Chapter 2

Structure and Bonding
An Overview of Organic Reactions

Chemical bonds: The octet rule

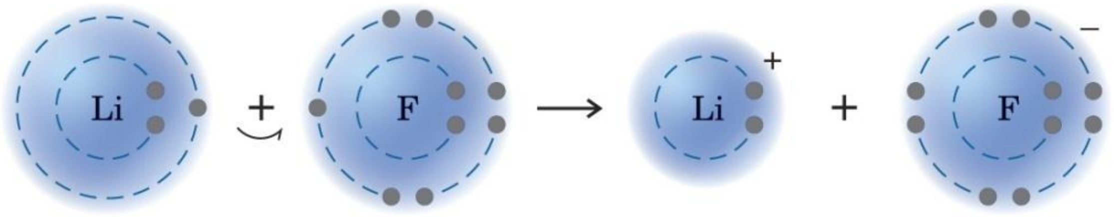
- Atoms form bonds to produce the electron configuration of a noble gas (because the electronic configuration of noble gases is particularly stable)
- For most atoms of interest, this means achieving a valence shell configuration of 8 electrons corresponding to that of the nearest noble gas (atoms close to helium achieve a valence shell configuration of 2 electrons)
- Atoms can form either ionic or covalent bonds to satisfy the octet rule.

Ionic bonds

- When ionic bonds are formed, atoms gain or lose electrons to achieve the electronic configuration of the nearest noble gas.

- The resulting oppositely charged ions attract and form ionic bonds. This generally happens between atoms of widely different electronegativities.

- Example:
  - Lithium loses an electron (to have the configuration of helium) and becomes positively charged.
  - Fluoride gains an electron (to have the configuration of neon) and becomes negatively charged.
  - The positively charged lithium and the negatively charged fluoride form a strong ionic bond (actually in a crystalline lattice) or static attraction.

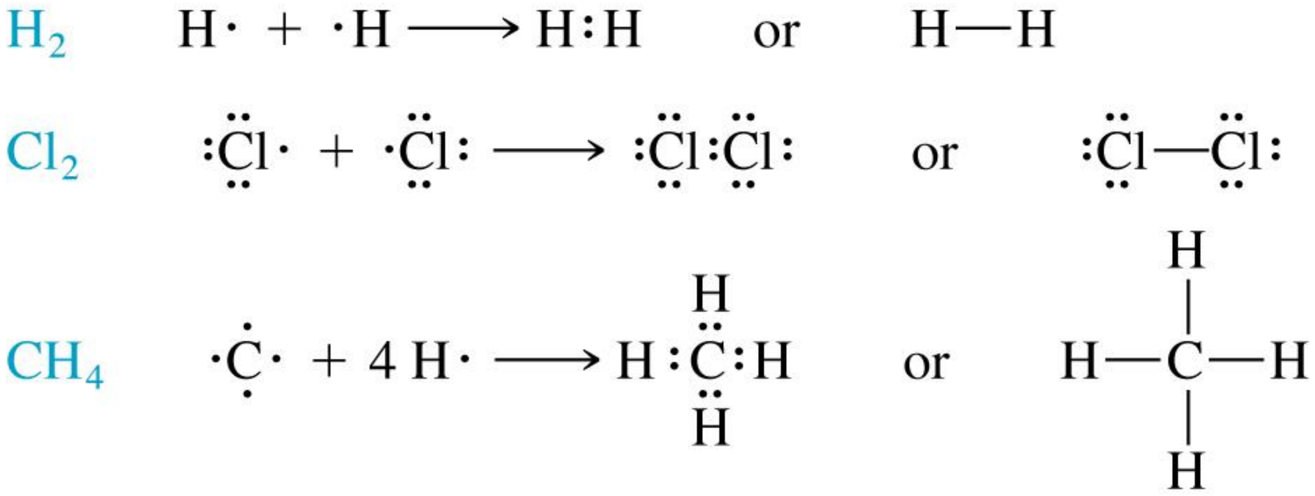


Covalent bonds

- Covalent bonds occur between atoms of similar electronegativity (close to each other in the periodic table). Atoms achieve octets by *sharing* of valence electrons. Molecules result from this covalent bonding.

- Covalent bonding, in which electrons are shared rather than transferred, is the most common type of bonding in organic compounds

- Valence electrons can be indicated by dots (electron-dot formula or Lewis structures) but this is time-consuming. The usual way to indicate the two electrons in a bond is to use a line (one line = two electrons)



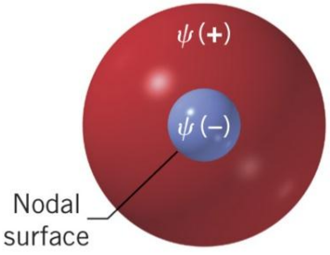
s and p orbitals

- 1*s* and 2*s* orbitals are spheres centered around the nucleus. Each orbital can accommodate 2 electrons. The 2*s* orbital is higher in energy and contains a nodal surface in its center.

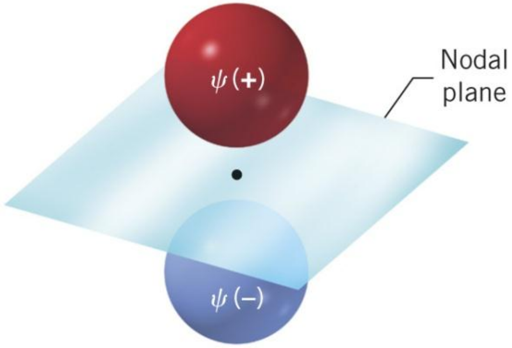
- Each 2*p* orbital has two nearly touching spheres (or **lobes**). One sphere has a positive phase sign and the other a negative phase sign; a nodal plane separates the spheres.

- There are three 2*p* orbitals which are perpendicular (orthogonal) to each other. Each *p* orbital can maximally accommodate 2 electrons for a total of 6 electrons. All three *p* orbitals are degenerate (equal in energy). The 2*p* orbitals are higher in energy than the 1*s* or 2*s*.

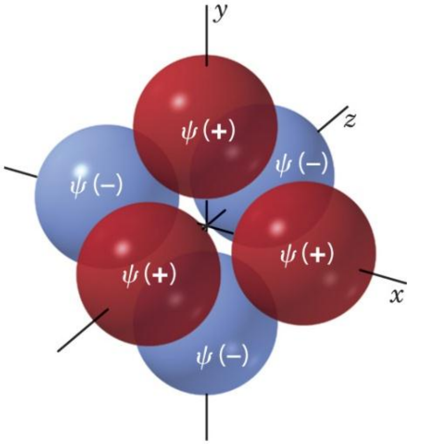
1*s* Orbital



2*s* Orbital



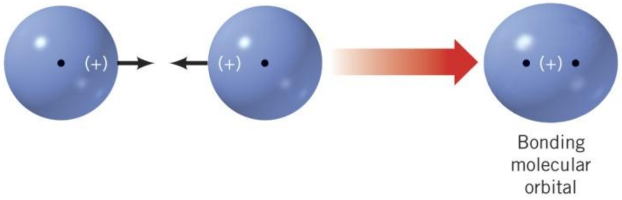
A pure 2*p* orbital (unhybridized)



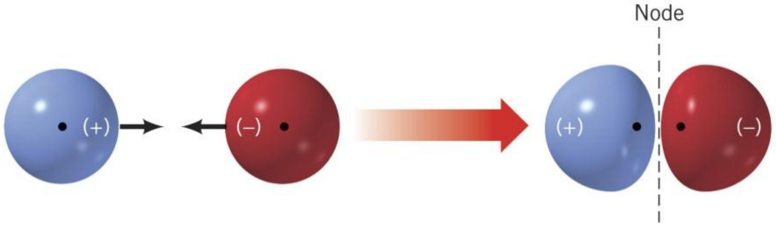
Three mutually perpendicular (orthogonal) 2p orbitals (unhybridized)

Summary of concepts from quantum mechanics

- Atomic orbital (AO): region in space around a nucleus where there is a high probability of finding an electron.
- Molecular orbital (MO): results from overlap of atomic orbitals.
- Bonding orbitals: when AOs of same sign overlap.



- Antibonding orbitals: when AOs of opposite sign overlap.



- The energy of electrons in a bonding orbital is less than the energy of the individual atoms.
  - The energy of electrons in an antibonding orbitals is more.

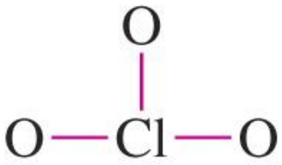
Drawing Lewis structures

- *Example:* Write the Lewis structure for the chlorate ion (ClO_3^-)

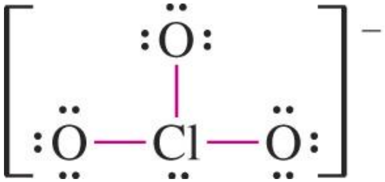
Step 1: The total number of valence electrons including the electron for the negative charge is calculated

$$\underset{\substack{\uparrow \\ \text{Cl}}}{7} + \underset{\substack{\uparrow \\ 3\,\text{O}}}{3(6)} + \underset{\substack{\uparrow \\ e^-}}{1} = 26$$

Step 2: Three pairs of electrons are used to bond the chlorine to the oxygens



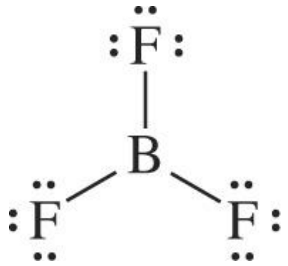
Step 3: The remaining 20 electrons are added to give each atom an octet



Exceptions to the octet rule

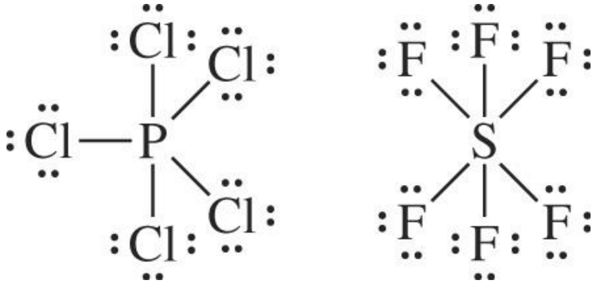
- The octet rule applies only to atoms in the **second** row of the periodic table (C, O, N, F) which are limited to valence electrons in the 2s and 2p orbitals. In second row elements *fewer* electrons are possible.

Example: BF_3 (boron trifluoride)



- In higher rows other orbitals are accessible and more than 8 electrons around an atom are possible.

Example: PCl_5 (phosphorus pentachloride) and SF_6 (sulfur hexafluoride)

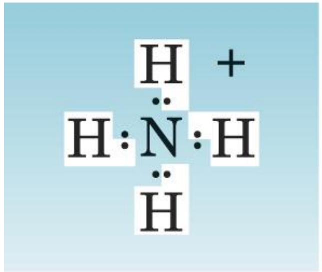


Formal charge

- A formal charge is a positive or negative charge on an individual atom. The sum of formal charges on individual atoms is the total charge of the molecule or ion.

Examples:

- Ammonium ion $(NH_4)^+$

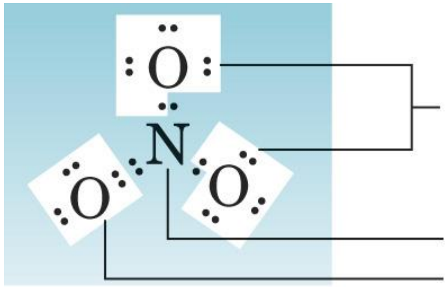


For hydrogen: valence electrons of free atom = 1
subtract assigned electrons = −1
Formal charge = 0

For nitrogen: valence electrons of free atom = 5
subtract assigned electrons = −4
Formal charge = +1

Charge on ion = 4(0) + 1 = +1

- Nitrate ion $(NO_3)^-$



Formal charge = 6 − 7 = −1

Formal charge = 5 − 4 = +1

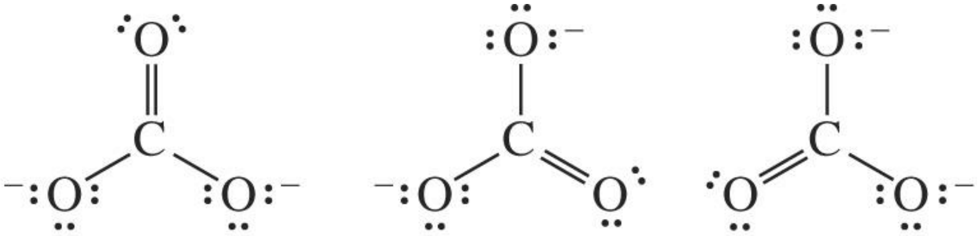
Formal charge = 6 − 6 = 0

Charge on ion = 2(−1) + 1 + 0 = −1

Resonance

- Often a single Lewis structure does not accurately represent the true structure of a molecule. In Lewis structure, all electrons are **localized**.

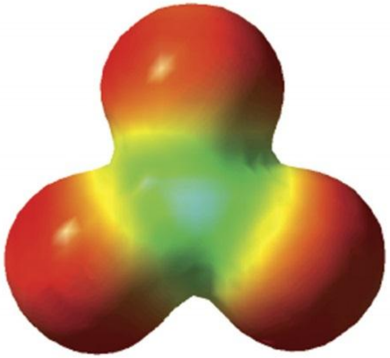
- The real carbonate ion is not represented by any of the structures 1,2 or 3.



1 **2** **3**

- Experimentally, carbonate is known not to have two carbon-oxygen single bonds and one double bond; all bonds are equal in length and the charge is spread equally over all three oxygens. The p and π are delocalized.

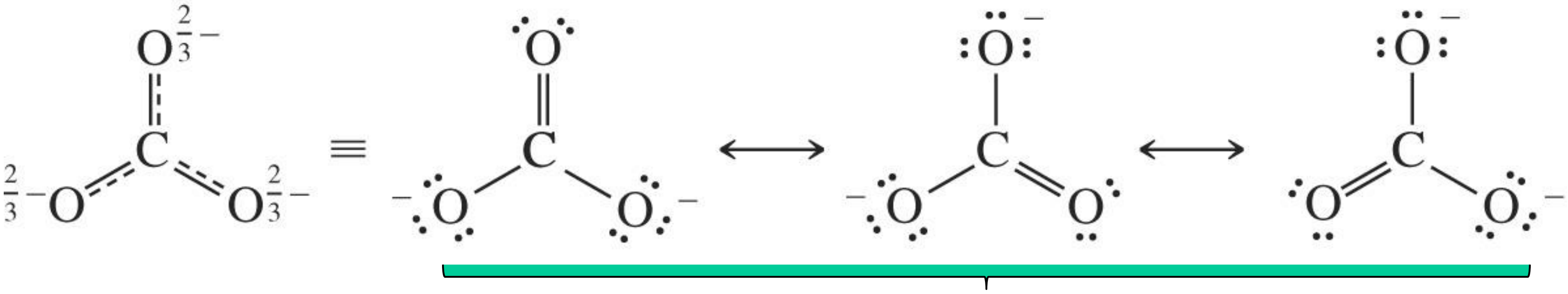
+ A calculated electrostatic potential map of carbonate clearly shows the electron density is spread equally among the three oxygens.



Resonance

- The real carbonate ion can be represented by a drawing in which partial double bonds to the oxygens are shown and partial negative charge exists on each oxygen. The real structure is a **resonance hybrid** or mixture of all three Lewis structures.

- Double headed arrows are used to show that the three Lewis structures are resonance contributors to the true structure. The use of equilibrium arrows is incorrect since the three structures do not equilibrate.

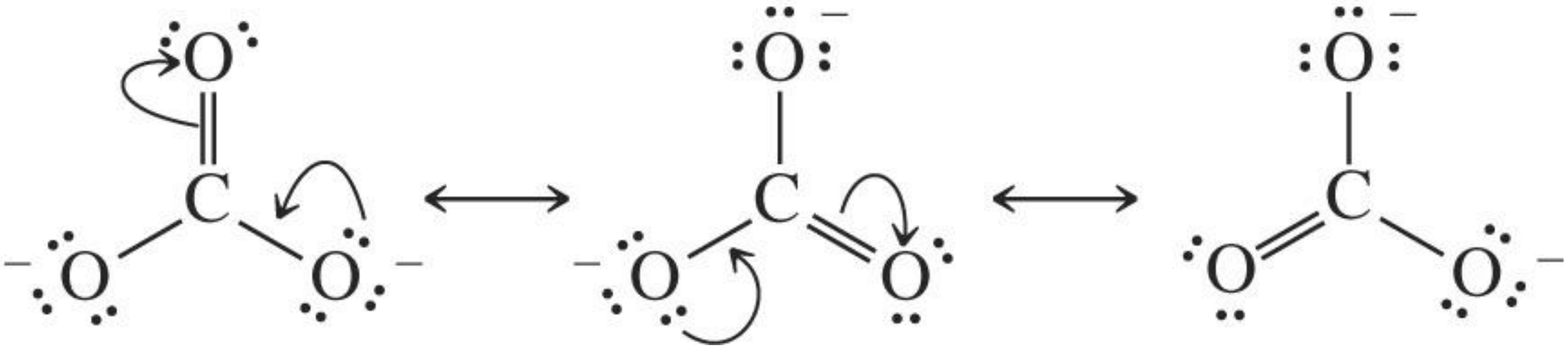


Resonance hybrid

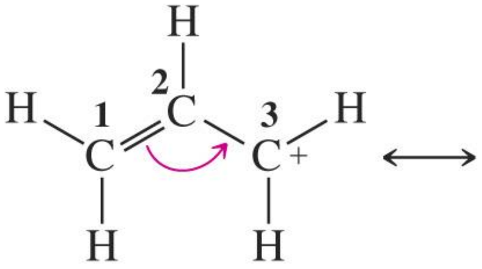
Resonance forms

- One resonance contributor is converted to another by the use of curved arrows which show the movement of electrons.

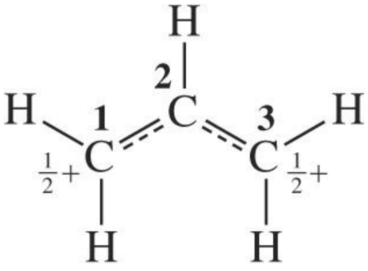
+ The use of these arrows serves as a bookkeeping device to assure all structures differ only in position of **p** and/or **π** electrons.



- Resonance theory predicts that the allyl cation is a hybrid of equivalent structures **D** and **E**:



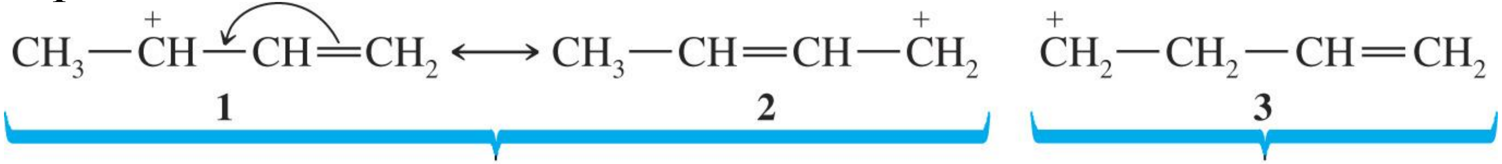
D **E**



F

Rules for resonance:

- Individual resonance structures exist only on paper.
  - The real molecule is a hybrid (average) of all contributing forms
  - Resonance forms are indicated by the use of double-headed arrow
- Only electrons are allowed to move between resonance structures.
  - The position of nuclei must remain the same
  - Only electrons in multiple bonds and nonbonding electrons can be move
- Example: 3 is NOT a resonance form because an atom has moved

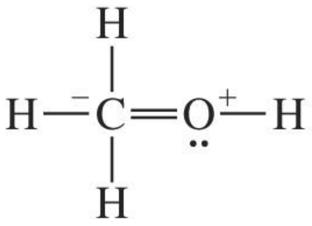


$CH_3-\overset{+}{C}H-CH=CH_2 \longleftrightarrow CH_3-CH=CH-\overset{+}{C}H_2 \qquad \overset{+}{C}H_2-CH_2-CH=CH_2$

These are resonance structures.

This is not a proper resonance structure of 1 or 2 because a hydrogen atom has been moved.

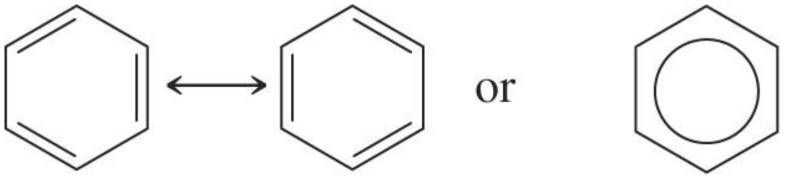
- All structures must be proper Lewis structures.



This is not a proper resonance structure for methanol because carbon has five bonds. Elements of the first major row of the periodic table cannot have more than eight electrons in their valence shell.

Rules for resonance:

- The energy of the actual molecule is lower than the energy of any single contributing form.
  - The lowering of energy is called resonance stabilization
- Equivalent resonance forms make equal contributions to the structure of the real molecule.
  - Structures with equivalent resonance forms tend to be greatly stabilized
  - Example: The two resonance forms of benzene contribute equally and greatly stabilize it



Resonance structures for benzene **Representation of hybrid**

- Unequal resonance structures contribute based on their relative stabilities.
  - More stable resonance forms contribute more to the structure of the real molecule.

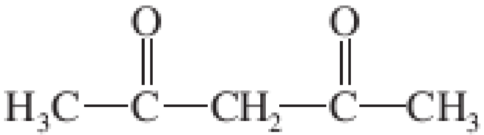
Resonance forms and tautomers

- Resonance forms can be compared using the following criteria, beginning with the most important:

1. As many octets as possible
2. As many bonds as possible
3. Any negative charges on electronegative atoms
4. As little charge separation as possible

PROBLEM 4-31

Acetylacetone (pentane-2,4-dione) reacts with sodium hydroxide to give water and the sodium salt of a carbanion. Write a complete structural formula for the carbanion, and use resonance forms to show the stabilization of the carbanion.



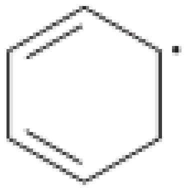
$$H_3C-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$$

acetylacetone (pentane-2,4-dione)

PROBLEM 4-32

Acetonitrile ($CH_3C\equiv N$) is deprotonated by very strong bases. Write resonance forms to show the stabilization of the carbanion that results.

Problem 10.5 Draw three resonance forms for the cyclohexadienyl radical.

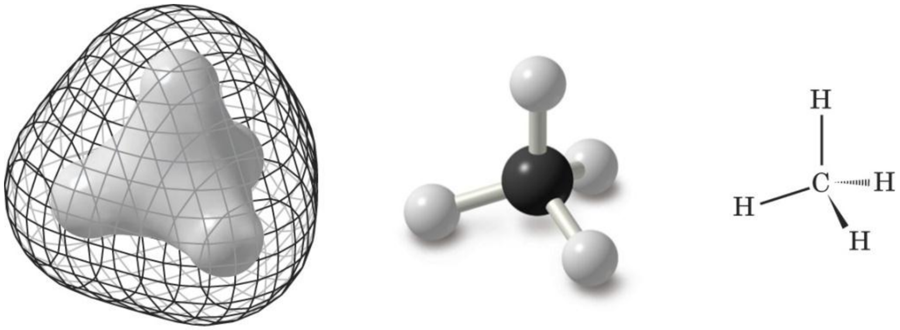


Cyclohexadienyl radical

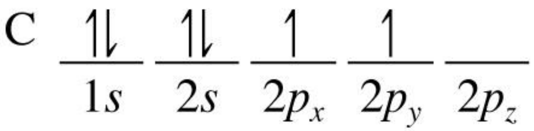
sp^3 Hybridization

- **The structure of methane:**

+ The structure of methane with its four identical tetrahedral bonds cannot be adequately explained using the electronic configuration of carbon.



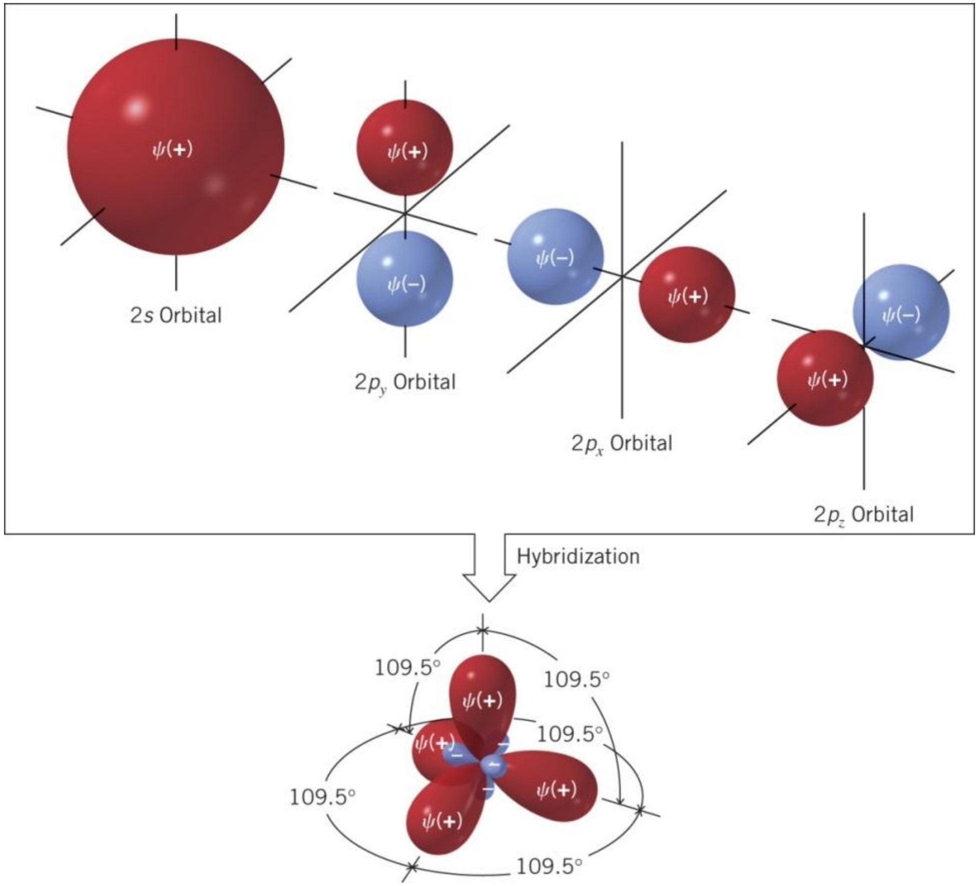
(*a*) (*b*) (*c*)



Ground state of a carbon atom

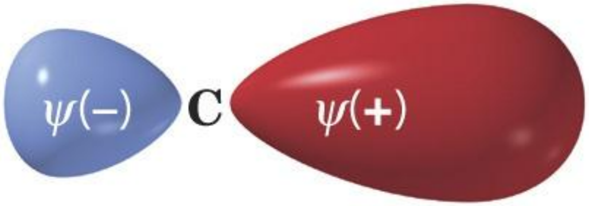
sp^3 Hybridization

- When one 2*s* orbital and three 2*p* orbitals are hybridized, four new and identical *sp*^{3} orbitals are obtained.
  - \+ Each new orbital has one part *s* character and 3 parts *p* character.
  - \+ The four identical orbitals are oriented in a tetrahedral arrangements.

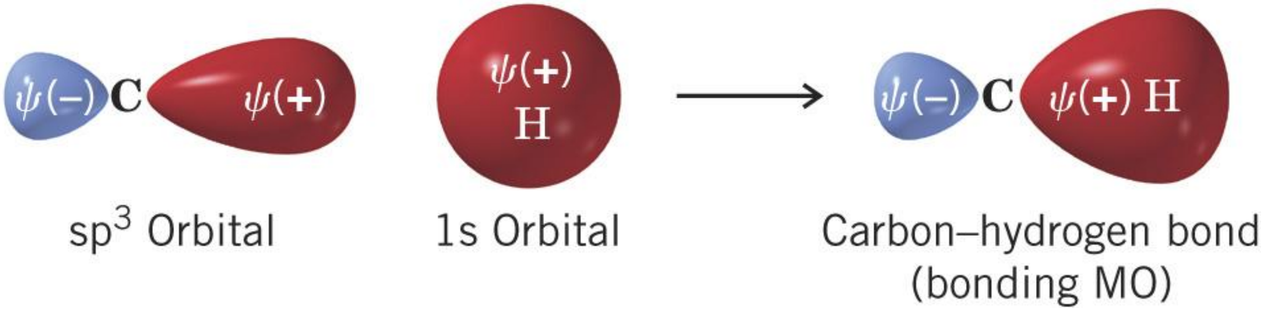


sp^3 Hybridization

- An *sp*^{3} orbital looks like a *p* orbital with one lobe greatly extended.



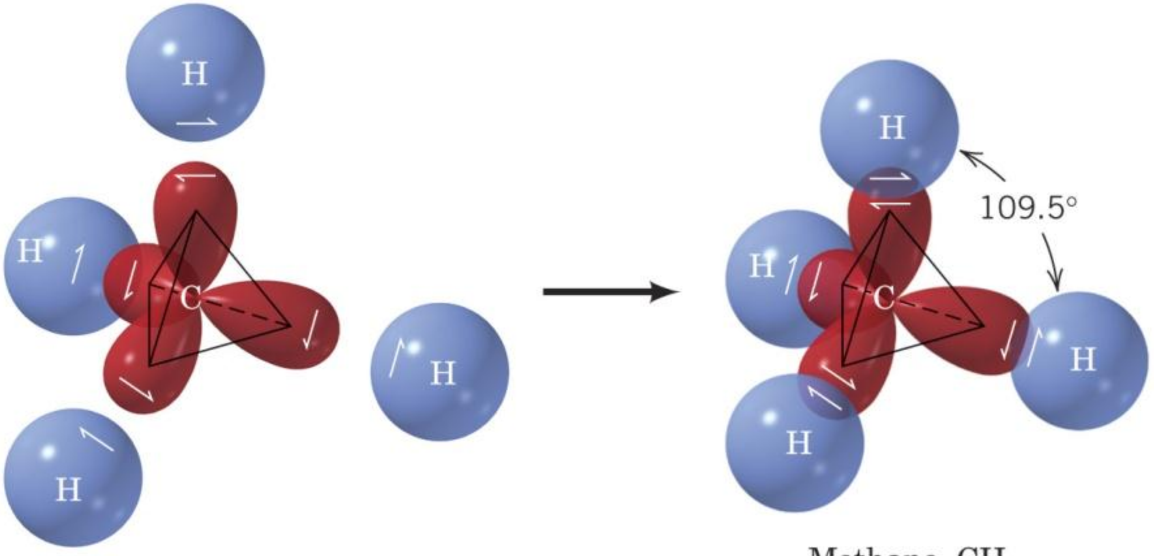
- The extended *sp*^{3} lobe can then overlap well with the hydrogen 1*s* to form a strong σ bond.



- The bond formed is called a sigma (s) bond because it is circularly symmetrical in cross section when view along the bond axis.

sp^3 Hybridization

- The four *sp*^{3} orbitals are then combined with the 1*s* orbitals of four hydrogens to give the molecular orbitals of methane. Each new molecular orbital can accommodate 2 electrons.

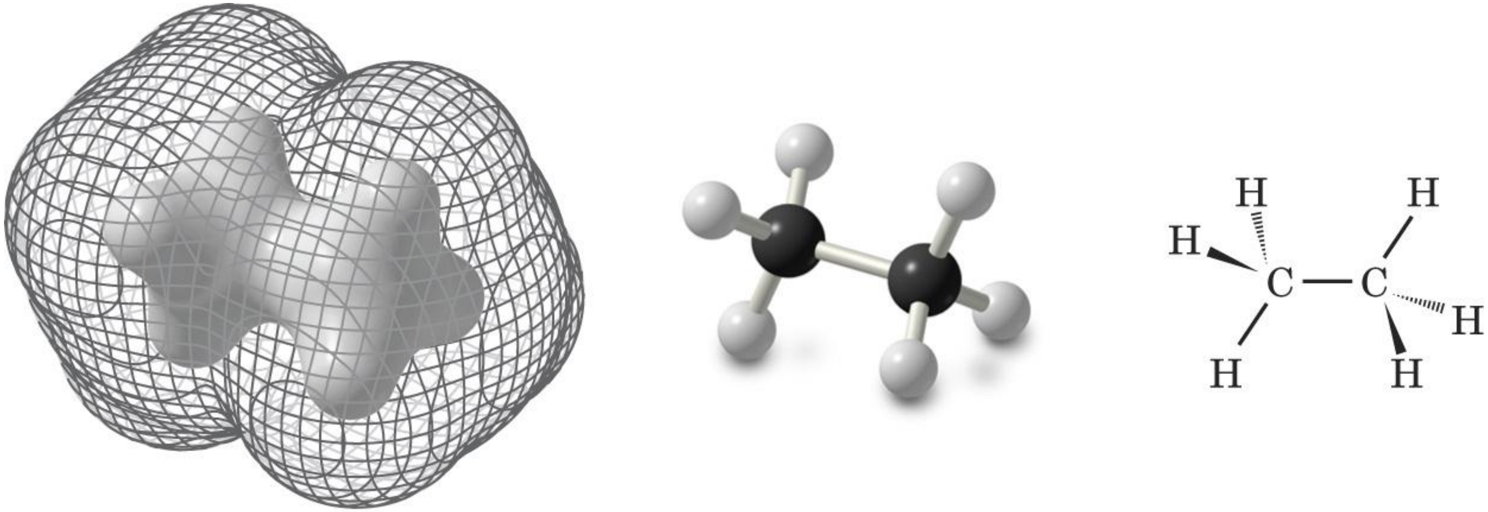


Methane, CH_4

Ethane (C_2H_6)

- The representations of ethane show the tetrahedral arrangement around each carbon.

  - a. calculated electron density surface
  - b. ball-and-stick model
  - c. typical 3-dimensional drawing.



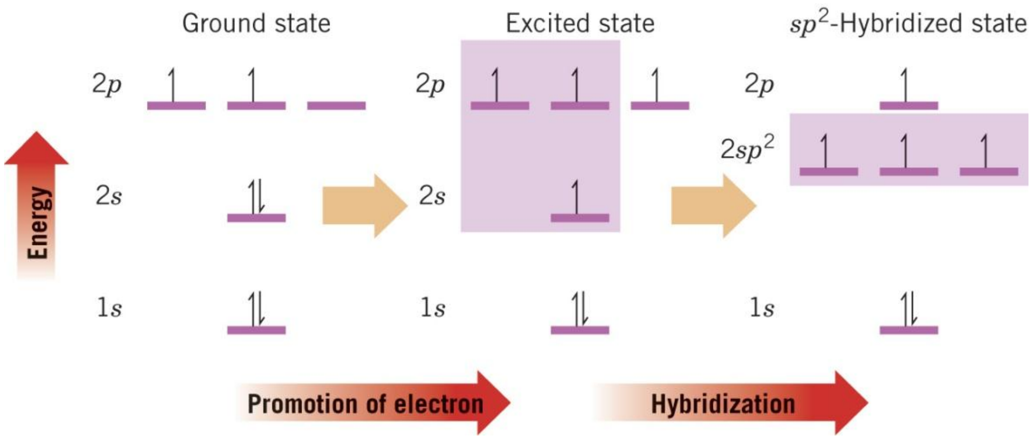
(*a*) (*b*) (*c*)

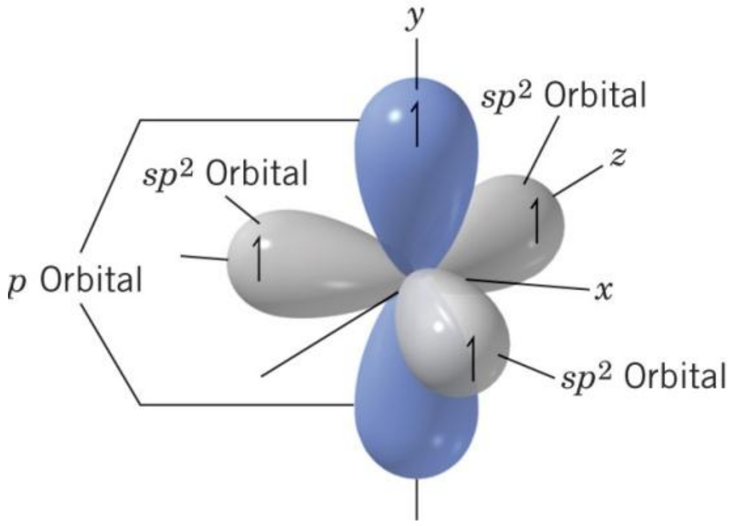
- Generally there is relatively free rotation about σ bonds.

  - **Very little energy (13-26 kcal/mol) is required to rotate around the carbon-carbon bond of ethane**

sp^2 Hybridization

- The three *sp^2* hybridized orbitals come from mixing one *s* and two *p* orbitals.
    - One *p* orbital is left unhybridized
- The *sp^2* orbitals are arranged in a trigonal planar arrangement.
    - The unhybridized *p* orbital is perpendicular (orthoganol) to the plane



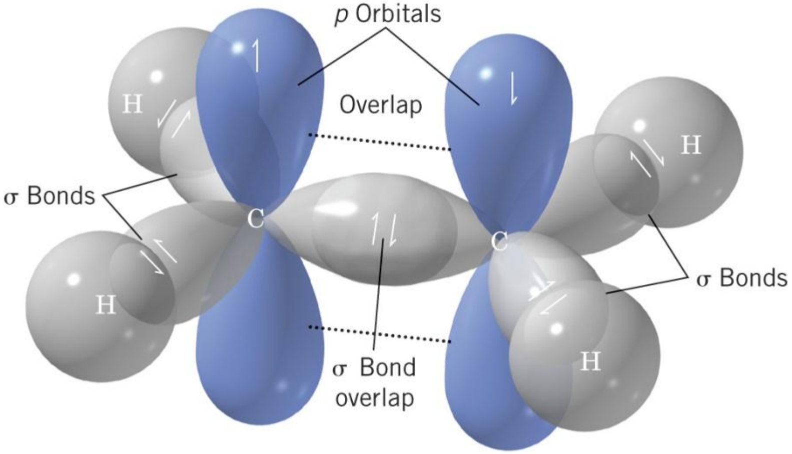


sp^2 Hybridization

- Overlap of *sp*^{2} orbitals in ethylene results in formation of a σ framework.

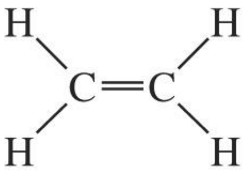
- The leftover *p* orbitals on each carbon overlap to form a bonding π (pi) bond between the two carbons.

- A π bond results from **side overlap** of *p* orbitals above and below the plane of the s bond.

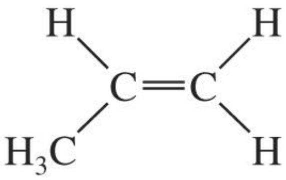


sp^2 Hybridization: The structure of ethene (ethylene)

- Ethene (C_2H_4) contains a carbon-carbon double bond and is in the class of organic compounds called *alkenes*.

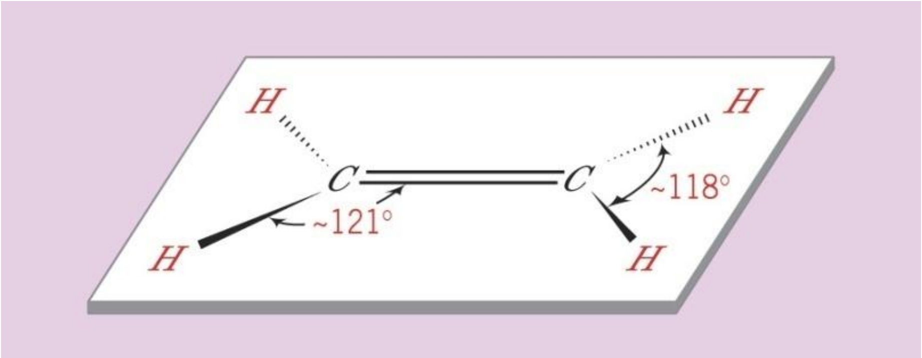


Ethene



Propene

- The geometry around each carbon is called *trigonal planar:* There are three σ bonds around each carbon of ethene and these are formed by using *sp*^{2} hybridized orbitals.
  - All atoms directly connected to each carbon are in a plane.
  - The bonds point towards the corners of a regular triangle.
  - The bond angle are approximately 120°.



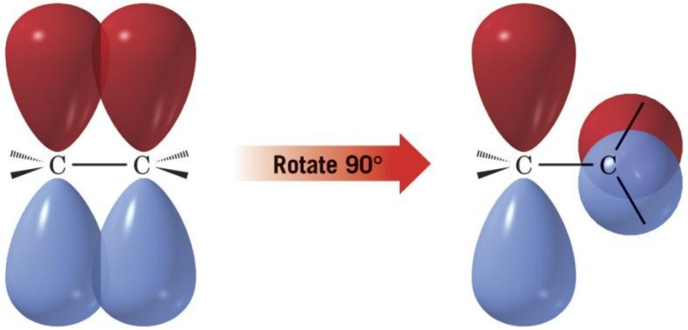
Restricted rotation and the double bond

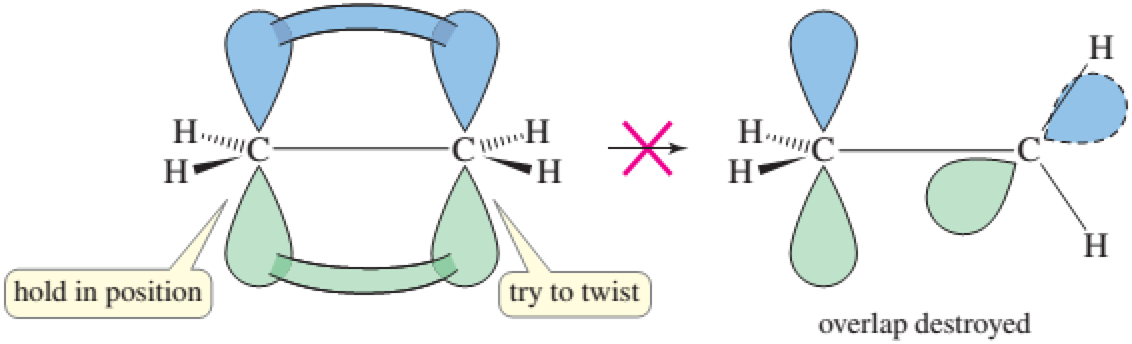
- There is a large energy barrier to rotation (about 264 kJ/mol) around the double bond.

  - This corresponds to the strength of a p bond.
  - The rotational barrier of a carbon-carbon single bond is 13-26 kJ/mol.

- This rotational barrier results because the *p* orbitals must be well aligned for maximum overlap and formation of the π bond.

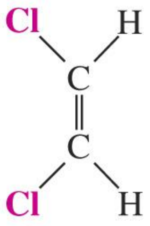
- Rotation of the *p* orbitals 90° totally breaks the π bond.



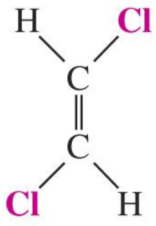


cis-trans Isomers

- *cis-trans* isomers are the result of restricted rotation about double bonds
- These isomers have the same connectivity of atoms and differ only in the arrangement of atoms in space
  - This puts them in the broader class of stereoisomers
- The molecules below do not *superpose* on each other
- One molecule is designated cis (groups on same side) and the other is trans (groups on opposite side)

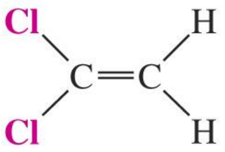


cis-1,2-Dichloroethene

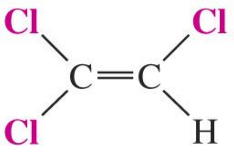


trans-1,2-Dichloroethene

- *cis-trans* isomerism is not possible if one carbon of the double bond has two identical groups



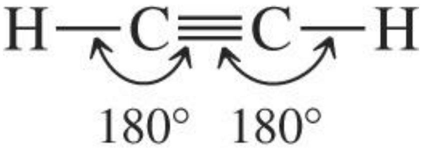
1,1-Dichloroethene
(no cis–trans isomerism)



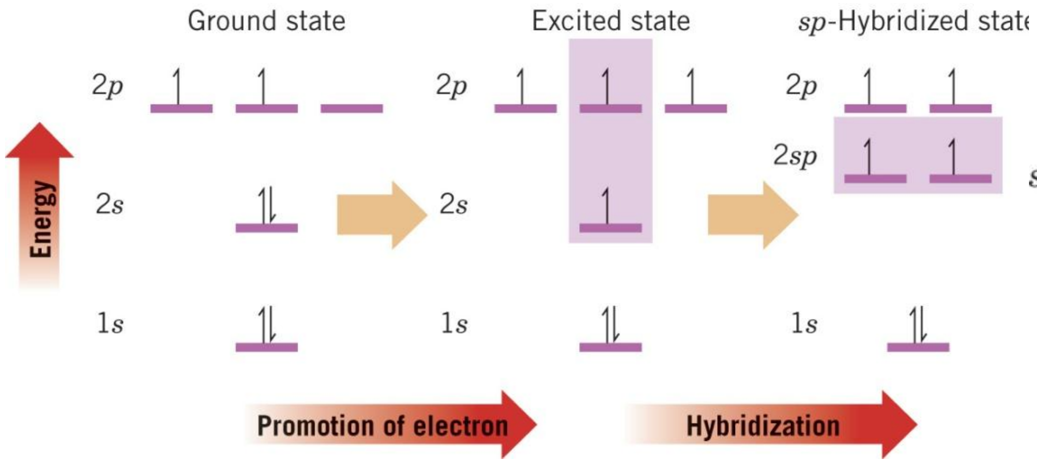
1,1,2-Trichloroethene
(no cis–trans isomerism)

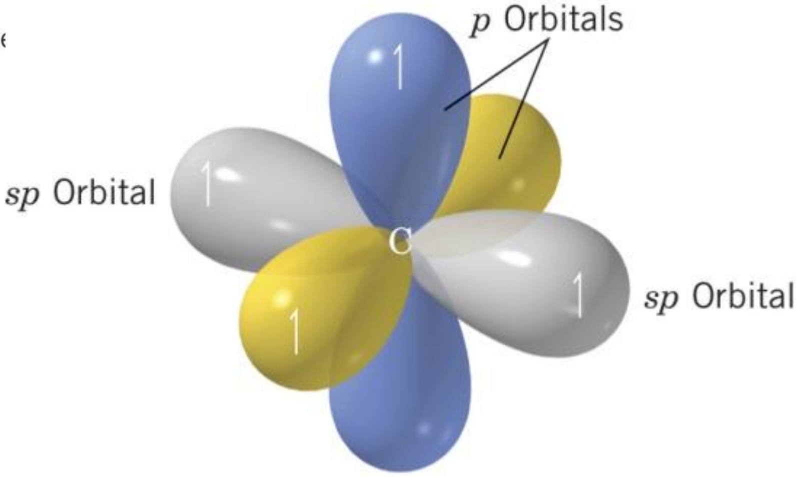
sp Hybridization

- Ethyne (acetylene) is a member of a group of compounds called alkynes which all have carbon-carbon triple bonds. The arrangement of atoms around each carbon is linear with bond angles 180°.



- The carbon in ethyne is *sp* hybridized.
  - One *s* and one *p* orbital are mixed to form two *sp* orbitals.
  - Two *p* orbitals are left un-hybridized.





- The two *sp* orbitals are oriented 180° relative to each other around the carbon nucleus. The two *p* orbitals are perpendicular to the axis that passes through the center of the *sp* orbitals.

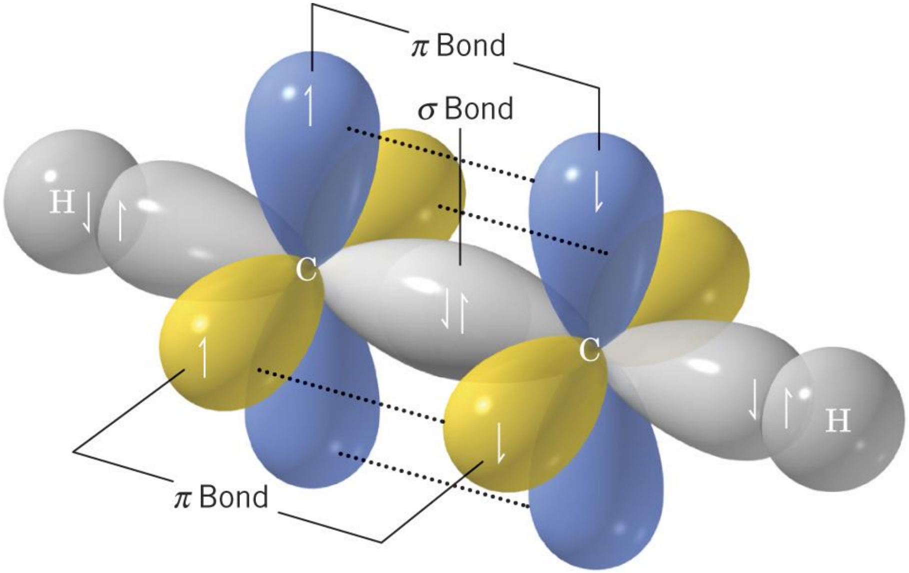
sp Hybridization

- In ethyne the *sp* orbitals on the two carbons overlap to form a sigma (σ) bond.

  - The remaining *sp* orbitals overlap with hydrogen 1s orbitals.

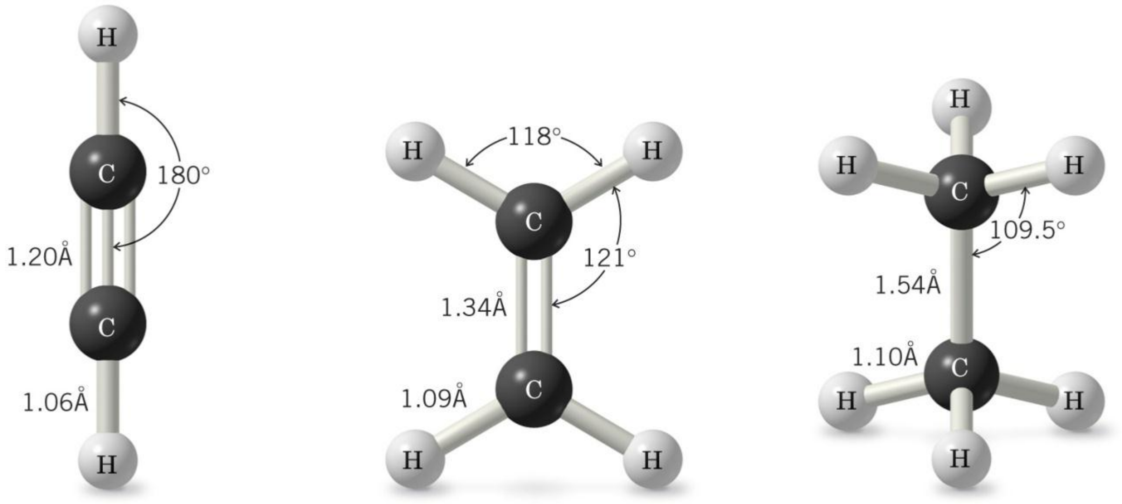
- The p orbitals on each carbon overlap to form two π bonds.

- The triple bond consists of one σ and two π bonds.



Bond lengths of ethyne, ethene and ethane

- The carbon-carbon bond length is shorter as more bonds hold the carbons together.
    - With more electron density between the carbons, there is more “glue” to hold the nuclei of the carbons together.
- The carbon-hydrogen bond lengths also get shorter with more *s* character of the bond.
    - 2*s* orbitals are held more closely to the nucleus than 2*p* orbitals.
    - A hybridized orbital with more percent *s* character is held more closely to the nucleus than an orbital with less *s* character.
    - The *sp* orbital of ethyne has 50% *s* character and its C-H bond is shorter.
    - The sp^3 orbital of ethane has only 25% s character and its C-H bond is longer.



Summary of hybridization

- The number of molecular orbitals formed equals the number of the atomic orbitals used.

- Hybridized orbitals are obtained by mixing the wave functions of different types of orbitals.

- Four sp^3 orbitals are obtained from mixing one *s* and three *p* orbitals.
  - The geometry of the four orbitals is tetrahedral
  - This is the hybridization used in the carbon of methane

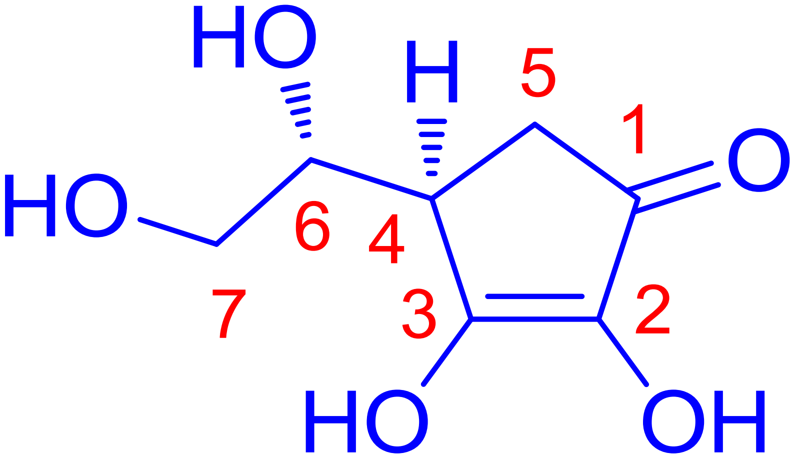
- Three sp^2 orbitals are obtained from mixing one *s* and two *p* orbitals.
  - The geometry of the three orbitals is trigonal planar
  - The left over *p* orbital is used to make a p bond
  - This is the hybridization used in the carbons of ethene

- Two *sp* orbitals are obtained from mixing one *s* and one *p* orbital.
  - The geometry of the two orbitals is linear
  - The two leftover *p* orbitals are used to make two p bonds
  - This is the hybridization used in the carbons of ethyne

- Sigma (s) bonds have circular symmetry when viewed along the bond axis.

- Pi (π) bonds result from **sideways overlap** of two p orbitals.

Vitamin C and scurvy disease



Ascobic acid (Vitamin C)

Polar covalent bonds

- Polar covalent bonds occur when a covalent bond is formed between two atoms of **differing electronegativities**.

  + The more electronegative atom draws electron density closer to itself.

  + The more electronegative atom develops a partial negative charge (δ-) and the less electronegative atom develops a partial positive charge (δ+).

  + A bond which is polarized is a dipole and has a **dipole moment**.

  + The direction of the dipole can be indicated by a **dipole arrow**. The arrow head is the negative end of a dipole, the crossed end is the positive end .

(positive end) ⟶ (negative end)

- Example: In the molecule HCl, The more electronegative chlorine draws electron density away from the hydrogen. Chlorine develops a partial negative charge.

- The dipole moment of a molecule can be measured experimentally.
  - + It is the product of the magnitude of the charges (in electrostatic units: esu) and the distance between the charges (in cm)
  - + The actual unit of measurement is a Debye (D) which is equivalent to 1 x 10^{-18} esu cm

$$\text{Dipole moment} = \text{charge (in esu)} \times \text{distance (in cm)}$$

$$\mu = e \times d$$

Molecular dipole

- In diatomic molecules, a dipole exists if the two atoms are of different electronegativity.

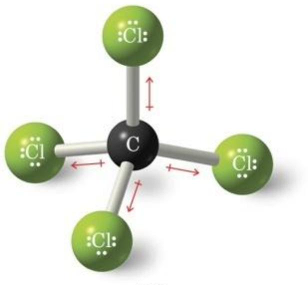
- In more complicated molecules, the molecular dipole is the sum of the bond dipoles.

- Some molecules with very polar bonds will have no net molecular dipole because the bond dipoles cancel out.

- **The center of positive charge and negative charge coincide in these molecules**

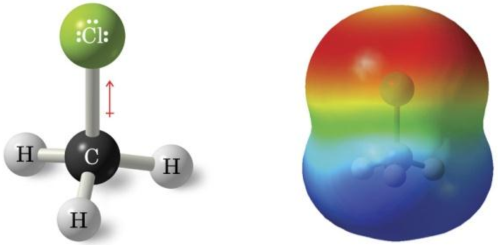
Formula	μ (D)	Formula	μ (D)
H_2	0	CH_4	0
Cl_2	0	CH_3Cl	1.87
HF	1.91	CH_2Cl_2	1.55
HCl	1.08	$CHCl_3$	1.02
HBr	0.80	CCl_4	0
HI	0.42	NH_3	1.47
BF_3	0	NF_3	0.24
CO_2	0	H_2O	1.85

➔In carbon tetrachloride the bond dipoles cancel and the overall molecular dipole is 0 Debye.



$\mu = 0$ D

➔In chloromethane the C-H bonds have only small dipoles but the C-Cl bond has a large dipole and the molecule is quite polar.

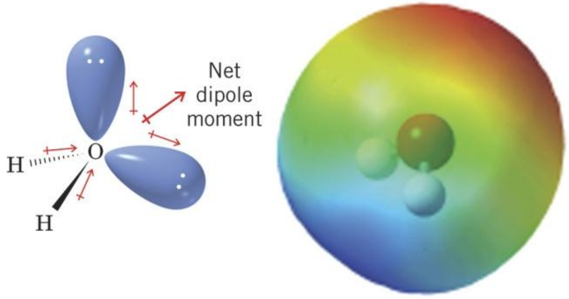


$\mu = 1.87$ D **Chloromethane**

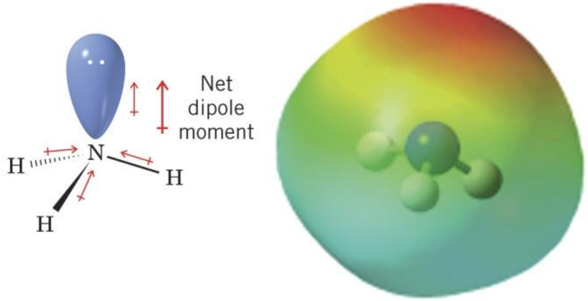
(*a*) (*b*)

➔An unshared pair of electrons on atoms such as oxygen and nitrogen contribute a great deal to a dipole.

- Water and ammonia have very large net dipoles



Water

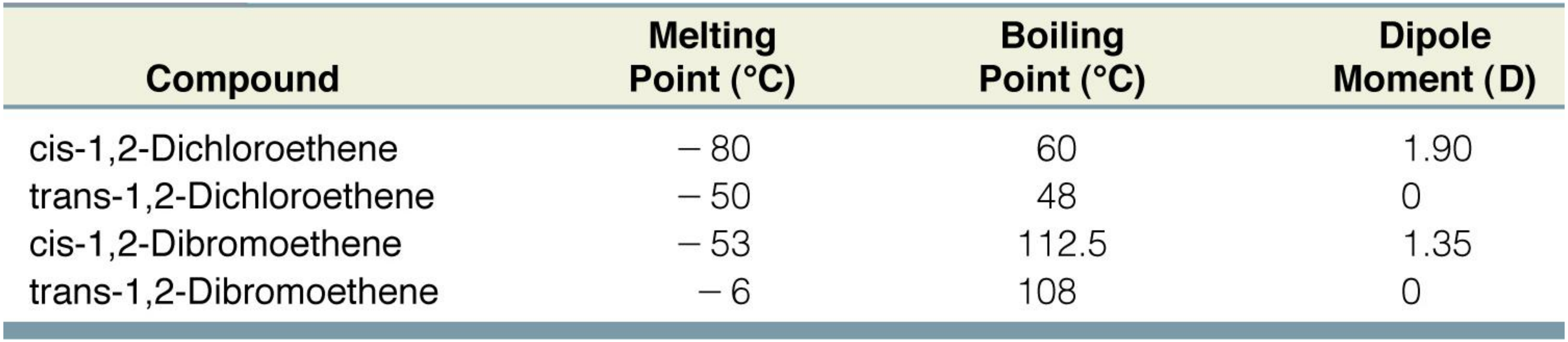


Ammonia

- Some cis-trans isomers differ markedly in their dipole moment.

➔In trans 1,2-dichloroethene the two carbon-chlorine dipoles cancel out and the molecular dipole is 0 Debye.

➔In the cis isomer the carbon-chlorine dipoles reinforce and there is a large molecular dipole.



Compound	Melting Point (°C)	Boiling Point (°C)	Dipole Moment (D)
cis-1,2-Dichloroethene	− 80	60	1.90
trans-1,2-Dichloroethene	− 50	48	0
cis-1,2-Dibromoethene	− 53	112.5	1.35
trans-1,2-Dibromoethene	− 6	108	0

The greater the dipole moment, the higher the boiling point and the melting point.

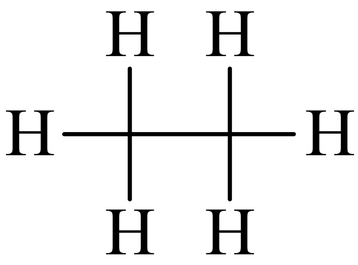
Inductive effects

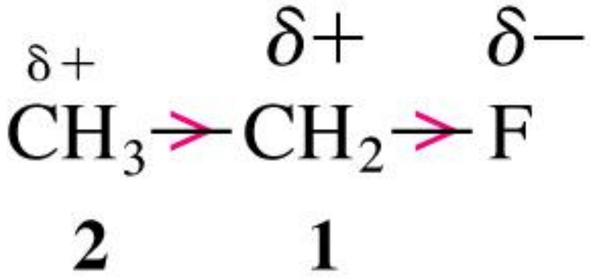
- Electronic effects that are transmitted through the sigma (σ) bonds of a molecule. These can be the electron donation or withdrawal through the sigma bonds of a molecule.

- In ethyl fluoride, the electronegative fluorine is withdrawing electron density away from the carbons.

☞ Fluorine is an electron withdrawing group (EWG).

	X
H	2.1
C	2.5
F	4.0





$$\underset{2}{\overset{\delta+}{CH_3}} \rightarrow \underset{1}{\overset{\delta+}{CH_2}} \rightarrow \overset{\delta-}{F}$$

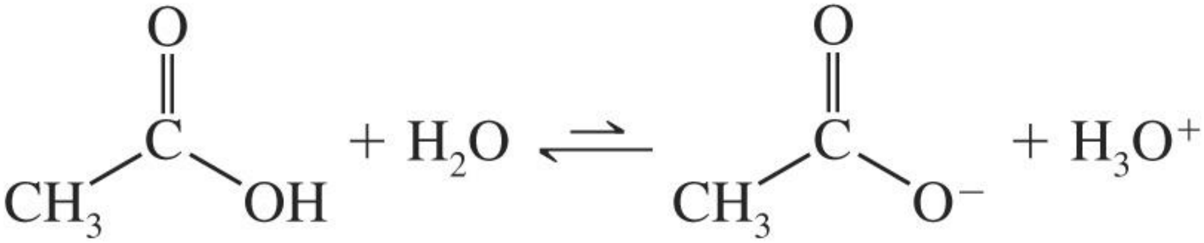
- The effect gets weaker with increasing distance.

- The effect is not affected by the geometry of the molecule.

Strengths of acids and bases

- **K_a and pK_a**

\+ Acetic acid is a relatively weak acid and a 0.1 M solution is only able to protonate water to the extent of about 1%.



\+ The equilibrium equation for this reaction is:

$$K_{eq} = \frac{[H_3O^+]\,[CH_3CO_2^-]}{[CH_3CO_2H][H_2O]}$$

- Any substituent that stabilizes the negatively charged carboxylate ion promotes dissociation and results in a stronger acid.

pK_a

- Acidity is usually expressed in terms of pK_a
  - pK_a is the negative log of K_a.
  - The pK_a for acetic acid is 4.75.

$$pK_a = -\log K_a$$

- The larger the pK_a, the weaker the acid.

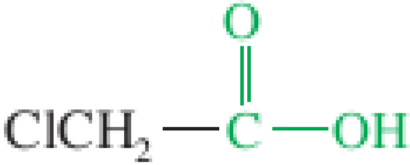
$$CH_3CO_2H < CF_3CO_2H < HCl$$

CH_3CO_2H	CF_3CO_2H	HCl
$pK_a = 4.75$	$pK_a = 0$	$pK_a = -7$
Weak acid		**Very strong acid**

Increasing acid strength →

The higher the electronegativity, the stronger the inductive effect.

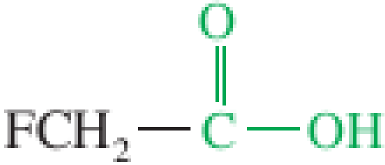
- Stronger electron-withdrawing groups stabilize the anion of the conjugate base more than weaker groups, leading to stronger acids.
- Electronegative atoms enhance the strength of an acid by withdrawing electron density from the carboxylate ion. This inductive effect can be quite large if one or more strongly electron-withdrawing groups are present on the carbon atom.



$ClCH_2-C(=O)-OH$

chloroacetic acid

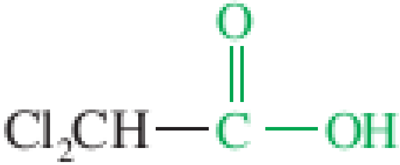
$pK_a = 2.86$



$FCH_2-C(=O)-OH$

fluoroacetic acid

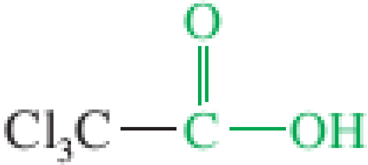
$pK_a = 2.59$



$Cl_2CH-C(=O)-OH$

dichloroacetic acid

$pK_a = 1.26$



$Cl_3C-C(=O)-OH$

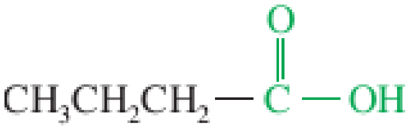
trichloroacetic acid

$pK_a = 0.64$

- Highly electronegative atoms withdrawal electron via inductive effect (negative, -*I*)

The longer the distance, the weaker the inductive effect

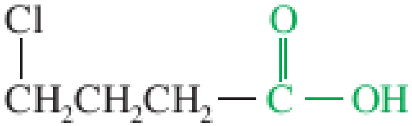
- The magnitude of this inductive effect depends on the number of bonds between the electronegative element (or other electron-with-drawing group) and the site of the negative charge. Note how adding a chlorine atom to butanoic acid increases its acidity, and the effect is larger if the chlorine atom is closer to the acidic group.



$CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-OH$

butanoic acid

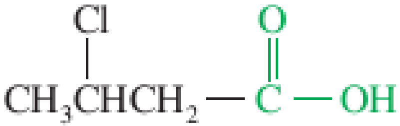
$pK_a = 4.82$



$\overset{\overset{Cl}{|}}{C}H_2CH_2CH_2-\overset{\overset{O}{\|}}{C}-OH$

4-chlorobutanoic acid

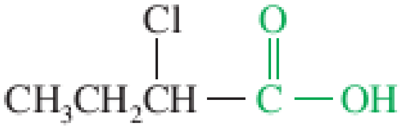
$pK_a = 4.52$



$CH_3\overset{\overset{Cl}{|}}{C}HCH_2-\overset{\overset{O}{\|}}{C}-OH$

3-chlorobutanoic acid

$pK_a = 4.05$



$CH_3CH_2\overset{\overset{Cl}{|}}{C}H-\overset{\overset{O}{\|}}{C}-OH$

2-chlorobutanoic acid

$pK_a = 2.86$

- More distant substituents have smaller effects on acidity, showing that inductive effects decrease rapidly with distance.

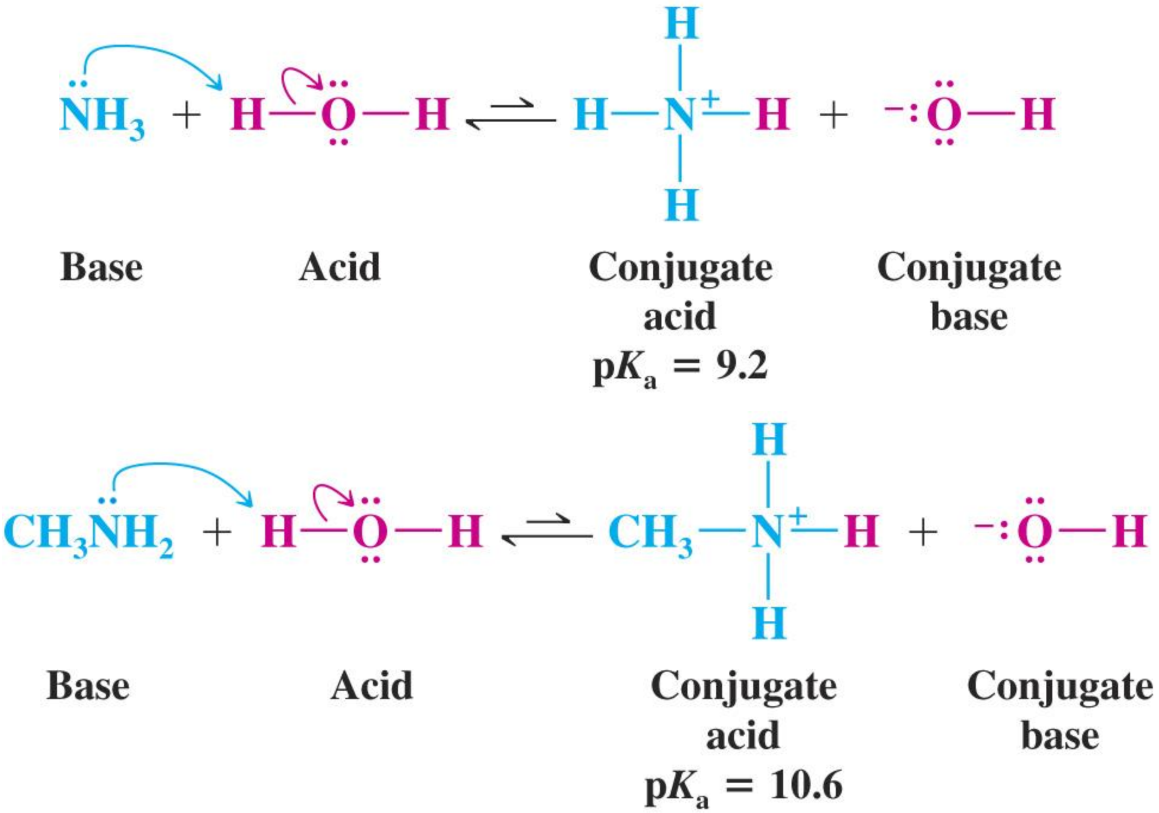
TABLE 20-4 Values of K_a and pK_a for Substituted Carboxylic Acids

Acid	K_a	pK_a
F_3CCOOH	5.9×10^{-1}	0.23
Cl_3CCOOH	2.3×10^{-1}	0.64
$Cl_2CHCOOH$	5.5×10^{-2}	1.26
$O_2N—CH_2COOH$	2.1×10^{-2}	1.68
$NCCH_2COOH$	3.4×10^{-3}	2.46
FCH_2COOH	2.6×10^{-3}	2.59
$ClCH_2COOH$	1.4×10^{-3}	2.86
$CH_3CH_2CHClCOOH$	1.4×10^{-3}	2.86
$BrCH_2COOH$	1.3×10^{-3}	2.90
ICH_2COOH	6.7×10^{-4}	3.18
CH_3OCH_2COOH	2.9×10^{-4}	3.54
$HOCH_2COOH$	1.5×10^{-4}	3.83
$CH_3CHClCH_2COOH$	8.9×10^{-5}	4.05
PhCOOH	6.46×10^{-5}	4.19
$PhCH_2COOH$	4.9×10^{-5}	4.31
$ClCH_2CH_2CH_2COOH$	3.0×10^{-5}	4.52
CH_3COOH	1.8×10^{-5}	4.74
$CH_3CH_2CH_2COOH$	1.5×10^{-5}	4.82

stronger acids ↑

Inductive effects of alkyl groups

- Methylamine is a stronger base than ammonia.
  - + The conjugate acid of methylamine is weaker than the conjugate acid of ammonia.

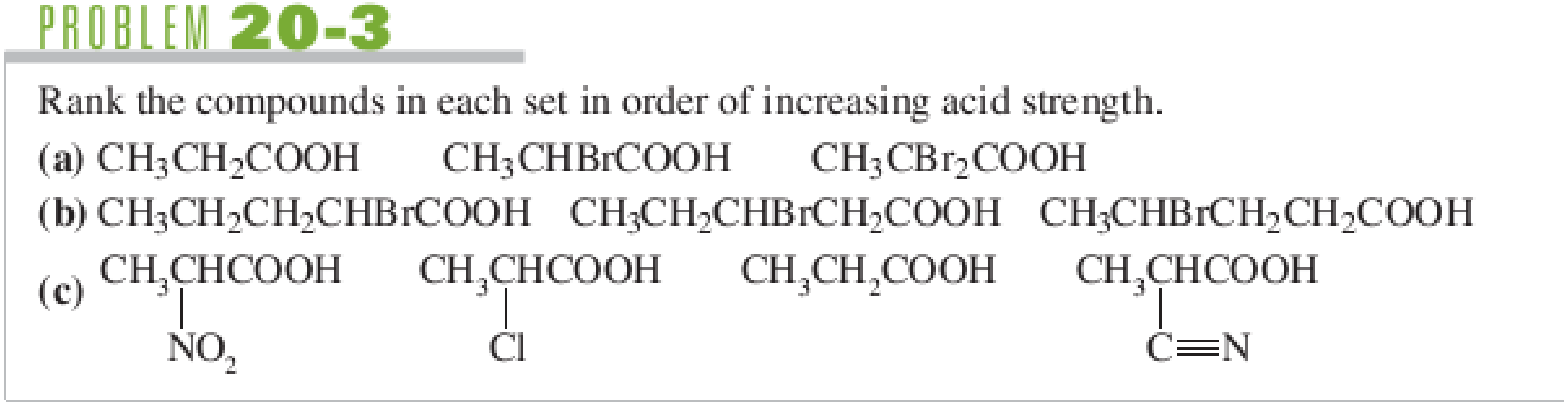


- Alkyl groups donate electron by inductive effect (positive, +*I*)

Summary

- Electron-withdrawing groups enhance acidity because they help to stabilize the negative charge of the conjugate base (the carboxylate ion). The amount of stabilization depends on:

1. The number of electron-withdrawing groups;
2. The strength of the electron-withdrawing groups; and
3. The distance of the electron-withdrawing groups from the COOH group.



PROBLEM 20-3

Rank the compounds in each set in order of increasing acid strength.

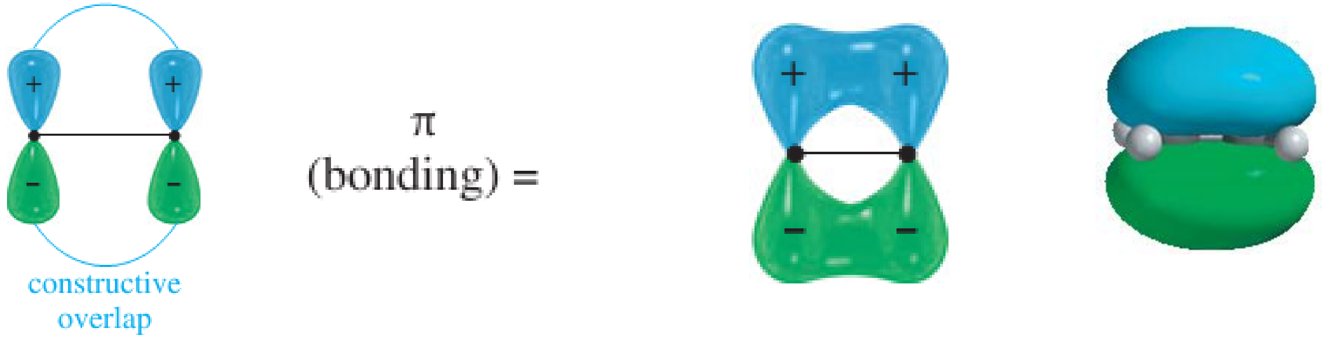
(a) CH_3CH_2COOH $CH_3CHBrCOOH$ CH_3CBr_2COOH

(b) $CH_3CH_2CH_2CHBrCOOH$ $CH_3CH_2CHBrCH_2COOH$ $CH_3CHBrCH_2CH_2COOH$

(c) $CH_3\underset{\displaystyle NO_2}{\underset{|}{C}}HCOOH$ $CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCOOH$ CH_3CH_2COOH $CH_3\underset{\displaystyle C\equiv N}{\underset{|}{C}}HCOOH$

π-π Conjugated systems

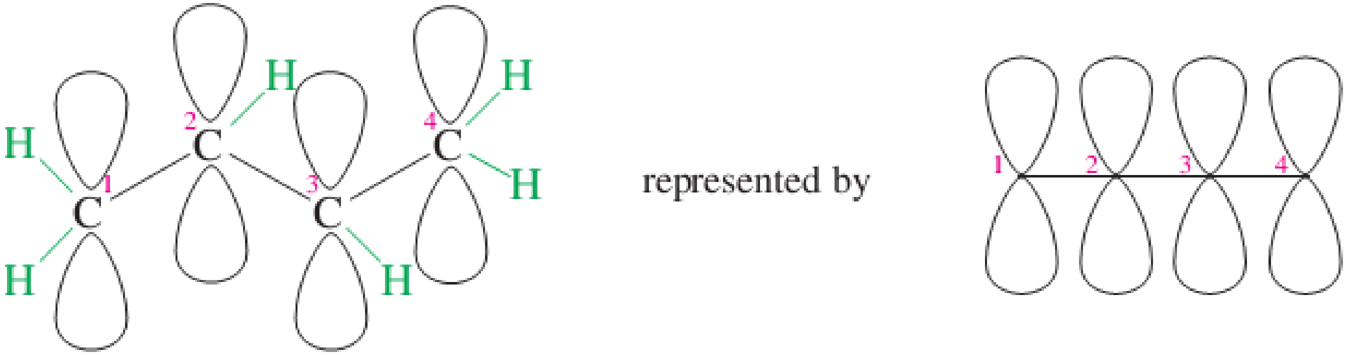
- The pi molecular orbitals of ethylene. The pi bonding orbital is formed by constructive overlap of un-hybridized p orbitals on the carbon atoms.



- The pi molecular orbitals of buta-1,3-diene:

+ Double bonds can interact with each other if they are **separated by just one single bond**. Such interacting double bonds are said to be conjugated.

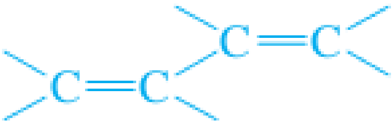
+ This is an typical example of **π-π conjugated systems.**



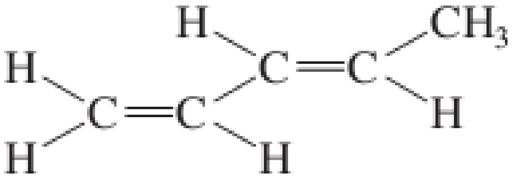
Conjugation effect

- Because of the interaction between the double bonds, systems containing conjugated double bonds tend to be more stable than similar systems with isolated double bonds.

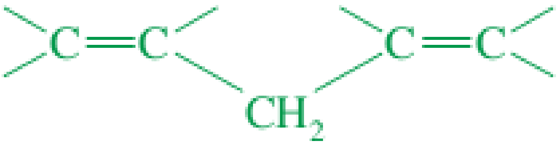
- Double bonds with two or more single bonds separating them have little interaction and are called isolated double bonds. For example, penta-1,3-diene has conjugated double bonds, while penta-1,4-diene has isolated double bonds.



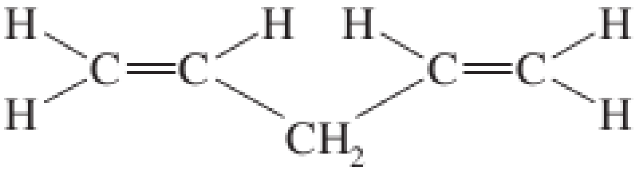
conjugated double bonds
(more stable than isolated double bonds)



penta-1,3-diene



isolated double bonds

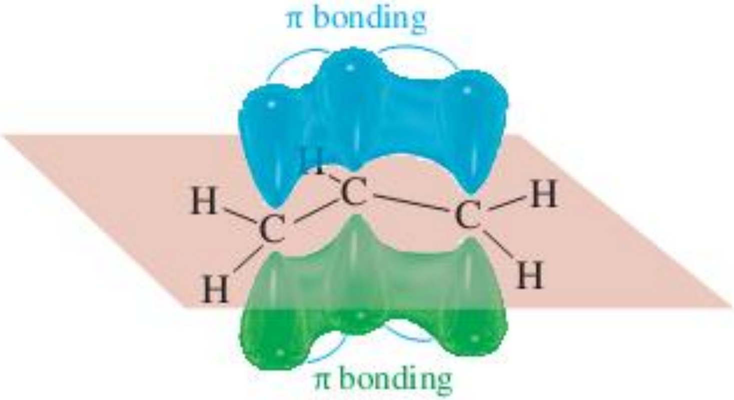


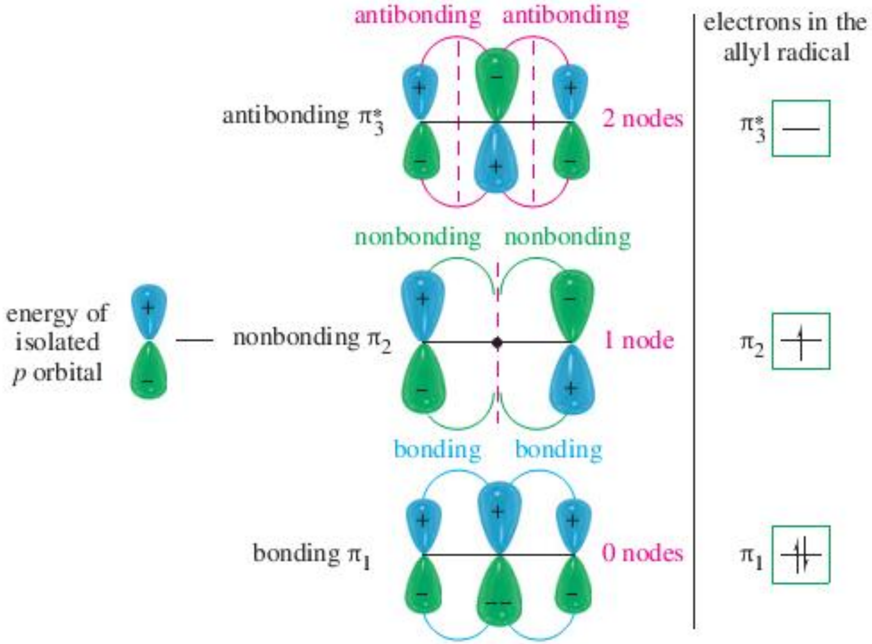
penta-1,4-diene

Lewis structures are inadequate to represent delocalized molecules such as buta-1,3-diene. To represent the bonding in conjugated systems accurately, we must consider molecular orbitals that represent the entire conjugated pi system, and not just one bond at a time.

p-π Conjugated systems

- Just as the four p orbitals of buta-1,3-diene overlap to form four molecular orbitals, the **three** atomic p orbitals of the allyl system overlap to form three molecular orbitals.





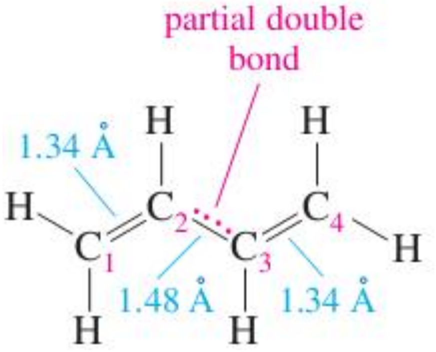
- p-π Conjugated unsaturated systems have a *p* orbital on an atom adjacent to a double bond or a triple bond.
  + The *p* orbital may be the empty *p* orbital of a carbocation or a *p* orbital with a single electron in it (a radical).
  + Conjugated molecules can be detected using UV spectroscopy.

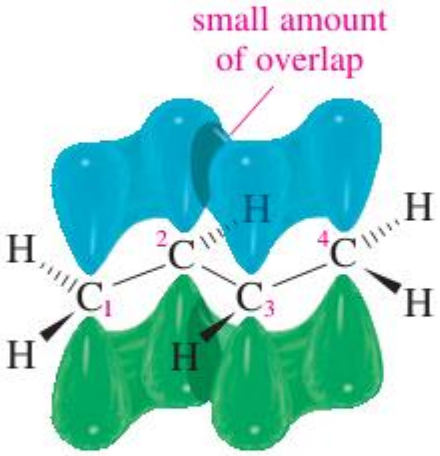
Conjugation effect: Electron delocalization

+ The double bonds of buta-1,3-diene have the expected length of regular double bonds.

+ The central bond is much shorter than a regular carbon-carbon single bond.

  - Ethane has a carbon-carbon bond length of 1.54 Å



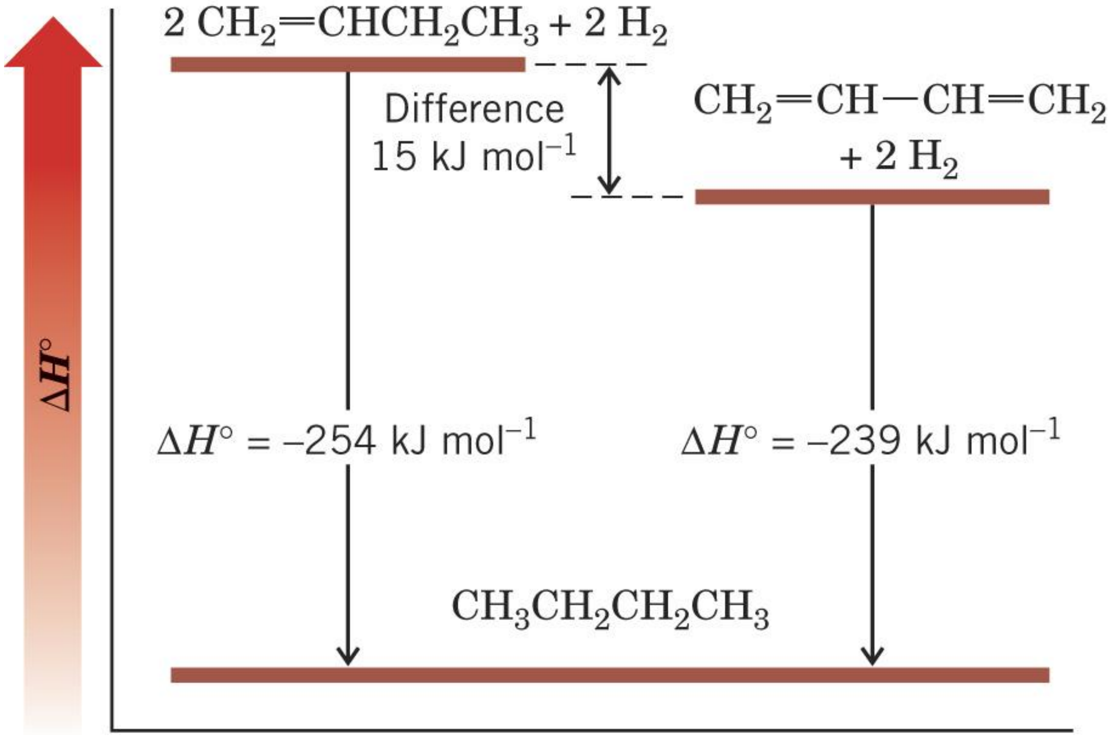


+ The central bond in buta-1,3-diene is shorter than that in ethane for two reasons.

  - The σ bond between C2 and C3 is made from sp^2-sp^2 overlap
  - There is significant overlap between the C2-C3 *p* orbitals

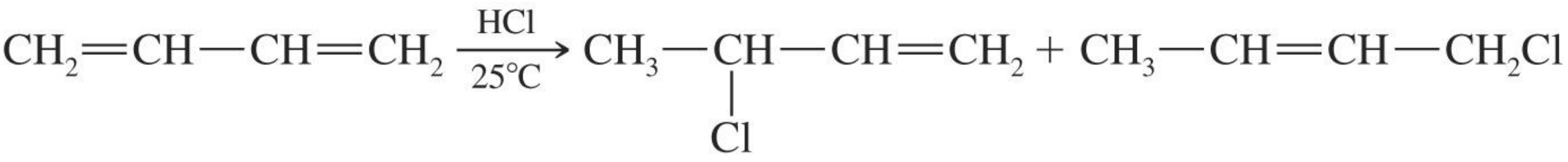
The stability of conjugated polyenes

- Buta-1,3-diene has a lower heat of hydrogenation by 15 kJ mol^{-1} than two molecules of 1-butene.
  - A lower heat of hydrogenation means 1,3-butadiene is more stable
  - These molecules can be compared directly because upon hydrogenation they lead to the same product



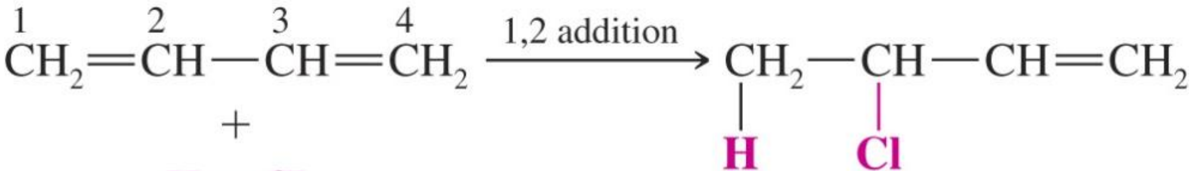
Chemical properties of long conjugated systems

- Electrophilic attack on conjugated dienes: 1,4 addition.
  - When 1,3-butadiene reacts with one equivalent of HCl at room temperature 78% of the 1,2 addition product and 22% of the 1,4 addition product are obtained.



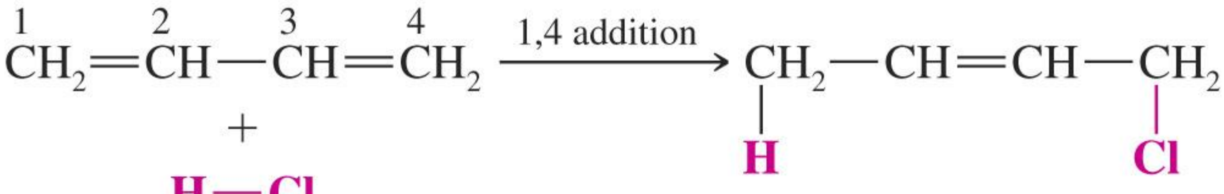
$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[25^\circ C]{HCl} CH_3{-}\underset{Cl}{CH}{-}CH{=}CH_2 + CH_3{-}CH{=}CH{-}CH_2Cl$$

1,3-Butadiene **3-Chloro-1-butene (78%)** **1-Chloro-2-butene (22%)**



$$\overset{1}{CH_2}{=}\overset{2}{CH}{-}\overset{3}{CH}{=}\overset{4}{CH_2} + H{-}Cl \xrightarrow{\text{1,2 addition}} \underset{H}{CH_2}{-}\underset{Cl}{CH}{-}CH{=}CH_2$$

3-Chloro-1-butene



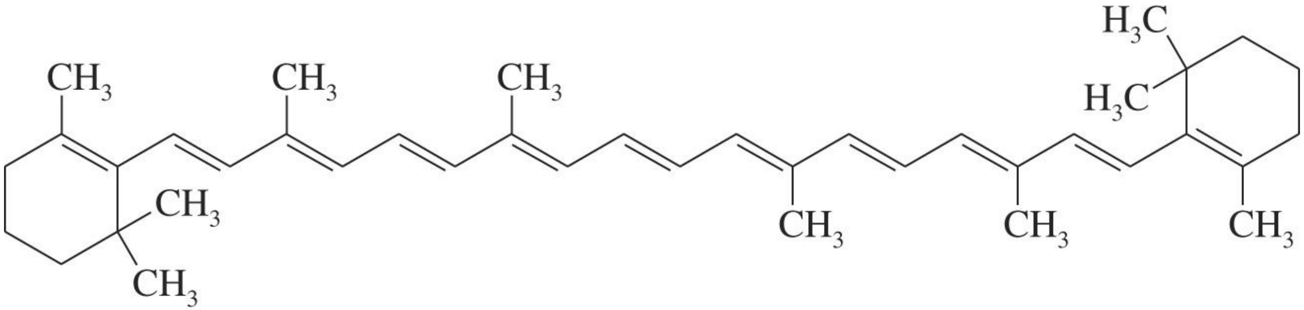
$$\overset{1}{CH_2}{=}\overset{2}{CH}{-}\overset{3}{CH}{=}\overset{4}{CH_2} + H{-}Cl \xrightarrow{\text{1,4 addition}} \underset{H}{CH_2}{-}CH{=}CH{-}\underset{Cl}{CH_2}$$

1-Chloro-2-butene

Physical properties of long conjugated systems

- The longer the conjugated system, the smaller the energy difference between the HOMO and the LUMO.

- A smaller energy gap results in longer λ_{max} in the ultraviolet-visible spectrum.
- β-Carotene has 11 conjugated double bonds and an absorbance maximum at 497 nm which is in the blue-green region of the visible spectrum.
- β-Carotene is perceived as red-orange, the complementary color of blue-green.

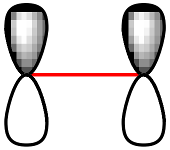


***β*-Carotene**

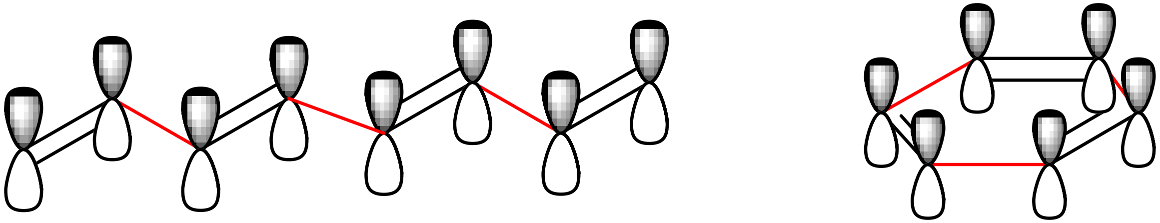
Pumpkins

Summary of conjugated systems

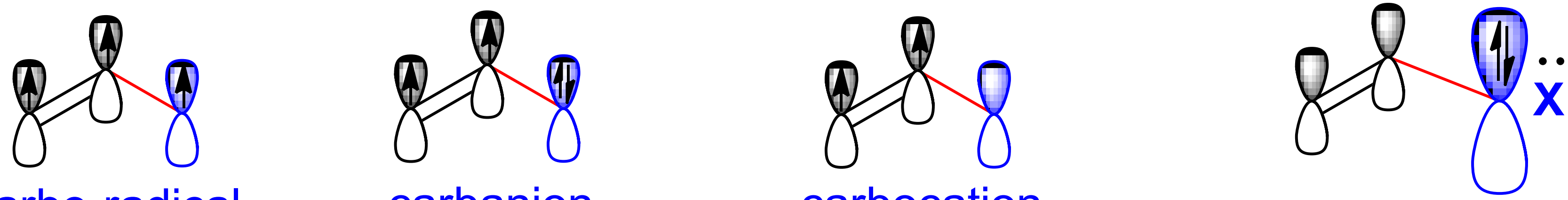
- Conjugated double bonds: double bonds that alternate with single bonds, with interaction by overlap of the p orbitals in the pi bonds.
- A conjugated system is a system of at least three connected p orbitals. Alternating single and multiple bonds or lone pairs (in p orbitals) are parts of the systems. This generally lowers the overall energy of the molecule and increases its stability.



π bond



alternating single and multiple bond:
π–π conjugated systems



carbo-radical

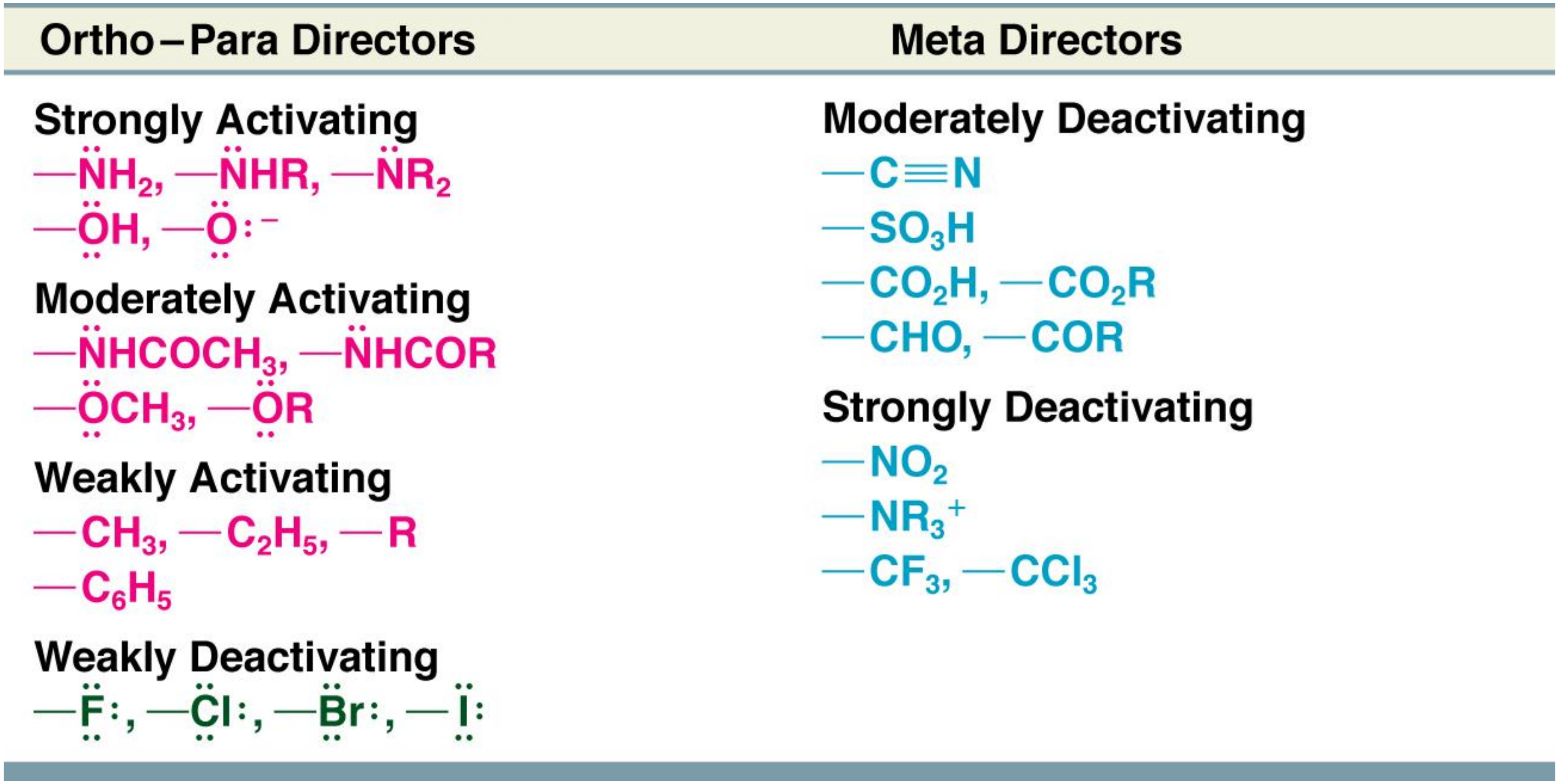
carbanion

carbocation

X: halogen, O, N, ...

A p orbital adjacent to a multiple bond:
p–π conjugated systems

Classification of substitutents

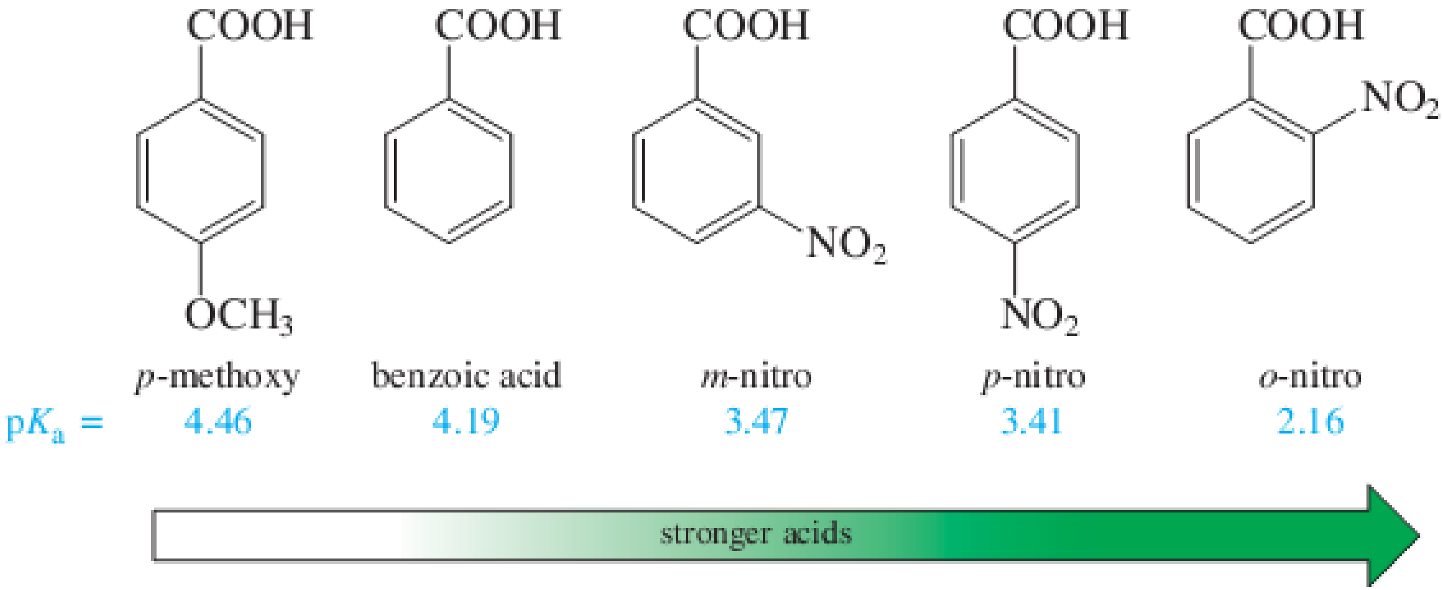


Ortho–Para Directors	Meta Directors
Strongly Activating $-\ddot{N}H_2$, $-\ddot{N}HR$, $-\ddot{N}R_2$ $-\underset{..}{\ddot{O}}H$, $-\underset{..}{\ddot{O}}:^-$	**Moderately Deactivating** $-C\equiv N$ $-SO_3H$ $-CO_2H$, $-CO_2R$ $-CHO$, $-COR$
Moderately Activating $-\ddot{N}HCOCH_3$, $-\ddot{N}HCOR$ $-\underset{..}{\ddot{O}}CH_3$, $-\underset{..}{\ddot{O}}R$	**Strongly Deactivating** $-NO_2$ $-NR_3^+$ $-CF_3$, $-CCl_3$
Weakly Activating $-CH_3$, $-C_2H_5$, $-R$ $-C_6H_5$	
Weakly Deactivating $-\underset{..}{\ddot{F}}:$, $-\underset{..}{\ddot{Cl}}:$, $-\underset{..}{\ddot{Br}}:$, $-\underset{..}{\ddot{I}}:$	

Characters of conjugation effect

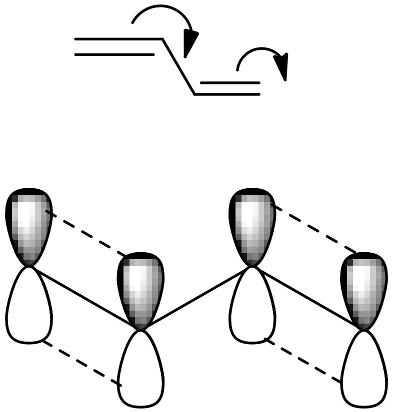
- It does not depend on the length of the conjugated system.
- It depends heavily on the planarity of the system.

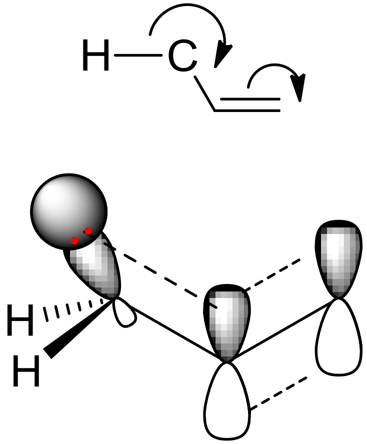
- Explain the trend of the strength of the following series of acids.

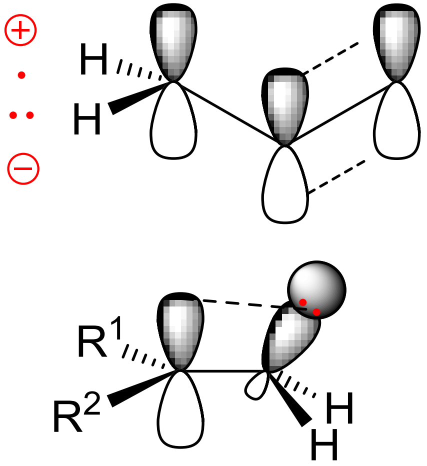


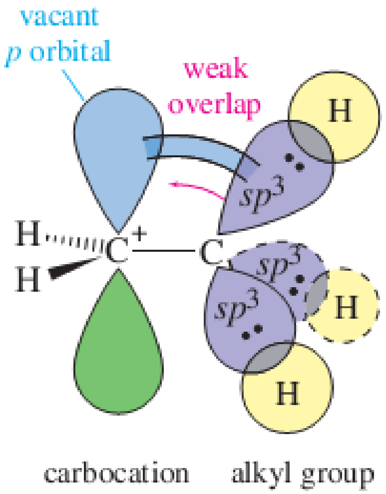
Hyperconjugation

- Alkyl substituents also have filled orbitals that can overlap with the empty p orbital on the positively charged carbon atom, further stabilizing the carbocation.
- The pair of electrons in this bond spreads out into the empty p orbital, stabilizing the electron-deficient carbon atom. This type of overlap between a p orbital and a sigma bond is called **hyperconjugation**.





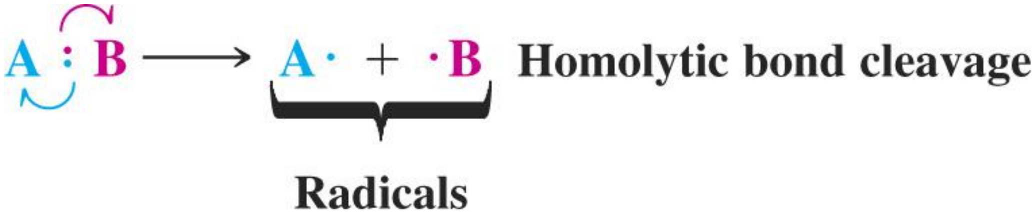




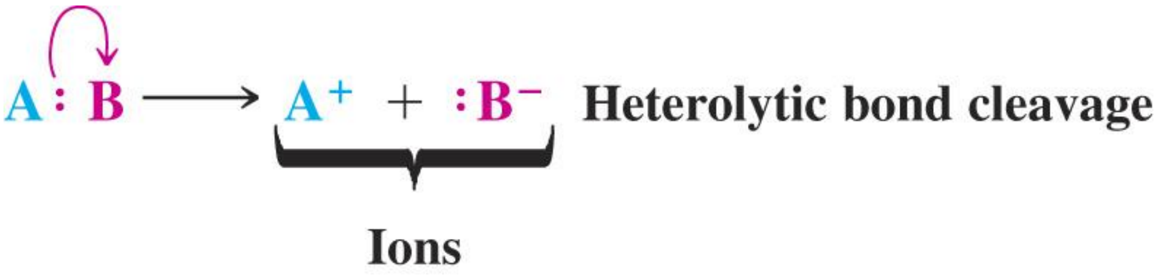
In general, conjugation effect plays a more important role than inductive and hyperconjugation effects.

Cleavage of covalent bonds

- **Homolysis**: Heterolytic reactions almost always occur at non-polar bonds.

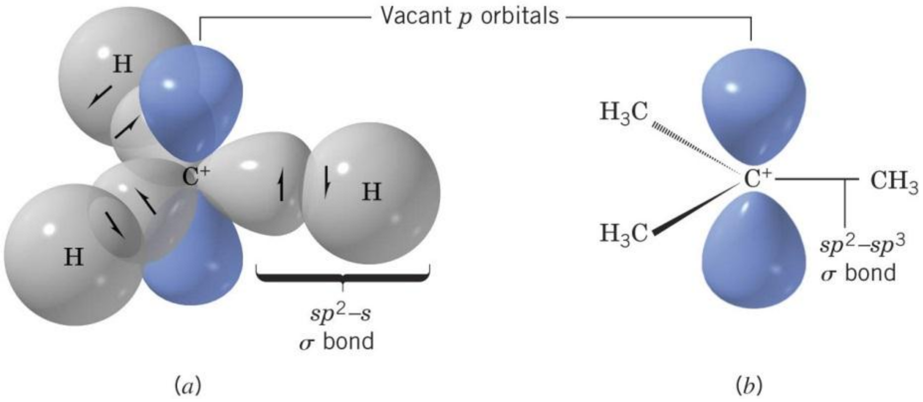


- **Heterolysis**: Heterolytic reactions almost always occur at polar bonds.



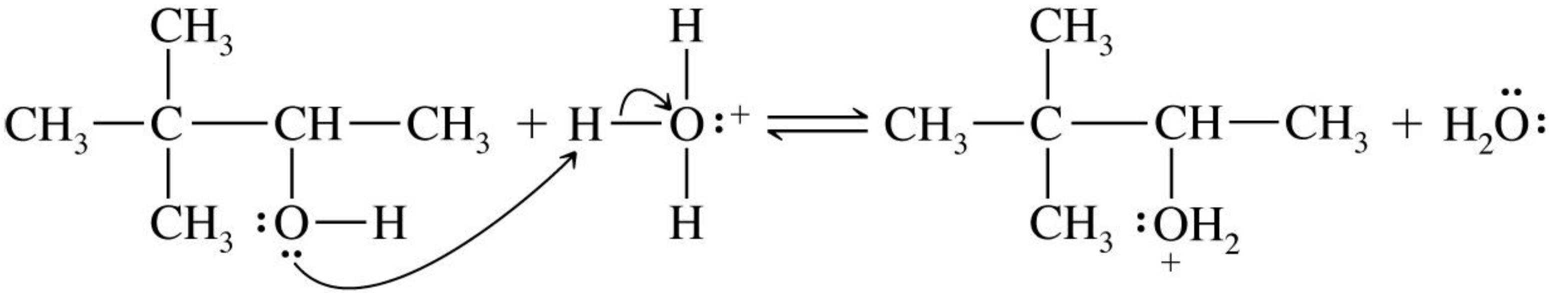
Carbocations

➔A carbocation has only 6 electrons, is sp^2 hybridized and has an empty *p* orbital. Carbocations are **electron-deficient** species.



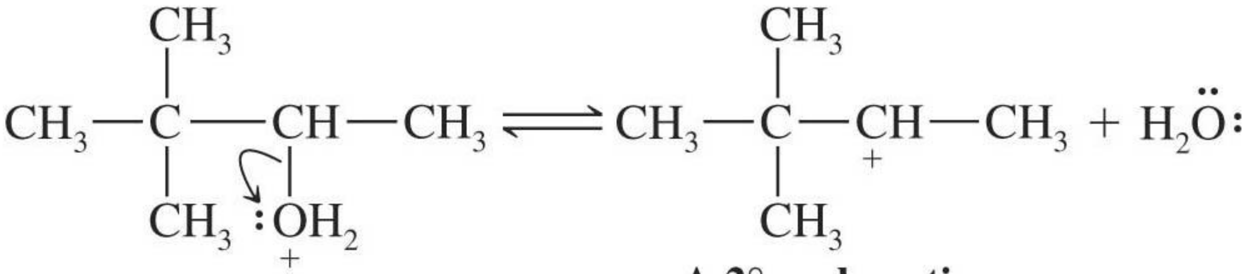
Formation of carbocations

Step 1



Protonated alcohol

Step 2

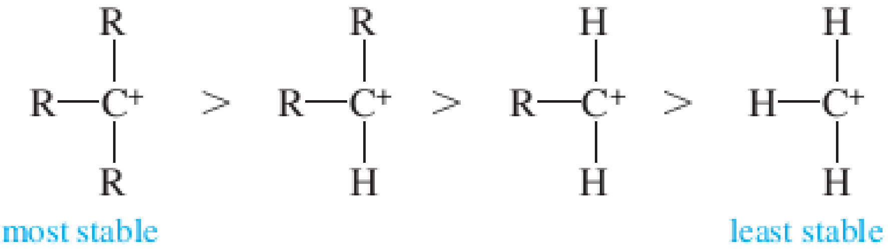


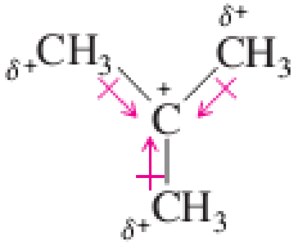
A 2° carbocation

Carbocations

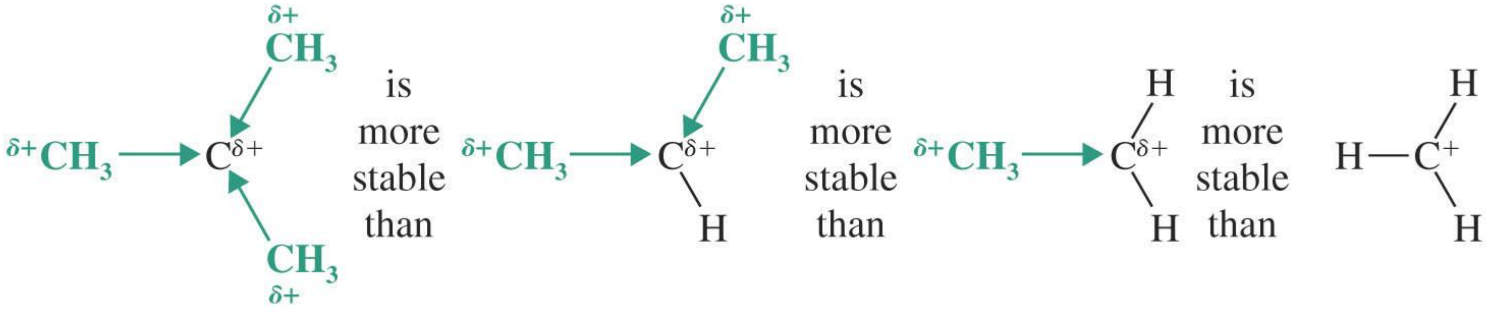
- Carbocations are stabilized by alkyl substituents. An alkyl group stabilizes an electron-deficient carbocation in two ways: (1) through an **inductive effect**, and (2) through the partial overlap of filled orbitals with empty ones.

+ The inductive effect is a donation of electron density through the sigma bonds of the molecule. The positively charged carbon atom withdraws some electron density from the polarizable alkyl groups bonded to it.





3° > 2° > 1° > methyl



***tert*-Butyl cation** **(3°) (most stable)**

Isopropyl cation **(2°)**

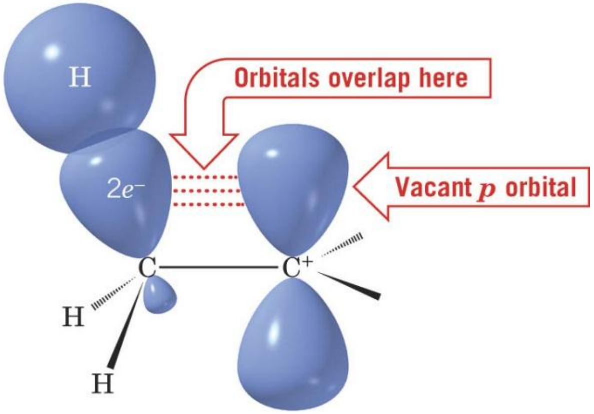
Ethyl cation **(1°)**

Methyl cation **(least stable)**

Carbocations

➔ Hyperconjugation stabilizes the carbocation by donation of electrons from an adjacent carbon-hydrogen or carbon-carbon σ bond into the empty *p* orbital.

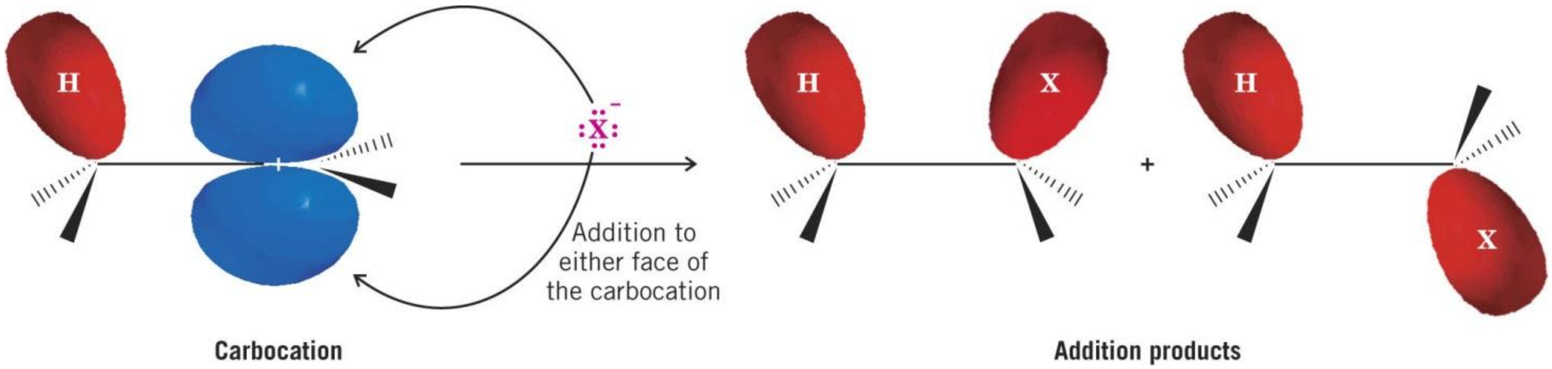
- More substitution provides more opportunity for hyperconjugation.



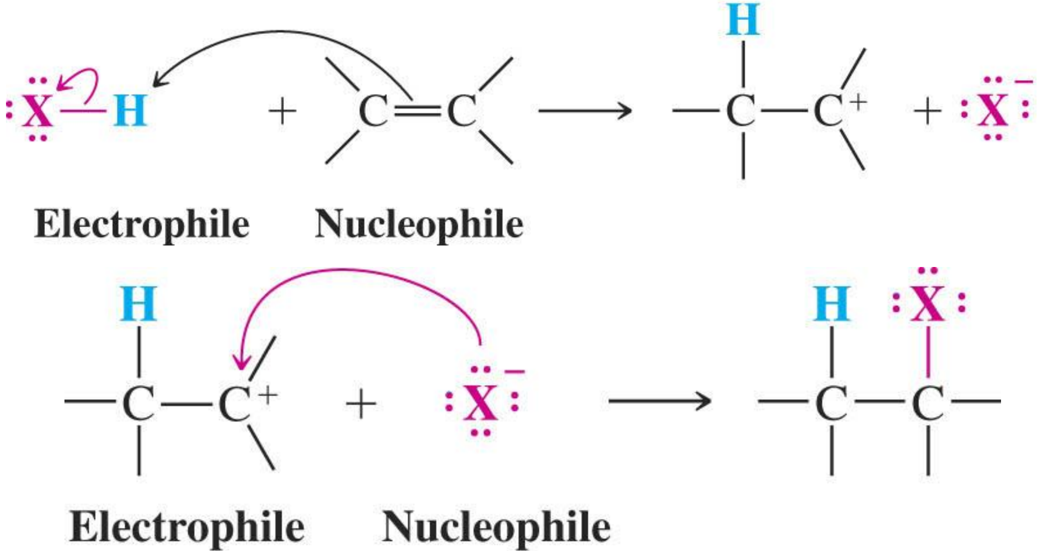
+ Alkyl substituents have filled orbitals that can overlap with the empty p orbital on the positively charged carbon atom, further stabilizing the carbocation. The pair of electrons in this bond spreads out into the empty p orbital, stabilizing the electron-deficient carbon atom. This type of overlap between a p orbital and a sigma bond is called **hyperconjugation**.

➔The carbocation produced is an electrophile

- It can react with a nucleophile such as a halide.



➔In addition reactions the alkene changes from a nucleophile in the first step to an electrophile in the second.

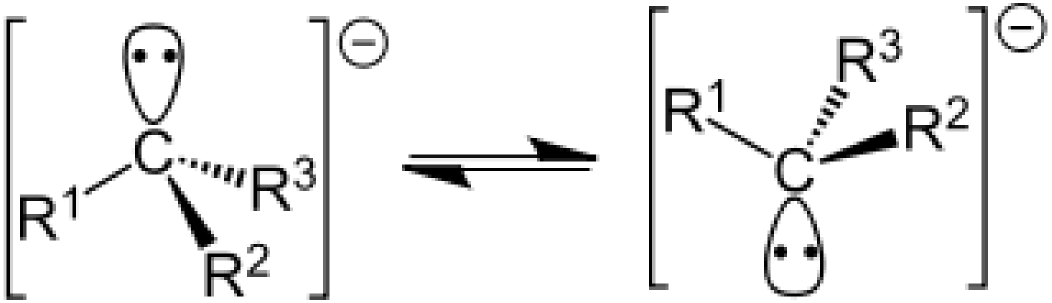


Carbanion

- Carbanion: A carbon anion, or substance that contains a trivalent, negatively charged carbon atom ($R_3C:^-$).

+ Carbanions are normally *sp*^{3}-hybridized.

+ Carbanions have 8 valence electrons and a negative charge.

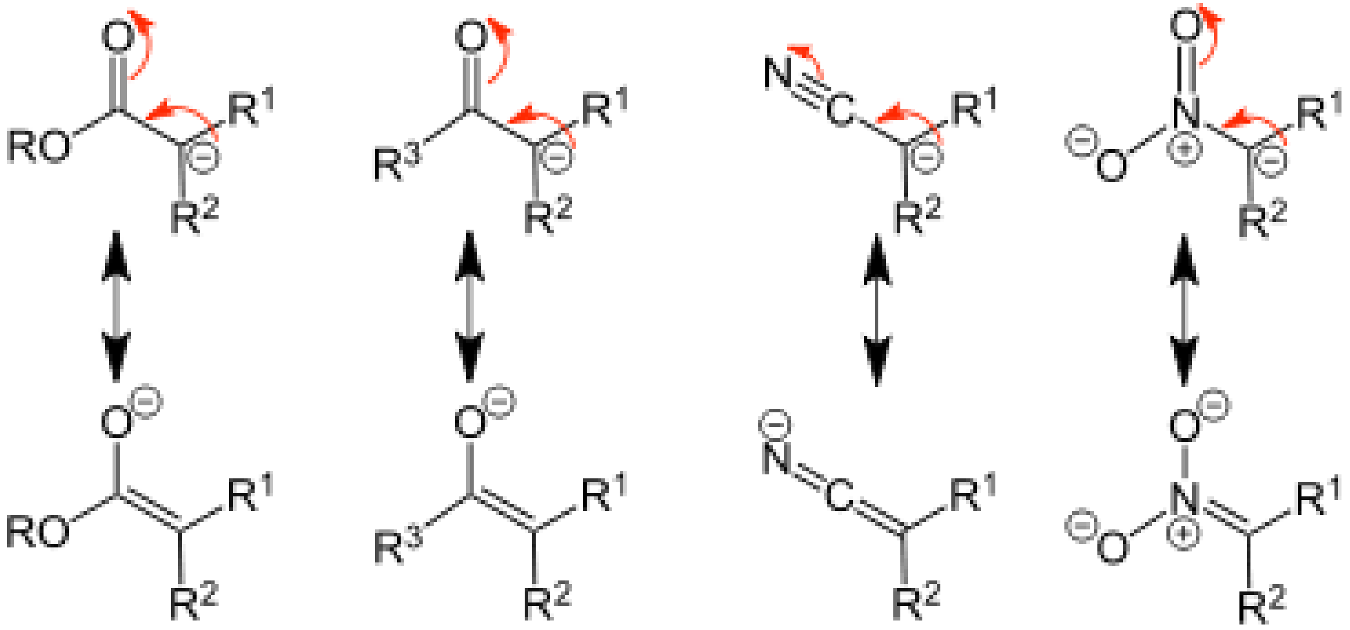


Stabily of carbanions

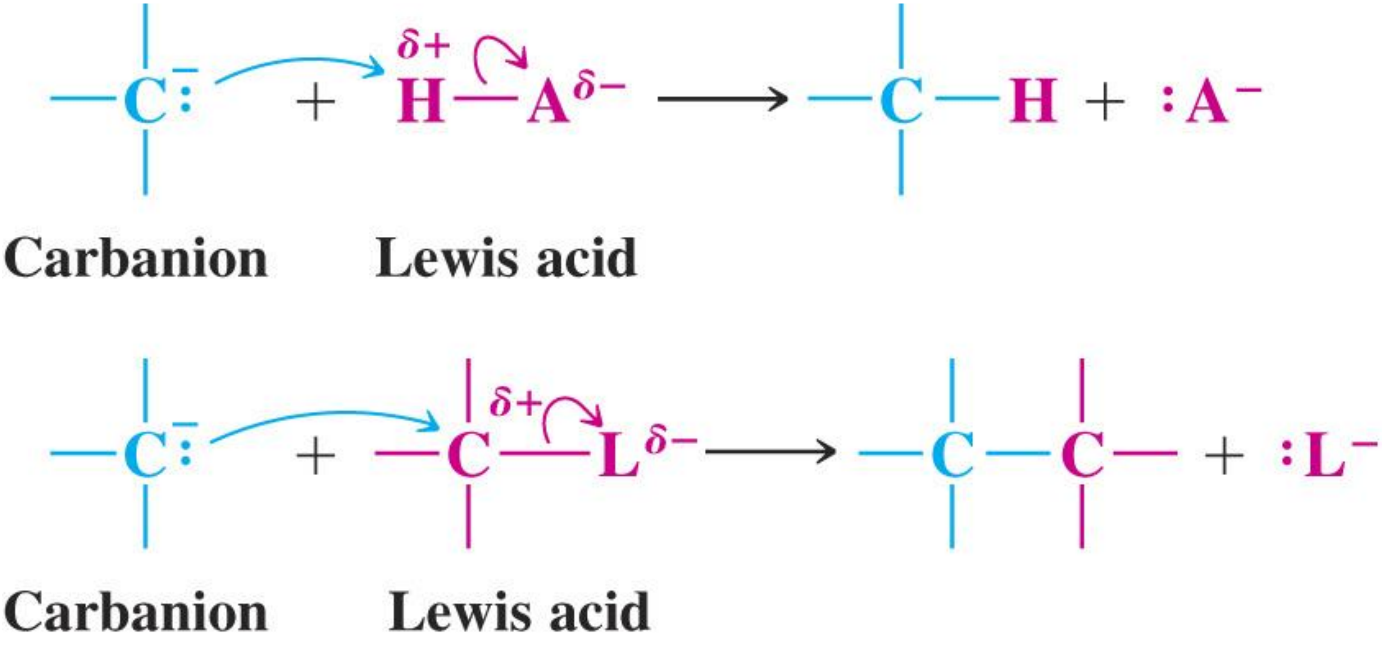
- The stability of carbanions can be explained by:

+ Resonance effect or

+ Electronic effects (Conjugation, Inductive or Hyperconjugation).



Reactions of carbanions



➔Electrophiles ("electron-loving" reagents): seek electrons to obtain a stable valence shell of electrons.

- Are electron-deficient themselves e.g. carbocations
- Proton, Lewis acids,…

➔Nucleophiles ("nucleus-loving" reagents): seek a proton or some other positively charged center.

- Are electron-rich themselves e.g. carbanions.
- A nucleophile may be any molecule with an unshared electron pair.

Reactions and their mechanisms

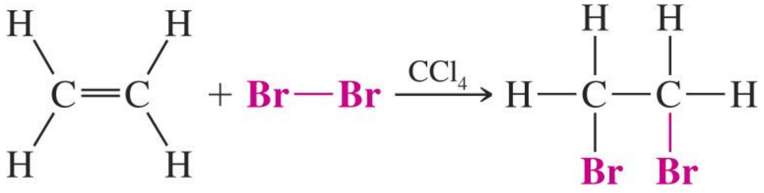
- **There are four general types of organic reactions**

➔**Substitutions**

$$H_3C{-}Cl + Na^{+}OH^{-} \xrightarrow{H_2O} H_3C{-}OH + Na^{+}Cl^{-}$$

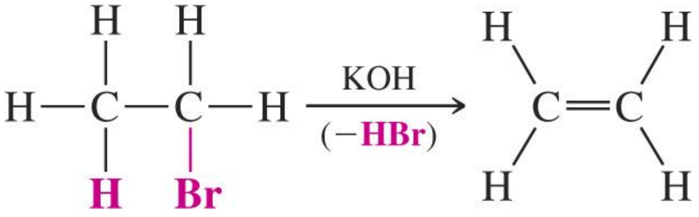
A substitution reaction

➔**Additions**



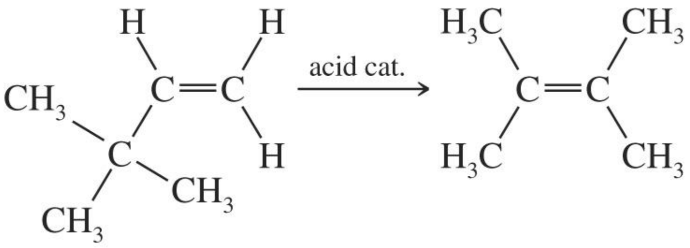
An addition reaction

➔**Eliminations**



An elimination reaction

➔**Rearrangements**

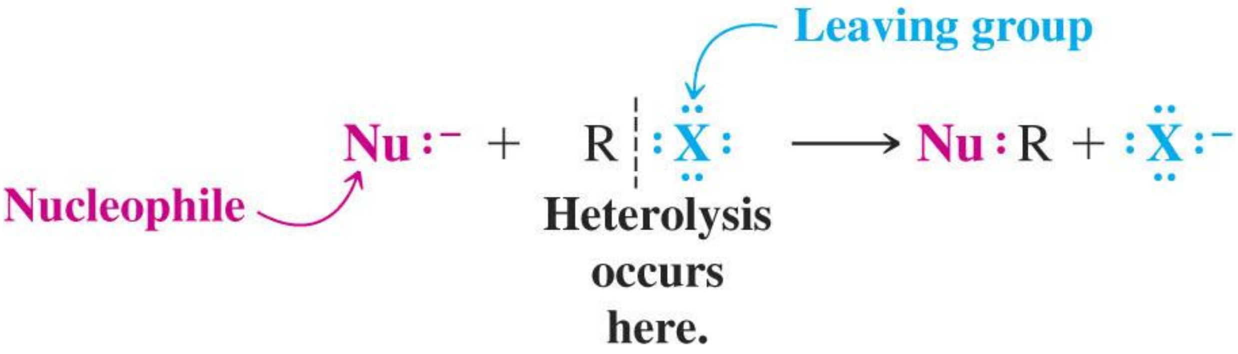


A rearrangement

Nucleophilic substitution reactions

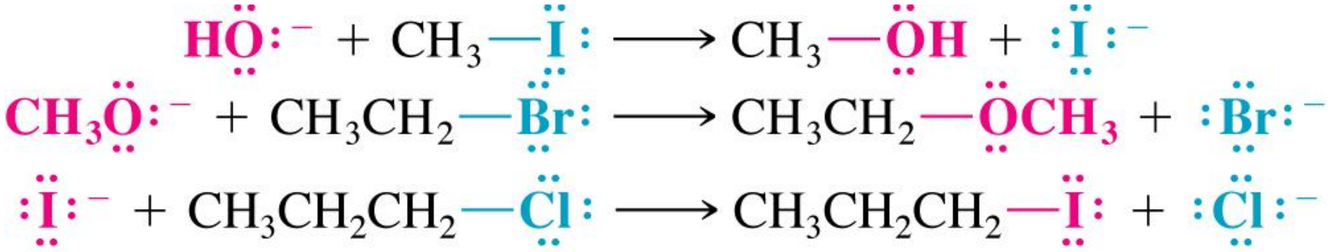
➔ In this reaction a nucleophile is a species with an unshared electron pair which reacts with an electron deficient carbon.

+ A leaving group is substituted by a nucleophile.



$$\text{Nu:}^- + \text{R} \vdots \text{:}\ddot{\underset{\cdot\cdot}{\text{X}}}\text{:} \longrightarrow \text{Nu:R} + \text{:}\ddot{\underset{\cdot\cdot}{\text{X}}}\text{:}^-$$

+ Examples of nucleophilic substitution



$$\text{H}\ddot{\underset{\cdot\cdot}{\text{O}}}\text{:}^- + \text{CH}_3\text{—}\ddot{\underset{\cdot\cdot}{\text{I}}}\text{:} \longrightarrow \text{CH}_3\text{—}\ddot{\underset{\cdot\cdot}{\text{O}}}\text{H} + \text{:}\ddot{\underset{\cdot\cdot}{\text{I}}}\text{:}^-$$

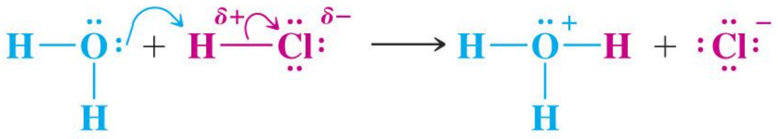
$$\text{CH}_3\ddot{\underset{\cdot\cdot}{\text{O}}}\text{:}^- + \text{CH}_3\text{CH}_2\text{—}\ddot{\underset{\cdot\cdot}{\text{Br}}}\text{:} \longrightarrow \text{CH}_3\text{CH}_2\text{—}\ddot{\underset{\cdot\cdot}{\text{O}}}\text{CH}_3 + \text{:}\ddot{\underset{\cdot\cdot}{\text{Br}}}\text{:}^-$$

$$\text{:}\ddot{\underset{\cdot\cdot}{\text{I}}}\text{:}^- + \text{CH}_3\text{CH}_2\text{CH}_2\text{—}\ddot{\underset{\cdot\cdot}{\text{Cl}}}\text{:} \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{—}\ddot{\underset{\cdot\cdot}{\text{I}}}\text{:} + \text{:}\ddot{\underset{\cdot\cdot}{\text{Cl}}}\text{:}^-$$

The use of curved arrows in illustrating reactions

- ➔Curved arrows show the flow of electrons in a reaction.
- ➔An arrow starts at a site of higher electron density (a covalent bond or unshared electron pair) and points to a site of electron deficiency.
- ➔Example: Mechanism of reaction of HCl and water.

$$H_2O + HCl \longrightarrow H_3O^+ + Cl^-$$

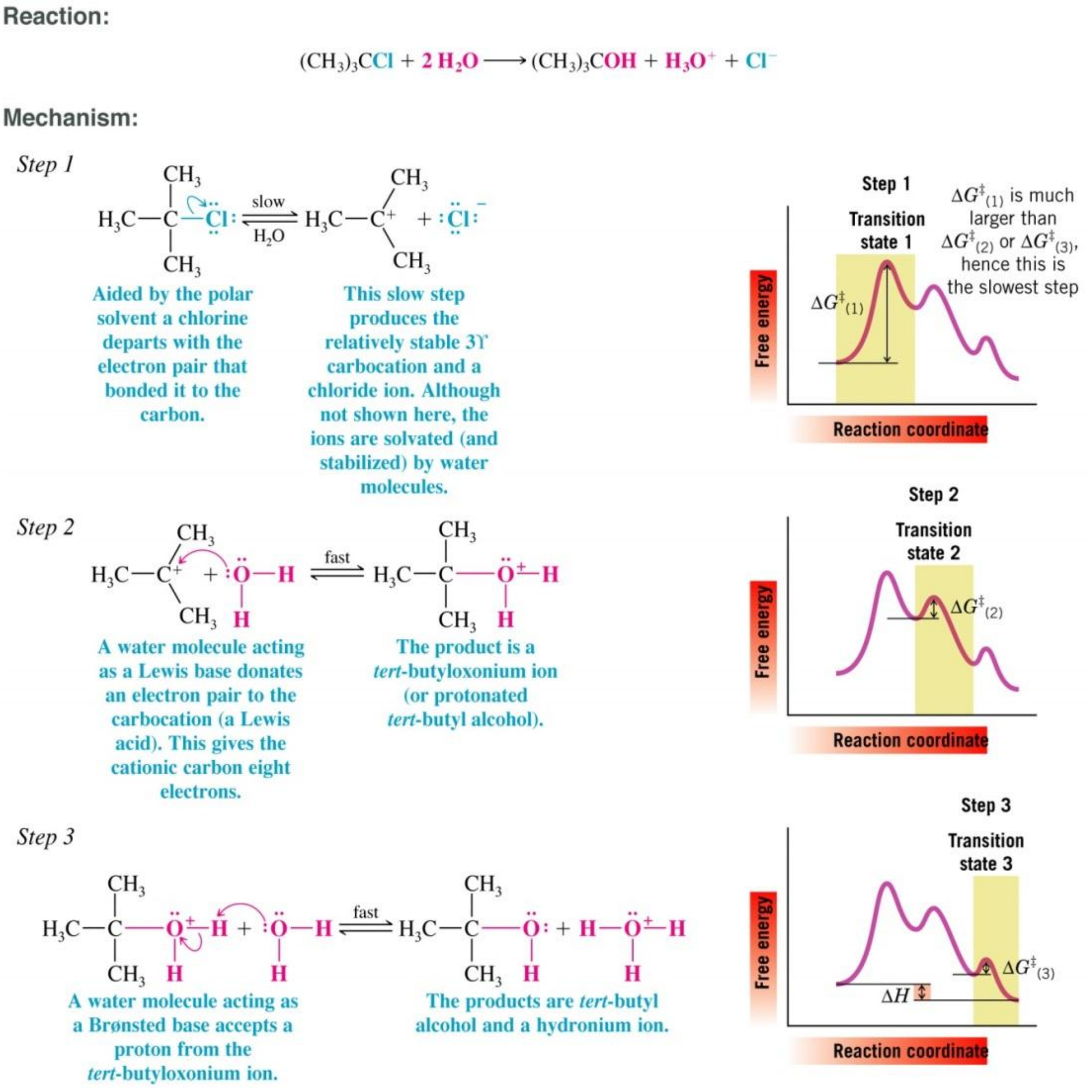


A water molecule uses one of the nonbonding electron pairs to form a bond to a proton of HCl. The bond between the hydrogen and chlorine breaks with the electron pair going to the chlorine atom.

This leads to the formation of a hydronium ion and a chloride ion.

A mechanism for the S_N1 reaction

- Step 1 is rate determining (slow) because it requires the formation of unstable ionic products.
- In step 1 water molecules help stabilize the ionic products.



Reaction:

$(CH_3)_3CCl + 2\ H_2O \longrightarrow (CH_3)_3COH + H_3O^+ + Cl^-$

Mechanism:

Step 1

Aided by the polar solvent a chlorine departs with the electron pair that bonded it to the carbon.

This slow step produces the relatively stable 3° carbocation and a chloride ion. Although not shown here, the ions are solvated (and stabilized) by water molecules.

Step 2

A water molecule acting as a Lewis base donates an electron pair to the carbocation (a Lewis acid). This gives the cationic carbon eight electrons.

The product is a *tert*-butyloxonium ion (or protonated *tert*-butyl alcohol).

Step 3

A water molecule acting as a Brønsted base accepts a proton from the *tert*-butyloxonium ion.

The products are *tert*-butyl alcohol and a hydronium ion.

$\Delta G^{\ddagger}_{(1)}$ is much larger than $\Delta G^{\ddagger}_{(2)}$ or $\Delta G^{\ddagger}_{(3)}$, hence this is the slowest step

Physical properties of organic compounds

➔The strength of intermolecular forces (forces between molecules) determines the physical properties (*i.e.* melting point, boiling point and solubility) of a compound

➔Stronger intermolecular forces result in high melting points and boiling points

- More energy must be expended to overcome very strong forces between molecules

➔The type of intermolecular forces are determined by its structure.

➔All things being equal, larger and heavier molecules have higher boiling points

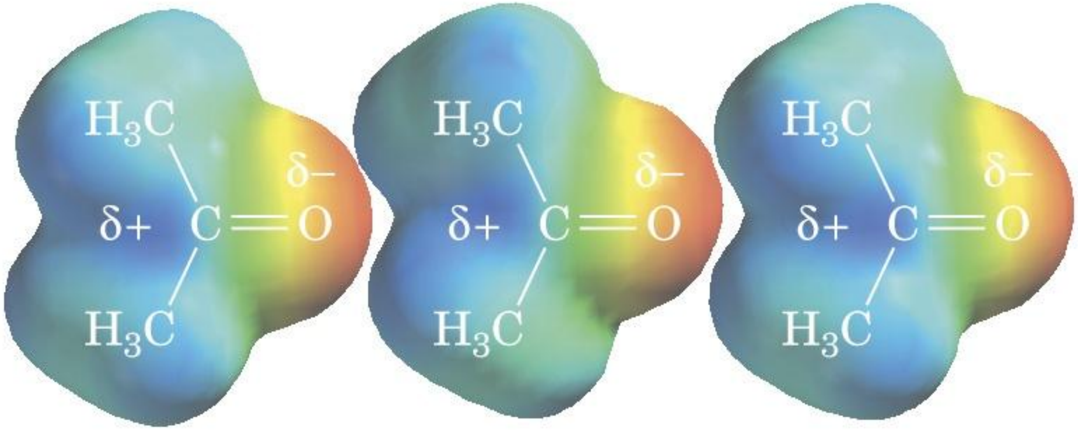
- Larger molecules need more energy to escape the surface of the liquid
- Larger organic molecules tend to have more surface area in contact with each other and so have stronger van der Waals interactions
- Methane (CH_4) has a boiling point of -162^{o}C whereas ethane (C_2H_6) has a boiling point of -88.2^{o}C

Compound	Structure	mp (°C)	bp (°C) (1 atm)[a]
Methane	CH_4	−182.6	−162
Ethane	CH_3CH_3	−183	−88.2
Ethene	$CH_2"CH_2$	−169	−102
Ethyne	$HC\#CH$	−82	−84 subl
Chloromethane	CH_3Cl	−97	−23.7
Chloroethane	CH_3CH_2Cl	−138.7	13.1
Ethyl alcohol	CH_3CH_2OH	−115	78.5
Acetaldehyde	CH_3CHO	−121	20
Acetic acid	CH_3CO_2H	16.6	118
Sodium acetate	CH_3CO_2Na	324	dec
Ethylamine	$CH_3CH_2NH_2$	−80	17
Diethyl ether	$(CH_3CH_2)_2O$	−116	34.6
Ethyl acetate	$CH_3CO_2CH_2CH_3$	−84	77

[a] In this table dec = decomposes and subl = sublimes.

Weak intermolecular forces: Van de Waals forces

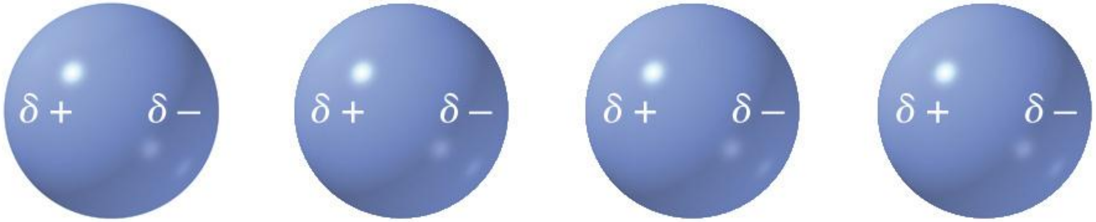
- Dipole-dipole forces: Dipole-dipole forces are between molecules with permanent dipoles.
  - There is an interaction between δ+ and δ- areas in each molecule;
  - Molecules align to maximize attraction of δ+ and δ- parts of molecules;
  - Example: acetone.



van der Waals forces: London or dispersion forces

➔London or dispersion forces result when a temporary dipole in a molecule caused by a momentary shifting of electrons induces an opposite and also temporary dipole in an adjacent molecule.

- These temporary opposite dipoles cause a weak attraction between the two molecules.
- Molecules which rely only on van der Waals forces generally have low melting points and boiling points.



Weak intermolecular forces: Hydrogen bonds

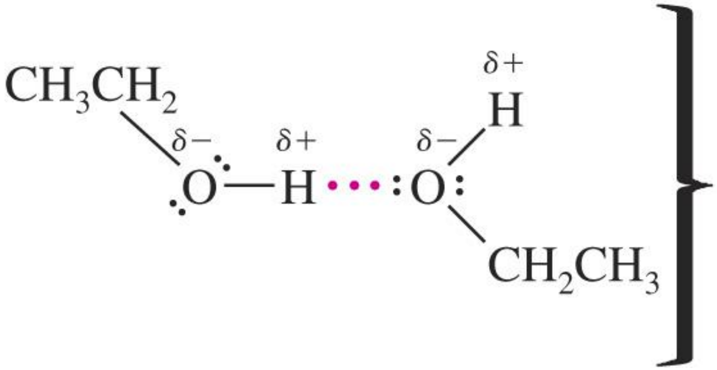
➔Hydrogen bonds result from very strong dipole-dipole forces.

➔There is an interaction between hydrogens bonded to strongly electronegative atoms (O, N or F) and nonbonding electron pairs on other strongly electronegative atoms (O, N or F).

Hydrogen bonds

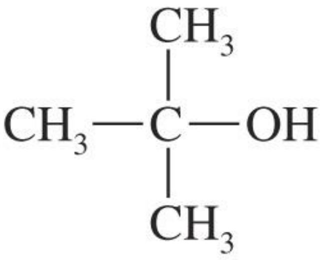
➔ **Ethanol (CH_3CH_2OH) has a boiling point of +78.5°C; its isomer methyl ether (CH_3OCH_3) has a boiling point of -24.9°C**

- **Ethanol molecules are held together by hydrogen bonds whereas methyl ether molecules are held together only by weaker dipole-dipole interactions**



The dotted bond is a hydrogen bond. Strong hydrogen bonding is limited to molecules having a hydrogen atom attached to an O, N, or F atom.

➔ **A factor in melting points is that symmetrical molecules tend to pack better in the crystalline lattice and have higher melting points**

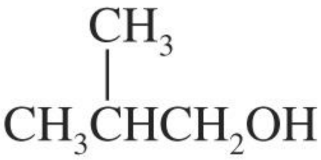


$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-OH$$

***tert*-Butyl alcohol**
(mp 25°C)

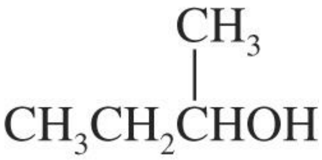
$CH_3CH_2CH_2CH_2OH$

Butyl alcohol
(mp −90°C)



$$CH_3\overset{\overset{\large CH_3}{|}}{C}HCH_2OH$$

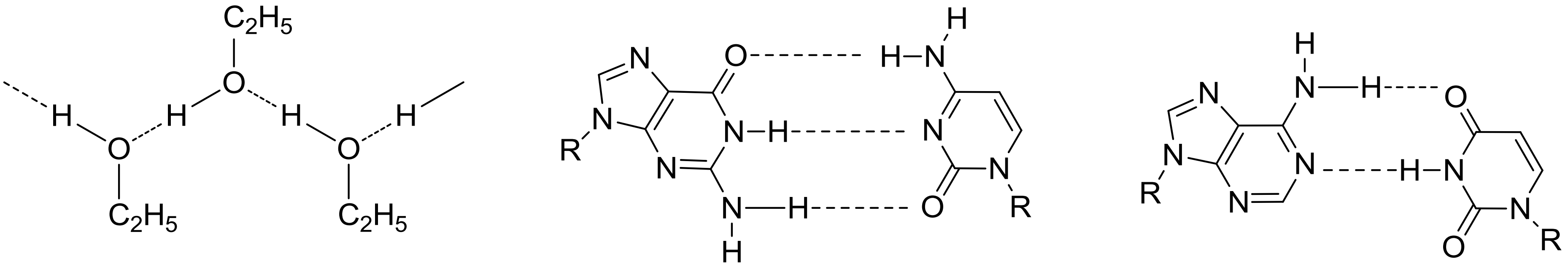
Isobutyl alcohol
(mp −108°C)



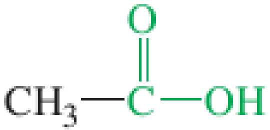
$$CH_3CH_2\overset{\overset{\large CH_3}{|}}{C}HOH$$

***sec*-Butyl alcohol**
(mp −114°C)

Hydrogen bonds



- **Boiling points**: Carboxylic acids boil at considerably higher temperatures than do alcohols, ketones, or aldehydes of similar molecular weights. For example, acetic acid (MW 60) boils at 118 °C, propan-1-ol (MW 60) boils at 97 °C, and propionaldehyde (MW 58) boils at 49 °C. The high boiling points of carboxylic acids result from formation of a stable, hydrogen-bonded dimer. This dimer contains an eight-membered ring joined by two hydrogen bonds, effectively doubling the molecular weight of the molecules leaving the liquid phase, and requiring more energy (higher temperature) to boil.

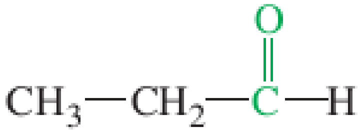


$CH_3-C(=O)-OH$

acetic acid, bp 118 °C

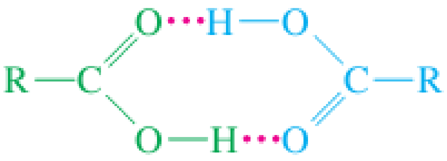
$CH_3-CH_2-CH_2-OH$

propan-1-ol, bp 97 °C



$CH_3-CH_2-C(=O)-H$

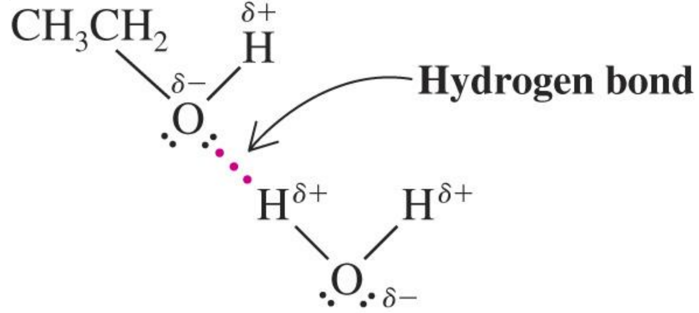
propionaldehyde, bp 49 °C



hydrogen-bonded acid dimer

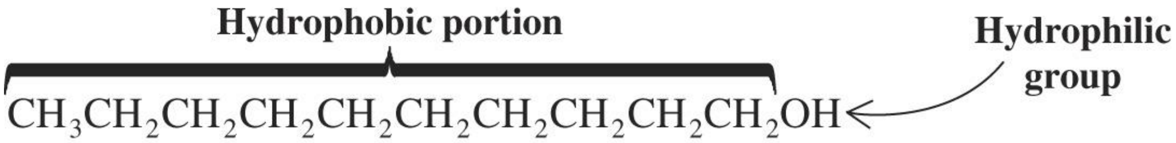
Solubilities: Generally like dissolves like

- Polar solvents tend to dissolve polar solids or polar liquids.
- Methanol (a water-like molecule) dissolves in water in all proportions and interacts using hydrogen-bonding to the water.



➔A large alkyl group can overwhelm the ability of the polar group to solubilize a molecule in water.

- **Decyl alcohol is only slightly soluble in water**
- **The large alkyl portion is hydrophobic ("water hating") and overwhelms the capacity of the hydrophilic ("water loving") hydroxyl**



$$\overbrace{CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2}^{\text{Hydrophobic portion}}OH$$

Decyl alcohol

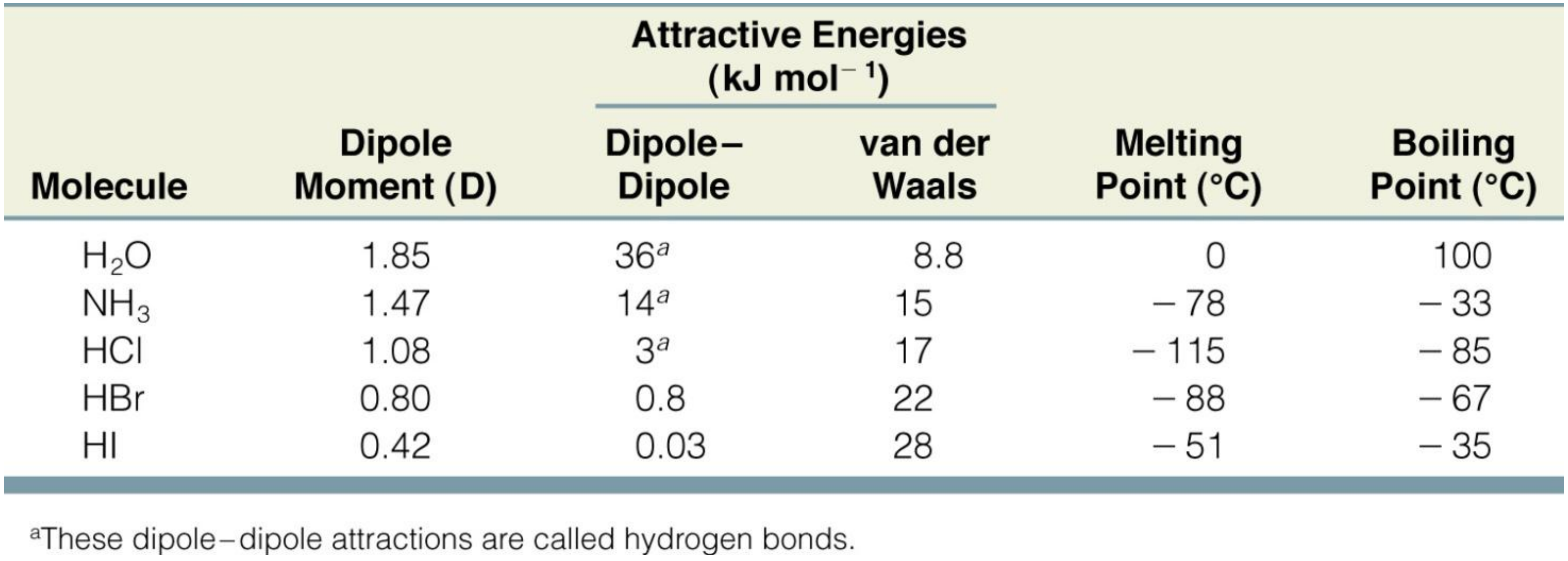
➔Generally one hydrophilic group (e.g. hydroxyl) can make a compound with 3 carbons completely soluble in water.

- One hydrophilic group can make a 5 carbon compound at least partially soluble.
- A compound is water soluble if at least 3g of it will dissolve in 100 mL water.

Polarizability

➔Polarizability predicts the magnitude of van der Waals interactions.

- Polarizability is the ability of the electrons on an atom to respond to a changing electric field.
- Atoms with very loosely held electrons are more polarizable.
- Iodine atoms are more polarizable than fluorine atoms because the outer shell electrons are more loosely held.
- Atoms with unshared electrons are more polarizable (a halogen is more polarizable than an alkyl of similar size).



		Attractive Energies (kJ mol^{-1})			
Molecule	**Dipole Moment (D)**	**Dipole–Dipole**	**van der Waals**	**Melting Point (°C)**	**Boiling Point (°C)**
H_2O	1.85	36[a]	8.8	0	100
NH_3	1.47	14[a]	15	−78	−33
HCl	1.08	3[a]	17	−115	−85
HBr	0.80	0.8	22	−88	−67
HI	0.42	0.03	28	−51	−35

[a] These dipole–dipole attractions are called hydrogen bonds.