
CHAPTER - II

EXPERIMENTAL TECHNIQUE

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The study of oxidation mechanism of alcohols has been an interesting problem since long time. Kinetic investigations regarding the oxidative processes involving alcohols and various oxidising agents have been reported by many workers¹⁻⁵ and the various oxidants used were other than chloramine-T. Very little is known about the kinetics and mechanism of oxidations involving chloramine-T⁶⁻⁸. Recently the polymeric reagents were shown to be quite effective in the oxidation of primary and secondary alcohols to aldehydes and ketones respectively in high yield. The polymeric reagents have been rapid development while reagents are not particularly expensive, their toxicity and associated environmental problems make easy recovery and separation from reaction products a practical necessity.

In this chapter, the kinetics of oxidation of benzyl alcohol and 4-methoxy benzyl alcohol by the polymer-supported chromates has been studied. The main aim has been to discuss the complete mechanism of the oxidation reaction and rate law.

PURITY OF THE CHEMICALS

All the chemicals used during the investigation were of AR grade. The chromic acid supported polymeric reagent prepared as mentioned in earlier communications⁹⁻¹¹.

The benzyl alcohol, 1:4 dioxane, carbon tetrachloride, benzene, chloroform, dichloromethane, methanol were distilled before use. The other chemicals used viz. chromic acid, potassium hydroxide, sodium thiosulphate, potassium iodide, sodium borohydride, sodium sulphate etc. were of AR grade.

PREPARATION OF 4-METHOXY-BENZYL ALCOHOL

A solution of 4-methoxy benzaldehyde (5ml) in methanol was cooled to 0°C to 5°C, Sodium borohydride (1.5gm) was added to it in small portions with stirring. The stirring was continued for two hours. The reaction mixture was slowly warmed to room temperature. The progress of reaction was monitored by TLC. After completion of the reaction methanol was removed under reduced pressure, followed by addition of saturated solution of ammonium chloride (20ml) and extraction with ether 3x10ml. The ether extraction washed with brine and dried over anhydrous sodium sulphate. Removal of solvent gave the corresponding alcohol which was purified by distillation (b.p. 257°C) and characterised by TLC and IR.

PREPARATION OF POLYMER-BOUND CHROMIUM(VI) OXIDE

To prepare the reagent 10 gms of the chloride form of Amberlyst A-26, a macroreticular anion exchange resin containing quaternary ammonium groups is stirred with

saturated aqueous solution of 5 gms of chromium trioxide in 30 ml of water for 30 minutes at room temperature, using a magnetic stirrer. Chloride ions were readily displaced and a HCrO_4^- form of the resin was quantitatively obtained in 30 min. The resin was successively rinsed with water, acetone, and ether and finally dried in vacuum at 50°C for 5 hours.

DETERMINATION OF THE CAPACITY OF POLYMERIC REAGENT

The capacity of the resin was determined by stirring overnight 0.5 gms of the resin with 10 ml of 2 N aqueous potassium hydroxide, filtering off and titrating iodometrically the obtained chromate solution. The determined average capacity of the dried resin was 3.6 mmol CrO_3/gm of resin. The resin thus obtained did not lose activity on storing in air at room temperature for several weeks nor on refluxing for 5 h in benzene or hexane⁹. This helps to use the same sample of polymeric reagent throughout the kinetic study.

UV SPECTRA

In the oxidation reaction of benzyl alcohol and 4-methoxy-benzyl alcohol using chromic acid polymeric reagent in 1:4 dioxane, benzaldehyde and 4-methoxy-benzaldehyde were the products. According to UV study benzaldehyde absorbs at 248 nm and 4-methoxy benzaldehyde absorbs at

271 nm. The kinetic investigation of these oxidation reactions was carried out at 258 nm for first oxidation reaction and at 276 nm for second oxidation reaction using Shimadzu 160-A UV VIS spectrophotometer.

PRESENT WORK

This chapter describes the kinetics and mechanism of oxidation of alcohols by polymer-supported chromic acid in 1:4 dioxane solvent. Oxidation of alcohols to the parent carbonyl compounds is achieved by a lot of reagents though the general problem can not be considered as definitely settled, particularly when chromium(VI) derivatives were used the efficiency was low^{12,13} and the work up of reaction mixture is some times complicated. The supported quaternary ammonium complex chromic acid exhibits effective oxidizing properties towards alcohols. Therefore we developed polymer-supported chromic acid as a new class of recyclable solid phase oxidizing agent.

MONITORING THE COURSE OF OXIDATION REACTION

Alcohol was added in 5ml of 1:4 dioxane and a known amount of polymeric reagent was added. This reaction mixture stirred on magnetic stirrer at a constant rate. At different time intervals 10 μ l of the reaction mixture was withdrawn using Wheatons micro pipette and care was taken that no solid particles were removed along with the

solution. The aliquots, thus withdrawn were taken in the test-tubes containing 5ml of 1:4 dioxane measured accurately with the help of measuring flask. The absorbance of the solution was measured at 258 nm for benzyl alcohol to benzaldehyde oxidation reaction and at 276 nm for 4-methoxy benzyl alcohol to 4-methoxy benzaldehyde oxidation reaction keeping the '0' time reading as reference. The following variations were studied.

- 1) Variation of concentration of polymeric reagent
- 2) Variation of concentration of substrate
- 3) Variation of solvent.

The observations, graphs and results are given and discussed in Chapter-III.

TEST FOR FREE RADICALS

The reaction was initiated by mixing polymer-supported chromate, alcohol and solvent at 45°C with continuous stirring. After 30 minutes about 0.5ml of reaction mixture was withdrawn in a test tube to which 1 ml of acrylo nitrile is added. Then this mixture is diluted with 2 ml distilled water, copious precipitation occurs on shaking which indicates the presence of free radicals.

PRODUCT ANALYSIS

In a 10ml 1:4 dioxane 150mg polymeric reagent and 15 μ l alcohol at 45⁰C stirred on magnetic stirrer. The progress of reaction was monitored by TLC. After the completion of reaction the resin was filtered off, washed with the solvent (5ml) and the product was isolated by the evaporation of filterate under reduced pressure. Then the product aldehyde is characterised by its 2:4 dinitrophenyl hydrazine derivative.

Aldehyde	2:4 Dinitrophenyl hydrazine Derivative M.P.
Benzaldehyde	236 ⁰ C
4-methoxy benzaldehyde	250 ⁰ C

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