Thermochimica Acta, 72 (1984) 219–224
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THERMAL DECOMPOSITION OF HYDRATED COPPER(II) 5-SUBSTITUTED SALICYLATES

L.H.J. LAJUNEN, P. KOKKONEN, A. NISSI and H. RUOTSALAINEN
Department of Chemistry, University of Oulu, SF-90570 Oulu 57 (Finland)

ABSTRACT

Trihydrates of copper(II) 5-chloro-, copper(II) 5-bromo-, and copper(II) 5-iodosalicylates and dihydrate of copper(II) 5-nitrosalicylate have been prepared and characterized on the basis of elemental analysis and IR studies. The thermal behaviour of these salicylate hydrates has been determined employing TG, DTG and DSC techniques. The decomposition reaction mechanism of these complexes was studied by analyzing the decomposition products with MS and IR spectroscopy. CuO has been detected as the final product in the decomposition processes.

INTRODUCTION

The donor properties of substituted salicylic acids have not been studied as extensively as those of unsubstituted salicylic acid. Plostinaru and Spacu (ref.1) have studied some lanthanide compounds with 5-chlorosalicylic acid and found that the anion is coordinated as a bidentate ligand. Melnik et al. (refs.2-3) have investigated the thermal, spectral and magnetic properties of solid copper(II) 5-chloro- and copper(II) 5-bromosalicylates. We have previously determined the composition and stability of complexes formed in aqueous solutions of copper(II) ions and 5-substituted salicylic acid as a ligand as well as the partition of copper(II) between aqueous sodium perchlorate solution and organic solvents such as n-butanol, CCl_4, $CHCl_3$, etc. in the presence of 5-chloro-, 5-bromo-, 5-iodo- or 5-nitrosalicylic acid (refs.4-5). The aim of the present work is to study the thermal decomposition of hydrated copper(II) 5-chloro-, copper(II) 5-bromo-, copper(II) 5-nitrosalicylates by means of TG, DTG, DSC, MS and IR.

EXPERIMENTAL

Materials

The ligands as well as anhydrous cupric sulfate were supplied commercially (Fluka AG) as the purest available grade and they were used without further purification.

0040-6031/84/$03.00

Preparation of the compounds

The complexes in question, $Cu(5\text{-}xsal)_2 \cdot 3\ H_2O$ (x = Cl, Br or I and sal = $C_6H_3\text{-}OHCOO^-$) and $Cu(5\text{-}NO_2sal)_2 \cdot 2\ H_2O$, were prepared by modifying the procedure described elsewhere (ref. 2). The pH of an aqueous or water-ethanol solution of the sodium salt of each ligand acid was adjusted to 4-5. Cupric sulfate was added to these solutions with a molar ratio of 1:2. The light green products which formed after some minutes or in the case of copper(II) 5-iodosalicylate after some hours were filtered, washed with water and dried at room temperature over silica gel in vacuum. The copper contents of compounds were determined by AAS (Pye Unicam SP9-800) and the carbon and hydrogen contents with an element analyzer manufactured by Leco Co. The elemental analysis data for these complexes are given in Table 1. No sodium was found by AAS.

TABLE 1

Analytical data for copper(II) 5-substituted salicylates.

Compound	Calc. (%)			Found (%)		
	Cu	C	H	Cu	C	H
$Cu(5\text{-}Clsal)_2 \cdot 3\ H_2O$	13.79	36.50	3.06	13.70	36.2	1.73
$Cu(5\text{-}Brsal)_2 \cdot 3\ H_2O$	11.56	30.59	2.57	11.64	30.70	2.54
$Cu(5\text{-}Isal)_2 \cdot 3\ H_2O$	9.87	26.14	2.19	10.39	26.40	1.63
$Cu(5\text{-}NO_2sal)_2 \cdot 2\ H_2O$	13.70	36.26	2.61	13.07	36.0	1.50

Methods

The infrared spectra of the studied compounds and some intermediate products were recorded in a KBr medium, in the 4000-250 cm^{-1} region, using a Perkin-Elmer 457 spectrometer. The TG, DTG and DSC studies were carried out in air on a Mettler TA3000 thermal analysis system, using samples varying in weight from 5 to 12 mg and a heating rate of 5 $^oC\ min^{-1}$. The temperature calibration was made by checking the transformation-temperatures of a sample composed of three metal samples which Curie-temperatures are known (alumel, trafoperm and μ-metal in alumina crucible) and the heat flow calibration was carried out by employing the heat of fusion of a quantity of indium which was known exactly. The evaporated decomposition products were condensed, collected and analyzed by IR and by a Kratos MS 80 RF Autoconsole mass spectrometer using a capillary gas chromatographic sample inlet system. The conditions for the gas chromatographic analysis were a OV-1 column, a temperature programme range of 80-250 ^oC employing a heating rate of 5 $^oC\ min^{-1}$ and the chamber temperature of the MS-spectrometer at 230 ^oC.

RESULTS AND DISCUSSION

The results from the IR spectral measurements are presented in Fig. 1.

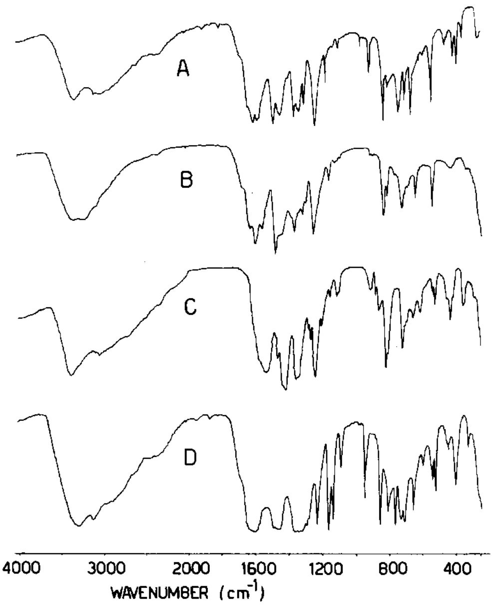

Fig. 1. The IR absorption spectra of Cu(5-Clsal)$_2$·3 H_2O (A); Cu(5-Brsal)$_2$·3 H_2O (B); Cu(5-Isal)$_2$· 3 H_2O (C); and Cu(5-NO_2sal)$_2$· 2 H_2O (D).

The IR spectra of the complexes consist of broad absorption bands in the 3150-3700 cm^{-1} region and the weak bands at 1620 cm^{-1} are due to water molecules (ref.6). The characteristic bands of the halogen and nitro groups can be observed at 650-790 cm^{-1} (C-Cl), 600-730 cm^{-1} (C-Br), 400-480 cm^{-1} (C-I) and 1550-1580 as well as 1300-1370 cm^{-1} (C-NO_2). The antisymmetrical COO^- stretch absorbs at 1630-1540 cm^{-1} and the symmetrical COO^- stretch is located in the range 1450-1300 cm^{-1}. There are not any bands found in the 1680-1700 cm^{-1} region which corresponds to the frequency of the COOH group ascribing to the free 5-xsalicylic acids (x = Cl, Br, I and NO_2) (ref.7).

Figures 2 and 3 show the TG, DTG and DSC plots of cu(5-xsal)$_2$· 3 H_2O complexes with the exception of Cu(5-NO_2sal)$_2$·2 H_2O which explodes at 370 °C and therefore its thermal behaviour has been determined only by TG.

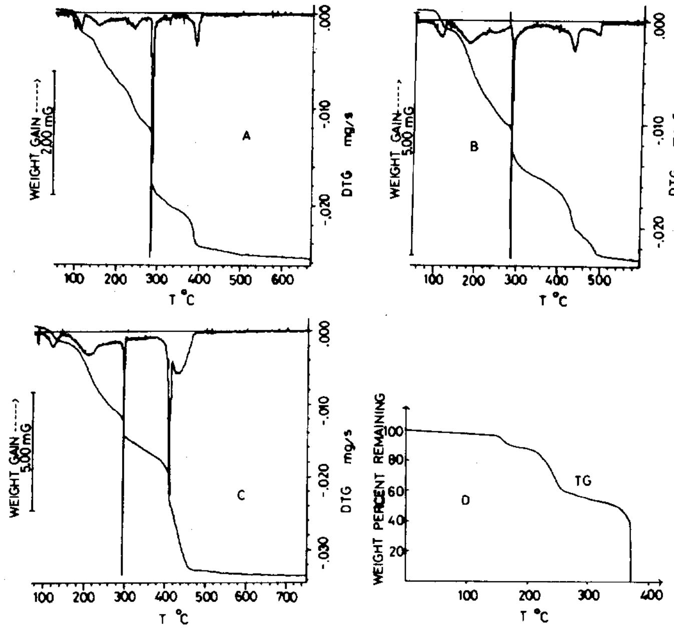

Fig. 2. TG and DTG plots of Cu(5-Clsal)$_2$ ·3 H_2O (A); Cu(5-Brsal)$_2$ · 3 H_2O (B); Cu(5-Isal)$_2$ ·3 H_2O (C); and Cu(5-NO_2sal)$_2$ ·2 H_2O (D).

TABLE 2

TG data for the first step of the dehydration process and the final product of decomposition.

	2 H_2O			CuO		
Complex	wt. loss (%)			residue		
	T °C	Found	Calcd.	T °C	Found	Calcd.
Cu(5-Clsal)$_2$ • 3 H_2O	80–124	8.3	7.8	500	17.2	17.3
Cu(5-Brsal)$_2$ • 3 H_2O	90–120	5.9	6.6	520	13.8	14.5
Cu(5-Isal)$_2$ • 3 H_2O	75–140	5.4	5.6	520	13.5	12.4
Cu(5-NO_2sal)$_2$• 2 H_2O	140–190	8.0	7.8	–	–	17.2

In all the complexes the first decomposition stage is the simultaneous release of two water molecules (Table 2). The expected endothermic behaviour for the release of water molecules has been observed from DSC curves in the same temperature ranges. In the second stage between 140-260 °C the third water molecule is relased, except for Cu(5-NO_2sal)$_2$ · 2 H_2O complex. Similarly for all the complexes the release of the ligand acid occurs which has been verified by IR and MS. This stage in the decomposition process of the complexes is a endothermic reaction. In the third stage a very rapid exothermic reaction takes place in the temperature range 280-300 °C. At this step the intermediate product is the corresponding halosubstituted phenol.

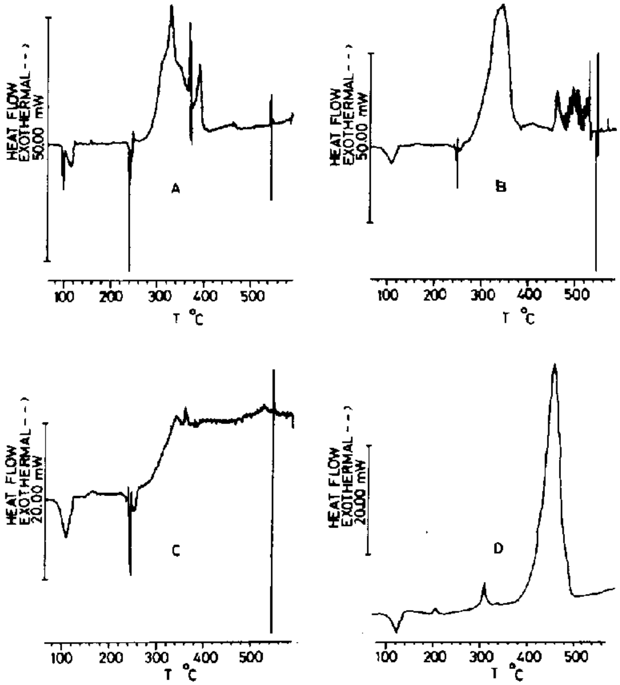

Fig. 3. DSC curves of $Cu(5\text{-}Clsal)_2 \cdot 3\ H_2O$ (A); $Cu(5\text{-}Brsal)_2 \cdot 3\ H_2O$ (B); $Cu(5\text{-}Brsal)_2 \cdot 3\ H_2O$ in N_2 atmosphere (C); and $Cu(5\text{-}Isal)_2 \cdot 3\ H_2O$ (D).

Figure 3 reveals that until this step the DSC curve for $Cu(5\text{-}Brsal)_2 \cdot 3\ H_2O$ is equal in an air and nitrogen atmosphere. In Fig. 4 the total ion chromatogramme of the sublimation products between 150-400 °C of $Cu(5\text{-}Brsal)_2 \cdot 3\ H_2O$ have been shown. The main components of the total ion chromatogramme were identified by MS-spectrometry and are given in the figure. So in the temperature range of 300-500 °C the main decomposition products, in addition to many minor intermediate components, are the corresponding halosubstituted phenols and carbon dioxide. Probably in this temperature range complicated redox-reactions of organic molecules occurs whereby the final product at 500 °C is the formation of CuO.

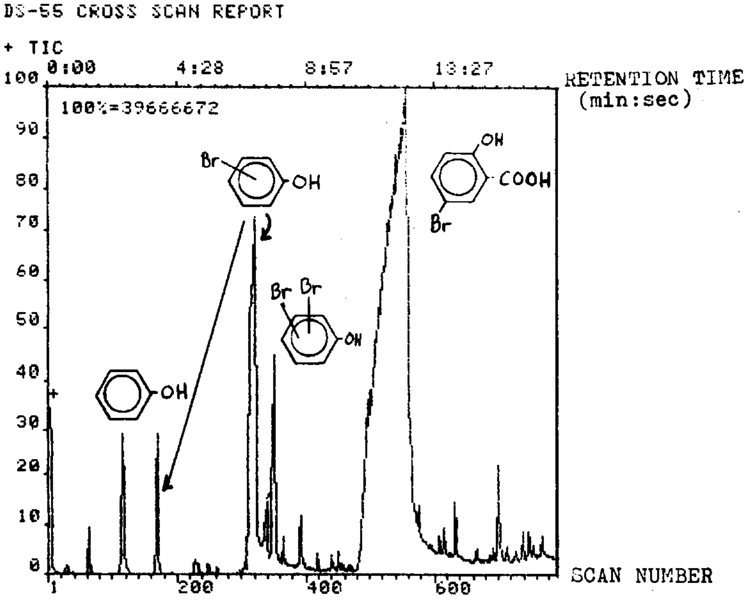

Fig. 4. The total ion chromatogramme of the sublimation products between 150–400 °C of Cu(5-Brsal)$_2$·3 H_2O.

REFERENCES

1 S. Plostinaru and P. Spacu, Rev. Roum. Chim. 19 (1974) 567.
2 M. Melnik, J. Inorg. Nucl. Chem. 40 (1978) 463.
3 M. Melnik, Z. Basik and H. Sandström, Acta Chem. Scand. A 33 (1979) 769.
4 L.H.J. Lajunen, H. Lippo and P. Kokkonen, Finn. Chem. Lett., in press.
5 L.H.J. Lajunen, P. Kokkonen and H. Lippo, Finn. Chem. Lett., in press.
6 D.H. Williams and I. Fleming, Spectroscopic methods in organic chemistry, 2. ed., McGraw-Hill Book Co., London 1973, p. 49.
7 The Sadler Standard Spectra, Sadler Research Laboratories, Philadelphia.