CHAPTER III

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The literature survey on oxidation of various organic compounds, including oxidation of alcohols by chromic acid, revealed that,

1) The present work of oxidation of various substituted alcohols, using polymer supported oxidizing agents is quite meagre. Although a large number of reagents are known in the literature, for such transformations, there still appears a need either to improvise the existing oxidation methods, or to introduce newer reagents, to obtain

a) Better selectivity under milder conditions.

b) Easy workup procedures. For example, oxidation of the Baylis – Hillman product is an extremely sluggish reaction with pyridinium chlorochromate (PCC), pyridinium dichromate (PDC) and with palladium catalysed oxidation.

Tremendous work has been carried out with potassium dichromate, pyridinium dichromate (PDC), quinolinium dichromate (QDC), quinolinium fluorochromate (QFC) pyridinium chlorochromate (PCC), and quinolinium chlorochromate (QCC) in aqueous acetic acid in the presence of perchloric acid.
2) Oxidation methods such as supporting the oxidizing agent,\textsuperscript{9,10,11} or oxidation under phase – transfer catalysis \textsuperscript{12} find wide application in synthetic organic chemistry. But using a polymer supported oxidising agent \textsuperscript{13} for kinetic and mechanistic study is limited.

3) The use and reuse of polymer-supported oxidizing agent without loss of capacity is another interesting factor, to undertake the present work.

4) The present work is also important for the easy workup and safety or a unique reaction outcome. It also decreases side reactions. The oxidation process stops at product aldehyde only.

5) Cross-linked polystyrenes (with varying \% of DVB) which are now a days widely used because of their chemical and mechanical stability and also because the polymer swells strongly in several solvents. The reactions carried out using such cross-linked polymers result into high yield transformations.

Considering all these advantages the present study is planned. The various alcohols selected for the study are

- Benzyl alcohol
- 4-methoxy benzyl alcohol
- 4-methyl benzyl alcohol
- 4-chloro benzyl alcohol
- 4-bromo benzyl alcohol
- 4-nitro benzyl alcohol
The objective of the present study is not only to develop a method for the oxidation of these alcohols to their corresponding aldehydes, but also to determine the order of reaction, to study the effect of crosslinked polymers on the rate of reaction and to propose the plausible mechanism of the reaction and order of reaction.

During our survey it is found that, particularly when chromium (VI) derivatives were used, the efficiency of the reaction was low \(^{14,15}\) and the work up of reaction mixture is sometimes complicated.

The chromic acid supported on commercially available Amberlyst A-26 (anion exchange resin) and tailor-made, cross-linked (3.5% and 6.5%) quaternary ammonium resins which were also supported by chromium (VI) oxide, exhibits effective oxidizing properties towards alcohols.

Hence present study includes the effect of cross-linking on the rate of reaction.

The polymer supported chromium (VI) oxide (including Amberlyst A-26, 3.5% and 6.5% quaternary ammonium anion exchange resins) acts as a new class of recyclable solid phase oxidizing agent.

**Materials and purity:**

The double distilled water was used throughout the work, obtained by redistillation of distilled water in the presence of few crystals of KMnO₄ and a few pallets of KOH using corning glass distillation assembly.
All the chemicals used during the investigation were of AR grade. Benzyl alcohol was distilled before use. 1,4 dioxane, carbon tetrachloride, chloroform, cyclohexane and methanol were of spectroscopic grade..

The other chemicals viz., chromic oxide (BDH) potassium hydroxide, sodium thiosulphate, potassium iodide sodium borohydride, sodium sulphate etc. were of AR grade. The solid alcohols were recrystallized and used.

**Preparation of polymer bound – Chromium (VI) oxide:**

To prepare the reagent\textsuperscript{16-18} 10 gms of the chloride form of Amberlyst A-26, a macroreticular anion exchange resin [(Fluka, (20-50 mesh)] containing quaternary ammonium group was 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 HCrO\textsubscript{4} form of the resin was quantitatively obtained in 30 min.

\[
\begin{align*}
\text{P} & \quad \text{N} \quad \text{Cl}^- \\
\text{CrO}_3 & \quad \text{CrO}_3 \\
\text{P} & \quad \text{N} \quad \text{HCrO}_4^-
\end{align*}
\]

The resin was successively rinsed with water, acetone and ether and finally dried in vacuum at 50 °C for 5 hours. The dried form of the resin was stored and used throughout our study.
The preparation of quaternary ammonium iodide form of the resin from 3.5% and 6.5% crosslinked chloromethylated polystyrene is explained in detail in Chapter V. The tailor-made resins were also supported by chromium (VI) oxide by applying the same above mentioned procedure.

**Determination of capacity of polymeric reagent**

The capacity of chromate form of Amberlyst A-26, 3.5% and 6.5% quaternary ammonium resins was determined by stirring overnight 0.5gm of the resin with 10ml of 2N aqueous potassium hydroxide, filtering off and titrating iodometrically, the obtained chromate solution. The determined average capacity of the dried resin was.

1) Chromate form of Amberlyst A-26 → 3.6 mmol/gm

2) Chromate form of 3.5% quaternary ammonium resin → 3.4 mmol/gm

3) Chromate form of 6.5% Quaternary ammonium resin → 3.4 mmol/gm.

The resin thus obtained did not loose activity on storing in air at room temperature for several weeks, nor on refluxing for 5 hours in benzene or hexane. This helped to use the same sample of polymeric reagent throughout our kinetic study.

**Method of following the Kinetics**

The main features of the experimental method are as follows.

1) The temperature of the reaction mixture was kept constant by immersing the vessel in constant temperature bath at 45 °C.
2) The standard glasswares were used throughout the experimental work.

3) The reaction was carried out in a stoppered round bottom flask.

4) The standard run was carried out in 1:4 Dioxane and the completion time of the reaction was noted, by monitoring the reaction with the help of TLC. The reaction goes to completion within 2 hours.

5) The calculated amount of alcohol was then added in 5 ml of 1:4 Dioxane and a known amount of polymeric reagent was added.

6) The reaction mixture was stirred on magnetic stirrer at constant rate.

7) At different time intervals 10 µl of the reaction mixture was withdrawn using Qualigens (Glaxo) 5 to 50 µl micropipette. Care was taken, that no solid particles were removed along with the aliquot.

8) The aliquot thus withdrawn were taken in stoppered test-tubes containing 5 ml of 1:4 Dioxane, measured accurately with the help of standard measuring flask.

9) The optical densities (O.D.) of the reaction mixture thus withdrawn were measured at different wavelengths corresponding to the wavelengths of product aldehydes, using Schimadzu 160 – A UV – VIS spectrophotometer and keeping the zero time reading as reference.
Prior to the above step, the wavelengths of all the alcohols under study were determined by diluting 1 mg of sample of alcohol in 100 ml of 1:4 Dioxane, keeping 1:4 Dioxane as a reference. The wavelengths determined are as follows.

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>$\lambda_{\text{max}}$ nm</th>
<th>Aldehyde</th>
<th>$\lambda_{\text{max}}$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyl alcohol</td>
<td>258</td>
<td>Benzaldehyde</td>
<td>248</td>
</tr>
<tr>
<td>4-methoxy benzyl alcohol</td>
<td>276</td>
<td>4-methoxy benzaldehyde</td>
<td>273</td>
</tr>
<tr>
<td>4-methyl benzyl alcohol</td>
<td>265</td>
<td>4-methyl benzaldehyde</td>
<td>255</td>
</tr>
<tr>
<td>4-chloro benzyl alcohol</td>
<td>268.4</td>
<td>4-chloro benzaldehyde</td>
<td>254</td>
</tr>
<tr>
<td>4-bromo benzyl alcohol</td>
<td>269</td>
<td>4-bromo benzaldehyde</td>
<td>246</td>
</tr>
<tr>
<td>4-nitro benzyl alcohol</td>
<td>272</td>
<td>4-nitro benzaldehyde</td>
<td>265</td>
</tr>
</tbody>
</table>

The following variations were studied:

1) Variation of concentration of polymeric reagent.

2) Variation of concentration of substrate (i.e. alcohol).

3) Variation of solvent.

4) Variation of temperature.

5) Variation of % of Cross linking in polymeric reagent.
6) **Test for free radical** :

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

**Product Analysis** :

The product formed, were analyzed by its 2:4 Dinitro phenyl hydrazone derivatives. For product analysis 10 ml of 1:4 Dioxane, 150 mg of polymeric reagent and 15 µl alcohol was stirred on magnetic stirrer at 45 °C. After completion of the reaction (2 hours), the resin was filtered off, washed with the solvent (5 ml) and the product was isolated by the evaporation of filtrate under reduced pressure. The 2:4 Dinitro phenyl hydrazone derivative was then prepared from the corresponding aldehydes.

<table>
<thead>
<tr>
<th>Aldehydes</th>
<th>2:4 dinitro phenylhydrazone derivative (m.p.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Benzaldehyde</td>
<td>236°C</td>
</tr>
<tr>
<td>2) 4-methoxy benzaldehyde</td>
<td>253°C</td>
</tr>
<tr>
<td>3) 4-methyl benzaldehyde</td>
<td>233°C</td>
</tr>
<tr>
<td>4) 4-chloro benzaldehyde</td>
<td>265°C</td>
</tr>
<tr>
<td>5) 4-nitro benzaldehyde</td>
<td>219°C</td>
</tr>
<tr>
<td>6) 4-bromo benzaldehyde</td>
<td>207°C (p-nitro phenyl hydrazone)</td>
</tr>
</tbody>
</table>

The observations, graphs and results are given and discussed in Chapter IV.
REFERENCES

15) Lederer P. Personal Communication.