On Nitration of Salicylhydroxamic Acid

by

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Preliminary experiments on nitration of salicylhydroxamic acid carried out by J. Nowak and one of us (T. U.) [1] led to the conclusion that, depending on the conditions of nitration, a high yield of picric acid can be obtained.

More detailed experiments were carried out by the authors of the present paper and produced the following conclusion:

When salicylhydroxamic acid was nitrated with nitric acid (d=1.50) alone at a temperature below 60°, 5-nitrosalicylic acid was formed with a total yield of 71% of theoretical. When the nitration was carried out with nitric acid (d=1.50) at a temperature above 65°, picric acid with a yield of c. 60% was obtained.

It is well known that picric acid (and 5-nitrosalicylic acid) can be formed by nitration of salicylic acid [2], [3]. The former is most probably produced by decarboxylation, which occurs simultaneously with the nitration. We repeated the experiments of Marchand and Hübner. We found that in the conditions of experiments of nitration of salicylhydroxamic acid with nitric acid leading to the formation of picric acid (i.e. above 65°), the yield of picric acid and of 5-nitrosalicylic acid from salicylic acid was c. 11% and 7% respectively.

This led us to a conclusion that the formation of picric acid from salicylhydroxamic acid cannot be explained solely as the result of an intermediate formation of salicylic acid and nitration, and subsequent decarboxylation.

However, we found that under action of nitric acid diluted with ether to a concentration of c. 40 per cent HNO₃ at c. −15°, a hydrolysis of salicylhydroxamic acid to salicylic acid occurred with a yield of 83%.

This seems to demonstrate that the first stage of nitration of salicylhydroxamic acid may partly consist in converting it into salicylic acid. The possibility of a reaction similar to the Lossen rearrangement was
considered. No experimental support for such a possibility has, however, been found so far.

When salicylhydroxamic acid was nitrated with a mixture of nitric acid \( (d=1.40) \) and sulphuric acid in the proportion 35 : 50 at a temperature of c. 95°, the main product of the reaction was 3,5-dinitrosalicylic acid with a yield of c. 20%.

When the reaction was carried out with a mixture of nitric acid \( (d=1.50) \) and acetic anhydride in the proportion 1 : 1, at temperatures of 20°-60°, two products — 5-nitrosalicylic and 3,5-dinitrosalicylic acids — were formed.

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REFERENCES