SUMMARY

A brief but critical survey of the present situation and secondary alcohols by groups and their reactions is presented in this chapter. This also includes an analysis of the concept of coordination — the ability of certain acids, bases, or bases of different oxidation to enhance the ionization rates of the phosphorus as well as other related reactions. Various factors have been subjected to a structure — solvent — reactivity correlations with a view to extend to the present-day knowledge on this subject.

As a necessary adjunct to the study of dielectric alcohols by Cr(VI) oxide, a dielectric study has been made of the formic acid and a number of related acids with the aim of understanding the correlation of the following trends in alcohol dielectric constant in detail. (i) 2-nitro (ii) 2-chloro (iii) 2-methoxy (iv) 2-methyl and 2-bromo alcohols.

It has been established that the photochemical reaction of Cr(VI) in aqueous basic solution is a first-order reaction.
SUMMARY

A brief, but critical survey of the oxidation of primary and secondary alcohols by chromic acid has been made in the Introductory chapter. This also includes an analysis of the phenomenon of cooxidation - the ability of oxalic acid, even while undergoing oxidation, to enhance the oxidation rates of other organic substrates. This phenomenon as well as the related one, catalysis of Cr(VI) oxidations, have been subjected to a structure - reactivity and solvent - reactivity correlations with a view to add substantially to the present-day knowledge on this subject.

As a necessary adjunct to the study of Cooxidation of benzyl alcohols by Cr(VI) oxide in the presence of oxalic acid, a complete kinetic study has been made of the chromic acid oxidation of a large number of suitably substituted benzyl alcohols. The normal and cooxidation of the following benzyl alcohols have been studied in detail. (i) 4-bromo (ii) 2-bromo (iii) 4-chloro (iv) 4-nitro (v) 2-nitro (vi) 4-methyl (vii) 2-methyl and (viii) 4-methoxy benzyl alcohols.

It has been established that the rate of oxidation of benzyl alcohols by Cr(VI) in aqueous acetic acid as solvent follows the rate-law

\[ \frac{-d[Cr(\text{VI})]}{dt} = k [\text{ROH}][Cr(\text{VI})][H^+]^{0.5} \]

The application of a Hammett treatment is a reaction constant
rho of -0.82. The results are analysed in the light of Westheimer’s
proton-abstraction theory and Roček’s hydride-abstraction theory.
On the basis of a comparison with a related reaction viz., the
oxidation of benzyl alcohols by HNO₃, it is concluded that the reaction
proceeds by a hydride abstraction from a preformed chromate ester
of benzyl alcohol.

The cooxidation of benzyl alcohols by chromium (VI) oxide
in the presence of oxalic acid is shown to follow a relatively
straightforward rate-law viz.,

$$\frac{-d[Cr(\text{VI})]}{dt} = k [\text{ROH}][\text{Cr(\text{VI})}][\text{OxH}_2][H^+]^{0.5}$$

The following mechanism is proposed on the basis of the rate-law,
and structural effects on the rate,

$$\text{OxH}_2 + \text{HCrO}_4^- + H^+ \xrightarrow{K_1} \text{Complex 1}$$

$$\text{Complex 1} + \text{ROH} \xrightarrow{K_2} \text{Complex 2}$$

$$\text{Complex 2} \xrightarrow{k_3} \text{ketone} + \text{CO}_2 + \text{CO}_2^- + \text{Cr(III)}$$

The mechanism envisages the formation of a ternary complex between
oxalic acid, benzyl alcohol and Cr(VI) and a slow decomposition of
this complex involving a synchronous three-electron movement.
This mechanism is justified on the basis of (i) the considerably
decrease in Hammett rho for the benzyl alcohol system in the cooxidation
reaction (ii) the small effect of solvent polarity on the reaction
rate (iii) the absence of any influence by added Mn(II) which demons-
trates the absence of any Cr(IV) intermediate in these oxidations.
Oxalic acid, while increasing the rate of Cr(VI) oxidation of a second substrate, also suffers decomposition. On the other hand, picolinic acid (PA), 1,10-phenanthroline (Phen) and 2,2'-bipyridyl (Bipy) catalyse the oxidation of benzyl alcohols without undergoing any significant decomposition. The detailed rate-law for this oxidation in aqueous acetic acid has been established to be

$$\frac{d[Cr(VI)]}{dt} = k [ROH][Cr(VI)][H^+]^{0.5} [CA]^x$$

where $x$, the fractional order dependence on the complexing agent (CA), is explained on the basis of an intermediate formation of a 1:1 complex between Cr(VI) oxide and the complexing agent which further reacts with the alcohol molecule to form a second chromate ester type of complex. The slow decomposition of this complex into a molecule of benzaldehyde and a ligand-bound Cr(IV) intermediate accounts for the experimental observations and for a low Hammett rho.

The temperature effect on the normal oxidation, cooxidation and catalysed oxidation of benzyl alcohol by Cr(VI) oxide has been studied and the thermodynamic parameters have been evaluated. The data obtained have been analysed on the basis of the Exner treatment and the isokinetic relationship. The solvent effects on these reactions have been examined on the generalised theory of Amsel correlating rate with dielectric constant and also on the basis of specific solvation effects as dealt with by the Grunwald-Weinstein equation.

The kinetics of the oxidation of a series of alcohols (both primary and secondary) by the Corey reagent, pyridinium chlorochromate
in 90%HAc – 10%H2O(v/v) has been studied in detail with the following systems:

(i) benzyl alcohols (ii) diphenyl methanols (iii) 1-phenyl ethanols and (iv) aliphatic secondary alcohols.

It is established that there is a point to point correspondence between the rates of oxidation of these alcohols by PCC and Cr(VI) oxide in the same solvent system. On the basis of the observed isotopic, stereo and substituent effects, it is shown that the oxidation of alcohols by PCC proceed by an equilibrium formation of an alkyl ester of pyridinium chlorochromate which decomposes in a slow step, via a hydride ion transfer, to yield the carbonyl product and a Cr(IV) intermediate.