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REACTIONS OF ORGANIC COMPOUNDS IN AQUEOUS HYDROFLUORIC ACID

Ch. Comninellis*, Ph. Javet and E. Plattner

Institut de Génie chimique, Ecole Polytechnique Fédérale de Lausanne
140 Rue du Centre, CH 1025 St-Sulpice, Suisse

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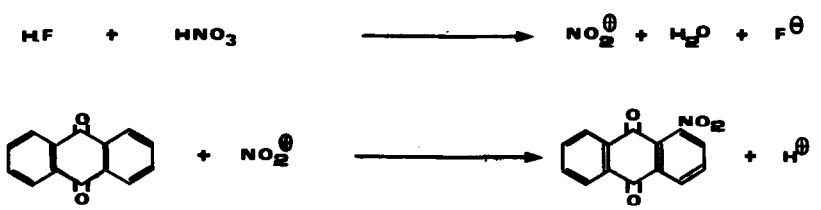
The literature gives much information about the catalytic effect of hydrogen fluoride on many organic reactions, e.g. acylation (1), ring closure (2), sulfonation (3), nitration (4), oxidation and other reactions (5,6). All these reactions were performed under anhydrous conditions and it was believed that only anhydrous hydrogen fluoride catalyses such reactions. In this paper we have found that 80-98 % aqueous hydrofluoric acid also catalyses some chemical reactions with high selectivity. This fact allows the use of hydrofluoric acid as a catalyst even in those reactions where water is formed.

We also confirm a theory proposed by Hebert (7) which revealed the existence of an active proton (of the form H_2F^+) in aqueous solutions of HF up to a concentration of 60 % HF.

Nitration

Anthraquinone is nitrated with HNO_3 or N_2O_4 in 80-98 % aqueous hydrofluoric acid. The experimental conditions are given in a recent Swiss patent application (8).

It has been found that the rate of nitration is constant between 80 and 98 % aqueous hydrofluoric acid but nitration occurs very slowly below 80 % aqueous hydrofluoric acid:



The reaction (1) occurs only if the hydrofluoric acid concentration is greater than 80 %.

The presence of water in the nitration medium has two advantages:

(i) The reaction temperature (30-40°C) can be obtained without external pressure. With anhydrous hydrogen fluoride the temperature at atmospheric pressure would be limited at 18-20°C.

(ii) The presence of water allows for an easy separation of the two isomers formed (1 nitro, 2 nitro) based on the difference of their solubility in aqueous hydrofluoric acid. The details of this separation are given elsewhere (8).

Oxidation

The oxidation of aliphatic thiols with nitrogen dioxide in aqueous hydrofluoric acid gives a high yield of sulfofluorides. E.g. octane is oxidised to octane sulfofluoride with 85 % yield.

$$n\text{-}C_8H_{17}SH + 3NO_2 + HF \longrightarrow n\text{-}C_8H_{17}SO_2F + 3NO + H_2O$$

The experimental conditions are given in a Swiss patent application (9)

The yield of the reaction depends on the concentration of the hydrofluoric acid solution, and the sulfofluoride is not obtained below 40 % hydrofluoric acid. With this low concentration the thiol is oxidised probably to the sulfonic acid as exhibited by the one phase educt.

In the region between 40-80 % hydrofluoric acid the educt has two phases and the yield of sulfofluoride increases and levels off at a value of 85 % for HF concentration of 80-98 %.

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