

The Formation of Salicylonitrile *via* the Thermal Decomposition of Bis(salicylaldimine)copper

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It is well known that the bis(salicylaldimine)-copper is a stable chelate. But the thermal properties of this chelate have not been fully studied. The authors have investigated on the preparation of nitriles from aldehydes and ammonia,¹⁾ the reaction catalysed by a copper cation, for example, and also on the thermal properties of copper halide complexes of ketimines.²⁾ In due course, the bis(salicylaldimine)copper is expected to yield salicylonitrile through the thermal decomposition. Wendlandt *et al.*³⁾ investigated on the thermal decomposition of this chelate and reported that this chelate decomposed at high temperatures with evolving water, carbon monoxide, carbon dioxide and nitrogen. But they did not study the fate of the ligand fully. Then, the present authors tried to detect salicylonitrile among the decomposition products.

The differential thermal analysis and thermogravimetric analysis were carried out and the results are shown in the Fig. 1. At about 215–240°C, the decomposition reaction proceeded, as was reported previously by Wendlandt.³⁾

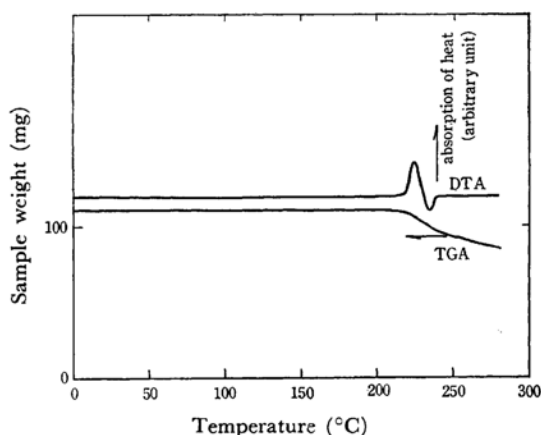


Fig. 1. The differential thermal analysis (DTA) and the thermogravimetric analysis (TGA).

Heating rate: 2.5°C/min under a dynamic nitrogen atmosphere the reference: α -alumina.

The chelate was set at the bottom of an ample under reduced pressure at 220°C; the volatile decomposition products were trapped on the water-cooled wall of the upper part of the ample. From the trapped material, a considerable amount of salicylonitrile (nearly the half of the total amount of the ligand contained) was obtained after suitable treatments. Among the trapped material, some resinous products were also found. The unvolatile part was dark purple in color after the decomposition reaction, which contained metallic copper.

The thermal decomposition may proceed through the internal oxidation-reduction, in which the central cation is reduced to its metallic form and the coordinated ligands lose their some hydrogen atoms by oxidation and yield the nitrile as the main product. Some residual products may contain the further reaction products of the nitrile. It has been made clear that the coordinated imino group could be dehydrogenated to the cyano group by the action of the central cation.

Experimental

The bis(salicylaldimine)copper(II) was synthesized according to Tyson and Adams.⁴⁾ (Found: C, 55.66; H, 4.05; N, 9.39%)

The chelate, 2.98 g (9.8 mmol) in weight, was set in the bottom of an ample, the upper part of which was cooled with water. The lower part of the ample was heated at about 220°C for 3 hr under reduced pressure (about 1 mmHg). The yellow material trapped on the water-cooled wall was dissolved into acetone (yield, 1.78 g). The infrared spectrum of this material showed a strong absorption signal at about 2220 cm^{-1} assigned as the $\text{C}\equiv\text{N}$ stretching (other main signals at about 3400–3000 (broad), 1605, 1460, 1310, 1280, 1240, 1160, 1030, 860, 850, 755 cm^{-1} : KBr disc method), but was not fully identical with that of a pure salicylonitrile. Salicylonitrile as the product was isolated according to the following procedure. The ether solution of the trapped material was treated with aqueous sodium hydroxide, and then the aqueous part was separated and acidified by hydrochloric acid. The aqueous solution thus obtained was again extracted with ether, and from the ethereal part, a yellow solid was obtained after evaporating the solvent. Its infrared spectrum was almost identical with that of a pure salicylonitrile (main signals at about 3290, 2220, 1605, 1505, 1460, 1360, 1310, 1275, 1240, 1160, 1100, 850, 750,

1) A. Misono, T. Osa and S. Koda, *This Bulletin*, **40**, 912 (1967); *ibid.*, 2875 (1967).

2) *Ibid.*, **41**, 373 (1968).

3) W. W. Wendlandt, S. I. Ali and C. H. Sternberg, *Anal. Chim. Acta*, **30**, 84 (1964).

4) G. N. Tyson and S. C. Adams, *J. Am. Chem. Soc.*, **62**, 1228 (1940).

735 cm^{-1} : KBr disc method). Gross yield, 0.98 g (8.2 mmol) Recry. from toluene after the treatment with activated carbon. Mp 95.7—96.5°C (the mixture with an authentic salicylonitrile showed the identical melting point), lit.⁵⁾ 96°C.

Found: C, 70.68; H, 4.16; N, 11.95; O, 14.35%.
Calcd for $\text{C}_7\text{H}_5\text{NO}$: C, 70.58; H, 4.23; N, 11.80; O, 13.34%.

5) M. Tanaka, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **78**, 1385 (1957).

In the X-ray diffraction pattern (Rigaku-Denki Co., Ltd., Geigerflex D-8C) of the unvolatile part (yield, about 1 g), strong signals were observed at about 43.5, 50.5, 74.0 and 90.0° of 2θ , which coincide with the signals of metallic copper. No other remarkable signals were observed.

The thermal analyses (TGA, DTA) were carried out with Rigaku-Denki Co., Ltd., differential thermal and thermogravimetric analyser. The decomposition was observed in a dynamic nitrogen atmosphere, at a heating rate of 2.5°C/min. Sample weight, 111 mg.