Chapter-IV

Results and discussion

The aim of the present study is to formulate the mechanism of the reactions under investigation and to suggest the suitable rate law and also to explain the relative reactivities of alcohols selected for the study. Hence it is necessary to review the various mechanistic criteria usually employed in the determination of reaction mechanism and to suggest the plausible mechanism on the basis of experimental facts.

In order to frame the most probable mechanism for the oxidation of the alcohols, it is necessary to summarize and discuss the results obtained in the present study.

Rate constants of the reaction:

The rate constant (k) of oxidation reaction of different alcohols under identical conditions are,

No.	Alcohols	k x10^{-4} min.$^{-1}$
1	4-Chlorobenzyl alcohol	4.11
2	Benzyl alcohol	7.61
3	4-Methoxybenzyl alcohol	8.63

The above results show that the rate of oxidation goes on increasing from 4-Chlorobenzyl alcohol to 4-Methoxybenzyl alcohol. Hence it is evident that the reaction is facilitated by electron donating group at para position.[1]

The linearity of absorbance against time plots and constancy of the zero order rate constants indicate that the reaction neither depends on the polymeric reagent nor on the alcohol concentration. This anomalous nature of the reaction may be because the oxidant is taken in the form of a solid supported on polymer. Therefore, the prior equilibra, before the rate determining or the step in which actual reaction takes place giving the product does not seem to contribute to the total rate since they are occurring in different phase i.e. solid phase. This was observed in earlier study of Benzoin oxidation by polymer supported N-Bromo sulphonamide.[2]

Effect of dielectric constant of solvent:

In the present study, it was observed that the rate of reaction increases with increase in dielectric constant of the medium indicating $r^* < r$ [where r^* and r refer to the radii of reactant species and the activated complex respectively].

In addition to this the high negative values[3] of $\Delta S^{\#}$ are also in favour of process in which activated complex is more solvated than the reacting species. The formation of free radical or radical ion during the course of reaction was confirmed from induced polymerization of acrylonitrile.

Effect of temperature:

The various parameters determined for oxidation reaction are as follows.

Thermodynamic parameters	4-Chloro benzyl alcohol	Benzyl alcohol	4-Methoxy benzyl alcohol
Energy of activation[Ea] Kcal	12.07	12.04	11.44
Frequency factor[A]x10^4	11.22	8.91	5.01
Temperature coefficient	1.77	1.78	2.00
Enthalpy of activation[$\Delta H^{\#}$] Kcal mol^{-1}	16.85	13.55	11.44
Entropy of activation[$\Delta S^{\#}$] e.u.	-21.04	-30.42	-36.71
Free energy of activation[$\Delta G^{\#}$] Kcal mol^{-1}	23.62	23.20	22.91

The energy of activation of substituted benzyl alcohols is in order.

4-Chlorobenzyl alcohol > Benzyl alcohol> 4-Methoxybenzyl alcohol

Ea values and order of reactivity reveals that, the activation energy value is the highest for the slowest reaction and vice versa.

The negative value of $S^{\#}$ in each case provides good evidence to state that, the rate determining step involves the association of molecules and there is loss of freedom of motion which reveals that the transition state is more ordered than the reactant molecules. The free energy of activation [$G^{\#}$] for all oxidation reaction is almost the same. These facts suggest that the probably the same mechanism prevails in all the reactions.

It reveals that the rate of oxidation goes on increasing from 4-Chlorobenzyl alcohol to 4-Methoxybenzyl alcohol. Hence, it is evident that the reaction is facilitated by electron donating group and it is retarded by electron withdrawing group.

Discussion:

The mechanism for one equivalent reducing agent, mainly inorganic ions, King and co-workers[4] proposed a sequence of three-one electron transfer steps to reduce chromium (VI) to chromium (III) with interconversion between chromium (V) and chromium (IV) as the slow step.

Mechanism of the oxidation of Alcohols:

The first serious attempt to understand the mechanism of the chromic acid oxidation of alcohols was made by Westheimer and Novick[5], who found the rate law for the oxidation of isopropyl alcohol to be:

$$= k_a\,[HCrO_4^-][R_2CHO][H^+] + K_b[HCrO_4^-][R_2CHO][H^+]^2$$

This rate law has been found to apply to the oxidation of all other primary or secondary alcohols which have been studied[6].

The most probable reaction sequence was:

$$R_2CHOH + Cr^{VI} \rightarrow R_2C=O + Cr^{IV}$$

$$Cr^{IV} + Cr^{VI} \rightarrow 2Cr^{V}$$

$$2\left(Cr^{V} + R_2CHOH \rightarrow R_2C=O + Cr^{III}\right)$$

Thus only one-third of the total oxidation is effected by chromium (VI) and two-third is effected by chromium (V).

Westheimer then proposed that the oxidation of primary and secondary alcohols proceeded via the acid chromate esters as intermediates.

$$R_2CHOH + HCrO_4^- + H^+ \rightarrow R_2CHOCrO_3H + H_2O$$

$$R_2CHOCrO_3H + H^+ \rightarrow R_2CHOCrO_3H_2^+$$

$$R_2CHOCrO_3H \xrightarrow{k_1} R_2C=O + Cr^{IV}$$

$$R_2CHOCrO_3H_2^+ \xrightarrow{k_2} R_2C=O + Cr^{IV}$$

There were several paths proposed for subsequent reaction of chromium (IV) thus making possible different mechanism for the oxidation of alcohols. According to Westheimer and Watanable[7,8] subsequent steps must involve chromium (VI).

Scheme (I)

$$Cr^{IV} + Cr^{VI} \rightarrow 2Cr^{V}$$

$$Cr^{V} + R_2CHOH \rightarrow R_2C{=}O + Cr^{III} + 2H^+$$

Scheme (II)

$$2Cr^{IV} \rightarrow Cr^{III} + Cr^{V}$$

$$Cr^{V} + \text{Red} \rightarrow Cr^{III} + \text{Oxi.}$$

The possibilities considered above are feasible when the reaction is carried out homogeneously. But if the oxidant is supported on polymer, which has certain advantages[9] over homogeneous reactions, the mechanism would be preferably according to Scheme II.

Chromium (VI) oxidation of alcohols as discussed earlier, proceed through formation of an ester. The ester thus formed will undergo internal oxidation reduction to produce chromium (IV). Since our oxidant was