General Organic Chemistry

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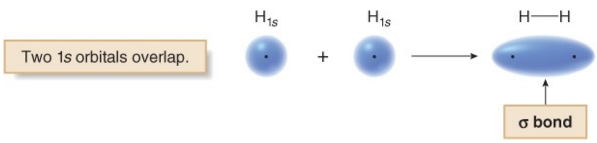
Orbitals and Bonding: Hydrogen

- When the 1*s* orbital of one H atom overlaps with the 1*s* orbital of another H atom, a sigma (σ) bond that concentrates electron density between the two nuclei is formed.
- This bond is cylindrically symmetrical because the electrons forming the bond are distributed symmetrically about an imaginary line connecting the two nuclei.



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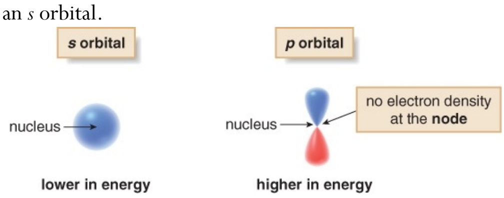
s and p Orbitals

- An *s* orbital has a sphere of electron density and is lower in energy than the other orbitals of the same shell.
- A *p* orbital has a dumbbell shape and contains a node of electron density at the nucleus. It is higher in energy than an *s* orbital.



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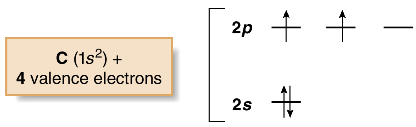
Orbitals and Bonding: Methane

- To account for the bonding patterns observed in more complex molecules, we must take a closer look at the 2*s* and 2*p* orbitals of atoms in the second row.
- Carbon has two core electrons, plus four valence electrons. To fill atomic orbitals in the most stable arrangement, electrons are placed in the orbitals of lowest energy. For carbon, this places two in the 2*s* orbital and one each in 2*p* orbitals.



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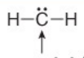
Orbitals and Bonding: Methane

- In this description, carbon should form only two bonds because it has only two unpaired valence electrons, and CH_2 should be a stable molecule.
- However, CH_2 is a very unstable species that cannot be isolated under typical laboratory conditions. Note that in CH_2, carbon would not have an octet of electrons.

Two bonds from two unpaired electrons



no octet (unstable)

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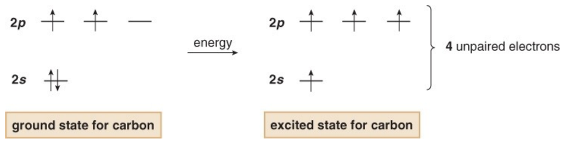
Orbitals and Bonding: Methane

- There is a second possibility. Promotion of an electron from a 2*s* to a vacant 2*p* orbital would form four unpaired electrons for bonding. This process requires energy because it moves an electron to a higher energy orbital. This higher energy electron configuration is called an electronically excited state.



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Orbitals and Bonding: Methane

- But this description is still not adequate. Carbon would form two different types of bonds: three with 2*p* orbitals and one with a 2*s* orbital. However, experimental evidence points to carbon forming four identical bonds in methane.

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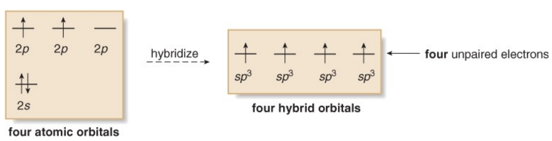
Orbitals and Bonding: Methane

- To solve this dilemma, chemists have proposed that atoms like carbon do not use pure *s* and pure *p* orbitals in forming bonds. Instead, atoms use a set of new orbitals called hybrid orbitals.
- *Hybridization* is the combination of two or more atomic orbitals to form the same number of hybrid orbitals, each having the same shape and energy.

Forming four sp^3 hybrid orbitals for carbon



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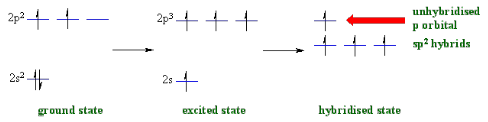
Hybridization



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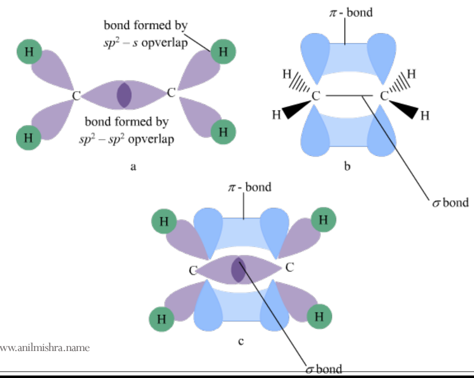
Hybridization



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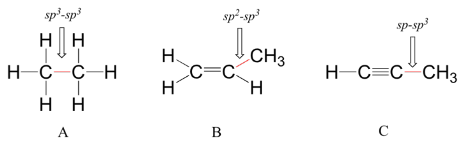
Hybridization



Carbon Atom Hybridization State Parameters

Hybridiztion State	# Of Hybrid Orbitals	# Of 2p Orbitals Left Over	# Of Groups Bonded To Carbon	# Of σ Bonds	# Of π Bonds	Geometry Around Carbon
sp^3	4	0	4	4	0	Tetrahedral
sp^2	3	1	3	3	1	Trigonal Planar
sp	2	2	2	2	2	Linear

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Understanding Organic Reaction

- Writing Equations
  - Equations for organic reactions are usually drawn with a single reaction arrow (→) between the starting material and product.
  - The reagent, the chemical substance with which an organic compound reacts, is sometimes drawn on the left side of the equation with the other reactants. At other times, the reagent is drawn above the arrow itself.

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Understanding Organic Reaction

- Although the solvent is often omitted from the equation, most organic reactions take place in liquid solvent.
- The solvent and temperature of the reaction may be added above or below the arrow.
- The symbols "hν" and "Δ" are used for reactions that require light and heat respectively.

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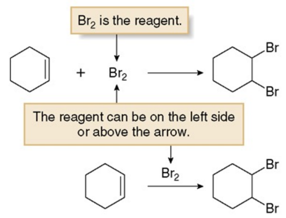
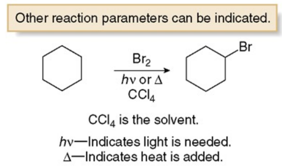
Ways of writing Organic Reactions





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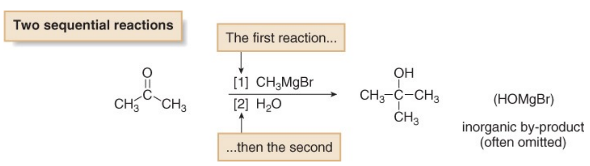
Ways of writing Organic Reactions

- When two sequential reactions are carried out without drawing any intermediate compound, the steps are usually numbered above or below the reaction arrow. This convention signifies that the first step occurs before the second step, and the reagents are added in sequence, not at the same time.



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Types of Organic Reactions

- Substitution Reactions
- Elimination Reactions
- Addition Reactions

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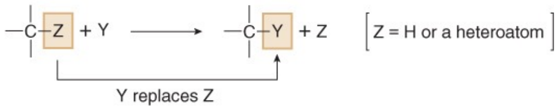
Substitution Reaction

- A substitution is a reaction in which an atom or a group of atoms is replaced by another atom or group of atoms.
- In a general substitution, Y replaces Z on a carbon atom.

A general substitution reaction



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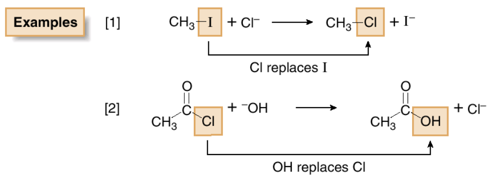
Substitution Reaction

- Substitution reactions involve σ bonds: one σ bond breaks and another forms at the same carbon atom.
- The most common examples of substitution occur when Z is a hydrogen or a heteroatom that is more electronegative than carbon.



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Elimination reactions

- Elimination is a reaction in which elements of the starting material are "lost" and a π bond is formed.

A general elimination reaction

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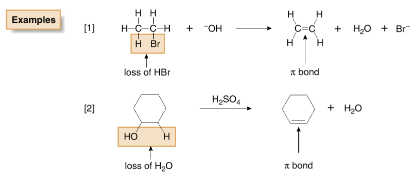
Elimination Reactions

- In an elimination reaction, two groups X and Y are removed from a starting material.
- Two σ bonds are broken, and a π bond is formed between adjacent atoms.
- The most common examples of elimination occur when X = H and Y is a heteroatom more electronegative than carbon.



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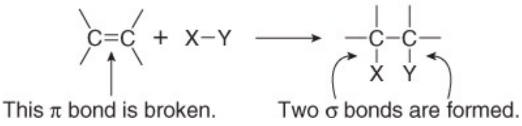
Addition Reactions

- Addition is a reaction in which elements are added to the starting material.

A general addition reaction



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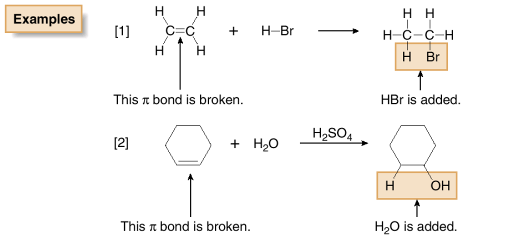
Addition Reactions

- In an addition reaction, new groups X and Y are added to the starting material. A π bond is broken and two σ bonds are formed.



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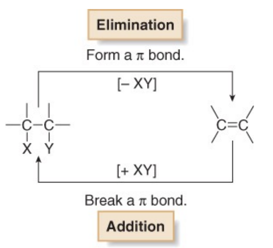
Elimination VS Addition

- Addition and elimination reactions are exactly opposite. A π bond is formed in elimination reactions, whereas a π bond is broken in addition reactions.



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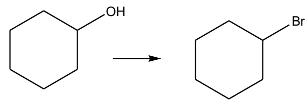
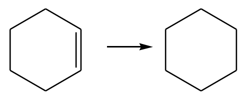
Classify each of the following as either substitution, elimination or addition reactions.

a)



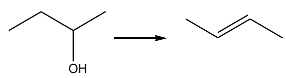
Substitution

b)



Addition

c)



Elimination

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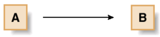
Bond Making and Bond Breaking

- A reaction mechanism is a detailed description of how bonds are broken and formed as starting material is converted into product.
- A reaction can occur either in one step or a series of steps.

- **A one-step reaction is called a *concerted reaction.*** No matter how many bonds are broken or formed, a starting material is converted *directly* to a product.



- **A stepwise reaction** involves more than one step. A starting material is first converted to an unstable intermediate, called a **reactive intermediate,** which then goes on to form the product.

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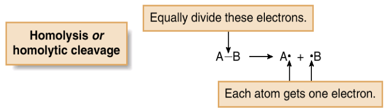
Bond Making and Bond Breaking

- Regardless of how many steps there are in a reaction, there are only two ways to break (cleave) a bond: the electrons in the bond can be divided equally or unequally between the two atoms of the bond.

- Breaking a bond by **equally dividing the electrons** between the two atoms in the bond is called **homolysis** or **homolytic cleavage.**



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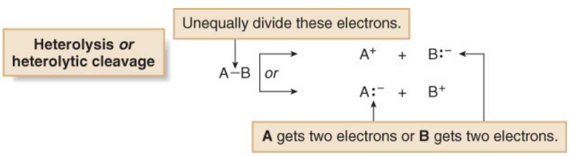
Bond Making and Bond Breaking

- Breaking a bond by **unequally dividing the electrons** between the two atoms in the bond is called **heterolysis** or **heterolytic cleavage.** Heterolysis of a bond between **A** and **B** can give either **A** or **B** the two electrons in the bond. When **A** and **B** have different electronegativities, the ***electrons end up on the more electronegative atom.***



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Bond Making and Bond Breaking

- Homolysis and heterolysis require energy.
- Homolysis generates uncharged reactive intermediates with unpaired electrons.
- Heterolysis generates charged intermediates.

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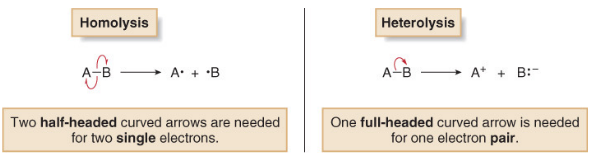
Arrow Notions

- To illustrate the movement of a single electron, use a half-headed curved arrow, sometimes called a fishhook.
- A full headed curved arrow shows the movement of an electron pair.



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Arrow Notions

- A number of types of arrows are used in describing organic reactions.

Arrow	Name	Use
⟶	Reaction arrow	Drawn between the starting materials and products in an equation
⇌	Double reaction arrows (equilibrium arrows)	Drawn between the starting materials and products in an equilibrium equation
⟷	Double-headed arrow	Drawn between resonance structures
⌒	Full-headed curved arrow	Shows movement of an electron pair
⌒	Half-headed curved arrow (fishhook)	Shows movement of a single electron

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Homolytic Cleavage

- Homolysis generates two uncharged species with unpaired electrons.
- A reactive intermediate with a single unpaired electron is called a radical.
- Radicals are highly unstable because they contain an atom that does not have an octet of electrons.

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Heterolytic Cleavage

- Heterolysis generates a carbocation or a carbanion.
- Both carbocations and carbanions are unstable intermediates. A carbocation contains a carbon surrounded by only six electrons, and a carbanion has a negative charge on carbon, which is not a very electronegative atom.

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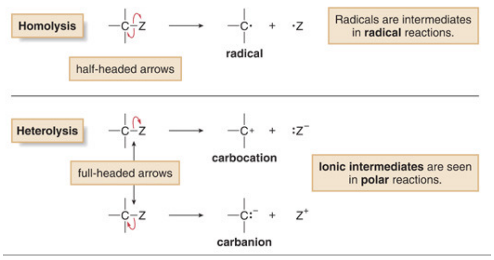
Reaction Intermediates

- Three reactive intermediates resulting from homolysis and heterolysis of a C – Z bond



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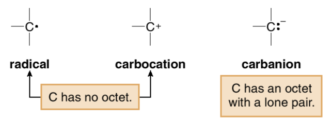
Reaction Intermediates

- Radicals and carbocations are electrophiles because they contain an electron deficient carbon.
- Carbanions are nucleophiles because they contain a carbon with a lone pair.



- Radicals and carbocations are electrophiles because they contain an electron-deficient carbon.
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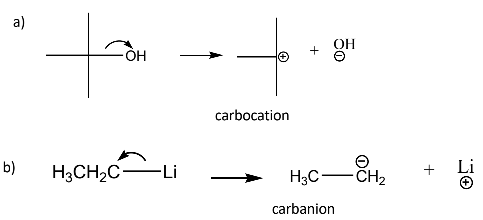
Reaction Intermediates



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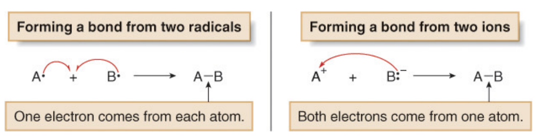
Bond Formation

- Bond formation occurs in two different ways.
  - Two radicals can each donate one electron to form a two-electron bond.
  - Alternatively, two ions with unlike charges can come together, with the negatively charged ion donating both electrons to form the resulting two-electron bond.
  - Bond formation always releases energy.



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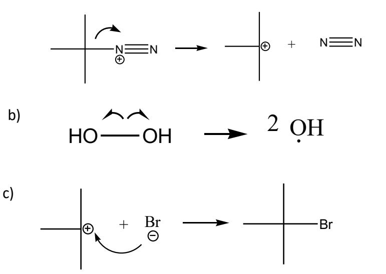
Use arrows to show the movement of electrons in the following reactions.

a)

b)

c)



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Bond Dissociation Energy

- The *bond dissociation energy* is the energy needed to homolytically cleave a covalent bond.

A–B ⟶ A• + •B $\Delta H°$ = bond dissociation energy

Homolysis requires energy.

- The energy absorbed or released in any reaction, symbolized by ΔH^0, is called the enthalpy change or heat of reaction.

- When $\Delta H°$ is positive (+), energy is absorbed and the reaction is *endothermic*.
- When $\Delta H°$ is negative (–), energy is released and the reaction is *exothermic*.

- Bond dissociation energy is the ΔH^0 for a specific kind of reaction—the homolysis of a covalent bond to form two radicals.

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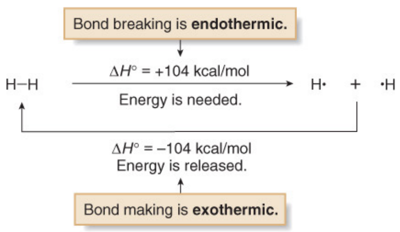
Bond Dissociation Energy

- Because bond breaking requires energy, bond dissociation energies are always positive numbers, and homolysis is always endothermic.
- Conversely, bond formation always releases energy, and thus is always exothermic. For example, the H—H bond requires +104 kcal/mol to cleave and releases –104 kcal/mol when formed.



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Bond Dissociation Energy

- Comparing bond dissociation energies is equivalent to comparing bond strength.
- The stronger the bond, the higher its bond dissociation energy.
- Bond dissociation energies decrease down a column of the periodic table.
- Generally, shorter bonds are stronger bonds.

Increasing size of the halogen ⟶

CH_3–F	CH_3–Cl	CH_3–Br	CH_3–I
$\Delta H°$ = 109 kcal/mol	84 kcal/mol	70 kcal/mol	56 kcal/mol

⟵ **Increasing bond strength**

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