INTERPRETATION OF TG CURVES WITH HELP OF HIGH RESOLUTION MASS SPECTROMETRY

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SUMMARY
    The use of high resolution mass spectrometry for the determination of the thermal decomposition mechanisms of metal salicylato complexes, $M(5-XHsal)_2 \cdot yH_2O$ (M is a divalent metal, $5-XH_2sal$ is 5-substituted salicylic acid and y is the number of crystal water molecules), is discussed. The decomposition of these complexes involves dehydration and loss of ligand acid in two successive steps. The final product is the corresponding metal oxide. This study was conducted to shown that for the resolving of the detailed reaction mechanism, decomposition products both in gaseous and solid state phases must be analyzed.

INTRODUCTION

    Thermal analysis in itself provides only weak clues pertaining to reaction mechanism, especially for the gaseous reaction products of thermal decomposition reactions. Therefore other methods, like mass spectrometry, are often used with thermogravimetry to reveal the thermal stabilities of products as well as the nature and consistency both of solid intermediate and gaseous reaction products. We have recently studied thermal behaviour of a number of metal complexes of aromatic o-hydroxycarboxylic acids (refs. 1-7). The use of high resolution mass spectrometry in connection of thermal analysis with these compounds will be demonstrated.

EXPERIMENTAL

Preparation and analysis of the compounds

    The preparation of the salicylato and 5-substituted salicylato complexes with copper(II), iron(II), manganese(II), nickel(II), zinc(II) and cadmium(II) and 1-hydroxy-4-sulfonato-2-naphthoic acid complex with copper(II) have been described earlier (refs. 1-7). The metal contents of the compounds were determined by atomic absorption spectrometry or direct current plasma atomic emission spectrometry, the crystal water content by the Karl Fischer titration, and the carbon and hydrogen contents with an element analyzer.

Methods

    TG and DTG curves were recorded on a Mettler TA-3000 thermoanalyzer. The sample weights and heating rates were from 5 to 12 mg and 5 K/min, respectively,

for each run.

For the analysis of volatile decomposition products by mass spectrometry, two different techniques have been used: (1) The decomposition products evaporated between desired temperature range were condensed and analyzed by a Kratos MS 80 RF autoconsole mass spectrometer using a capillary gas chromatographic sample inlet system. A Tecator Digestion System, equipped with an automatic temperature control (Autostep 1012 Controller) and a cold finger trap was used for collecting decomposition products. (2) In the second technique a direct insertion probe was employed. With a JEOL JMS-D300 mass spectrometer the sample was heated at a rate of 10 K/min in a quartz capillary of the direct inlet probe. The spectra of decomposition products were recorded every five seconds. The mass spectra with a Kratos mass spectrometer were determined with the direct inlet technique by heating the sample at 30 K intervals and by recording the mass spectra of formed decomposition products in a vacuum. The mass spectra were produced both by a chemical ionization with isobutane as a reagent gas and by electron ionization techniques. By the direct inlet system it is possible to follow the changes in the decomposition products as a function of temperature.

X-ray measurements were carried out on a Philips PW1050 X-ray diffractometer using CuK_α radiation.

RESULTS AND DISCUSSION

For the analysis of volatile decomposition products by high resolution mass spectrometry, we have used two different techniques: (1) The evaporated decomposition products were condensed, collected and analyzed by mass spectrometer using a capillary gas chromatographic sample inlet system, or (2) volatile decomposition products were analyzed by mass spectrometer using a direct insertion probe with a constant heating rate. The disadvantage of the latter method is that the gaseous phases of MS and TG runs are completely different. For example, 4(5)-(2,3-dimethylbenzyl)imidazole (detomidine) hydrochloride monohydrate was found to decompose differently according to the experimental conditions (ref. 8). In air and under normal pressure the following steps in the thermal decomposition takes place: first the release of water, then the simultaneous evaporation of hydrochloric acid and detomidine base followed by the decompostion of detomidine left in the crucible. On the basis of the mass spectra the thermal decomposition in vacuum involves only the release of water and evaporation of HCl and detomidine base, which shows that the molecule skeleton is not broken at the increased temperature under decreased pressure.

The structure of the complex compound between copper(II) and 1-hydroxy-4-sulfonato-2-naphthoic acid is not yet fully characterized, but the elemental

analysis of the compound gives the following empiric formula: $Cu(C_{11}H_7O_6S)_2 \cdot$
$9\ H_2O$ (ref. 1). The TG curve of the compound has four stages. The first three
stages are the release of water. The decomposition of the complex begins at
about 453 K, and the most dramatical weight loss (48.8 %) takes place at 603 K.
The final product was found to be CuO. To find out gaseous decomposition prod-
ucts, a complex sample was heated in a digestion system up to 673 K, and evap-
orated decomposition products were collected on a cold finger, dissolved in
ether and injected into the mass spectrometer using a silica capillary gas
chromatograph. According to the total ion chromatogram there are three main
condensed decomposition products of the ligand. These are 1-naphthol, 1,4-
naphthoquinone and phthalic acid anhydride.
acid anhydride.

In the next example it will be demonstrated how high resolution mass spectro-
metry can be used in determination of reaction mechanisms of decomposition
processes. We have studied thermal behaviour of a number of different metal(II)
salicylato complexes. According to the chemical analysis the general formula
of all these compounds is $M(5-XHsal)_2 \cdot yH_2O$. M is either copper(II), iron(II),
cadmium(II), zinc(II), nickel(II) or manganese(II), X is H, Cl, Br, I or NO_2
substituent in 5-position to the carboxylate group, and H_2sal denotes salicylic
acid. The amount of crystal water molecules (y) is either 2 or 4 depending on
the central atom. The complexation takes place via the carboxylate group, the
hydroxyl group is protonated, and the crystal water molecules are attached to
the central atom. The structure and bonding in copper, zinc and manganese
salicylato dihydrate complexes were recently determined by the single crystal
X-ray diffraction method (ref. 9). The X-ray analysis confirmed our earlier
proposal for the structures of these compounds.

Fig. 1 shows TG and DTG curves for bis(5-chlorosalicylato)zinc(II) dihydrate,
bis(5-bromosalicylato)iron(II) dihydrate and bis(5-bromosalicylato)cadmium(II)
dihydrate. The thermal decomposition of all these compounds takes place in
three separate stages: dehydration, the loss of free ligand acid and the loss
of second ligand acid which decomposes to the corresponding phenole and carbon
dioxide.

The search of the decomposition mechanism of various salicylato complexes
was conducted by collecting data both from gaseous and solid state phases, and
verifying results obtained to the corresponding TG and DTG curves. For analy-
sis of intermediate and final products in solid state, MS, X-ray diffraction,
IR-spectrometry and scanning electron microscopy were used. Gaseous decomposi-
tion products were identified with mass spectrometry using a direct inlet
system.

The search of the gaseous phase was in each case begun by making a total ion
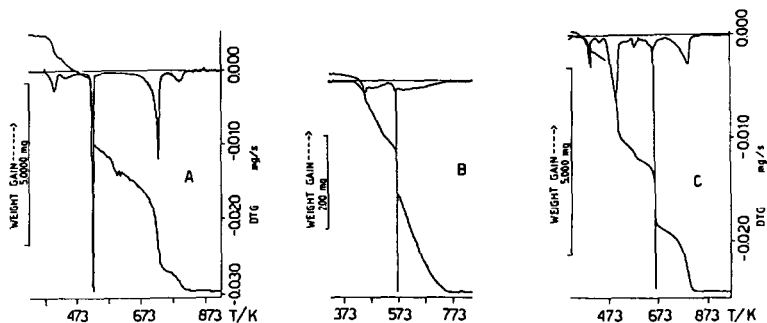chromatogram (Fig. 2). Then the main products evolved were identified on the

Fig. 1. TG and DTG curves for $Zn(5-ClHsal)_2 \cdot 2H_2O$ (A), $Fe(5-BrHsal)_2 \cdot 2H_2O$ (B), and $Cd(5-BrHsal)_2 \cdot 2H_2O$ (Refs. 4, 6, 7)

basis of the mass spectra obtained in the selected points of the total ion chromatogram (points 1 – 5 in Fig. 2). In the next step the mass chromatograms of the main products were reconstructed (Fig. 3).
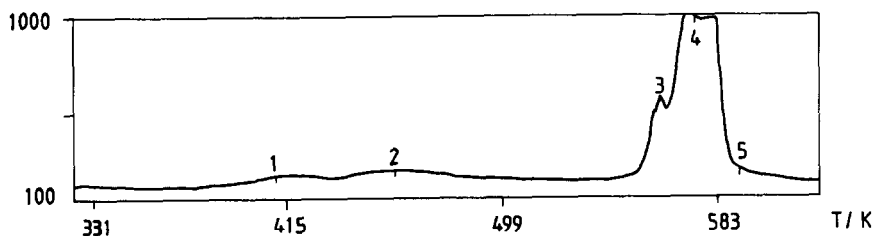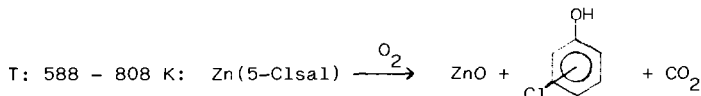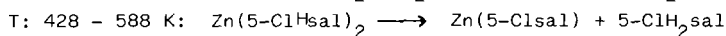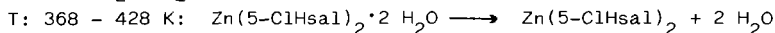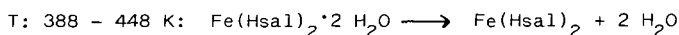

Fig. 2. The total ion chromatogram of $Zn(5-ClHsal)_2 \cdot 2H_2O$ (Ref. 7).

On the basis of TG and DTG curves, mass spectra of the volatile decomposition products, and X-ray diffraction analysis of the intermidiate and final products in solid state, we propose the following decomposition scheme for $Zn(5-ClHsal)_2 \cdot 2 H_2O$:

T: 368 – 428 K: $Zn(5-ClHsal)_2 \cdot 2 H_2O \longrightarrow Zn(5-ClHsal)_2 + 2 H_2O$

T: 428 – 588 K: $Zn(5-ClHsal)_2 \longrightarrow Zn(5-Clsal) + 5-ClH_2sal$

T: 588 – 808 K: $Zn(5-Clsal) \xrightarrow{O_2} ZnO +$ $+ CO_2$

In the case iron(II) and copper(II) salicylato complexes the decomposition mechanism is the same as that for the zinc salicylato complexes, except in the second step the complex decomposes totally and metal carbonate is formed. In the last step the carbonate and ligand acid decompose:
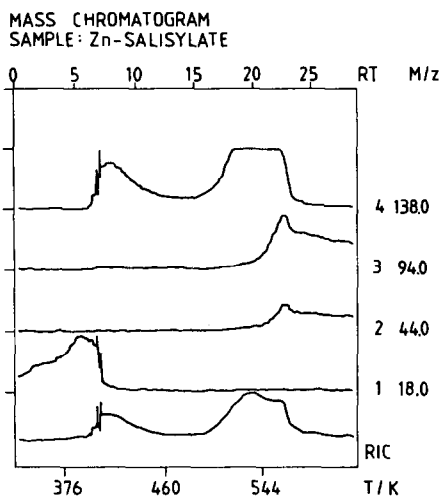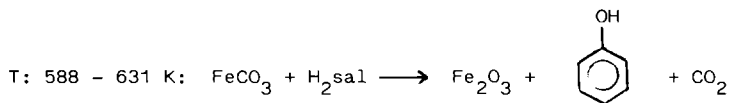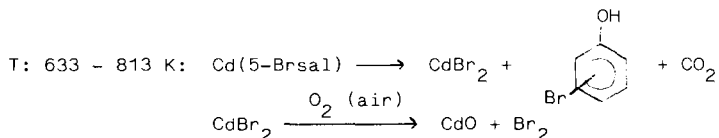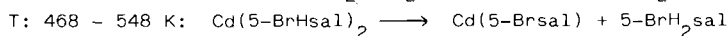
T: 388 – 448 K: $Fe(Hsal)_2 \cdot 2 H_2O \longrightarrow Fe(Hsal)_2 + 2 H_2O$

T: 448 – 588 K: $Fe(Hsal)_2 \longrightarrow FeCO_3 + H_2sal$ + gaseous products

T: 588 – 631 K: $FeCO_3 + H_2sal \longrightarrow Fe_2O_3 +$ [phenol structure, OH] $+ CO_2$
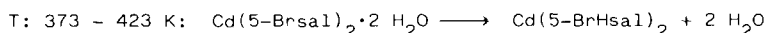
MASS CHROMATOGRAM
SAMPLE: Zn-SALISYLATE

Fig. 3. Mass chromatograms of the main decomposition products for $Zn(Hsal)_2 \cdot 2$ H_2O (Ref. 10.). Values of M/Z refer to water (18), carbon dioxide (44), phenol (94) and salicylic acid (138).

The decomposition scheme of $Cd(Hsal)_2 \cdot 2$ H_2O follows the same scheme as that of the zinc salicylato complexes. The decomposition of various 5–halosalicylato complexes of cadmium is different. The decomposition of these compounds in-volves four steps, from which the two last steps are overlapping. Before the formation of cadmium oxide, the corresponding cadmium halide was found to form. This was detected by scanning electron microscopy together with micro analysis, and X-ray diffraction analysis:

T: 373 – 423 K: $Cd(5-Brsal)_2 \cdot 2$ $H_2O \longrightarrow Cd(5-BrHsal)_2 + 2$ H_2O

T: 468 – 548 K: $Cd(5-BrHsal)_2 \longrightarrow Cd(5-Brsal) + 5-BrH_2sal$

T: 633 – 813 K: $Cd(5-Brsal) \longrightarrow CdBr_2 +$ [bromophenol structure, OH, Br] $+ CO_2$

$CdBr_2 \xrightarrow{O_2 \text{ (air)}} CdO + Br_2$

High resolution mass spectrometry is a powerfull technique for determination of decomposition mechanisms of metal complexes. However, for the entire decom-position scheme also other methods for analyses of the intermediate and final products in solid state phase is needed.

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