

#### Characteristics of Alkanes, alkenes, and alkynes



#### Polarity is due to charge distribution within the molecule:



Alkynes have higher boiling point, melting point, and density. Polarity drops from alkynes to alkanes as well as reactivity and boiling point values (polar substances stick together more strongly than non-polar)

### **Deprotonating acetylenes**





KOH will not deprotonate acetylene because it is a weaker base than acetylenes conjugate base (acetylide).

н— <del>—</del> —н	+	NaOH	<u> </u>	-—Н	+	H <sub>2</sub> O
pka 26 Weak acid		weaker base		strong base		pKa 16 Strong acid
H──═N pKa 9 strong acid	+	NaOH stronger base	<u> </u>	- <b>≕</b> N weaker base	+	H <sub>2</sub> O weaker acid

### More examples:



- Equilibrium lies to the left in each of these reactions as alkanes, alkenes, and alkynes are very weakly acidic.
- On the other hand, KNH<sub>2</sub> will deprotonate acetylene, as the resulting acetylide is a weaker base. Ammonia pKa is 36. Other bases such as NaCH<sub>3</sub> can also be used to deprotonate acetylene.

## **Example:**



Both substitution reactions involving methyl iodide and ethyl iodide are  $S_N 2$ , as the primary and secondary carbons will not hold the positive charge that is characteristic of an  $S_N 1$  intermediate (tertiary carbocation).

### HCN vs C<sub>2</sub>H<sub>2</sub>



- HCN is more acidic with a pKa of 9.0 due to the N atom being more electronegative than C atom (**Note:** the N atom is pulling the electron density away).

## Addition to Alkene and Alkynes Reaction:

- Large amount of negative charge concentrated on the  $\pi$ -bond ( $\delta^{-}$ ). An **electrophile**, a species that seeks negative charge (electron-loving), would then get attacked by the electrons in the  $\pi$ -bond, hence forming a new bond.

## **General Mechanism**



A is an electrophile – seeks electrons B is a nucleophile – seeks nucleus Alkene = olefin

## Hydrogenation Addition of H<sub>2</sub>



This reaction is **stereospecific**, meaning that the stereochemistry of the starting material determines the stereochemistry of the product (in this reaction, cis). Needs a catalyst for the reaction to proceed. The metals palladium (Pd), nickel (Ni), rhodium (Rh), and platinum (Pt) act as catalysts to facilitate this reaction.



**Catalysts** accelerate the reaction rate by providing a lower energy pathway (red curve above). In general, they are not permanently converted to other products **Mechanism of hydrogenation** 



Hydrogenation examples

Example 1: 1,2-dimethylcyclobutene



# 1,2-dimethylcyclobutene

# cis-1,2-dimethylcyclobutane

The hydrogenation can occur from the top or the bottom, which in this case produces the same product (cis isomer of 1,2-dimethylcyclobutane). The starting material is achiral, and the product is a meso compound (two stereogenic centers, but a plane of symmetry)

Example 2: Pentene



## trans-2-pentene

Energy is released in each of these reactions, the energy released implies stabilization caused from transforming the starting material into the product



# **Reaction Coordinate**

 $\Delta G$  trans-isomer <  $\Delta G$  cis-isomer <  $\Delta G$  1-pentene isomer

Alkenes with more substituents are more stable. Carbons in a double bond have a  $\delta$ + (electrondeficient), this is stabilized by the **electron donating effects** of alkyl groups. Hydrogens are less electron donating and so less substituted alkenes are less stable.

Cis alkenes are less stable than trans alkenes as they have methyl groups facing the same direction which causes unfavorable steric interactions.

Stability