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Note

Thermal analysis of 8-quinolinol sulfate

VERONICA VALENTI and HAROLD JACOBSON
Squibb Institute for Medical Research, New Brunswick, N. J. 08903 (U. S. A.)
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INTRODUCTION

In the application of differential thermal analysis (DTA) to the quality control of 8-quinolinol sulfate, endotherms were observed at 134 and 177 °C (Fig. 1A). The former endotherm was considerably larger than the latter. However, that at 177 °C coincides with the accepted melting point (175–178 °C)[1]. This study was undertaken to elucidate the meaning of the first endotherm[2], previously not associated with any phenomena. As will become evident, the thermal properties of 8-quinolinol sulfate are important and have a direct bearing on the composition of this substance, a chemical of commerce.

EXPERIMENTAL

Materials. — 8-Quinolinol (reagent grade), 8-quinolinol sulfate, and 8-quinolinol-5-sulfonic acid were obtained from Matheson, Coleman, and Bell.

Apparatus. — Thermal analyses were performed with the DuPont Differential Thermal Analyzer, Model 900 and the Thermogravimetric Analyzer, Model 950. A temperature increment rate of 15 °C/minute was used for the DTA in capillary tubes in the presence of air. The thermogravimetric analysis (TGA) was made under isothermal conditions of 135 °C under vacuum (2 mm Hg).

Sublimation was carried out in a Werner–Klein micro sublimation unit at 134 °C under a partial vacuum of 100 mm Hg.

Elemental analyses were performed with the Perkin–Elmer 240 Elemental Analyzer. Infrared spectra were taken with the Perkin–Elmer 21, using KBr pellets.

RESULTS AND DISCUSSION

Visual observations of the sample of 8-quinolinol sulfate made during the taking of a differential thermogram showed no obvious events at the endotherm occurring at 134 °C. At the temperature of the second endotherm (177 °C), the material melted with decomposition (progressive discoloration).

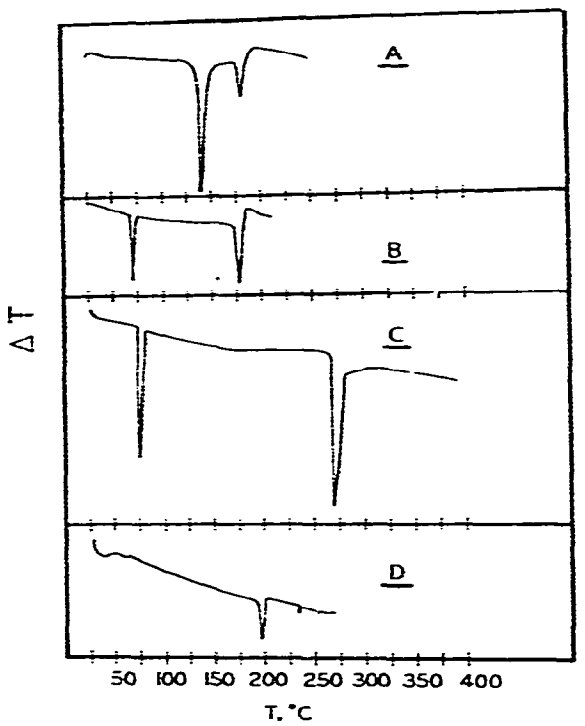

Fig. 1. Differential thermograms of: A, 8-quinolinol sulfate; B, 8-quinolinol sulfate that had been heated to 140°C and cooled; C, sublimate obtained from 8-quinolinol sulfate; D, residue after sublimation of 8-quinolinol sulfate.

When the material was heated just past the first endotherm to 140°C and allowed to cool, an exotherm was observed. (The exotherm occurred at 45°C, but because supercooling is almost invariably observed in this apparatus, the actual temperature is not as significant as is the presence of the exotherm.)

When the material was reheated, endotherms were observed at 70 and 177°C (Fig. 1B). The large endotherm previously present at 134°C was absent.

The isothermal TGA (at 136°C and 2 mm Hg pressure) resulted in a 41.0% weight loss. Under the conditions used, the weight loss required a relatively long time; it was concluded that the endotherm observed at 134°C during the DTA was not due solely to vaporization.

Subjection of this material to sublimation resulted in the formation of a white sublimate and a yellow residue, the latter unchanged in color from the original material. Thermograms of the sublimate and residue are shown in Figs. 1C and 1D, respectively. The sublimate showed a melting endotherm at 73°C and a boiling endotherm at 263°C. The residue gave a single endotherm at 190°C, representing a melting with decomposition. Samples of both sublimate and residue were also subjected to infrared and elemental analysis, as were, for comparison purposes 8-quinolinol, 8-quinolinol sulfate, and 8-quinolinol-5-sulfonic acid.

Both the infrared spectra and DTA showed the sublimate to be identical to

8-quinolinol. Further confirmation was given by elemental analysis: Found: C 74.36% H 5.10%, N 9.46%, S 0% (Theoretical: C 74.47%, H 4.86%, N 9.65%).

The infrared spectra of the residue did not lead to a clear identification. Elemental analysis, however, indicated it to be 8-quinolinol bisulfate; Found: C 44.50%, H 4.10%, N 5.70%, SO_4 38.55% (Theoretical: C 44.44%, H 3.73%, N 5.76%, SO_4 39.54%). The sulfur was determined as the sulfate. Supportive evidence is also given by the 41.0% weight loss observed by TGA, as mentioned above; the theoretical loss for 8-quinolinol sulfate yielding 8-quinolinol and 8-quinolinol bisulfate is 37.4%, with the former compound volatilizing.

It is concluded that 8-quinolinol sulfate, when subjected to relatively mild heating, dissociates and simultaneously sublimes to give 8-quinolinol and 8-quinolinol bisulfate. The first endotherm observed at 134°C (Fig. 1A) represents, principally, the dissociation. Sublimation is retarded by the close fit of the thermocouple in the capillary containing the sample. The exotherm observed on cooling from 140°C is the refreezing of the 8-quinolinol arising from the dissociation referred to above. The endotherm observed on reheating is the melting point of this compound. The endotherm at 177°C is due to the melting of the bisulfate with decomposition. The melting point for 8-quinolinol sulfate is probably not observable. That listed in the literature actually pertains to the bisulfate and is depressed, since the bisulfate is heavily "contaminated" with the 8-quinolinol.

REFERENCES

1 P. G. Stecher (Ed.), *The Merck Index*, Merck and Co., Inc., Rahway, N. J., 8th ed., 1968, p. 555.
2 R. G. W. Hollingshead, *Oxine and its Derivatives*, Butterworth, London, 1955.