

CHAPTER - 3:
EXPERIMENTAL SECTION

All the solutions were prepared in double distilled water. Crotonaldehyde, crotonic, maleic, fumaric and citraconic acids, sodium tungstate, sodium molybdate and sodium orthovanadate were (B.D.H.) reagent Grade. Solutions of α, β -unsaturated acids and of catalysts-sodium tungstate, sodium molybdate and sodium vanadate were prepared by weighing in double distilled water. Hydrogen peroxide used in this investigation was of (B.D.H) AnalaR. Fresh solution of hydrogen peroxide was prepared for each series of experiments and was standardized by potassium permanganate solution.¹¹⁴ The unsaturated compounds- maleic acid, fumaric acid, crotonic acid, and crotonaldehyde solutions were standardized using bromate-bromide procedure¹¹⁵ which is as follows: A calculated excess (10 to 15%) of 0.1N bromate-bromide solution (about 25 ml) was run from a burette into a 300 ml conical flask having a ground glass stopper bearing a sealed in stop cock (The first analysis was only approximate and was carried out with a large excess of bromate bromide solution. From this preliminary result the desired excess was calculated. Following the evacuation of the flask by means of a water aspirator, 5 ml of 6N sulphuric acid was added and the flask was allowed to stand

2 to 3 minutes while bromine was being liberated. 15 ml of 0.2N mercuric sulphate and the solution to be analyzed, which had about 2 milliequivalents of unsaturation in 15 ml of CCl_4 , were added next. After the flask, wrapped in a black cloth, was shaken for about 7 minutes, 15 ml of 2N NaCl and 15 ml of 20% of KI were added in succession and the shaking was continued for half a minute. The vacuum was broken and the titration made with 0.05N $\text{Na}_2\text{S}_2\text{O}_3$ using starch. A blank without the sample and with one-third of the amount of bromate-bromide solution used in the analysis, was run at the same time, and under the same conditions.

The ionic strength of the reaction mixture was maintained by the addition of sodium perchlorate. The pH in the epoxidation of α, β -unsaturated acids - maleic, fumaric, crotonic and citraconic acids were maintained by the addition of triethanolamine but in case of crotonaldehyde, the pH was maintained by the addition of perchloric acid. In kinetic runs, the concentration of hydrogen peroxide was measured colorimetrically.¹¹⁶

Procedure:- Although the order of the mixing did not have any influence on the reaction rate, the reactants were always mixed in the order; water (to make up the volume to

100 ml', substrate, triethanolamine or perchloric acid and finally the hydrogen peroxide. The pyrex flask containing the above reaction mixture and a test-tube containing $M/500$ catalyst solution were kept immersed in a thermostatic bath. With occasional shaking both the solutions attained the temperature of the bath within 15 minutes.

After bringing the reactants to the thermostat temperature, the reaction was started by the addition of the catalyst. The kinetics were followed by examining 5 ml aliquot portions of reaction mixture for hydrogen peroxide. The aliquots were added to test tubes containing 5 ml titanium sulphate* solution to stop the reaction. Optical density was measured by Bausch and Lomb Spectronic 20, at 420 m μ , and the concentration of hydrogen peroxide was read from the calibration graph. The catalyst concentration was too small to affect the colorimetric estimation of hydrogen peroxide.

(*Preparation of the Titanium Sulphate Solution):-

The titanium sulphate solution was prepared by treating one gram of titanium dioxide with 100 ml concentrated sulphuric acid for 20 hours at about 150°C and filtered off the

undissolved material and made it to one litre by double distilled water).

In order to check the dependence of reaction on atmosphere, two identical reaction mixtures were studied, by bubbling oxygen through the first and nitrogen through the second. Rate constants were almost the same in both the cases. Therefore, no care was taken to maintain inert atmosphere and the reaction was studied in open vessels.

IDENTIFICATION OF THE PRODUCTS

The presence of trans-epoxysuccinic acid, cis-epoxy-succinic acid, 1,3-epoxybutyraldehyde, and 1,3-epoxybutyric acid were confirmed by Jungnickel, et al.¹¹⁷ method. Instead of methanolic sodium hydroxide, an aqueous solution was used for titration. Tartaric acid was detected¹¹⁸ in the reaction mixture of maleic and fumaric acids, whose pH was lower than 4. The form of tartaric acid was confirmed by using Buchhan chromatographic method.¹¹⁹ The procedure is described below:

Paper chromatography was carried out with a descending solvent as recommended by Consden, Gordon and Martin.¹²⁰ Purified solvents were employed throughout. Whatman No. 1 filter paper was cut into 10x20 cms sheets and spot of

solutions obtained by fumaric acid reaction mixture and maleic acid reaction mixture were applied in the usual manner. The solvent (water, n-butanol-acetic acid and concentrated HCl in the ratio 25:25:5:1 by volume) was added to the boat of the Shendon apparatus after conditioning of the paper. When the solvent had descended to an adequate extent, it was taken out, and dried for 5 minutes at 80°C to remove the solvent. A thin spray of 2% sodium-meta-periodate was applied, and the oxidation was allowed to proceed for 7 minutes at 60°C, in an atmosphere of nitrogen. Sulphur dioxide was passed on the paper until all of the liberated iodine was consumed and the paper was finally sprayed with Schiff's reagent. Coloured zones usually appeared in three hours. R_f values were not found to be reproducible-but the R_f of maleic acid product was always less than that of fumaric acid product. According to Buchanan R_f value of dl-form is higher than that of meso form. Therefore, it was inferred from this test that maleic acid gave meso form, while fumaric acid gave dl-form of tartaric acid. As R_f values were not reproducible sodium-metavanadate test was made to confirm the form of tartaric acid in the reaction mixture. Sodium-metavanadate gives a

red complex with dl form and does not react with meso form of tartaric acid. The test procedure adopted is given below.¹²¹

Two reaction mixtures one with maleic and other with fumaric acids were prepared as described above and the reactions were started by adding suitable amount of the catalyst. After 15 minutes of interval, 2 ml aliquots were taken out and added to test tubes containing sodium metavanadate solution which on standing gave a red colour with the fumaric acid reaction mixture and no colour change was noticed with maleic acid product.