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KINETIC AND MECHANISTIC STUDIES ON THE DECOMPOSITION OF SOME HYDROUS IRON(II) SALICYLATO COMPLEXES

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ABSTRACT

Hydrous iron(II) salicylate, iron(II) 5-chloro-, iron(II) 5-bromo-, iron(II) 5-iodo-, and iron(II) 5-nitrosalicylato complexes have been prepared and their mode of thermal decomposition investigated by thermogravimetry, differential scanning calorimetry, and mass spectrometry. The results show that the decomposition of the compounds occurs in three stages and the final product, at about 700–773 K, is Fe_2O_3 for all complexes. The kinetics and thermodynamics of the isothermal dehydration of the complexes were studied by thermogravimetry and differential scanning calorimetry. The dehydration process seems to follow most closely a phase boundary reaction mechanism.

INTRODUCTION

Salicylic acid and its derivatives can act as an oxygen donor ligand and form chelate compounds with a great variety of metal ions. Some metal salicylato complexes have been used as additives in medicine [1]. Salicylate was introduced into medicine over a century ago, and, at present, acetyl salicylic acid (Aspirin) is used as an analgesic and antipyretic, and as an anti-inflammatory agent [2,3].

From the medicinal point of view it is interesting to know in which form salicylates exist in the body fluids. Therefore, the metal complex formation constants for salicylic acid, and its derivatives with many metal ions, provide useful information, and many stability constants have already been determined potentiometrically [3–5]. The composition and stability of complexes formed in aqueous sodium perchlorate solutions of iron(III) and copper(II) ions with salicylic, 5-chloro-, 5-bromo-, and 5-iodosalicylic acids at 298.15 K, and the use of these complexes in analytical applications, have been investigated [6,7]. In order to explain the mechanism of action of metal salicylates in various physicochemical processes, it is important to also know the thermal behaviour of these compounds. Mechanisms for the thermal decomposition of cobalt and nickel salicylates have been determined by

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Kishore and Nagarajan [8,9]. Recently, the thermal decomposition and kinetics of hydrous copper(II) 5-substituted salicylates have been studied [10,11]. In the present study, unsubstituted and 5-substituted iron(II) salicylates have been synthesized, characterized, and their mechanism and kinetics of decomposition investigated. This paper presents the results of these studies.

EXPERIMENTAL

The ligand acids, as well as ferrous sulfate, were supplied commercially (Fluka AG, Merck, and Janssen Chimica) as the purest available grade and were used without further purification.

Preparation of the compounds

Bis(2-hydroxybenzoato)iron(II)dihydrate (**A**); bis(2-hydroxy-5-chlorobenzoato)iron(II)dihydrate (**B**); bis(2-hydroxy-5-bromobenzoato)iron(II)dihydrate (**C**); bis(2-hydroxy-5-iodobenzoato)iron(II)dihydrate (**D**); and bis(2-hydroxy-5-nitrobenzoato)iron(II)trihydrate (**E**), were prepared by modifying the procedure described elsewhere [10,12]. The pH of an aqueous (complexes **A**–**C**) or 1 : 1 water–ethanol solution (complexes **D**–**E**) of the sodium salt of each ligand acid was adjusted to 4–7 by sulfuric acid. Ferrous sulfate was then added to these solutions with a molar ratio of 1 : 2. The powdered dark violet (**A**–**D**) or brick red (**E**) compounds which formed after 24–48 h were filtered, washed with water and ethanol, and dried at room temperature over silica gel in vacuum. The elemental analysis data for the complexes (Table 1) show that all of them, except **E**, were kept as dihydrates.

Methods

The following methods and instruments were used for elemental analysis: atomic absorption spectrometry (Pye Unicam SP9-800); direct current plasma atomic emission spectrometry (Spectra Span IIIB); and automatic element analyzer (Leco IR 12). IR spectra were recorded as KBr pellets in the range 250–4000 cm^{-1} with a Perkin-Elmer 457 spectrophotometer. Thermogravimetry (TG), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC) studies were carried out in air on a Mettler TA 3000 thermal analysis system, including a TG 50 thermobalance, DSC 20 differential scanning calorimetry and TC 10 TA processor. A sample weight of 5–8 mg was used, and a heating rate of 5 K min^{-1} was employed. The temperature and heat flow calibrations were carried out as previously described [10]. The decomposition products of the complexes were collected at about 20 K intervals on a Digestion System 20 combined with the

TABLE 1

Analytical data for iron(II)-5-substituted salicylates

Compound [a]	Analysis (%) [b]			IR bands (cm^{-1})		
	Fe	C	H_2O	$\nu_{as}(COO^-)$	$\nu(OH)$	νother
(**A**) $Fe(sal)_2 \cdot 2\ H_2O$	15.0 (15.2)	48.1 (45.9)	–	1600 s	3370 s	1230 (CO) s
(**B**) $Fe(5\text{-}Clsal)_2 \cdot 2\ H_2O$	12.6 (12.8)	40.3 (38.7)	8.7 (8.3)	1595 m	3390 s	730 (Cl) m
(**C**) $Fe(5\text{-}Brsal)_2 \cdot 2\ H_2O$	10.5 (10.7)	33.4 (32.1)	6.5 (6.9)	1590 m	3400 s	700 (Br) m
(**D**) $Fe(5\text{-}Isal)_2 \cdot 2\ H_2O$	8.8 (9.1)	27.5 (27.3)	5.7 (5.8)	1580 m	3400 s	685 (I) m
(**E**) $Fe(5\text{-}NO_2sal)_2 \cdot 3\ H_2O$	13.8 (11.8)	32.9 (35.5)	–	1590 s	3300 s	1330 (NO_2) s

[a] sal = $C_6H_3\text{–}OHCOO^-$.

[b] Calculated values are given in parentheses.

Autostep 1012 Controller made by Tecator (Sweden). The mass spectra of the decomposition products were obtained with a Kratos MS 80 RF Autoconsole mass spectrometer using a capillary gas chromatographic sample inlet system. Studies of the decomposition of the complexes in the mass spectrometer inlet system were made with a Jeol JMS-D300 mass spectrometer by heating the sample in the quartz capillary of the direct inlet probe of the mass spectrometer with a heating rate of 10 K min^{-1}. The energy of bombing electrons was 70 eV. The X-ray measurements were carried out on a Philips PW1050 X-ray diffractometer using Cu K_α radiation. The samples of the compounds were prepared by spreading their fine powders on a glass plate. Analyses of water contents were made by a Beckman KF4 aqua-meter.

Rate constants and activation parameters were calculated by least-squares procedures on a Univac 1100/22 computer.

RESULTS AND DISCUSSION

IR studies

Some main IR bands of iron(II) complexes are given in Table 1. Wide bands at ~ 3370 cm^{-1} can be attributed to the antisymmetric and symmetric OH stretching modes of the water molecules. The phenolic O–H bending vibrations are seen at 1360 cm^{-1}. If the phenolic-O is uncoordinated, the bonding should occur at a higher frequency. Therefore, it is possible that the salicylates act as a bidentate ligand as previously suggested [9,13]. The antisymmetric and symmetric COO^- stretches absorb at 1590 and 1420 cm^{-1}, respectively. No bands are found in the 1680–1700 cm^{-1} region, which corresponds to the frequency of the COOH group ascribing to the free ligand acid. The characteristic bands of the halogen and nitro groups can also be observed from the IR spectra (Table 1).

TG and mass spectrometric studies

TG and DTG curves between 323 and 923 K for complexes **A**–**D** are shown in Fig. 1. Typical mass chromatograms for the decomposition of the complexes studied are presented in Fig. 2. These two figures reveal three main steps in the decomposition of complexes **A**–**D**; the first step, below 460 K, is mainly due to the simultaneous loss of two coordinated water molecules, in the second step, 360–580 K, the main decomposition product is the ligand acid, and in the third step 420–770 K, it loses the corresponding phenol or halosubstituted phenol and carbon dioxide molecules. The final decomposition product is Fe_2O_3. The maxima in the ionic mass chromatogram for H_2O, ligand acid, carbon dioxide, and phenol molecules are at about 400, 465, 550 and 543 K, respectively. On the basis of weight loss in

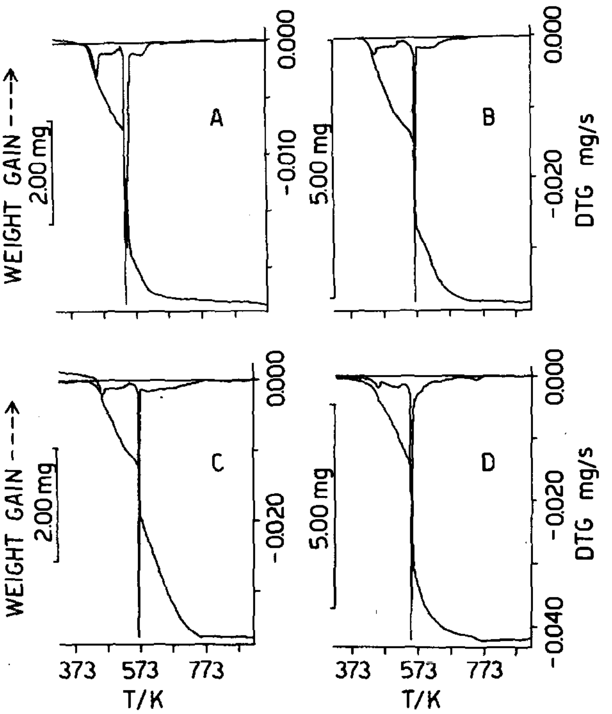
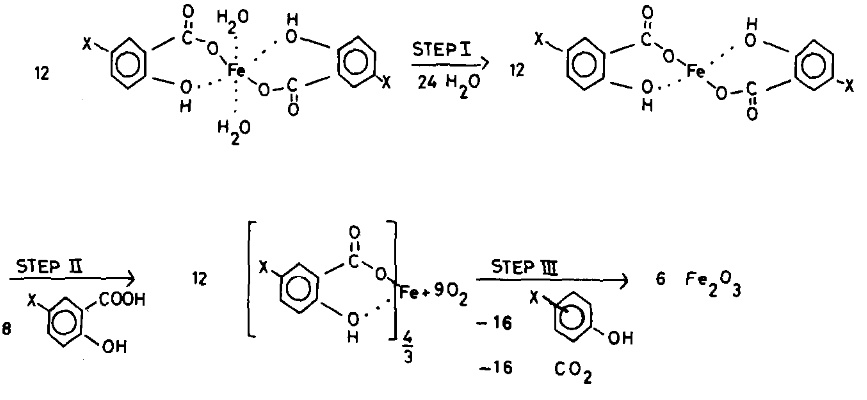


Fig. 1. TG and DTG plots of bis(2-hydroxybenzoato)iron(II)dihydrate (**A**); bis(2-hydroxy-5-chlorobenzoato)iron(II)dihydrate (**B**); bis(2-hydroxy-5-bromobenzoato)iron(II)dihydrate (**C**); and bis(2-hydroxy-5-iodobenzoato)iron(II)dihydrate (**D**).

TG measurements, and IR and mass spectral studies the following reaction mechanism is possible for the decomposition of complexes **A**–**D**.



(1)

where X = H (**A**), Cl (**B**), Br (**C**) or I (**D**). For these complexes, the experimental and calculated amounts of the final product as mass percent are within ±0.4. The final product was verified by comparing the X-ray diffractogram and IR spectrum of the residual product with the corresponding spectra obtained under the same circumstances from the extra pure

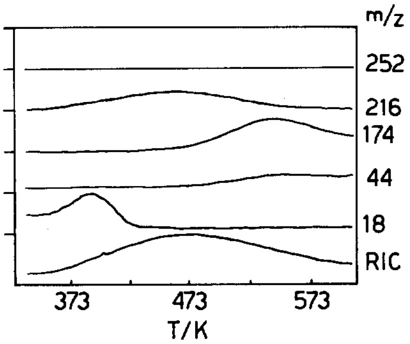


Fig. 2. Mass chromatograms of the main decomposition products obtained with a Jeol JMS-D300 mass spectrometer from the bis(2-hydroxy-5-bromobenzoato)iron(II)dihydrate. Values of *m/z* refer to water (18), carbon dioxide (44), bromophenol (174), 2-hydroxy-5-bromobenzoic acid (216), and dibromophenol (252).

Fe_2O_3. It was also interesting to observe, using the same spectral methods, that the oxidation of iron(II) ions to iron(III) ions occurs during the decomposition process at ~ 673 K both in the air and nitrogen atmospheres. This means that, in addition to the main decomposition scheme proposed, other oxidation–reduction reactions also occur during step III, because, in the nitrogen atmosphere, the oxygen for the formation of Fe_2O_3 must come from a substantial decomposition of the ligand.

The mass spectra of the decomposition products show that, in addition to the main volatile products, small amounts of di- and trihalophenols occur in connection with complexes **B**–**D**, due to various side-reactions occurring during the decomposition.

For the nitrocomplex (**E**), which was found to decompose explosively at 569 K, the TG curve between 293 and 473 K is shown in Fig. 3. According

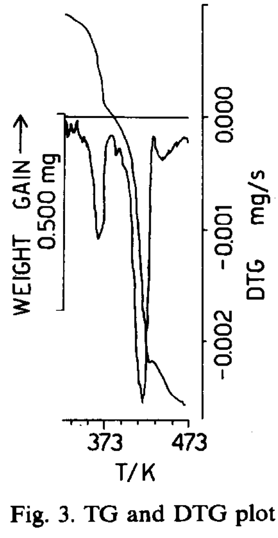


Fig. 3. TG and DTG plot of bis(2-hydroxy-5-nitrobenzoato)iron(II)trihydrate.

to the TG and mass spectral data the decomposition of complex **E** includes two steps before explosion. The first step (363 K) corresponds to the loss of one uncoordinated H_2O molecule. In the second stage (420 K) the two coordinated H_2O molecules are lost simultaneously.

DSC studies

On the basis of earlier DSC studies concerning copper(II) 5-substituted salicylates [10] it was possible to assume a very similar kind of thermal behaviour between complexes **A–D** and, therefore, DSC measurements were carried out only for complex **B** (Fig. 4). There is a weak endothermic peak centred at 363 K which is due to the loss of two water molecules. The enthalpy change for this decomposition step is 148.4 kJ mol^{-1}. The strong exothermic peak at about 590 K represents the organic redox reactions which occur in decomposition stage III.

Kinetic studies

The kinetics and thermodynamics of the thermal dehydration of powdered complexes, step I for **A–D** and step II for **E**, were studied by means of TG and DSC techniques at constant temperatures. For the isothermal dehydration reactions of hydrated iron(II) salicylates, **A–E**, the following equation is used

$$f(\alpha) = kt \tag{2}$$

where $f(\alpha)$ is a function dependent on the isothermal dehydration mechanism, α is the fraction dehydrated at time t, and k is the rate constant. The

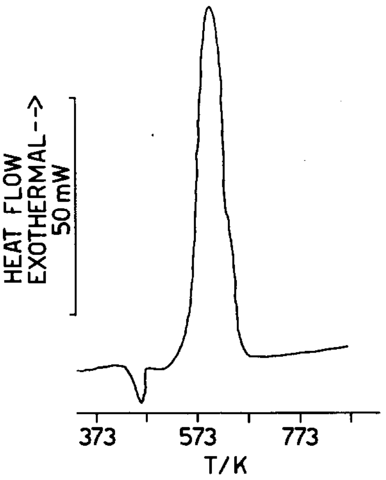


Fig. 4. DSC curve of bis(2-hydroxy-5-chlorobenzoato)iron(II)dihydrate.

commonly-used kinetic functions for the solid decomposition, including a random nucleation and subsequent growth, autocatalytical (Prout–Tompkins' function), diffusion and phase boundary reaction mechanisms, presented in detail elsewhere, were applied for the calculation of rate constants

TABLE 2

Rate constants, k, derived from TG or DSC measurements at different constant temperatures in the range 0.1–0.9

Complex	Method	T (K)	k ($\times 10^4$ s^{-1})	r	δ ($\times 10^2$)[a]
A	TG ($R_{3.2}$)	428.15	4.32	0.9998	0.11
		433.15	6.75	0.9993	0.31
		436.15	8.61	0.9988	0.53
		438.15	9.96	0.9983	0.74
		440.15	11.33	0.9974	1.03
B	TG ($R_{3.2}$)	433.15	3.27	0.9999	0.02
		438.15	5.31	0.9999	0.03
		443.15	8.52	0.9999	0.06
		448.15	13.25	0.9998	0.22
		451.15	17.05	0.9995	0.39
	DSC ($R_{2.2}$)	438.15	3.99	0.9999	0.04
		443.15	6.46	0.9999	0.04
		446.15	8.57	0.9999	0.10
		448.15	10.36	0.9999	0.14
		451.15	13.81	0.9999	0.25
C	TG ($R_{2.0}$)	438.15	8.30	0.9997	0.16
		440.15	9.82	0.9997	0.21
		443.15	12.75	0.9998	0.23
		446.15	16.45	0.9997	0.35
		448.15	19.50	0.9995	0.50
		451.15	25.01	0.9996	0.56
D	TG ($R_{1.2}$)	433.15	14.58	0.9999	0.13
		435.15	16.87	0.9999	0.14
		438.15	20.99	0.9999	0.20
		441.15	26.29	0.9997	0.56
		443.15	30.39	0.9996	0.71
E	TG ($R_{3.2}$)	393.15	1.71	0.9990	0.05
		398.15	3.24	0.9998	0.05
		403.15	5.96	0.9995	0.13
		408.15	10.44	0.9999	0.09
		413.15	18.60	0.9999	0.04
		418.15	32.53	0.9995	0.75

[a] δ is the error defined by the equation, $\delta = [\sum_{i=1}^{N} \epsilon_i^2/(N-1)]^{1/2}$, where ϵ_i is the deviation from the straight line, and N is the number of experimental data.

TABLE 3

Kinetic parameters derived from the Arrhenius plot by means of isothermal TG or DSC data

Complex	Method	$E_a/(\mathrm{kJ\ mol^{-1}})$	ln $A(s^{-1})$
A	TG ($R_{3.2}$)	126.9 ± 3.8	27.9 ± 1.0
B	TG ($R_{3.2}$)	149.2 ± 1.3	33.9 ± 0.4
	DSC ($R_{2.2}$)	156.6 ± 0.7	35.2 ± 0.2
C	TG ($R_{2.0}$)	139.8 ± 0.4	32.6 ± 0.2
D	TG ($R_{1.2}$)	117.5 ± 0.7	26.1 ± 0.2
E	TG ($R_{3.2}$)	160.4 ± 0.8	40.4 ± 0.3

[11,14]. The $f(\alpha)$ pertinent to the dehydration was searched for by plotting it against t; the appropriate plot should give a straight line with a slope k. On the basis of our calculations it could be deduced that the phase boundary reaction mechanism was the optimum.

Table 2 lists the rate constants, k, at various temperatures determined from TG and DSC data by means of the phase boundary reaction mechanism R_n determined by

$$f(\alpha) = 1 - (1 - \alpha)^{1/n} \tag{3}$$

where $n = 1.0, \ldots, 3.2$. In the table the correlation coefficient, r, and the error, δ, as a measure of the linearity are given. The results show that at the same temperature, 438.15 K, the rate constant increases as the size of the halogen atom increases in the case of complexes **B**–**D**, and, the activation energies calculated from the Arrhenius plot decrease in the same order (Table 3).

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