CHAPTER V

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IDENTIFICATION OF OXIDATION PRODUCTS

A knowledge of the products formed in a reaction subjected to kinetic study is an important step in elucidation of the mechanism of the reaction. Therefore it was considered necessary to identify the various products formed in these reactions.

Amide solution was mixed with equal quantities of $K_2S_2O_8$ and the silver catalyst. The reaction mixture after keeping for 24 hours was treated with a pinch of potassium chloride to precipitate out the silver chloride. The solution was filtered. The filterate was boiled till the whole solution of $K_2S_2O_8$ was decomposed(tested with KI and starch). The solution was further concentrated and the following tests were carried out.

TEST FOR ACID

Carboxylic acids can be converted into hydroxamic acids. All hydroxamic acids give a red or violet colour with ferric chloride in weak acid solution. This colour is due to acid CONHOH group, which is present in all hydroxamic acids.

Carboxylic acids cannot be converted into hydroxamic acids by direct action with hydroxylamine. The acid chloride must be formed first and it then readily gives the alkali salt of hydroxamic acid on treatment with hydroxylamine and alkali.

PROCEDURE

A drop of the test solution is evaporated to dryness in a microcrucible, or a minute portion of the solid is taken. Then two drops of thionyl chloride is added. The mixture is evaporated to dryness to convert the carboxylic acid into its chloride. Two drops of alcoholic solution of hydroxylamine hydrochloride are then added and two drops of alcoholic caustic soda until the liquid is alkaline to litmus paper. Reaction takes place on heating. The mixture is acidified with a few drops of dilute hydrochloric acid and treated with a dilute solution of ferric chloride. The colour changes from brown red to dark violet. This shows the presence of fumaric or azelaic acid. This test was performed according to Feigl.[195].

TEST FOR DETECTION OF NITROGEN

Test by ignition of calcium oxide (lime test).

1) When organic compounds containing nitrogen and hydrogen are strongly heated with lime then ammonia results. The paths by which ammonia is formed are not known. It is possible that calcium cyanide and calcium cyanamide are the initial products and these then hydrolyses on heating with water to produce ammonia. The necessary water is provided in the lime tests by the combustion of the hydrogen almost always a contained in the sample and reacts at the site of its production as superheated

steam. The ammonia produced in the lime test can be detected by indicator papers. Filter paper moistioned with silver nitrate, manganese nitrate solution are very effective. On contracts with ammonia a grey or black fleck appears on white paper. The stain is due to a mixture of free silver and manganous dioxide resulting from the reaction.

$$2Ag^{+} + Mn^{2+} + 4OH^{-} \longrightarrow 2Ag^{\circ} + MnO_2 + 2H_2O$$

PROCEDURE FOR TEST :

A little of the sample is mixed in a small hard glass tube with an ignited mixture of lime and manganese dioxide (10:1). Alternately, a drop of the test solution is evaporated to dryness in the tube. The open end of the tube is covered with filter paper moistioned with the reagent (manganese nitrate and silver nitrate solution) the glass stopper was kept in place and the tube is slowly heated to redness. A black or grey stain appears on the paper, shows the presence of nitrogen present. The stain immediately turns blue on spotting with benzidine solution. The above test was carried out according to Feigl.[195].

2) The formation of nitrogen was also shown by passing the gaseous reaction products (after completely freeing at from ammonia) over heated magnesium under nitrogen free atmosphere when Mg_3N_2 was obtained which produced ammonia on treatment with water.

Thus it can be concluded that the amide first undergoes hydrolytic decomposition and the hydrolytic products are oxidised by the radicals generated in the reaction medium.

Based on the above findings, a general reaction mechanism for the oxidation of amides suggested.