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THERMAL DECOMPOSITION OF BIS(1-HYDROXY-4-SULFONATO-2-NAPHTHOIC ACID)COPPER(II) NONAHYDRATE

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ABSTRACT

A 1:2 copper(II) complex of 1-hydroxy-4-sulfonato-2-naphthoic acid, $Cu(C_{11}H_7O_6S)_2 \cdot 9H_2O$, has been prepared and characterized on the basis of elemental analysis and IR spectrometry. The thermal behaviour of the compound has been studied using TG, DTG and DSC techniques. The decomposition mechanism of the complex has been interpreted by analyzing the decomposition products with mass and IR spectrometry. The first three stages in the TG curve are the release of the water molecules. According to the MS spectra there are three evaporated decomposition products at 330 °C which are 1-naphthol, 1,4-naphthoquinone and phthalic anhydride. The final decomposition product is CuO.

INTRODUCTION

The present paper continues our studies on the chemistry of aromatic sulfo-substituted o-hydroxycarboxylic acids. In some earlier papers we have reported the thermal behaviour of five sodium salts of sulfonated 1-hydroxy-2-naphthoic and 3-hydroxy-2-naphthoic acids (ref. 1-3). In this study a 1:2 copper(II) complex of 1-hydroxy-4-sulfonato-2-naphthoic acid has been prepared. The thermal behaviour of the compound was studied by means of TG, DTG and DSC techniques. With respects to interpreting the mechanism of the decomposition reaction, mass and IR spectroscopies were used.

EXPERIMENTAL

Materials

The preparation and purification of sodium 1-hydroxy-4-sulfonato-2-naphthoic acid have been described elsewhere (ref. 4). Anhydrous copper(II) nitrate was supplied commercially (Fluka AG, pa) and it was used without further purification.

Preparation and characterization of the complex compound

The complex compound studied was prepared by adding an excess of copper(II) nitrate to an aqueous solution of sodium 1-hydroxy-4-sulfonato-2-naphthoic acid (C_L = 0.02 M, $C_{Cu}:C_L$ = 3). The green crystals formed at room temperature were filtered, washed with water and dried in a vacuum desigator

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over silica gel. The copper and sodium contents of the compound were determined by AAS and the crystal water content by means of the Karl Fischer titration. On the basis of the above the composition of the present complex is $Cu(C_{11}H_7O_6S)_2 \cdot 9H_2O$. The calculated and determined copper and crystal water amounts are 8.36 and 8.39 %, and 21.3 and 20.2 %, respectively. No sodium was found.

Instrumentation and methods

The infrared spectra were recorded in a KBr medium in the 4 000 - 250 cm^{-1} region on a Perkin-Elmer 457 IR spectrometer. TG, DTG and DSC curves were recorded on a Mettler TA-3000 thermoanalyzer. The sample weights and heating rates were from 5 to 12 mg and 5 $^{o}C\ min^{-1}$, respectively, for each run. The decomposition products evaporated between 20 and 400 ^{o}C were condensed and analyzed by a Kratos MS 80 RF Autoconsole mass spectrometer using a capillary gas chromatographic sample inlet system and an IR spectrometer described above. Copper and sodium were determined with a Pye Unicam SP9-800 atomic absorption spectrometer equipped with a SP9 computer. A Tecator Digestion System, equipped with an automatic temperature control (Autostep 1012 Controller) and a cold finger trap, was used for collecting decomposition products. The crystal water amount was evaluated with a Beckman KF4 Aquameter.

RESULTS AND DISCUSSION

The thermoanalytical curves are presented in Fig. 1. The first three stages in the TG curve are the release of water. The change of weight for $Cu(C_{11}H_7O_6S)_2 \cdot 9H_2O$ in the first, second and third steps was 7.6, 4.4 and 4.1 %, respectively. The calculated weight loss for the dehydration of three and two H_2O molecules are 7.1 and 4.7 %, respectively. That reveals the simultaneous loss of three, two and two water molecules at about 85 - 113, 113 - 140 and 140 - 180 ^{o}C, respectively. The last two H_2O molecules are probably released between 180 and 295 ^{o}C. On the other hand, at that region the observed weight loss is 19.9 %. This means that the decomposition of the complex begins at about 180 ^{o}C. The most dramatical weight loss (48.8 %) takes place at 330 ^{o}C. So as to discover more details about the decomposition reaction, a complex sample was heated in a digestion system (temperature was risen up to 400 ^{o}C), and evaporated decomposition products were collected on a cold finger, dissolved in ether and analyzed by a mass spectrometer. The ether solution was injected into the mass spectrometer using a silica capillary gas chromatograph. The total ion chromatogramme of the run is given in Fig. 2. According to this run there are three main condensed decompositin products. On the basis of the mass spectroscopical analysis the decomposition products are 1-naphthol (MW = 144), 1,4-naphthoquinone (158) and phthalic anhydride (148). The end-product is pure CuO.

In the DSC curve two endothermic peaks (at 80 - 130 °C and 130 - 160 °C) and one exothermic peak (at 295 - 405 °C) are noted. The endothermic peaks are due to the dehydration and the large exothermic peak probably results from the oxidation of the decomposition products.

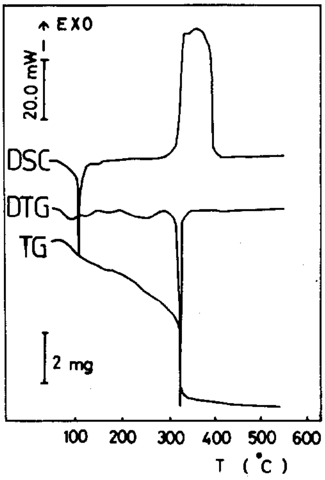

Fig. 1. TG, DTG and DSC curves from the thermal decomposition of bis(1-hydroxy-4-sulfonato-2-naphthoic acid)copper(II) nonahydrate.

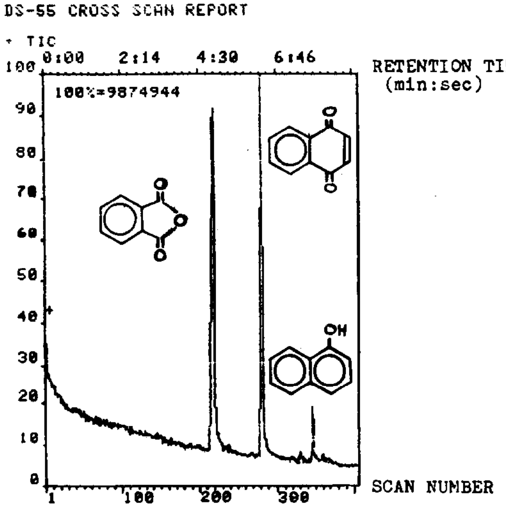

Fig. 2. The total ion chromatogramme for the condensed decomposition products evaporated at 330 °C in the thermal decomposition of bis(1-hydroxy-4-sulfonato-2-naphthoic acid)copper(II) nonahydrate.

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