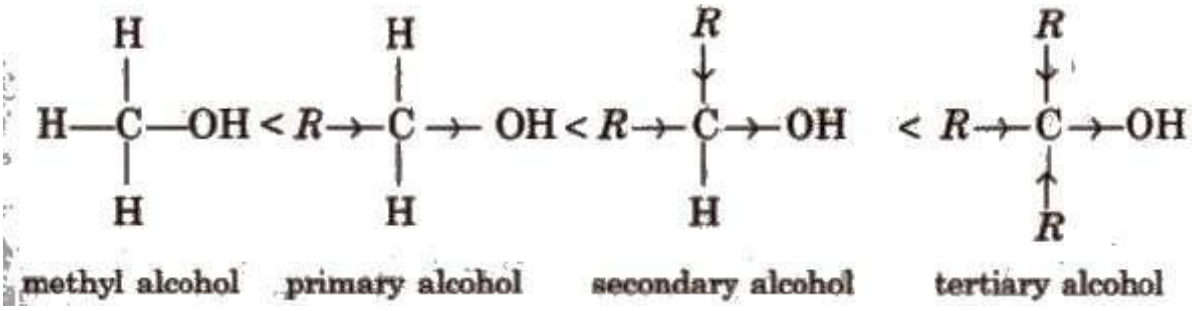
Alcohols, Phenols and Ethers

(ii) Reaction involving cleavage of C-O bond in alcohols

In these reactions, the reactivity order of different alcohols :



Alkyl group due to +1 effect increases the electron density on the carbon and oxygen atom of C-OH bond. As a result, the bond cleavage becomes easy. Greater the number of alkyl groups present, more will be the reactivity of alcohol. Thus, the relative order of reactivity of the alcohols is justified.

(a) Reaction with halogen acids Alcohols can be converted into haloalkanes by the action of halogen acids.

$$R - OH + HX\ (HCl, HBr, HI) \rightarrow R\text{-}X + H_2O$$

Alcohols Halogen acids Haloalkanes

For a given alcohol order of reactivity of HX is **H-I > H-Br > H-Cl**

For a given halogen acid order of reactivity of alcohols

Tertiary > Secondary > Primary

Lucas test

Primary alcohols	Secondary alcohols	Tertiary alcohols
$RCH_2OH \xrightarrow[Anhy.ZnCl_2]{Conc\ HCl}$	$R_2CH{-}OH \xrightarrow[Anhy.ZnCl_2]{Conc\ HCl}$	$R_3C{-}OH \xrightarrow[Anhy.ZnCl_2]{Conc\ HCl}$
No reaction and hence, no white cloudiness or turbidity at room temperature.	R_2CHCl White cloudiness or turbidity appears with in about 5 minutes.	R_3CCl White cloudiness or turbidity appears immediately.

(b) Reaction with phosphorus halides

$$ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$$

$$3ROH + PBr_3 \xrightarrow{P/Br_2} 3RBr + H_3PO_3$$

$$3ROH + PI_3 \xrightarrow{P/I_2} 3RI + H_3PO_3$$

(c) Reaction with thionyl chloride

$$ROH + SOCl_2 \longrightarrow RCl + SO_2\uparrow + HCl\uparrow$$

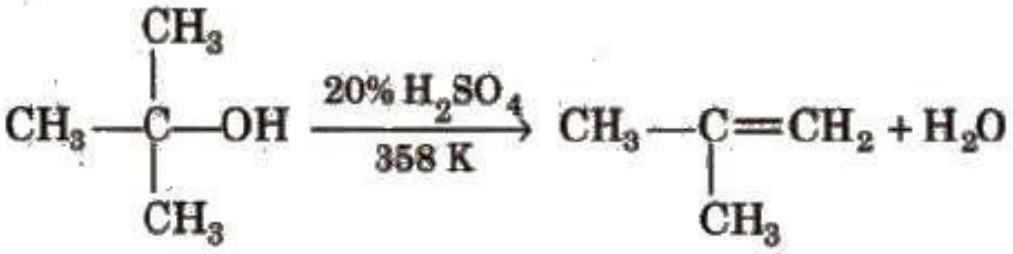
(d) **Dehydration of alcohols**

It requires acid catalyst and the reaction proceeds via intermediate carbonium ion. Acidic catalyst converts hydroxyl group into a good leaving group.

Since, the rate determining step is the formation of carbocation, the ease of dehydration is

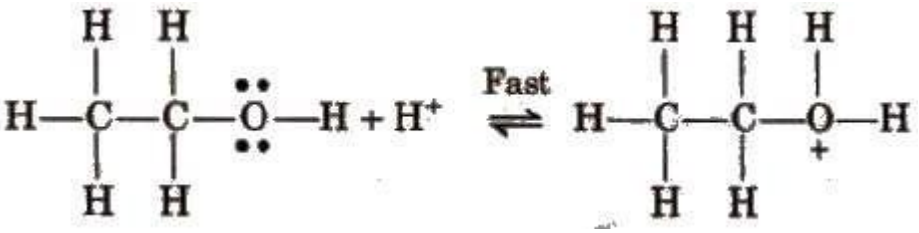
$$3^\circ > 2^\circ > 1^\circ$$

$$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2{=}CH_2 + H_2O$$



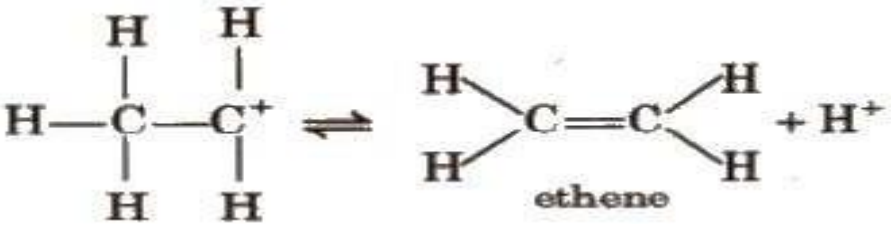
Mechanism

Step I. Formation of protonated alcohol



Step II Formation of carbocation

Step III Formation of ethene by elimination of a proton

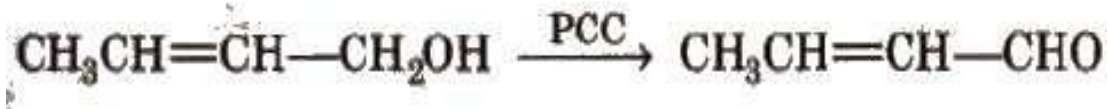


In dehydration reaction, highly substituted alkene is the major product and if the major product is capable of showing cis-trans isomerism, trans-product is the major product. (Saytzeff's rule).

(e) Oxidation reactions: Oxidising reagents used for the oxidation of alcohols are neutral, acidic or alkaline $KMnO_4$ and acidified $K_2Cr_2O_7$.

Primary alcohols	Secondary alcohols	Tertiary alcohols
CH_3CH_2OH	$CH_3CHOH—CH_3$	$(CH_3)_3C—OH$
$\downarrow[O]$	$\downarrow[O]$	$\downarrow[O]$
CH_3CHO	CH_3COCH_3	$CH_3COCH_3 + CO_2 + H_2O$
$\downarrow[O]$	$\downarrow[O]$	$\downarrow[O]$
CH_3COOH	$CH_3COOH + CO_2 + H_2O$	$CH_3COOH + CO_2 + H_2O$

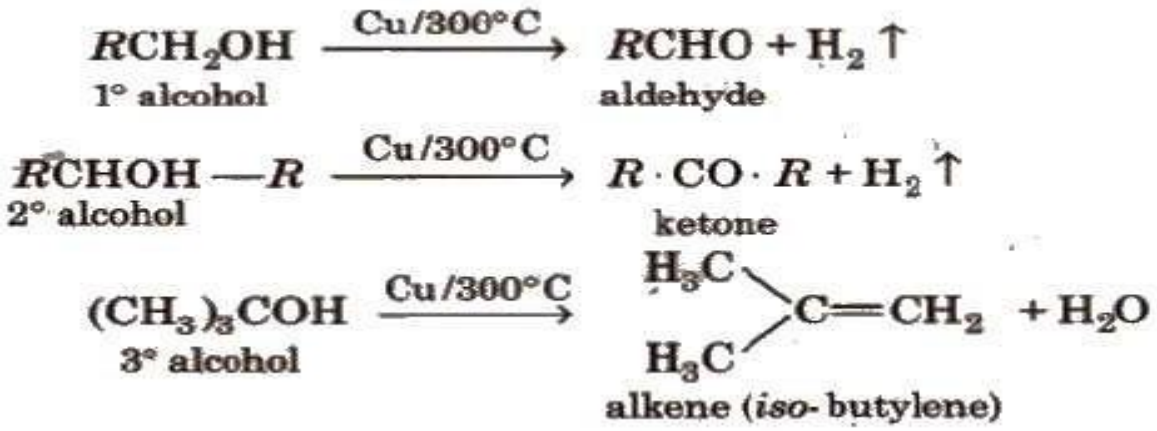
A common reagent that selectively oxidises a primary alcohol to an aldehyde (and no further) is pyridinium chlorochromate (PCC).



Distinction among 1°,2° and 3° Alcohols

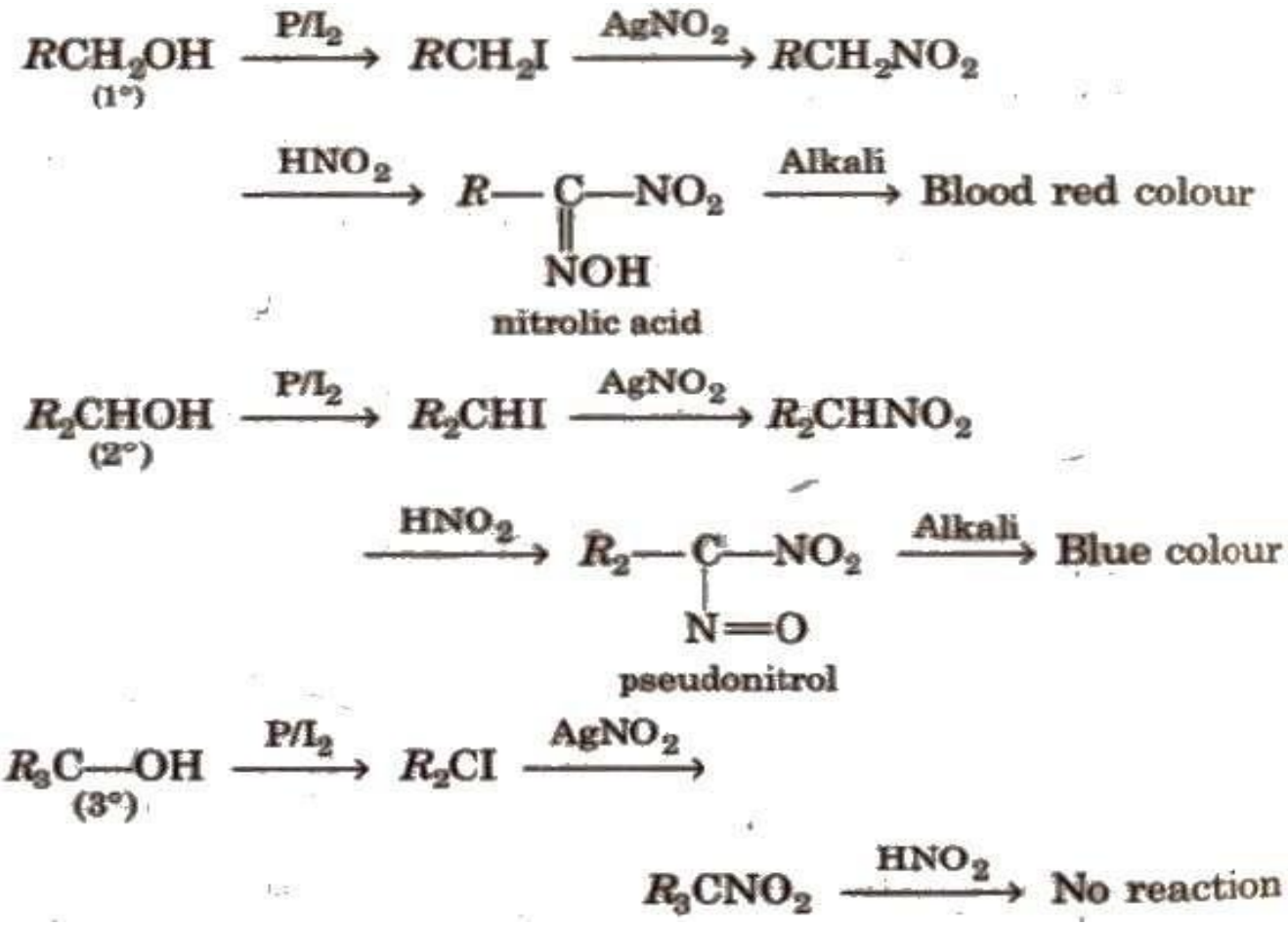
(f) Dehydrogenation

1°, 2° and 3° alcohols are distinguished by Lucas test, oxidation and reduced copper.



Victor Meyer's test is also used to distinguish them.

In this test, primary (1°) alcohols give red colour,
secondary (2°) alcohols give blue colour
and tertiary (3°) alcohols give no colouration.



****