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# STUDIES ON THE THERMAL DECOMPOSITION OF SALICYLHYDROXAMIC ACID AND ITS METAL COMPLEXES WITH Ni(II), Co(II), Fe(II), Mn(II) AND Zn(II)

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## ABSTRACT

The thermal decomposition of salicylhydroxamic acid and its metal complexes with Ni(II), Co(II), Fe(II), Mn(II) and Zn(II) has been studied by TG, DTG, DTA and IR spectroscopy. All the compounds investigated decompose to yield intermediate *N*-hydroxylactams.

Decomposition schemes have been proposed and reaction enthalpies and kinetic parameters have been calculated.

## INTRODUCTION

Recently, we have reported some thermal results on several complexes of 5,5′-methylenedisalicylhydroxamic acid (MEDSHA) [1]. These compounds decompose through three major steps, dehydration, transformation of the anhydrous hydroxamates to intermediate *N*-hydroxylactams, and, finally, decomposition to yield metal oxides as final products.

Since MEDSHA carries two SHA (salicylhydroxamic acid) moieties bridged through $-CH_2-$, it seems reasonable to assume that both compounds should show similar thermal behaviour. Therefore, it is of interest to study the thermal properties of SHA and its metal complexes. In this communication we report the kinetics, the associated $\Delta H$ values and mechanisms of the thermal decomposition of SHA and its metal complexes with Ni(II), Co(II), Fe(II), Mn(II) and Zn(II).

## EXPERIMENTAL

### *Preparation of reagent and chelates*

All chemicals used in this work were of reagent grade. Salicylhydroxamic acid was prepared by the procedure of Bhaduri [2].

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TABLE 1

Analytical data

| Complex[a] | Colour | Metal (%) | | Carbon (%) | | Hydrogen (%) | | Nitrogen (%) | |
|---|---|---|---|---|---|---|---|---|---|
| | | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. |
| $(RH)_2Zn \cdot 2\ H_2O$ | White | 17.11 | 17.53 | 38.95 | 38.57 | 3.97 | 3.74 | 6.91 | 6.61 |
| $(RH)_2Fe \cdot 2\ H_2O$ | Dark red | 13.88 | 14.09 | 42.15 | 42.45 | 3.82 | 4.07 | 7.27 | 7.07 |
| $(RH)_2Ni$ | Light green | 15.81 | 16.17 | 46.20 | 46.33 | 3.38 | 3.32 | 7.81 | 7.72 |
| $(RH)_2Co$ | Pink | 16.00 | 16.22 | 46.53 | 46.30 | 3.41 | 3.33 | 7.60 | 7.71 |
| $(RH)_2Mn$ | Dirty-white | 15.43 | 15.29 | 46.91 | 46.82 | 3.42 | 3.37 | 7.67 | 7.80 |

[a] $RH_2 = C_7H_7NO_3$ (salicylhydroxamic acid).

The Zn(II), Fe(II) and Ni(II) salicylhydroxamates were synthesized by the addition of calculated amounts of SHA in ethanol to the metal salts ($Zn(NO_3)_2 \cdot 6\ H_2O$, $(NH_4)_2Fe(SO_4)_2 \cdot 6\ H_2O$ and $Ni(NO_3)_2 \cdot 6\ H_2O$) in 30% aqueous ethanol and stirring. Ammonium hydroxide (2 N) was then gradually added to adjust the pH of the solutions to between 5.5 and 7.0. The mixtures were warmed and allowed to stand on a water-bath for 30 min with occasional stirring. The precipitates were filtered, washed with 30% aqueous ethanol, and finally dried in a vacuum desiccator over anhydrous calcium chloride.

In a similar manner, Co(II) and Mn(II) salicylhydroxamates were prepared by the treatment of the corresponding metal salts ($Co(NO_3)_2 \cdot 6\ H_2O$ and $MnCl_2 \cdot 4\ H_2O$) with SHA at 0°C under a nitrogen atmosphere and in the absence of light.

The solid complexes were characterised by chemical analysis (Table 1).

### *Apparatus*

The simultaneous TG, DTG and DTA were performed with a Setaram GDTD-10 thermoanalyzer fitted with a B-70 electrobalance with thermocouples of Pt/Pt–Rh in an alumina base. All the thermal experiments were done in static air, with alumina crucibles as sample holders, using calcinated $\alpha$-alumina as reference material. The sample weight amounted to about 10 mg and the heating rates were 2.2, 4.6, 7.3 and 14.6°C $min^{-1}$.

The activation energy, $E$, and the order of the reaction, $n$, were determined by the methods described in the literature [3–5].

Reaction enthalpies were determined from peak areas (DTA) [6]. The $\Delta H$ values are referred to the melting $\Delta H$ value of indium (6.80 cal $g^{-1}$).

Infrared spectra were recorded with a Beckman 4240 IR spectrophotometer in the 4000–250 $cm^{-1}$ range, using the KBr pellet technique.

The procedure for decomposition products analysis has been reported earlier [1].

## RESULTS AND DISCUSSION

### *Decomposition of salicylhydroxamic acid*

Figure 1 presents the TG, DTG and DTA plots of SHA. The course of the DTG curve suggests two transformations. The DTA curve presents first an endothermic effect at 165°C, corresponding to the melting of the reagent, followed by an exothermic one involving a continuous weight loss with a break at 185°C (17% weight loss). Around the latter temperature, a crystalline white product condensed on the pyrolysis tube walls in the TGA cell. This sublimated product, obtained from isothermal heating at 180°C, was

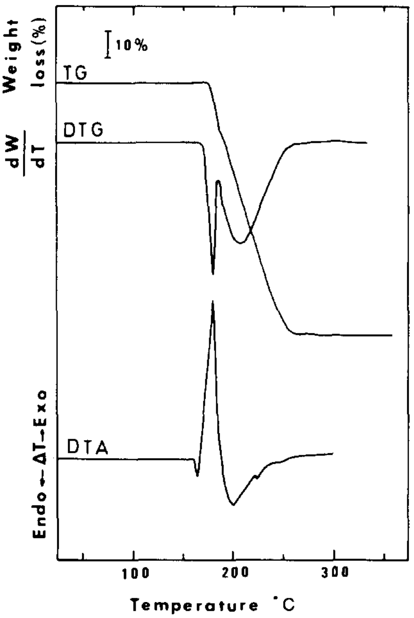
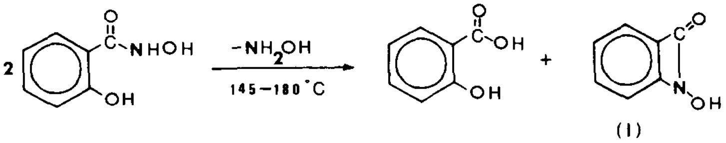


Fig. 1. DTA, TG and DTG curves for salicylhydroxamic acid.

identified by IR spectroscopy to have the same spectrum as that of the salicylic acid. In addition, the non-volatile residue isolated in this experiment was analyzed. Its IR spectrum showed the characteristic $\nu$C=O band around 1760 $cm^{-1}$ attributed to the stretching of a carbonyl group belonging to a four-membered ring [7]. Further, bands corresponding to N–H stretching (3282 $cm^{-1}$) and N–H bending (1575 $cm^{-1}$) disappeared. These modifications in the IR spectrum can be attributed to the *N*-hydroxylactam (**I**) formation. Chemical analysis of the products at this stage also supports the IR data.

All the above observations allow us to propose the following decomposition scheme.



Scheme 1

Further weight loss between 185 and 255°C corresponds to decomposition of all the *N*-hydroxylactam (**I**), as indicated by a complete weight loss on the TG curve. The peak corresponding to this change is also indicated on the DTA curve (200°C).

## *Decomposition of salicylhydroxamates*

The thermal curves of the complexes (Figs. 2 and 3) show two (anhydrous complexes) or three (hydrated complexes) major steps of decomposition.

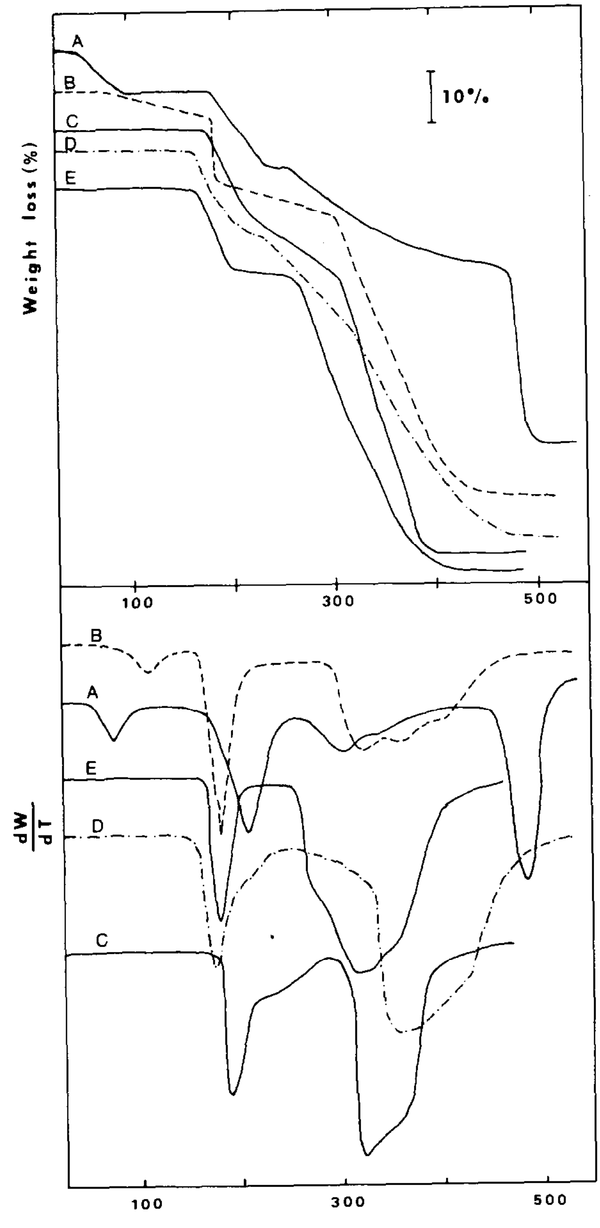


Fig. 2. TG and DTG curves of the metal chelates of salicylhydroxamic acid. A, $(RH)_2Zn\cdot 2H_2O$; B, $(RH)_2Fe\cdot 2H_2O$; C, $(RH)_2Ni$; D, $(RH)_2Co$; E, $(RH)_2Mn$.

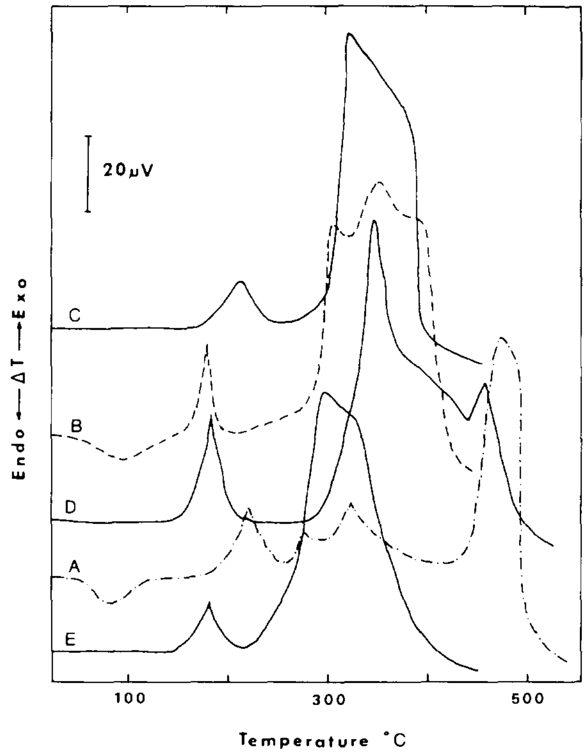


Fig. 3. DTA curves for the metal chelates of salicylhydroxamic acid. A, $(RH)_2Zn \cdot 2\ H_2O$; B, $(RH)_2Fe \cdot 2\ H_2O$; C, $(RH)_2Ni$; D, $(RH)_2Co$; E, $(RH)_2Mn$.

TABLE 2

Thermal data for the decomposition of salicylhydroxamates

| Complex | Temp. range (°C) | TG loss (wt%) | | DTA peak |
|---|---|---|---|---|
| | | Found | Calcd. | |
| $(RH)_2Zn \cdot 2\ H_2O$ | 50–90 | 8.4 | 8.87 | Endo (80) |
| | 180–233 | 14.7 | 15.03 | Exo (222) |
| | 255–500 | 55.5 | 56.04 | Exo (475) |
| $(RH)_2Fe \cdot 2\ H_2O$ | 60–170 | 5.0 | 4.54 | Endo (91) |
| | 178–185 | 12.9 | 12.88 | Exo (183) |
| | 185–450 | 62.9 | 62.42 | Exo (304, 358) |
| $(RH)_2Mn$ | 159–198 | 15.9 | 16.99 | Exo (184) |
| | 198–436 | 60.9 | 61.78 | Exo (293) |
| $(RH)_2Ni$ | 173–219 | 17.1 | 16.82 | Exo (212) |
| | 219–389 | 62.2 | 62.60 | Exo (318) |
| $(RH)_2Co$ | 159–223 | 16.9 | 16.81 | Exo (186) |
| | 223–488 | 60.5 | 61.09 | Exo (342, 453) |

TABLE 3

Fundamental frequency assignment [a]

| Compound | Frequencies of vibration ($cm^{-1}$) | | | |
|---|---|---|---|---|
| | $\nu$(C=O) hydroxamic | $\nu$(C=O) *N*-hydroxylactam | $\nu$(C=O) carboxylic (salicylic) | $\nu$NH |
| $(RH)_2Zn \cdot 2\ H_2O$ | 1603 vs [a] | — | — | 3320 s |
| 230°C sinter | 1590 vs | 1750 m | 1650 s | — |
| $(RH)_2Fe \cdot 2\ H_2O$ | 1600 vs | — | — | 3300 s |
| 200°C sinter | 1595 vs | 1750 m | 1640 sh | — |
| $(RH)_2Mn$ | 1601 vs | — | — | 3310 s |
| 198°C sinter | 1596 vs | 1750 m | 1630 sh | — |
| $(RH)_2Ni$ | 1603 vs | — | — | 3330 s |
| 205°C sinter | 1598 vs | 1750 s | 1650 sh | — |
| $(RH)_2Co$ | 1608 vs | — | — | 3330 vs |
| 200°C sinter | 1598 s | 1755 m | 1650 sh | — |

[a] vs = very strong; s = strong; m = medium; sh = shoulder.

The temperatures and the characteristics of the peaks occurring on the DTA curves for all investigated products are shown in Table 2.

The thermal curves of the Zn(II) and Fe(II) complexes show water loss. The DTA plots exhibit one identifiable dehydration step, and their decomposition stoichiometries may be expressed by the reactions

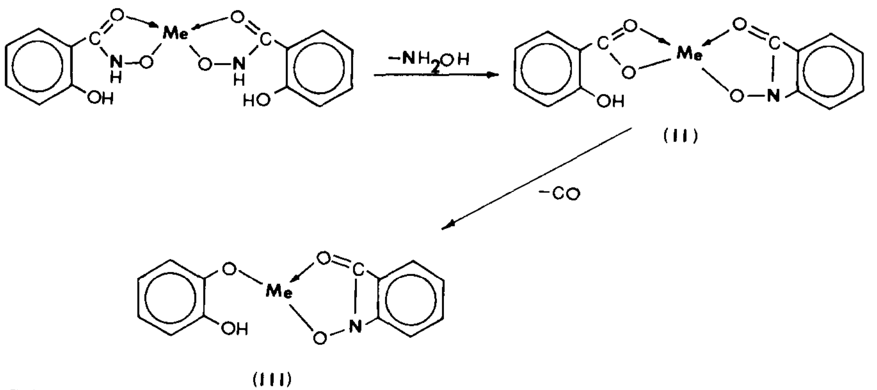
$$(RH)_2Zn \cdot 2\ H_2O \xrightarrow[50-90^{\circ}C]{-2H_2O} (RH)_2Zn$$

$$(RH)_2Fe \cdot 2\ H_2O \xrightarrow[60-170^{\circ}C]{-H_2O} (RH)_2Fe \cdot 1\ H_2O$$

The anhydrous salts, i.e., $(RH)_2Mn$, $(RH)_2Ni$, $(RH)_2Co$ and $(RH)_2Zn$, decompose in two stages, liberating 1 mole of hydroxylamine and 1 mole of carbon monoxide in the first stage between 150 and 240°C. This change clearly appears on the DTA curves as a medium exothermic peak. The data for calculated and observed weight losses and the corresponding temperature ranges are also given in Table 2.

Samples obtained from isothermal heating at the above temperature interval were analyzed by IR spectroscopy (Table 3). It can be seen that all of the compounds heated contain a new absorption centered around 1750 $cm^{-1}$, which is assigned to the *N*-hydroxylactam $\nu$(C=O) mode, and a shoulder at approximately 1650 $cm^{-1}$. This last band has been attributed to the $\nu$C=O vibration of salicylate [8]. In addition, we observed that the heated compounds did not contain the characteristic hydroxamic $\nu$(NH) mode in the region 3250–3350 $cm^{-1}$ [9].

All the above observations and results suggest an intramolecular interaction which leads to the following proposed decomposition scheme



Scheme 2

However, it is clear from the shape of the curves that the two processes overlap.

In contrast to this behaviour, the mass losses for $Fe(RH)_2 \cdot 2\ H_2O$ suggest that one water molecule is lost initially (60–170°C) and that the second step involves further loss of water together with $NH_2OH$.

These general features agree markedly with the free ligand, SHA, and the 5,5′-methylenedisalicylhydroxamates [1] both of which show *N*-hydroxylactam formation.

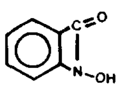
Finally, all the complexes decompose to oxides between 180 and 500°C,

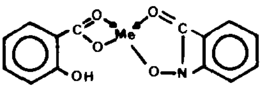
TABLE 4

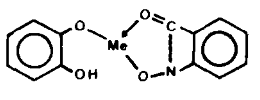
Reaction order ($n$), activation energy ($E$) and enthalpy change ($\Delta H$) for the decompositions to *N*-hydroxylactams

| Reaction [a] | A [b] | | B [b] | | C [b] | $\Delta H$(kcal mol$^{-1}$) |
|---|---|---|---|---|---|---|
| | $n$ | $E$(kcal mol$^{-1}$) | $n$ | $E$(kcal mol$^{-1}$) | $E$(kcal mol$^{-1}$) | |
| $RH_2 \rightarrow$ (I)+vp | — | — | 1 | 45.2 | — | 24.2 |
| $(RH)_2Zn \rightarrow$ (III)+vp | 1 | 46.2 | 1 | 45.7 | 44.7 | 17.5 |
| $(RH)_2Fe \cdot 1\ H_2O$ $\rightarrow$ (II)+vp | 1 | 95.3 | 1 | 92.4 | — | 20.0 |
| $(RH)_2Mn \rightarrow$ (III)+vp | 1 | 40.7 | 1 | 39.2 | — | 16.9 |
| $(RH)_2Ni \rightarrow$ (III)+vp | 1 | 56.8 | 1 | 67.6 | — | 5.0 |
| $(RH)_2Co \rightarrow$ (III)+vp | 1 | 69.8 | 1 | 69.0 | — | 26.6 |

[a] vp = Volatile products.

(I) =


(II) =


(III) =


[b] A = Dave and Chopra method (DTG); B = Coats–Redfern method (TG); C = Piloyan et al. method (DTA).

showing one or two exothermic effects due to the combustion of the organic matter.

### *Kinetic parameters and associated* $\Delta$H *values*

The non-isothermal decomposition to intermediate *N*-hydroxylactams of SHA and the metal complexes under study is a one-step decomposition reaction which can be kinetically probed for kinetic parameters using the expressions of Dave and Chopra [3] and Coats–Redfern [4]. The activation energies, $E$, and the associated reaction orders, $n$, were calculated from TG and DTG curves and the values are reported in Table 4. The values obtained using the different procedures are quite comparable. Only in one of the five complexes, namely that of Zn(II), could the activation energy be calculated from the DTA curve, following the expressions of Piloyan et al. [5].

The reaction order of decomposition to *N*-hydroxylactam was found to be 1 for all of the compounds examined.

The $\Delta H$ values associated with these reactions are also reported in Table 4.

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