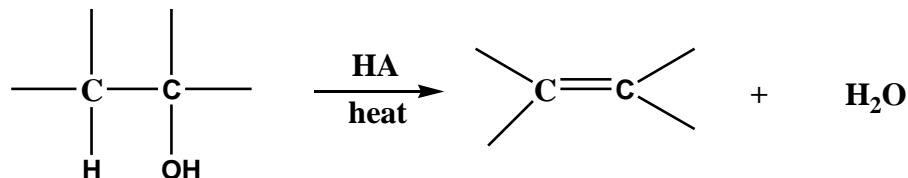


Synthesis of Alkenes From Alcohols:

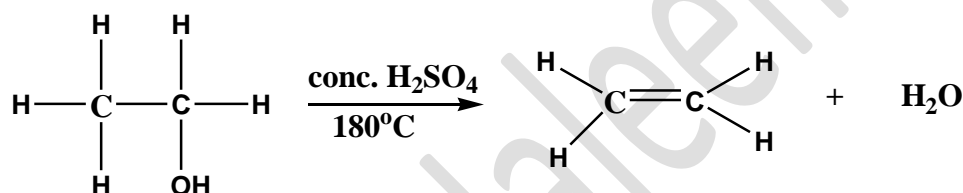
Alkenes can be synthesized from alcohols by a process called dehydration. When alcohols are heated with strong acid, they lose a molecule of water (dehydration) and form an alkene.



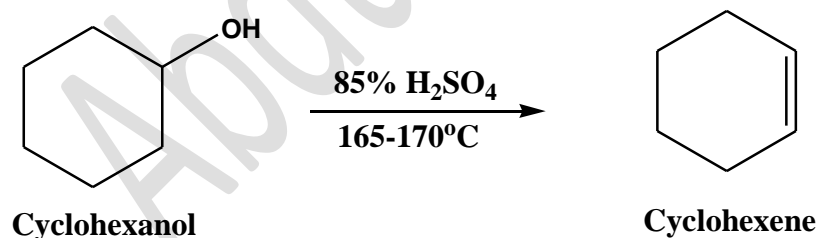
This is an elimination reaction and is favoured at higher temperatures. The most common acids that are used for dehydration of alcohols are the bronsted acids like sulfuric acid and phosphoric acid. Lewis acids like Alumina are often used in the industrial gas phase dehydration.

The experimental conditions i.e., the temperature and acid concentration required to bring about dehydration depend on the structure of the individual alcohol.

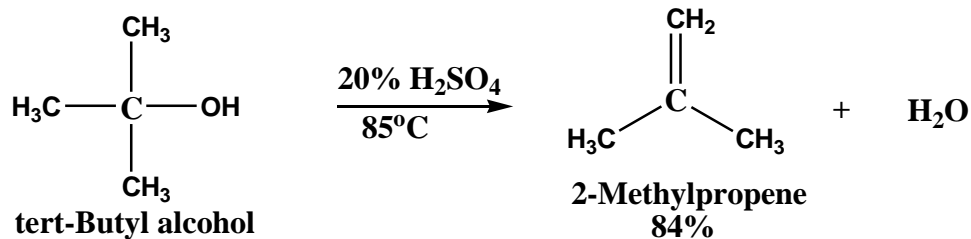
Primary alcohols are the most difficult to dehydrate. Ethanol, for example, requires concentrated sulfuric acid at a temperature of 180 degree Celsius.



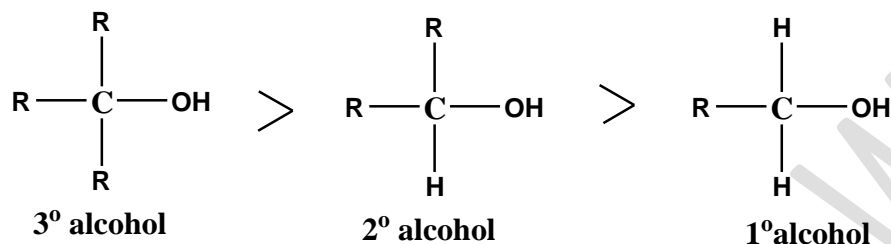
Secondary alcohols usually dehydrate under mild conditions. For example, dehydration of cyclohexanol in 85% phosphoric acid at 165 to 170 degree Celsius.



Tertiary alcohols get easily dehydrated and extremely mild conditions are used. For example, tertiary butyl alcohol dehydrates in 20% aqueous sulfuric acid at a temperature of 85 degree Celsius.



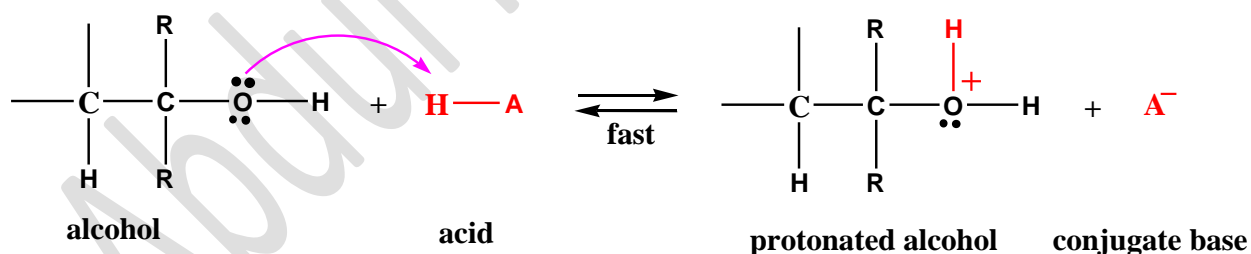
Thus, the relative ease with which alcohols undergo the hydration is in the following order.



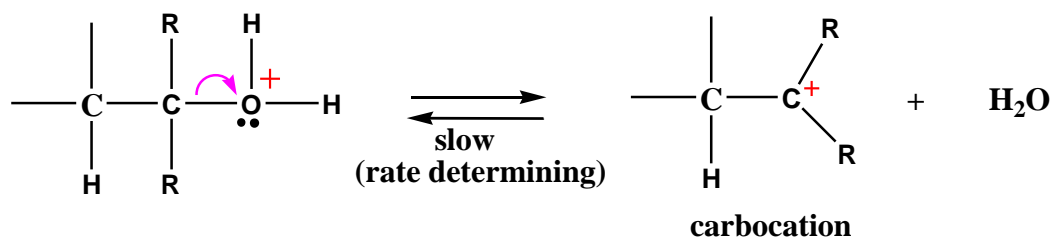
Mechanism for Dehydration of Secondary and Tertiary Alcohols:

The dehydration of secondary and tertiary alcohols follows E1 mechanism in which the substrate is a protonated alcohol or an alkyloxonium ion.

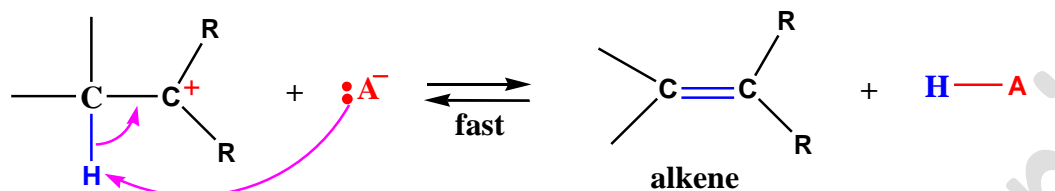
The first step is an acid base reaction in which a proton is rapidly transferred from the acid to one of the electron pairs of the alcohol. This Proton transfer creates a positive charge on the oxygen and weakens all bonds from oxygen including the carbon oxygen bond.



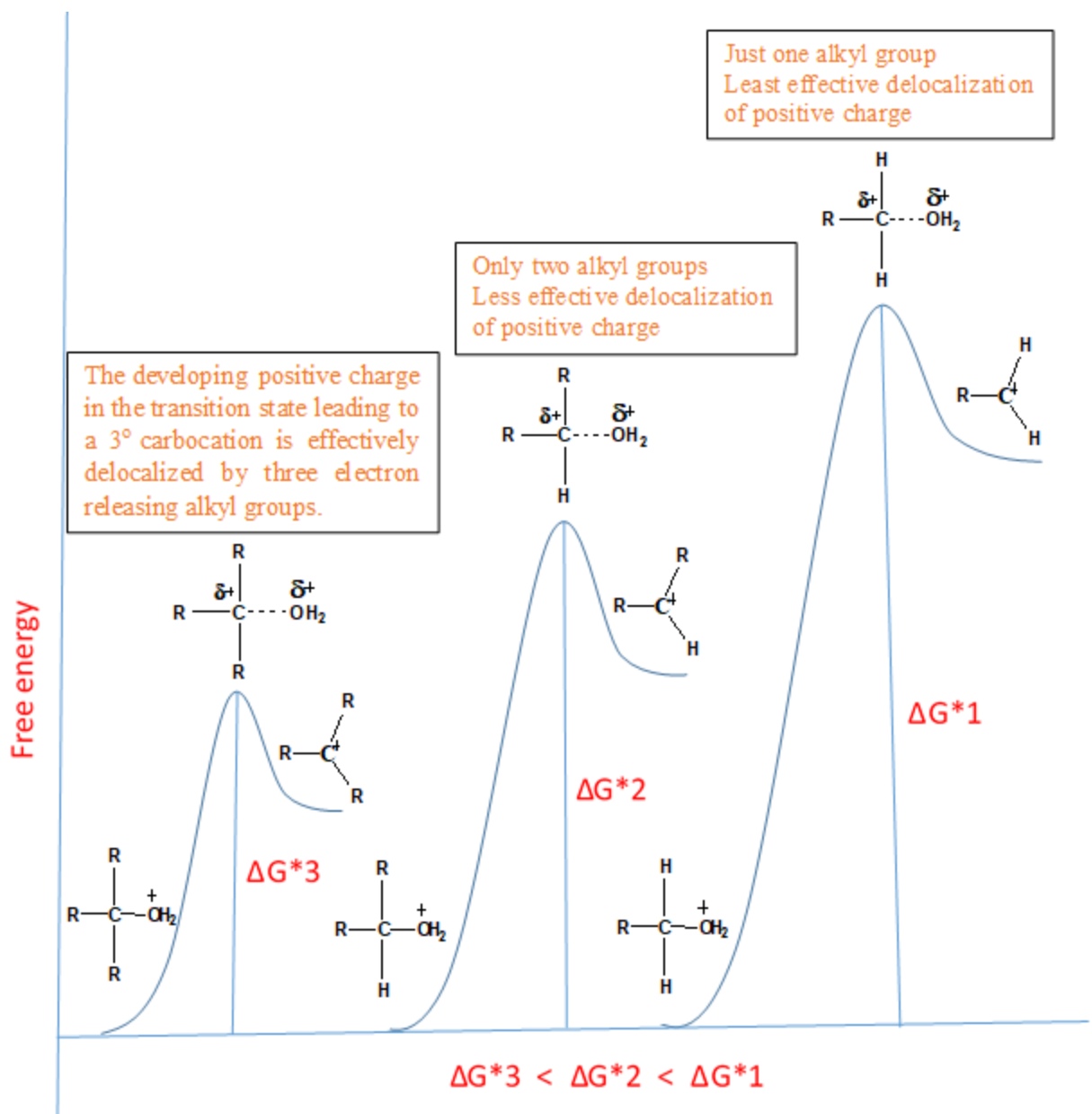
In step 2 the carbon oxygen Bond breaks. a molecule of water is lost leaving behind a carbocation.



Finally, in step 3 the carbocation transfers a proton to a base (water, another molecule of alcohol or conjugate base of the acid). The result is the formation of an alkene. This is again an acid base reaction. Any of the protons available on the adjacent carbon can be transferred to a molecule of water/base. The electron pair left behind becomes the second bond of the double bond.

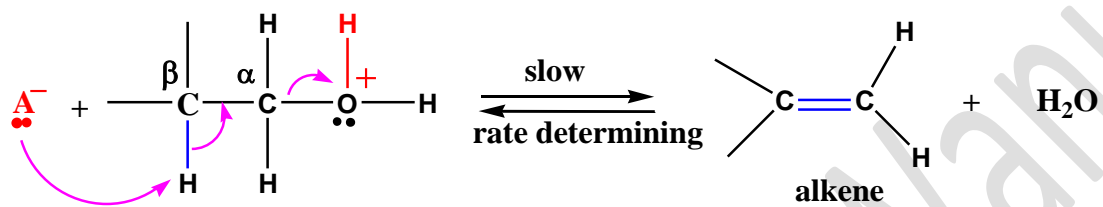
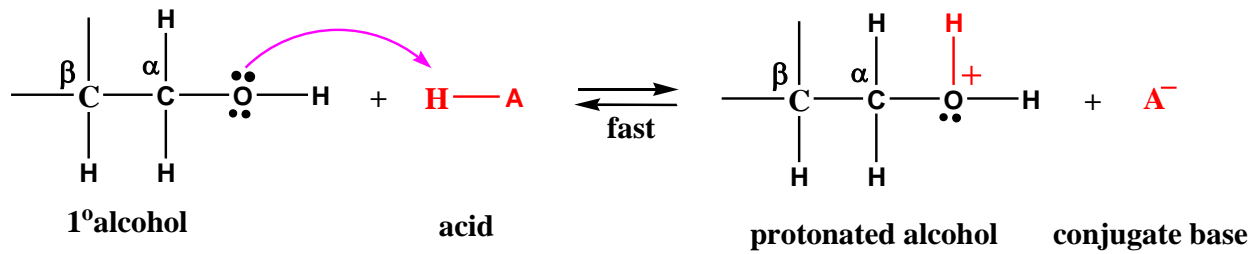


The formation of carbocation as an intermediate explains the relative ease with which alcohols undergo dehydration. Since step 2 is the rate determining step, it is this step that determines the reactivity of alcohols towards dehydration. Tertiary alcohols lead to the formation of a tertiary carbocation. The free energy of activation (ΔG^{\ddagger}) for its formation is the lowest and hence tertiary alcohols are most easily dehydrated. Secondary alcohols are dehydrated relatively slowly as compared to tertiary alcohols as the free energy of activation for their dehydration is higher (since these involve the formation of less stable secondary carbocation as an intermediate). The free energy of activation for dehydration of primary alcohols is so high that they do not undergo dehydration by E1 mechanism.



Mechanism for Dehydration of Primary Alcohols: An E2 Reaction

The first step in the dehydration of 1° alcohols is the protonation of hydroxyl oxygen. The Lewis base in the reaction mixture removes a β -hydrogen simultaneously with the formation of the alkene double bond and the departure of the protonated hydroxyl group.



Abdul Haleem Wani