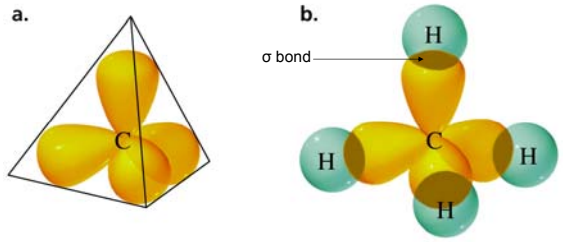
Hybrid Orbitals

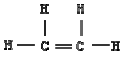
- **Hybrid orbitals are mixed orbitals --- they result from combining orbitals.**
- **The concept of combining orbitals, called orbital hybridization, was first proposed by Linus Pauling in 1931.**
- **All single bonds are sigma bonds.**

The orbitals used in bond formation determine the bond angles



- **Tetrahedral bond angle: 109.5°; non-polar.**
- **Electron pairs spread themselves into space as far from each other as possible.**

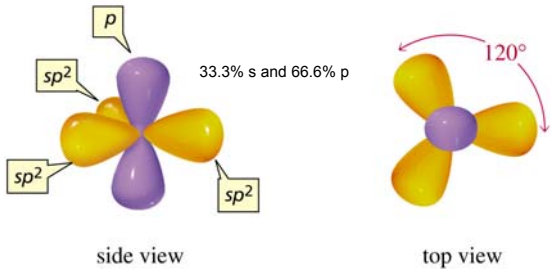
1.8 Ethene: Double Bond



- Ethene: $CH_2=CH_2$
- Electron configuration:
  H: $1S^1$
  C: $1S^2 2S^2 2P^2$

Element	Total Electrons	Orbital Diagram 1s	2s	2p	3s	Electron Configuration
C	6	↑↓	↑↓	↑ ↑		$1s^2\,2s^2\,2p^2$

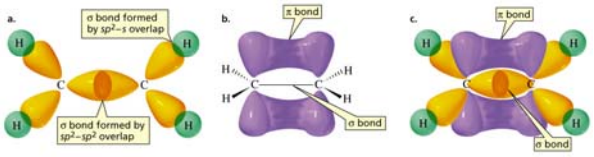
An sp^2-Hybridized Carbon



- The bond angle in the sp^2 carbon is 120°
- The sp^2 carbon is the trigonal planar carbon

Bonding in Ethene: A Double Bond

Ethene: $CH_2=CH_2$, sp^2 hybridization



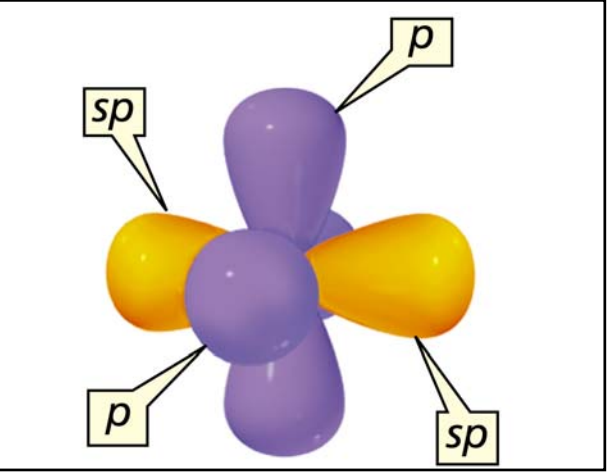
A double bond has one sigma bond and one pi bond.

1.9 Bonding in Ethyne: A Triple Bond

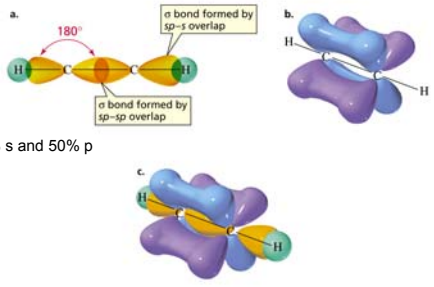
H — C ≡ C — H

- Ethyne: CH Ξ CH
- Electron configuration:
  H: $1S^1$
  C: $1S^22S^22P^2$

Element	Total Electrons	Orbital Diagram 1s	2s	2p	3s	Electron Configuration
C	6	↿⇂	↿⇂	↿ ↿		$1s^2\,2s^2\,2p^2$



Bonding in Ethyne: A Triple Bond

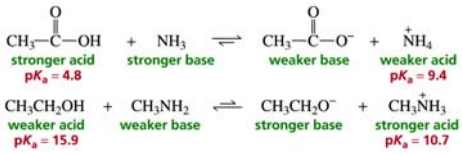


50% s and 50% p

- A triple bond consists of one σ bond and two π bonds
- Bond angle of the *sp* carbon: 180°

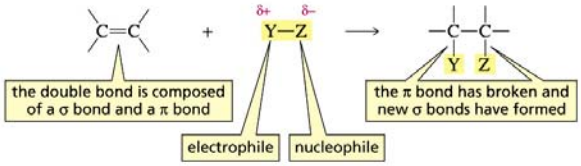
1.16 Brønsted–Lowry Acids and Bases

- Acid donates a proton
- Base accepts a proton

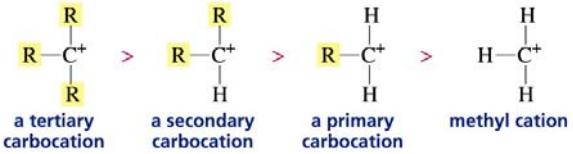


- Strong reacts to give weak
- The weaker the base, the stronger is its conjugate acid
- Stable bases are weak bases

Electrophilic Addition of Alkenes

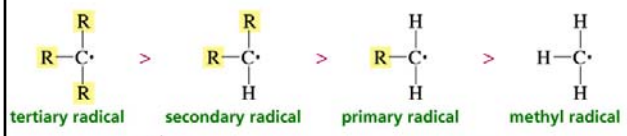


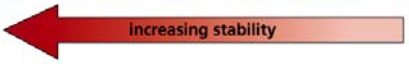
4.2 Carbocation Stabilities



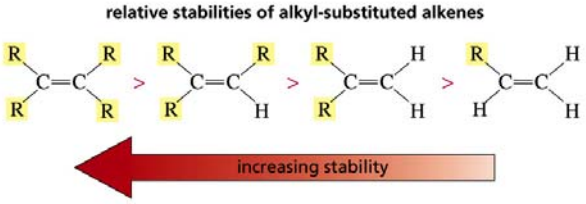
Similar to the stability of radicals!

Relative Stabilities of Alkyl Radicals

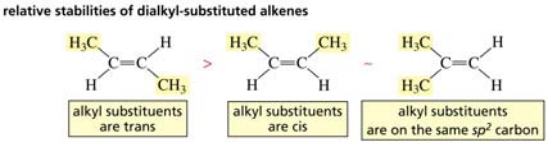




Relative Stabilities of Alkenes



Relative Stabilities of Dialkyl-Substituted Alkenes



9.1 Alkanes are very unreactive compounds because they have only strong s bonds and atoms with no partial charges

However, alkanes do react with Cl_2 and Br_2 at high T or in the presence of light.
Halogenation Reaction

$$CH_4 + Cl_2 \xrightarrow[\text{or } h\nu]{\Delta} \underset{\text{methyl chloride}}{CH_3Cl} + HCl$$

$$CH_3CH_3 + Br_2 \xrightarrow[\text{or } h\nu]{\Delta} \underset{\text{ethyl bromide}}{CH_3CH_2Br} + HBr$$

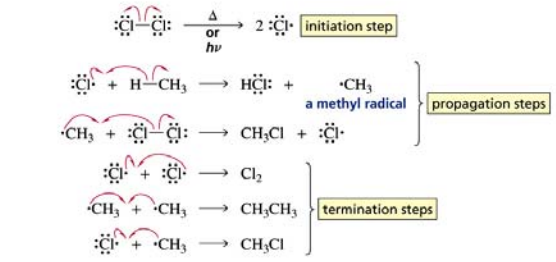
Free Radical

- **A radical (often called a free radical) is a species containing an atom with unpaired electron.**

- **A radical is highly reactive because it needs to acquire an electron to complete its octet.**

9.2 Reaction of Alkane with Cl_2 or Br_2

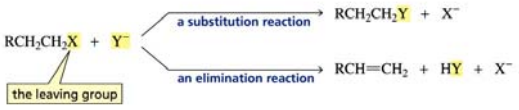
mechanism for the monochlorination of methane



Excess alkane present is preferred.

Also called radical substitution reaction.

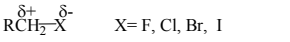
What is a substitution reaction?



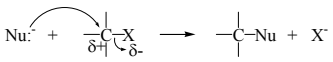
The atom or group that is substituted or eliminated in these reactions is called a leaving group

10.1 Alkyl halides have relatively good leaving groups: nucleophilic substitution reaction

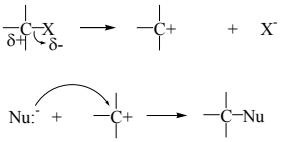
How do alkyl halides react?



X= F, Cl, Br, I



Alternatively …



Because a nucleophile substitutes for the halogen, these reactions are known as nucleophilic substitution reactions

The reaction mechanism which predominates depends on the following factors:

- **the structure of the alkyl halide**
- **the reactivity of the nucleophile**
- **the concentration of the nucleophile**
- **the solvent of the reaction**

10.2 The Mechanism of an S_N2 Reaction

$$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$$

Consider the kinetic of the reaction:

Rate = *k*[alkyl halide][nucleophile]

a second-order reaction

S_N2: S for substitution, N for nucleophilic, 2 for biomolecular.

10.5 Experimental Evidence for an S_N1 Reaction

1. **The rate of the reaction depends only on the concentration of the alkyl halide**
2. **The rate of the reaction is favored by the bulkiness of the alkyl substituent**
3. **In the substitution of a chiral alkyl halide, a racemic mixture of product is obtained**

10.9 Competition Between S_N2 and S_N1 Reactions

Table 10.5 Comparison of S_N2 and S_N1 Reactions

S_N2	S_N1
A one-step mechanism	A stepwise mechanism that forms a carbocation intermediate
A bimolecular rate-determining step	A unimolecular rate-determining step
No carbocation rearrangements	Carbocation rearrangements
Product has inverted configuration relative to the reactant	Products have both retained and inverted configurations relative to the reactant
Reactivity order: methyl > 1° > 2° > 3°	Reactivity order: 3° > 2° > 1° > methyl

Table 10.6 Summary of the Reactivity of Alkyl Halides in Nucleophilic Substitution Reactions

Methyl and 1° alkyl halides	S_N2 only
Vinylic and aryl halides	Neither S_N1 nor S_N2
2° alkyl halides	S_N1 and S_N2
1° and 2° benzylic and 1° and 2° allylic halides	S_N1 and S_N2
3° alkyl halides	S_N1 only
3° benzylic and 3° allylic halides	S_N1 only

When an alkyl halide can undergo either S_N1 or S_N2,

- the concentration of the nucleophile,
- the reactivity of the nucleophile,
- and the solvent of the reaction
- will determine which reaction will predominate

An S_N2 reaction is favored by a high concentration of a good nucleophile

An S_N1 reaction is favored by a low concentration of a nucleophile or by a poor nucleophile

The Role of Solvent in S_N2 and in S_N1 Reactions

one or more reactants charged in the rate-limiting step	none of the reactants is charged in the rate-limiting step
increase the polarity of the solvent	increase the polarity of the solvent
decrease the rate of the reaction	increase the rate of the reaction

In addition to substitution, an alkyl halide can undergo an elimination reaction

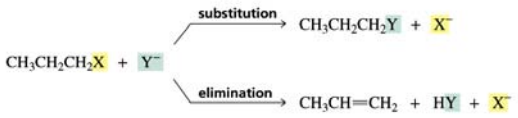


Table 11.4 Stereochemistry of Substitution and Elimination Reactions

Mechanism	Products
S_N1	Both stereoisomers (*R* and *S*) are formed (more inverted than retained).
E1	Both *E* and *Z* stereoisomers are formed (more of the stereoisomer with the bulkiest groups on opposite sides of the double bond).
S_N2	Only the inverted product is formed.
E2	Both *E* and *Z* stereoisomers are formed (more of the stereoisomer with the bulkiest groups on opposite sides of the double bond is formed) unless the β-carbon of the reactant is bonded to only one hydrogen, in which case only one stereoisomer is formed, with a configuration that depends on the configuration of the reactant.

11.8 Competition Between Substitution and Elimination

Alkyl halides can undergo S_N2, S_N1, E2 and E1

1) decide whether the reaction conditions favor S_N2/E2 or S_N1/E1

- **S_N2/E2 reactions are favored by a high concentration of nucleophile/strong base**
- **S_N1/E1 reactions are favored by a poor nucleophile/weak base**

2) decide how much of the product will be the substitution product and how much of the product will be the elimination product

Consider the S_N2/E2 conditions

Table 11.5 Relative Reactivities of Alkyl Halides

In an S_N2 reaction:	$1° > 2° > 3°$	In an S_N1 reaction:	$3° > 2° > 1°$
In an E2 reaction:	$3° > 2° > 1°$	In an E1 reaction:	$3° > 2° > 1°$

Consider S_N1/E1 conditions

Table 11.6 Summary of the Products Expected in Substitution and Elimination Reactions

Class of alkyl halide	S_N2 versus E2	S_N1 versus E1
Primary alkyl halide	Primarily substitution, unless there is steric hindrance in the alkyl halide or nucleophile, in which case elimination is favored	Cannot undergo S_N1/E1 reactions
Secondary alkyl halide	Both substitution and elimination; the stronger and bulkier the base, the greater is the percentage of elimination	Both substitution and elimination
Tertiary alkyl halide	Only elimination	Both substitution and elimination