular ions nor those corresponding to the elimination of one ligand from the parent ions are detected. This

Table 2 Most relevant mass spectral peaks of 2-hydroxyaryloximes and some of their Fe(III) chelates

Compound	$m/e$ ( $R/I$ ) <sup>a</sup>
Hapox	28(100), 51(56), 52(42), 53(42), 55(21), 62(30), 63(79), 64(83), 65(93), 66(32), 67(22), 75(21), 76(24), 77(62), 78(71), 79(39), 89(23), 90(68), 91(97), 92(69), 93(23), 94(26), 103(21), 104(61), 105(49), 106(49), 107(24), 119(44), 120(33), 132(35), 133(94), 134(87), 135(34), 151(47), 152(47)
Hmpox	28(100), 51(65), 52(48), 53(43), 55(13), 62(10), 63(28), 64(10), 65(28), 66(14), 76(15), 77(98), 78(95), 79(44), 89(14), 90(11), 91(63), 92(25), 93(12), 103(19), 104(47), 105(52), 106(27), 107(21), 108(10), 117(14), 118(57), 119(78), 120(20), 121(11), 132(36), 133(31), 134(13), 146(81), 147(94), 148(69), 164(14), 165(54), 166(38)
Hppox	51(29), 52(23), 53(17), 54(11), 56(12), 62(10), 63(38), 64(41), 65(49), 66(10), 76(10), 77(34), 78(19), 79(13), 90(14), 91(51), 92(33), 93(12), 102(18), 103(30), 104(20), 105(23), 107(10), 115(10), 118(20), 119(51), 120(51), 121(14), 131(10), 132(40), 133(18), 146(37), 147(14), 148(26), 165(100), 166(18)
Hbpx	28(100), 51(40), 52(13), 63(20), 64(15), 65(22), 76(14), 77(83), 78(18), 91(16), 92(15), 104(15), 118(17), 119(11), 152(11), 165(16), 166(17), 167(80), 168(16), 181(16), 195(60), 196(25), 213(49), 214(8)
Hopox	51(53), 52(22), 63(23), 65(17), 69(12), 77(100), 78(26), 79(25), 91(33), 95(10), 103(12), 104(19), 105(26), 106(9), 107(19), 108(10), 115(16), 118(28), 119(37), 122(13), 124(11), 139(8), 146(12), 147(24), 149(12), 151(26), 161(13), 165(29), 167(11), 182(53), 183(12), 196(11), 210(14), 211(14), 225(57), 226(20), 227(27), 228(20), 232(10), 243(45), 244(8)

Table 2 Continued

Compound	<i>m/e</i> ( <i>R/I</i> ) <sup>a</sup>
Fe(mpox) <sub>3</sub>	51(36), 52(21), 53(11), 56(7), 62(7), 63(14), 64(3), 65(7), 66(6), 76(5), 77(42), 78(60), 79(13), 89(4), 91(29), 92(7), 103(5), 104(19), 105(30), 106(6), 107(40), 117(4), 118(83), 119(45), 120(5), 132(9), 133(11), 134(7), 146(15), 147(38), 148(21), 149(20), 165(100), 166(9), 203(5)
Fe(ppox) <sub>3</sub>	51(16), 52(11), 53(9), 54(5), 55(6), 56(7), 62(6), 63(23), 64(23), 65(30), 66(4), 77(18), 78(8), 79(6), 90(7), 91(100), 92(20), 102(10), 103(17), 104(10), 105(12), 107(5), 115(5), 118(6), 119(100), 120(35), 121(8), 131(5), 132(27), 133(10), 146(23), 147(5), 148(13), 149(15), 165(100), 166(10), 203(5), 312(1)
Fe(opox) <sub>3</sub>	51(33), 56(6), 58(13), 63(10), 65(6), 77(44), 78(22), 91(17), 95(8), 103(5), 104(6), 105(15), 106(3), 107(10), 115(10), 122(12), 124(8), 149(39), 151(20), 167(17), 182(75), 183(14), 196(8), 210(10), 211(25), 225(58), 226(39), 227(50), 228(25), 243(100), 244(19), 281(10), 389(3), 391(1)

<sup>a</sup>*R/I*: relative intensity

was expected because of their high molecular and thermal instability, which makes it difficult to give a complete fragmentation pattern. A representative spectrum for the chelate  $\text{Fe}(\text{opox})_3$  is given in Fig. 1, together with the spectrum of the free oxime Hopox.

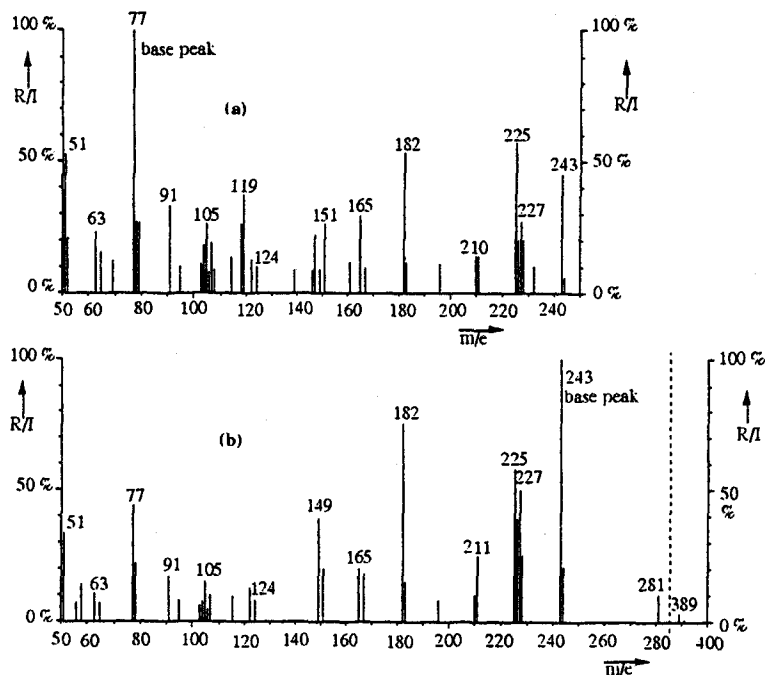


Fig. 1 Mass spectra of (a) the ligand Hopox and (b) the chelate  $\text{Fe}(\text{opox})_3$ .

The two mass spectra exhibit few, but significant differences in their profiles. On the basis of these differences (peaks at  $m/e$  389, 281, 149 and 56), a mechanistic approach to a fragmentation pathway is attempted in Scheme 1 for the chelate  $\text{Fe}(\text{opox})_3$ .

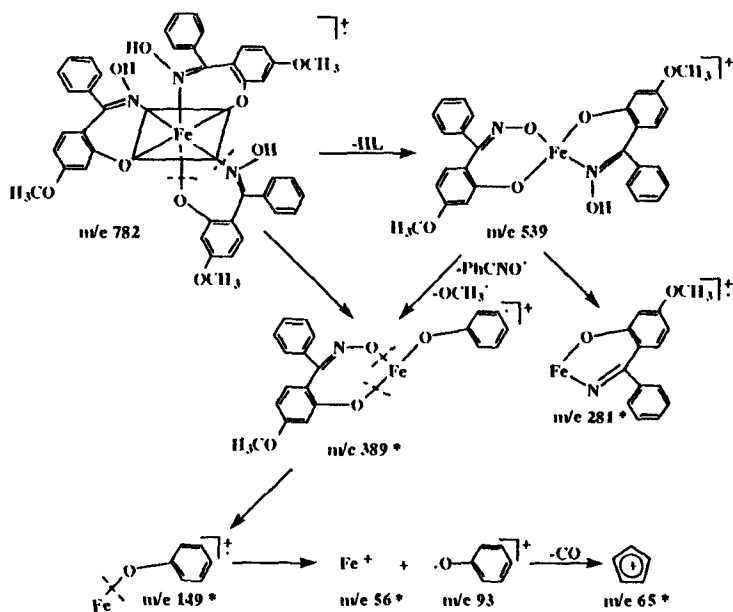
It can be deduced that, besides the scission of the coordinative bond and the escape of one hydroxyoxime molecule from the chelate, cleavages of other bonds in the chelate ring may initiate a decomposition process.

In the low mass-number region, the observed peaks correspond to the released oxime ( $m/e$  243, base peak) and its fragments. The fragmentation pattern of the released oxime Hopox is similar to that of the free ligand and it is given in Scheme 2.

The temperature-dependent loss of water from the oxime ion is the main process, while the other routes give daughter ions derived from the oxime ion by elimination of the groups  $-\text{NO}_2$ ,  $-\text{NO}$ ,  $-\text{PhCNO}$  or  $-\text{OCH}_3$ .

The mass spectra of all the studied 2-hydroxyaryloximes reveal that their fragmentation processes are not affected by the substituents of the oximic group and they agree with those reported for salicylaldoxime [27, 28]. In the case of the 5-methyl-





\* Ions that have been detected

Scheme 1 Possible fragmentation pathways for  $\text{Fe}(\text{opox})_3$

substituted benzene ring (Hmpox), however, another secondary pathway can possibly take place (Scheme 3).

This fragmentation process is in agreement with that suggested for 2-hydroxy-5-alkylphenylethanoneoxime [29].

### Thermal behaviour

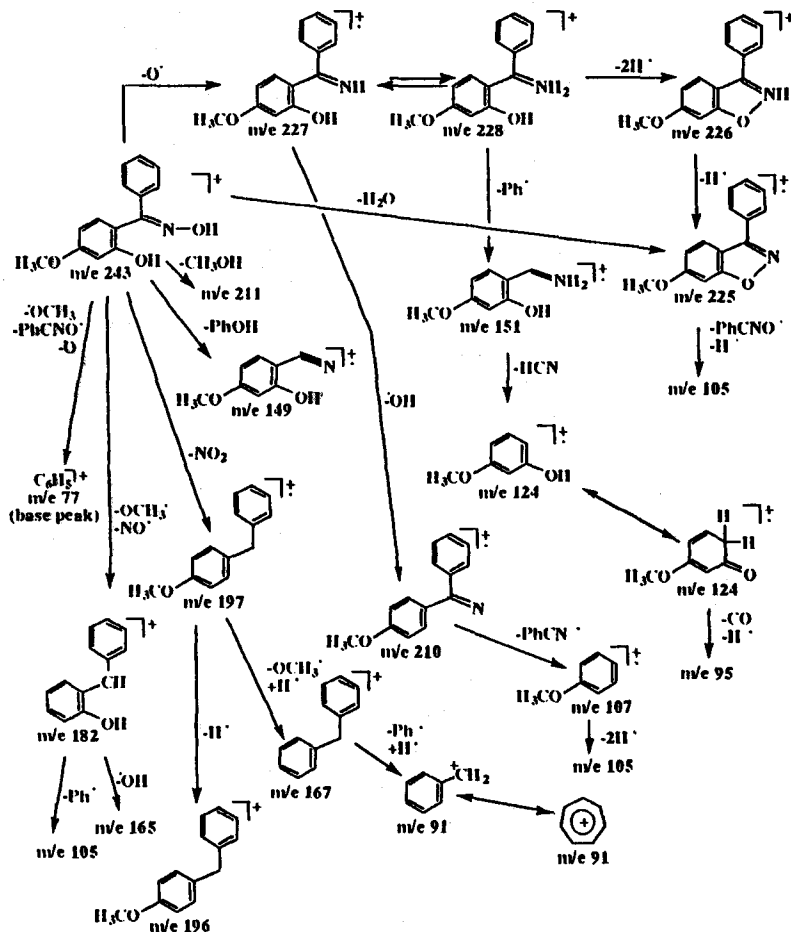
Three of the studied iron(III) complexes were subjected to TG-DTA analysis from ambient temperature up to 800°C in static air atmosphere.

Their thermoanalytical curves are presented in Fig. 2, while the temperature ranges, the determined percentage mass losses and the thermal effects accompanying the decomposition reactions are given in Table 3.

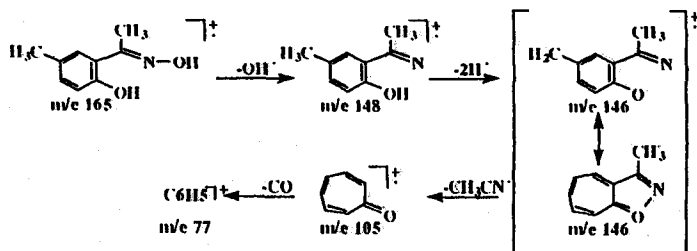
The DTA endotherms at 170, 205 and 260°C indicate that melting takes place just before decomposition for all the complexes studied, while the two well-defined degradation stages are accompanied by exothermic effects. The initial decomposition temperatures indicate that the thermal stabilities of the complexes under investigation follow the series  $\text{Fe}(\text{opox})_3 \geq \text{Fe}(\text{mpox})_3 > \text{Fe}(\text{ppox})_3$ , which is in agreement with our previous results regarding analogous complexes of Cu(II), Ni(II) and Pd(II) with the same ligands [15].

For all the investigated compounds, the thermal decomposition mode suggested by the TG-DTA curves seems to follow the same model. The first decomposition

stage proceeds with a sudden and considerable mass loss (67–75%), which is attributed to the rupture of both coordination bonds (eliminating two ligand mole-



Scheme 2 Possible fragmentation pattern for the released ligand 4-methoxybenzophenone-oxime



Scheme 3 Possible secondary pathway for Hmpox

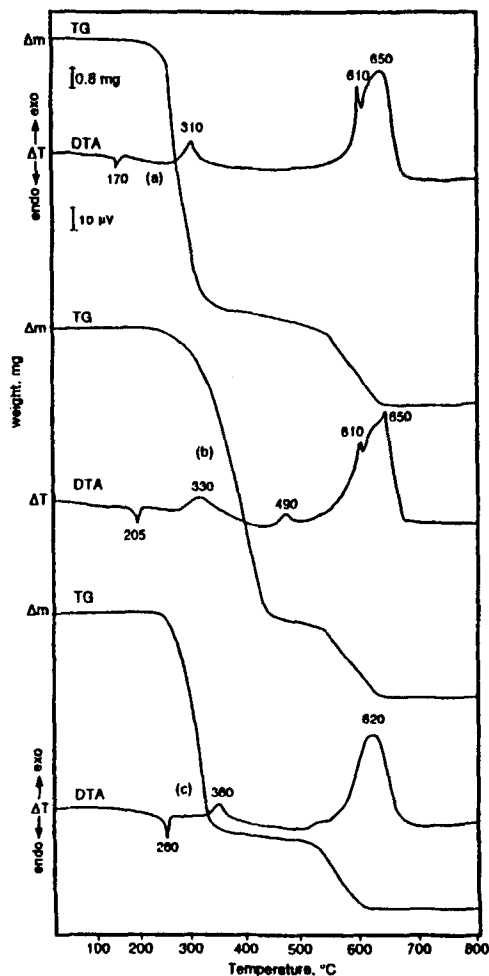


Fig. 2 Thermoanalytical curves of (a)  $\text{Fe}(\text{ppox})_3$ , (b)  $\text{Fe}(\text{opox})_3$  and (c)  $\text{Fe}(\text{mpox})_3$  in air

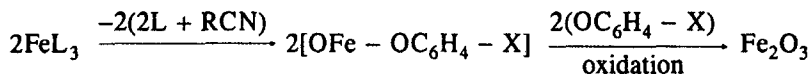
cules) plus the rupture of bonds inside the ligands (possibly involving elimination of one molecule of  $\text{RCN}$ , where  $R$ =methyl, ethyl or phenyl). The intermediates formed, corresponding to the formula  $\text{OFeO}-\text{C}_6\text{H}_4-\text{X}$ , where  $X$ =H, 5- $\text{CH}_3$ , or 4- $\text{OCH}_3$ , are unstable. At higher temperatures, they undergo further decomposition and gradually oxidation until the stable  $\text{Fe}_2\text{O}_3$  is formed at about  $700^\circ\text{C}$ , as expected [30] and verified from the X-ray powder diffraction data.

In addition to the peaks already mentioned, an extra exothermic peak in the DTA curve is observed at  $490^\circ\text{C}$  for the complex  $\text{Fe}(\text{opox})_3$ . The origin of this peak can only be tentatively assumed. It may be due to the diffusion of the gaseous products of the first decomposition stage with oxygen, since the liberated ligand opox is less volatile than the ligands ppox and mpox [15].

Table 3 Thermoanalytical results (TG-DTA) for some iron(III) 2-hydroxyaryloximates in air

Compound	Stage	T/°C	DTA		Mass loss/ %	Evolved moiety formula	Mass calcd./ %	E*/ kJ mol <sup>-1</sup>
			Endo(-)	Exo(+)				
Fe(mpox) <sub>3</sub>	1	250-500	260	360	67.5	2L + CH <sub>3</sub> CN	67.4	132
	2	500-700	600, 620		17.5	CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O + oxidation FeO → Fe <sub>2</sub> O <sub>3</sub>	18.0	
	Residue	700			15	Fe <sub>2</sub> O <sub>3</sub>	14.6	
Fe(ppox) <sub>3</sub>	1	170-520	170	310	69.6	2L + C <sub>2</sub> H <sub>5</sub> CN	70.0	108
	2	520-700	310, 650		16.0	C <sub>6</sub> H <sub>5</sub> O + oxidation FeO → Fe <sub>2</sub> O <sub>3</sub>	15.5	
	Residue	700			14.4	Fe <sub>2</sub> O <sub>3</sub>	14.6	
Fe(opox) <sub>3</sub>	1	252-520	205	330, 490	75	2L + C <sub>6</sub> H <sub>5</sub> CN	75.1	128
	2	520-700	610, 650		15.5	CH <sub>3</sub> OC <sub>6</sub> H <sub>5</sub> O + oxidation FeO → Fe <sub>2</sub> O <sub>3</sub>	14.7	
	Residue	700			9.5	Fe <sub>2</sub> O <sub>3</sub>	10.2	

The overall decomposition path may be expressed by the reaction:



### Decomposition kinetics

The first stage of decomposition in air for the studied complexes was chosen for detailed study. The kinetic parameters (activation energy  $E^*$ , reaction order  $n$  and pre-exponential factor  $Z$ ) were evaluated graphically by employing the Coats-Redfern equation. The validity range of  $\alpha$  (fraction decomposed) for the first decomposition is 0.05–0.90 for all the complexes studied. A typical curve is given in Fig. 3 for  $\text{Fe}(\text{mpox})_3$ .

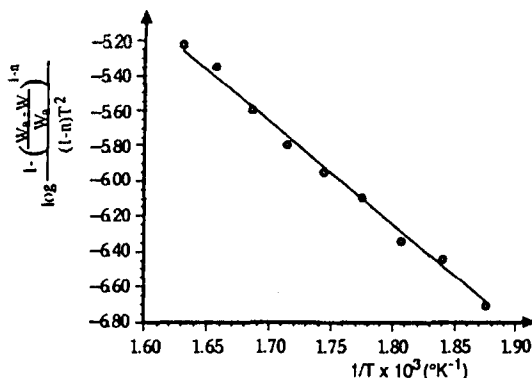


Fig. 3 Coats-Redfern plot for  $\text{Fe}(\text{mpox})_3$

All the linear plots were evaluated by regression analysis and the corresponding correlation coefficients  $r$  were calculated and found to be equal to 0.992–0.997. The best linear plots were obtained for a reaction order of 0.75.

The  $E^*$  values found for the complexes  $\text{Fe}(\text{ppox})_3$ ,  $\text{Fe}(\text{mpox})_3$  and  $\text{Fe}(\text{opox})_3$ , were 108, 132 and 128  $\text{kJ mol}^{-1}$ , respectively, which are in agreement with their thermal stability series, as discussed previously. The  $Z$  values are of the order  $10^8 \text{ s}^{-1}$ . Moreover, it seems that the thermal stabilities of the studied  $\text{Fe}(\text{III})$  2-hydroxyarylloximates, as indicated by their initial temperatures and their activation energies, are quite close to the thermal stabilities of the analogous complexes of copper(II) [15]. The latter complexes exhibit biological activity, as recently reported [31 and references therein]. This observation may be of significant importance since both copper and iron are found in the human body and play an important role in our biological system.

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