

Ch. 4: Alcohols and Alkyl Halides



alcohol

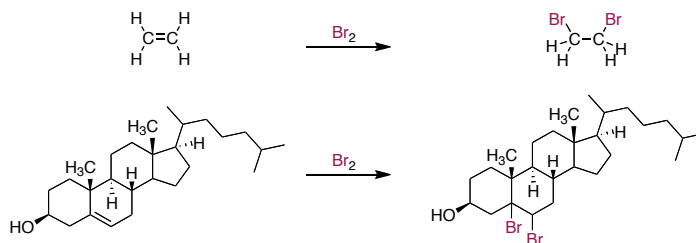


alkyl halide (X= F, Cl, Br, I)

4.1: Functional Groups - >11 million organic compounds which are classified into families according to structure and reactivity.

Functional Group (FG): a group of atoms, which are part of a larger molecule, that have characteristic chemical behavior. FG's behave similarly in every molecule they are part of.

The chemistry of organic molecules is defined by the function groups it contains



75



Alkanes

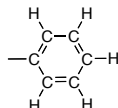
Carbon - Carbon Multiple Bonds



Alkenes

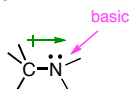


Alkynes



Arenes

Carbon-heteroatom single bonds

X= F, Cl, Br, I
Alkyl Halide

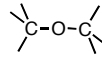
amines



nitro alkane



alcohols



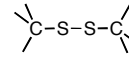
ethers



epoxide

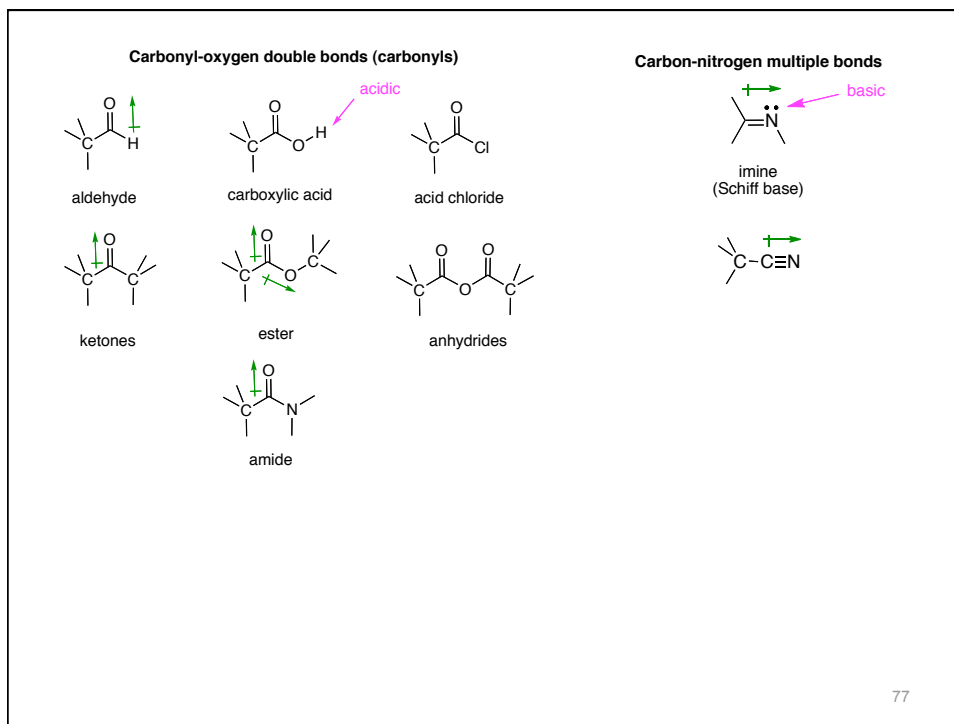


thiols

sulfides
(thioethers)

disulfide

76



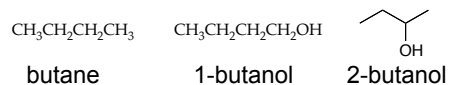
4.2: IUPAC Nomenclature of Alkyl Halides (please read)

Use the systematic nomenclature of alkanes; treat the halogen as a substituent of the alkane.

F- fluoro, Cl- chloro, Br- bromo, I- iodo

4.3: IUPAC Nomenclature of Alcohols

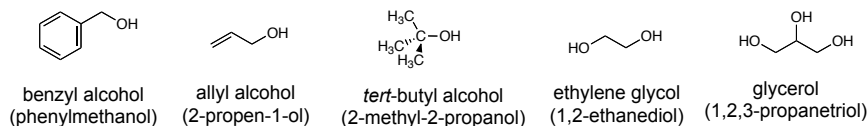
- In general, alcohols are named in the same manner as alkanes; replace the -ane suffix for alkanes with an -ol for alcohols



- Number the carbon chain so that the hydroxyl group gets the lowest number
- Number the substituents and write the name listing the substituents in alphabetical order.

78

Many alcohols are named using non-systematic nomenclature

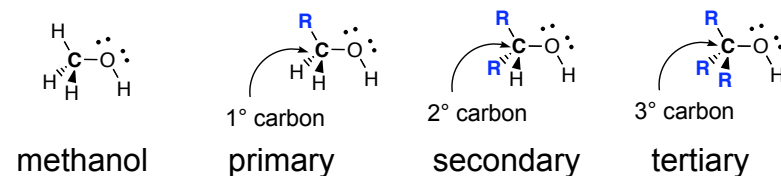
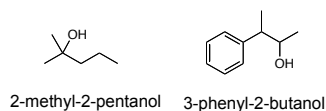


4.4: Classes of Alcohols and Alkyl Halides - Alcohols and alkyl halides are classified as according to the degree of substitution of the carbon bearing the halogen or -OH group

primary (1°) : one alkyl substituent

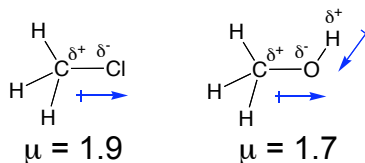
secondary (2°) : two alkyl substituents

tertiary (3°) : three alkyl substituents

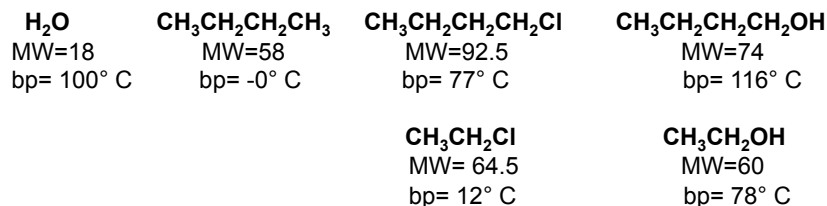


79

4.5: Bonding in Alcohols and Alkyl Halides - the C-X bond of alkyl halides and C-OH bond of alcohols has a significant dipole moment.

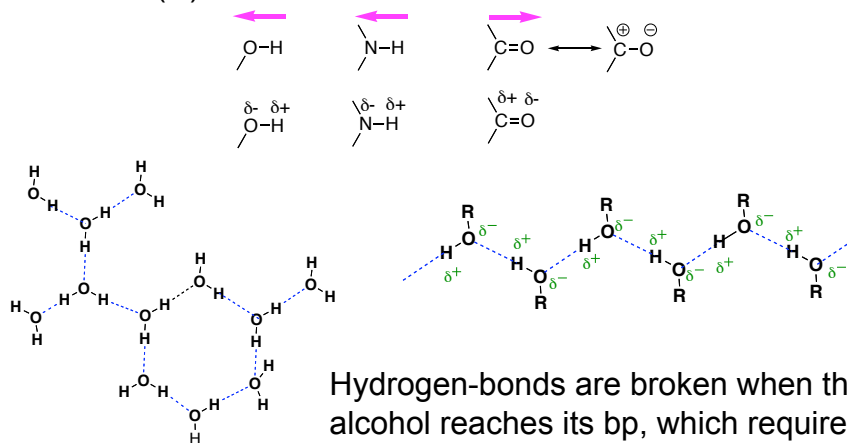


4.6: Physical Properties of Alcohols and Alkyl Halides: Intermolecular Forces



80

Like water, alcohols can form *hydrogen bonds*: a non-covalent interaction between a hydrogen atom (δ^+) involved in a polar covalent bond, with the lone pair of a heteroatom (usually O or N), which is also involved in a polar covalent bond (δ^-)



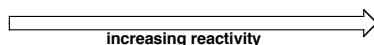
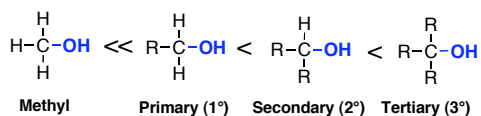
Hydrogen-bonds are broken when the alcohol reaches its bp, which requires additional energy

81

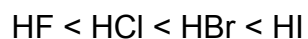
4.7: Preparation of Alkyl Halides from Alcohols and Hydrogen Halides



Reactivity of the alcohol:



Reactivity of the H-X : parallels the acidity of HX



82

4.8: Mechanism of the Reaction of Alcohols with Hydrogen Halides

Curved Arrow Convention

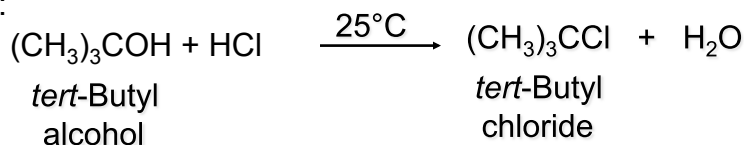
- Curved arrows show the movement (flow) of electron during bond breaking and/or bond making processes. The foot of the arrow indicates where the electron or electron pair originates, the head of the arrow shows where the electron or electron pair ends up.
 - The movement of a single electron is denoted by a curved single headed arrow (fishhook or hook).
 - The movement of an electron pair is denoted by a curved double headed arrow.
- If an electron pair moves in on a new atom, another electron pair must leave so that the atom does not exceed a full valance of eight electrons. There are two common exceptions:
 - When an atom already has an incomplete valance (R_3C^+).
 - With second row (or below) elements the octet rule may be violated.
- The arrows completely dictate the Lewis structure of the product. 83

Curved Arrow Convention

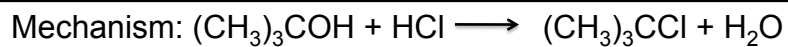
Other Suggestions for Proper Arrow Pushing:

- The natural polarization of double bonds between unlike atoms is in the direction of the more electronegative atom and this will be the important direction of electron movement.
- In drawing a mechanism, the formal charges of atoms in the reactants may change in the product. Use your knowledge of Lewis structures and formal charge to determine this.
- The first step in writing a mechanism is to identify the nucleophile (Lewis base) and the electrophile (Lewis acid). The first arrow is always from the nucleophile to the electrophile.

The generally accepted mechanism for the reaction of *t*-butyl alcohol and HCl involves to give *t*-butyl chloride has three basic steps:

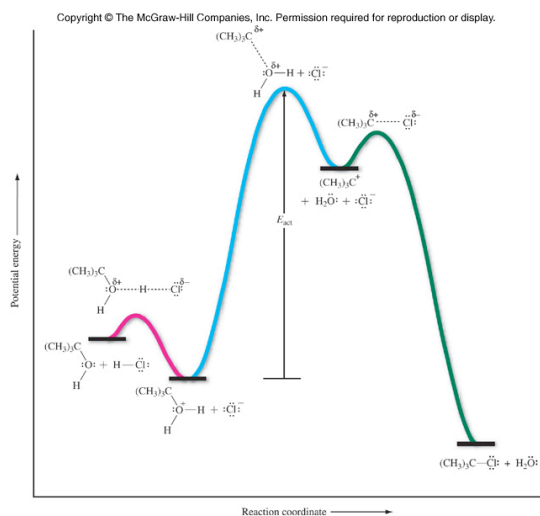


84



85

4.9: Potential Energy Diagrams for Multistep Reactions: The $\text{S}_{\text{N}}1$ Mechanism



The rate of oxonium ion formation is very fast
The rate of carbocation formation (dissociation of the oxonium ion) is slow

The rate of reaction between the carbocation and for X^- is fast

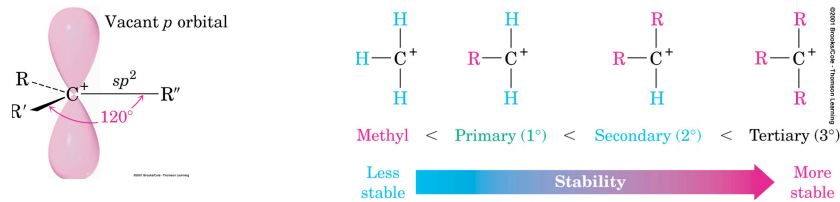
The overall rate is dependent of the slowest step (rate limiting step)

rate = k [oxonium ion] , where k is the rate constant

86

4.10: Structure, Bonding, and Stability of Carbocations -

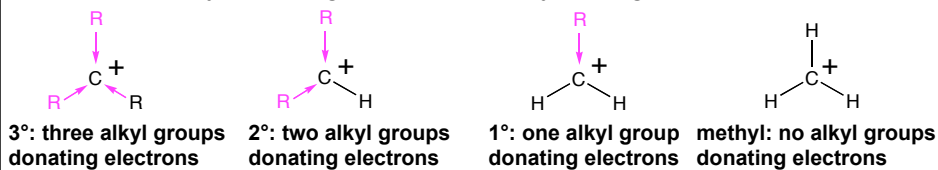
Carbocations are sp^2 hybridized and have a trigonal planar geometry



Substituents stabilize a carbocation through:

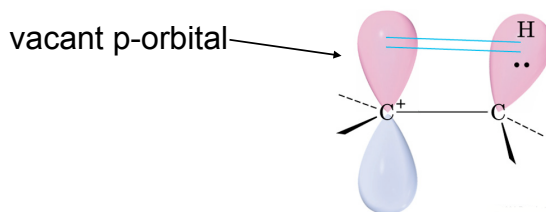
a. Inductive Effects: shifting of electrons in a σ -bond in response to the electronegativity of a nearby atom (or group).

Carbon is a good electron donor. Substitution can also stabilize carbocations by donating electron density through the σ -bond.



87

b. Hyperconjugation: The C-H σ -bond on the neighboring carbon lines up with the vacant p-orbital and can donate electron density to the carbon cation. This is a “bonding” interaction and is stabilizing. More substituted carbocations have more possible hyperconjugation interactions.



4.11: Effect of Alcohol Structure on Reaction Rate.

The order of reactivity for the reaction:

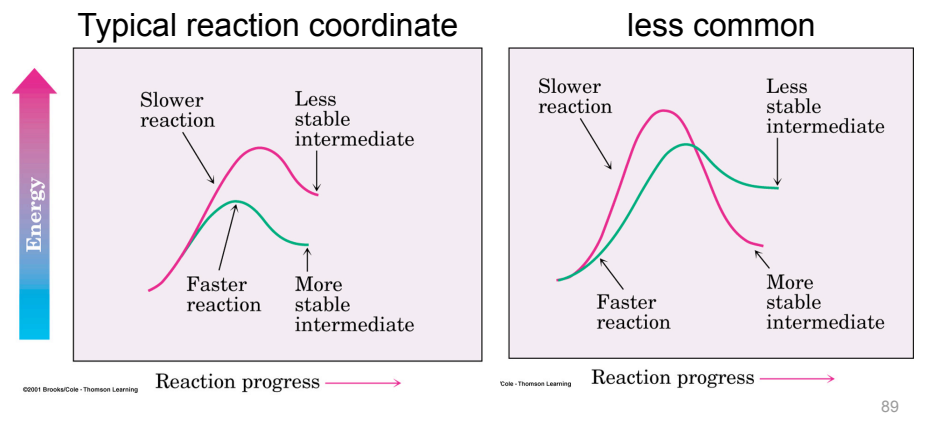


where 3° alcohols are most reactive and 1° alcohols are least reactive, reflects the stability of the intermediate carbocation.

88

The rate of a reaction is dependent of the activation energy (E_{act})
 There is no formal relationship between ΔG_{act} and ΔG°
 What is the structure of a transition state?
 How can the structures of the reactants and products affect ΔG_{act}

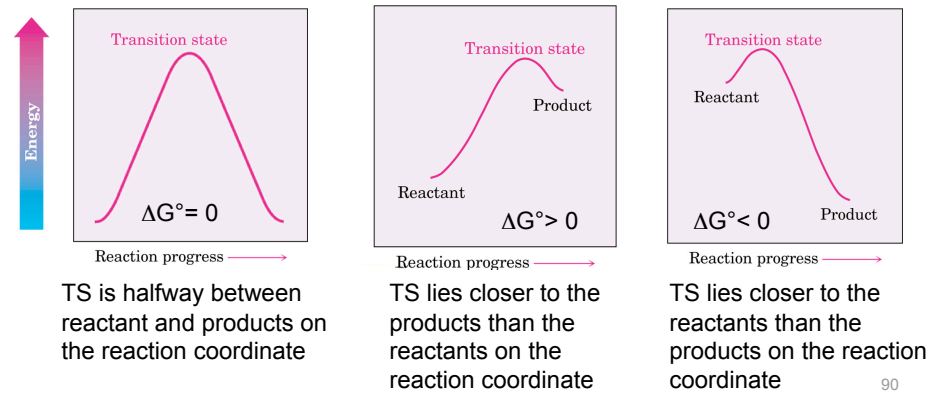
The *Hammond Postulate* provides an intuitive relationship
 Between rate (ΔG_{act}) and product stability (ΔG°).

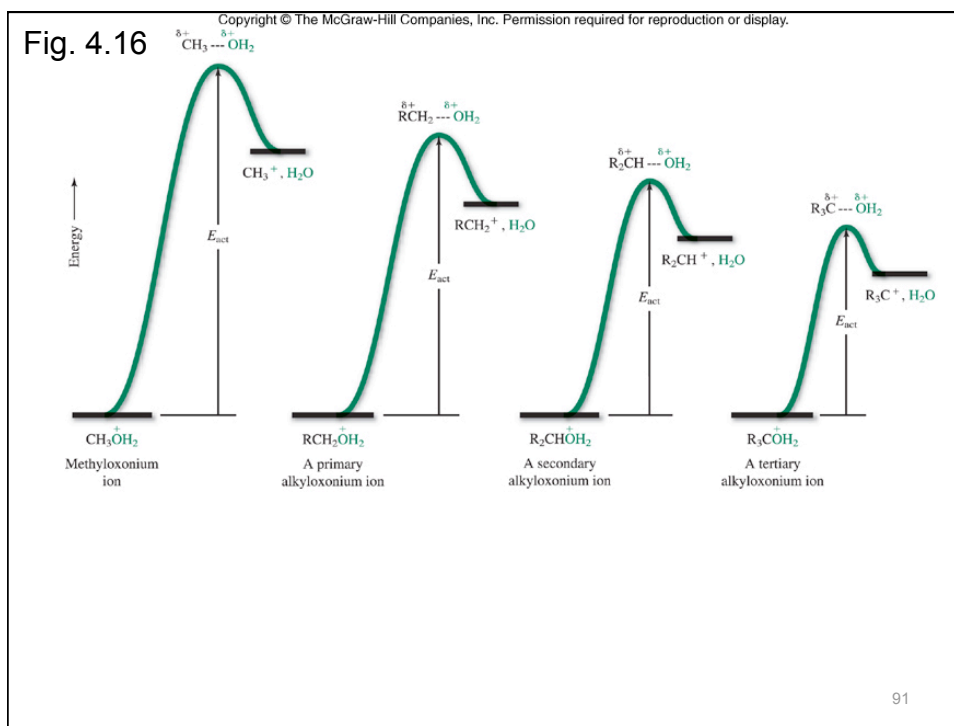


The Hammond Postulate: The structure of the transition state more closely resembles the nearest stable species (i.e., the reactant, intermediate or product)

For an endothermic reaction ($\Delta G^\circ > 0$), the TS is nearer to the product. The structure of the TS more closely resembles that of the product. Therefore, factors that stabilize the product will also stabilize the TS leading to that product.

For an exothermic reaction ($\Delta G^\circ < 0$), the TS is nearer to the reactant. The structure of the TS more closely resembles that of the reactants.





4.12: Reaction of Primary Alcohols with Hydrogen Halides. The $\text{S}_{\text{N}}2$ Mechanism:

Methyl and primary carbocations are the least stable, and they are not likely to be intermediates in reaction mechanism

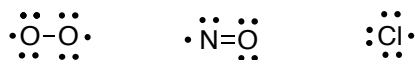


$\text{S}_{\text{N}}2$ (substitution-nucleophilic-bimolecular).

92

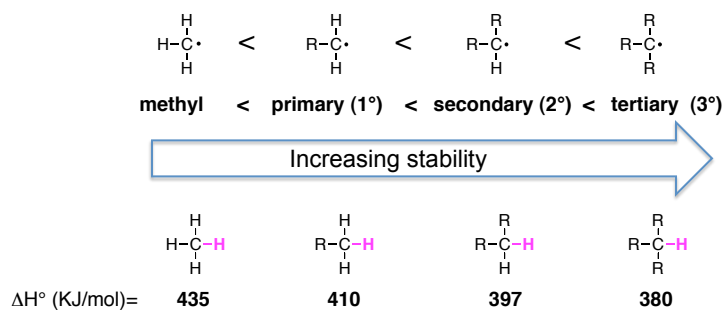
4.16: Structure and Stability of Free Radicals

Free radical: species that contain unpaired electrons



Organic (alkyl) radicals are usually highly reactive.

The stability and structure of alkyl radicals parallels those of carbocations:



Radicals are also stabilized by hyperconjugation

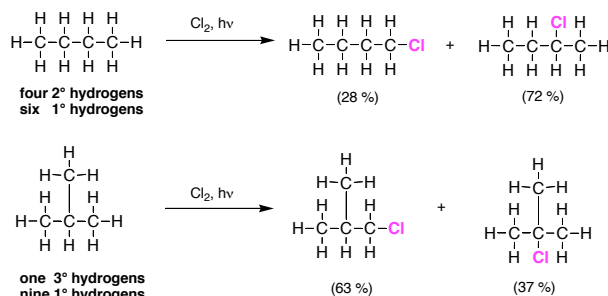
95

4.17: Mechanism of Chlorination of Methane

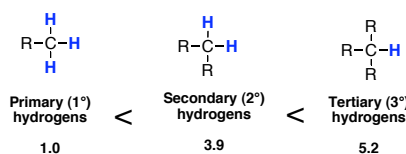
Free-radical chain mechanism:

96

4.18: Halogenation of Higher Alkanes – free radical chlorination of more substituted carbons is favored, reflecting the stability of the intermediate radical.

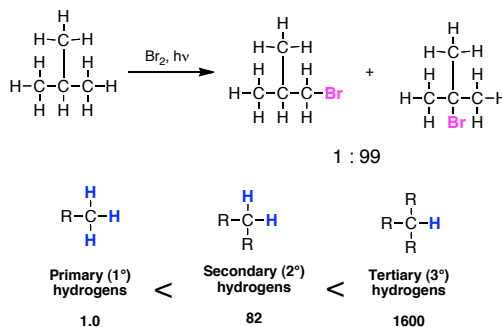


Relative rates of free radical chlorination



97

Free radical bromination is highly selective



The propagation step for free radical bromination is endothermic, Whereas chlorination which is exothermic. According to the Hammond postulate the transition state for bromination should resemble the product radical, and therefore be more selective for the product going through the more stable radical intermediate

98