# Aromaticity

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The compound we know as benzene was first isolated in 1825 by Michael Faraday, who extracted the compound from a liquid residue obtained after heating whale oil under pressure to produce a gas used to illuminate buildings in London. Because of its origin, chemists suggested that it should be called "pheno" from the Greek word phainein ("to shine"). In 1834, Eilhardt Mitscherlich correctly determined benzene's molecular formula and decided to call it benzin because of its relationship to benzoic acid, a known substituted form of the compound. Later its name was changed to benzene. Compounds like benzene, which have relatively few hydrogens in relation to the number of carbons, are typically found in oils produced by trees and other plants. Early chemists called such compounds aromatic compounds because of their pleasing fragrances. In this way, they were distinguished from aliphatic compounds, with higher hydrogen-to-carbon ratios, that were obtained from the chemical degradation of fats. The chemical meaning of the word "aromatic" now signifies certain kinds of chemical structures. We will now examine the criteria that a compound must satisfy to be classified as aromatic.

Aromaticity may be defined as extra stability possessed by a molecule that meets specific criteria: Pi bonds all must lie within a cyclic structure, loop of p orbitals, p orbitals must be planar and overlap, must follow Hückel's Rule. In the nineteenth century, it was recognized that aromatic compounds differ greatly from unsaturated aliphatic compounds, but for many years chemistswere hard pressed to arrive at a mutually satisfactory definition of aromatic character. Qualitatively, there has never been real disagreement. Definitions have taken the form that aromatic compounds are characterized by a special stability and that they undergo substitution reactions more easily than addition reactions. The difficulty arises because these definitions are vague and not easy to apply in borderline cases. Definitions of aromaticity must encompass molecules ranging form polycyclic conjugated hydrocarbons, to heterocyclic compounds of various ring sizes, to reactive intermediates.

Criteria for Aromaticity

Benzene is a planar, cyclic compound with a cyclic cloud of delocalized electrons above and below the plane of the ring . Because of its delocalised pi electrons, all the carbon-carbon bonds have the same length—partway between the length of a typical single and a typical double bond. We also saw that benzene is a particularly stable compound because it has an unusually large resonance energy (36 kcal/mol or 151 kJ/mol). Most compounds with delocalized electrons

a.

b.

c.
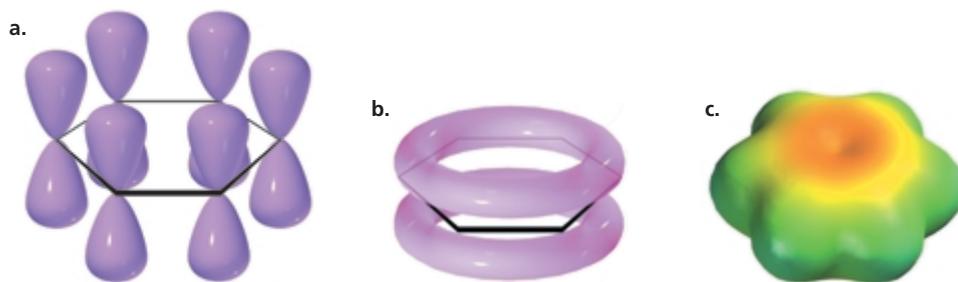
◀ **Figure**
(a) Each carbon of benzene has a *p* orbital. (b) The overlap of the *p* orbitals forms a cloud of π electrons above and below the plane of the benzene ring. (c) The electrostatic potential map for benzene shows that all the carbon–carbon bonds have the same electron density.

have much smaller resonance energies. Compounds such as benzene with unusually large resonance energies are called aromatic compounds. How can we tell whether a compound is aromatic by looking at its structure? In other words, what structural features do aromatic compounds have in common?

To be classified as aromatic, a compound must meet both of the following criteria:

1. *It must have an uninterrupted cyclic cloud of π electrons* (often called a π cloud) *above and below the plane of the molecule.* Let's look a little more closely at what this means:

   For the π cloud to be cyclic, *the molecule must be cyclic.*

   For the π cloud to be uninterrupted, *every atom in the ring must have a* p *orbital.*

   For the π cloud to form, each *p* orbital must overlap with the *p* orbitals on either side of it. Therefore, *the molecule must be planar.*

2. *The π cloud must contain an odd number of pairs of π electrons.*

Benzene is an aromatic compound because it is cyclic and planar, every carbon in the ring has a *p* orbital, and the π cloud contains *three* pairs of π electrons.

The German chemist Erich Hückel was the first to recognize that an aromatic compound must have an odd number of pairs of π electrons. In 1931, he described this requirement by what has come to be known as **Hückel's rule**, or the **4*n* + 2 rule**. The rule states that for a planar, cyclic compound to be aromatic, its uninterrupted π cloud must contain $(4n + 2)\pi$ electrons, where *n* is any whole number. According to Hückel's rule, then, an aromatic compound must have 2 ($n = 0$), 6 ($n = 1$), 10 ($n = 2$), 14 ($n = 3$), 18 ($n = 4$), etc., π electrons. Because there are two electrons in a pair, Hückel's rule requires that an aromatic compound have 1, 3, 5, 7, 9, etc., pairs of π electrons. Thus, Hückel's rule is just a mathematical way of saying that an aromatic compound must have an *odd* number of pairs of π electrons.

Aromatic compounds are particularly stable.

For a compound to be aromatic, it must be cyclic and planar and have an uninterrupted cloud of π electrons. The π cloud must contain an odd number of pairs of π electrons.

PROBLEM

a. What is the value of *n* in Hückel's rule when a compound has nine pairs of π electrons?

b. Is such a compound aromatic?

Aromatic Hydrocarbons

Monocyclic hydrocarbons with alternating single and double bonds are called **annulenes**. A prefix in brackets denotes the number of carbons in the ring. Cyclobutadiene, benzene, and cyclooctatetraene are examples.

cyclobutadiene
[4]-annulene

benzene
[6]-annulene

cyclooctatetraene
[8]-annulene
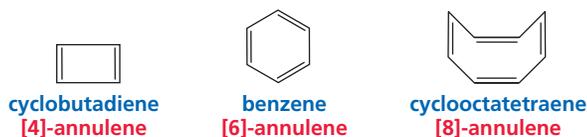
Cyclobutadiene has two pairs of π electrons, and cyclooctatetraene has four pairs of π electrons. Unlike benzene, these compounds are *not* aromatic because they have an *even* number of pairs of π electrons. There is an additional reason why cyclooctatetraene is not aromatic—it is not planar but, instead, tub-shaped. Earlier, we saw that, for an eight-membered ring to be planar, it must have bond angles of $135°$, and we know that sp^2 carbons have $120°$ bond angles. Therefore, if cyclooctatetraene were planar, it would have considerable angle strain. Because cyclobutadiene and cyclooctatetraene are not aromatic, they do not have the unusual stability of aromatic compounds.

Now let's look at some other compounds and determine whether they are aromatic. Cyclopropene is not aromatic because it does not have an uninterrupted ring of p orbital-bearing atoms. One of its ring atoms is sp^3 hybridized, and only sp^2 and sp hybridized carbons have p orbitals. Therefore, cyclopropene does not fulfill the first criterion for aromaticity.

cyclopropene   **cyclopropenyl cation**   **cyclopropenyl anion**

The cyclopropenyl cation is aromatic because it has an uninterrupted ring of p orbital-bearing atoms and the π cloud contains *one* (an odd number) pair of delocalized π electrons. The cyclopropenyl anion is not aromatic because although it has an uninterrupted ring of p orbital-bearing atoms, its π cloud has *two* (an even number) pairs of π electrons.

When drawing resonance contributors, remember that only electrons move, atoms never move.

resonance contributors of the cyclopropenyl cation

resonance hybrid
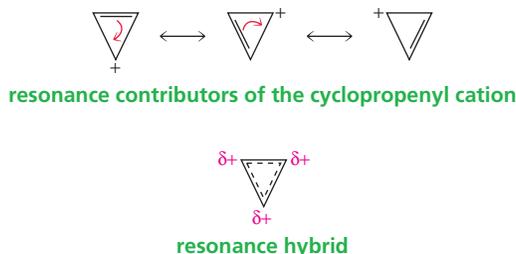
Cycloheptatriene is not aromatic. Although it has the correct number of pairs of π electrons (three) to be aromatic, it does not have an uninterrupted ring of p orbital-bearing atoms because one of the ring atoms is sp^3 hybridized. Cyclopentadiene is also not aromatic: It has an even number of pairs of π electrons (two pairs), *and* it does not have an uninterrupted ring of p orbital-bearing atoms. Like cycloheptatriene, cyclopentadiene has an sp^3 hybridized carbon.

cycloheptatriene   **cyclopentadiene**
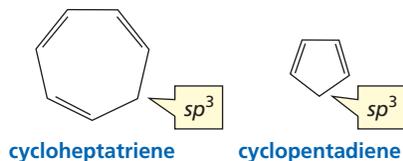
The criteria for determining whether a monocyclic hydrocarbon compound is aromatic can also be used to determine whether a polycyclic hydrocarbon compound is aromatic. Naphthalene (five pairs of π electrons), phenanthrene (seven pairs of π electrons), and chrysene (nine pairs of π electrons) are aromatic.

**naphthalene**   **phenanthrene**   **chrysene**
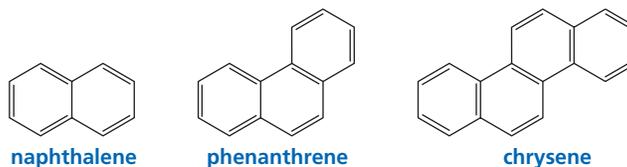
PROBLEM

The [10]- and [12]-annulenes have been synthesized, and neither has been found to be aromatic. Explain.

Aromatic Heterocyclic Compounds

A compound does not have to be a hydrocarbon to be aromatic. Many *heterocyclic compounds* are aromatic. A **heterocyclic compound** is a cyclic compound in which one or more of the ring atoms is an atom other than carbon. A ring atom that is not carbon is called a **heteroatom**. The name comes from the Greek word *heteros*, which means "different." The most common heteroatoms found in heterocyclic compounds are N, O, and S.

heterocyclic compounds

pyridine   pyrrole   furan   thiophene
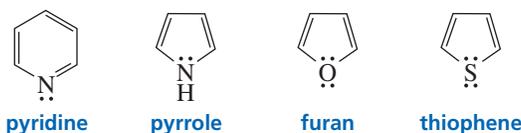
Pyridine is an aromatic heterocyclic compound. Each of the six ring atoms of pyridine is sp^2 hybridized, which means that each has a p orbital; and the molecule contains three pairs of π electrons. Don't be confused by the lone-pair electrons on the nitrogen; they are not π electrons. Because nitrogen is sp^2 hybridized, it has three sp^2 orbitals and a p orbital. The p orbital is used to form the π bond. Two of nitrogen's sp^2 orbitals overlap the sp^2 orbitals of adjacent carbon atoms, and nitrogen's third sp^2 orbital contains the lone pair.

this is a
p orbital

these electrons are in an sp^2 orbital perpendicular to the p orbitals

orbital structure of pyridine
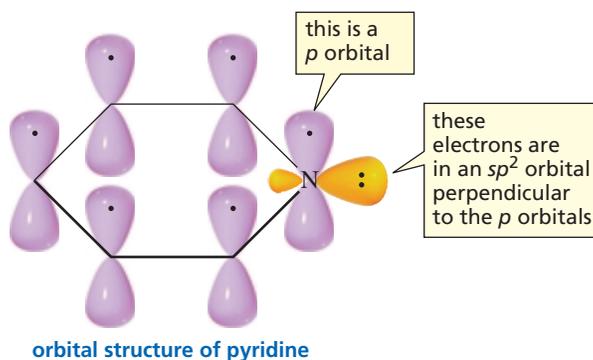
It is not immediately apparent that the electrons represented as lone-pair electrons on the nitrogen atom of pyrrole are π electrons. The resonance contributors, however, show that the nitrogen atom is sp^2 hybridized and uses its three sp^2 orbitals to bond to two carbons and one hydrogen. The lone-pair electrons are in a p orbital that overlaps the p orbitals on adjacent carbons, forming a π bond—thus, they are π electrons. Pyrrole, therefore, has three pairs of π electrons and is aromatic.

**resonance contributors of pyrrole**

orbital structure of pyrrole   **orbital structure of furan**
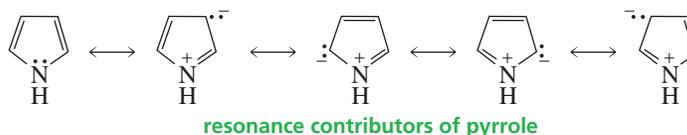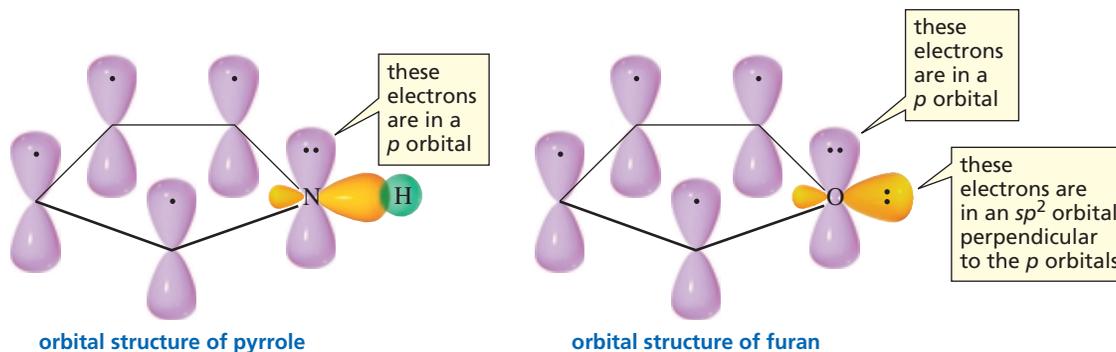
Similarly, furan and thiophene are stable aromatic compounds. Both the oxygen in the former and the sulfur in the latter are sp^2 hybridized and have one lone pair in an sp^2 orbital. The second lone pair is in a p orbital that overlaps the p orbitals of adjacent carbons, forming a π bond. Thus, they are π electrons.

resonance contributors of furan
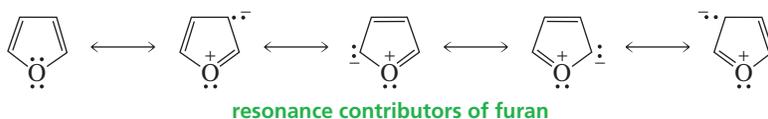
Quinoline, indole, imidazole, purine, and pyrimidine are other examples of hetero-cyclic aromatic compounds.

quinoline   **indole**   **imidazole**   **purine**   **pyrimidine**
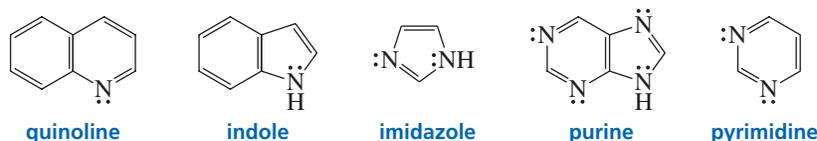
PROBLEM

In what orbitals are the electrons represented as lone pairs when drawing the structures of quinoline, indole, imidazole, purine, and pyrimidine?

PROBLEM

Answer the following questions by examining the electrostatic potential maps on p. 598:

a. Why is the bottom part of the electrostatic potential map of pyrrole blue?
b. Why is the bottom part of the electrostatic potential map of pyridine red?
c. Why is the center of the electrostatic potential map of benzene more red than the center of the electrostatic potential map of pyridine?

Some Chemical Consequences of Aromaticity

The pK_a of cyclopentadiene is 15, which is extraordinarily acidic for a hydrogen that is bonded to an sp^3 hybridized carbon. Ethane, for example, has a pK_a of 50.

cyclopentadiene   **cyclopentadienyl anion**
$pK_a = 15$

$$CH_3CH_3 \rightleftharpoons CH_3\ddot{C}H_2 \ + \ H^+$$

ethane   **ethyl anion**
$pK_a = 50$

Why is the pK of cyclopentadiene so much lower than that of ethane? To answer this question, we must look at the stabilities of the anions that are formed when the compounds lose a proton. (Recall that the strength of an acid is determined by the stability of its conjugate base: The more stable its conjugate base, the stronger is the acid;) All the electrons in the ethyl anion are localized. In contrast, the anion that is formed when cyclopentadiene loses a proton fulfills the requirements for aromaticity: It is cyclic and planar, each atom in the ring has a p orbital, and the π cloud has three pairs of delocalized π electrons. The negatively charged carbon in the cyclopentadienyl anion is sp^2 hybridized because if it were sp^3 hybridized, the ion would not be aromatic. The resonance hybrid shows that all the carbons in the cyclopentadienyl anion are equivalent. Each carbon has exactly one-fifth of the negative charge associated with the anion.

resonance contributors of the cyclopentadienyl anion

resonance hybrid
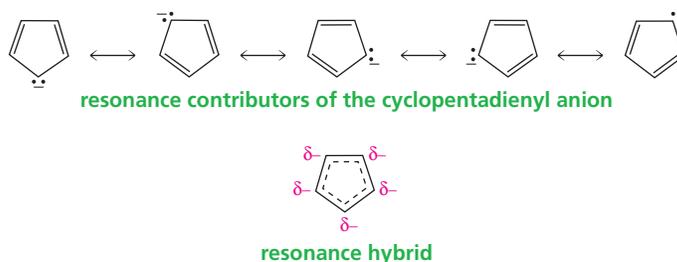
As a result of its aromaticity, the cyclopentadienyl anion is an unusually stable carbanion. This is why cyclopentadiene has an unusually low pK_a. In other words, it is the stability conveyed by the aromaticity of the cyclopentadienyl anion that makes the hydrogen much more acidic than hydrogens bonded to other sp^3 carbons.

PROBLEM

Predict the relative pK_a values of cyclopentadiene and cycloheptatriene.

PROBLEM

a. Draw arrows to show the movement of electrons in going from one resonance contributor to the next in
   1. the cyclopentadienyl anion
   2. pyrrole
b. How many ring atoms share the negative charge in
   1. the cyclopentadienyl anion?
   2. pyrrole?

Another example of the influence of aromaticity on chemical reactivity is the unusual chemical behavior exhibited by cycloheptatrienyl bromide. Recall that alkyl halides tend to be relatively nonpolar covalent compounds— they are soluble in nonpolar solvents and insoluble in water. Cycloheptatrienyl bromide, however, is an alkyl halide that behaves like an ionic compound—it is insoluble in nonpolar solvents, but readily soluble in water.

covalent
cycloheptatrienyl bromide

ionic
cycloheptatrienyl bromide
tropylium bromide
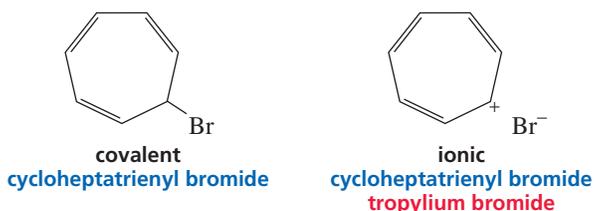
Cycloheptatrienyl bromide is an ionic compound because its cation is aromatic. The alkyl halide is *not* aromatic in the covalent form because it has an sp^3 hybridized carbon, so it does *not* have an uninterrupted ring of p orbital-bearing atoms. In the ionic form, however, the cycloheptatrienyl cation (also known as the tropylium cation) *is* aromatic because it is a planar cyclic ion, all the ring atoms are sp^2 hybridized (which means that each ring atom has a p orbital), and it has three pairs of delocalized π electrons. The stability associated with the aromatic cation causes the alkyl halide to exist in the ionic form.
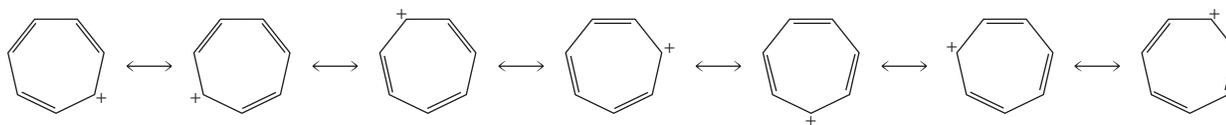
resonance contributors of the cycloheptatrienyl cation
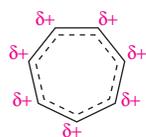
resonance hybrid

PROBLEM-SOLVING STRATEGY

Which of the following compounds has the greater dipole moment?
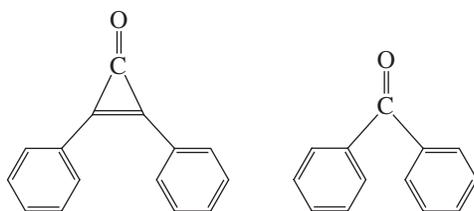
Before attempting to answer this kind of question, make sure that you know exactly what the question is asking. You know that the dipole moment of these compounds results from the unequal sharing of electrons by carbon and oxygen. Therefore, the more unequal the sharing, the greater is the dipole moment. So now the question becomes, which compound has a greater negative charge on its oxygen atom? Draw the structures with separated charges, and determine their relative stabilities. In the case of the compound on the left, the three-membered ring becomes aromatic when the charges are separated. In the case of the compound on the right, the structure with separated charges is not aromatic. Because being aromatic makes a compound more stable, the compound on the left has the greater dipole moment.
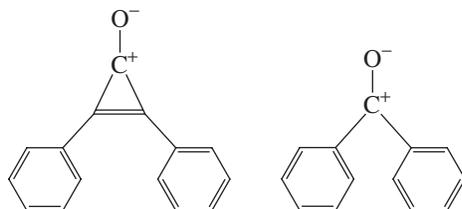
PROBLEM

Draw the resonance contributors of the cyclooctatrienyl dianion.

a. Which of the resonance contributors is the least stable?
b. Which of the resonance contributors makes the smallest contribution to the hybrid?

Antiaromaticity

An aromatic compound is *more stable* than an analogous cyclic compound with localized electrons. In contrast, an **antiaromatic** compound is *less stable* than an analogous cyclic compound with localized electrons. *Aromaticity is characterized by stability, whereas antiaromaticity is characterized by instability*.

relative stabilities

aromatic compound > cyclic compound with localized electrons > antiaromatic compound

increasing stability
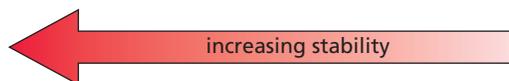
A compound is classified as being antiaromatic if it fulfills the first criterion for aromaticity but does not fulfill the second criterion. In other words, it must be a planar, cyclic compound with an uninterrupted ring of p orbital-bearing atoms, and the π cloud must contain an *even* number of pairs of π electrons. Hückel would state that the π cloud must contain $4n$ π electrons, where n is any whole number—a mathematical way of saying that the cloud must contain an *even* number of pairs of π electrons.

Cyclobutadiene is a planar, cyclic molecule with two pairs of π electrons. Hence, it is expected to be antiaromatic and highly unstable. In fact, it is too unstable to be isolated, although it has been trapped at very cold temperatures. The cyclopentadienyl cation also has two pairs of π electrons, so we can conclude that it is antiaromatic and unstable.

**cyclobutadiene**   **cyclopentadienyl cation**

PROBLEM

a. Predict the relative pK_a values of cyclopropene and cyclopropane.
b. Which is more soluble in water, 3-bromocyclopropene or bromocyclopropane?

A Molecular Orbital Description of Aromaticity and Antiaromaticity

Why are planar molecules with uninterrupted cyclic π electron clouds highly stable (aromatic) if they have an odd number of pairs of π electrons and highly unstable (antiaromatic) if they have an even number of pairs of π electrons? To answer this question, we must turn to molecular orbital theory.

The relative energies of the π molecular orbitals of a planar molecule with an uninterrupted cyclic π electron cloud can be determined—without having to use any math—by first drawing the cyclic compound with one of its vertices pointed down. The relative energies of the π molecular orbitals correspond to the relative levels of the vertices   . Molecular orbitals below the midpoint of the cyclic structure are bonding molecular orbitals, those above the midpoint are antibonding molecular orbitals, and any at the midpoint are nonbonding molecular orbitals. This scheme is sometimes called a Frost device (or a Frost circle) in honor of Arthur A. Frost, an
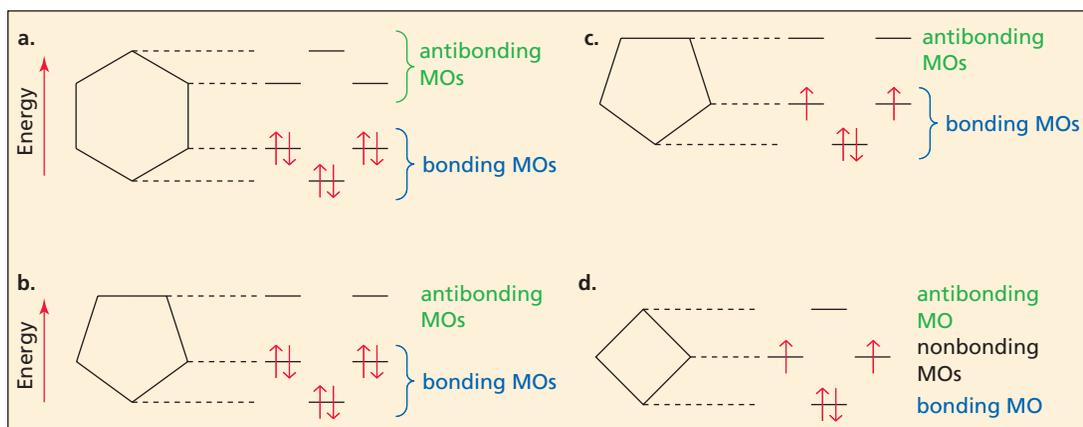
The distribution of electrons in the π molecular orbitals of (a) benzene, (b) the cyclopentadienyl anion, (c) the cyclopentadienyl cation, and (d) cyclobutadiene. The relative energies of the π molecular orbitals in a cyclic compound correspond to the relative levels of the vertices. Molecular orbitals below the midpoint of the cyclic structure are bonding, those above the midpoint are antibonding, and those at the midpoint are nonbonding.

American scientist who devised this simple method. Notice that the number of π molecular orbitals is the same as the number of atoms in the ring because each ring atom contributes a p orbital.

The six π electrons of benzene occupy its three bonding π molecular orbitals, and the six π electrons of the cyclopentadienyl anion occupy *its* three bonding π molecular orbitals. Notice that there is always an odd number of bonding orbitals because one corresponds to the lowest vertex and the others come in degenerate pairs. This means that aromatic compounds—such as benzene and the cyclopentadienyl anion—with an odd number of pairs of π electrons have completely filled bonding orbitals and no electrons in either nonbonding or antibonding orbitals. This is what gives aromatic molecules their stability.

Aromatic compounds are stable because they have filled bonding π molecular orbitals.

Antiaromatic compounds have an even number of pairs of π electrons. Therefore, either they are unable to fill their bonding orbitals (cylopentadienyl cation) or they have a pair of π electrons left over after the bonding orbitals are filled (cyclobutadiene).

Hund's rule requires that these two electrons go into two degenerate orbitals . The unpaired electrons are responsible for the instability of antiaromatic molecules.

PROBLEM

How many bonding, nonbonding, and antibonding π molecular orbitals does cyclobutadiene have? In which molecular orbitals are the π electrons?

PROBLEM

Can a radical be aromatic?

Reaction Intermidiates

Definition: a reaction intermediate or an intermediate as a molecular entity (atom, ion, molecule...) with a lifetime appreciably longer than a molecular vibration that is formed (directly or indirectly) from the reactants and reacts further to give (either directly or indirectly) the products of a chemical reaction.

Main carbon reactive intermediates:

- Carbocations and their stabilized equivalents such as oxonium ions
- Carbanions and their stabilized equivalents such as enolates
- Free radicals
- Carbenes

Common features

♦ Low concentration
♦ Dot not obey the Lewis octet rule with the exception of carbanions, hence the high reactivity
♦ Often generated on chemical decomposition
♦ It is often possible to prove the existence of this species by spectroscopic means
♦ Cage effects have to be taken into account
♦ Often stabilisation by conjugation or resonance
♦ Often difficult to distinguish from a transition state
♦ Prove existence by means of chemical trapping

CARBOCATIONS

o A **carbocation** is an ion with a positively-charged carbon atom.

$$Carbocation \begin{cases} \textit{Carbenium ion (trivalent positive species)} \\ CH_3^+, C_2H_5^+ ... \\ \\ \textit{Carbonium ion (pentavalent positive species,} \\ \text{nonclassical carbocation)} \end{cases}$$
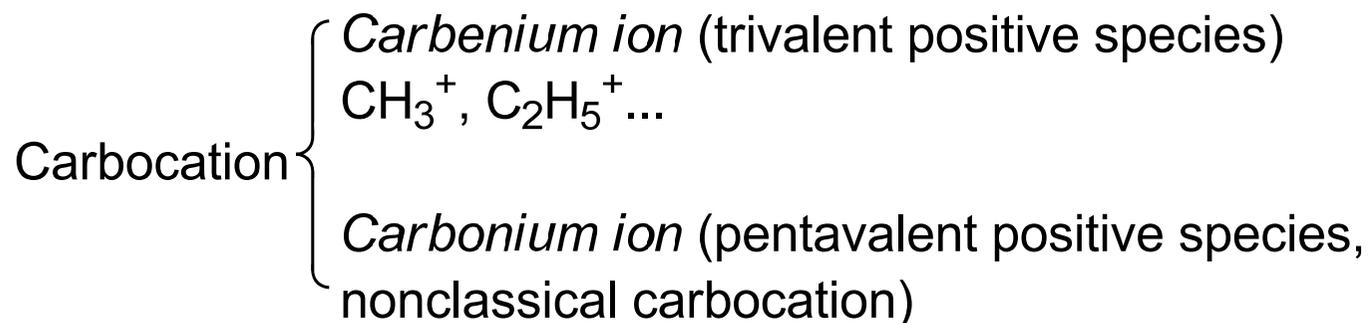
Norris and Kehrman (1902):

deep yellow
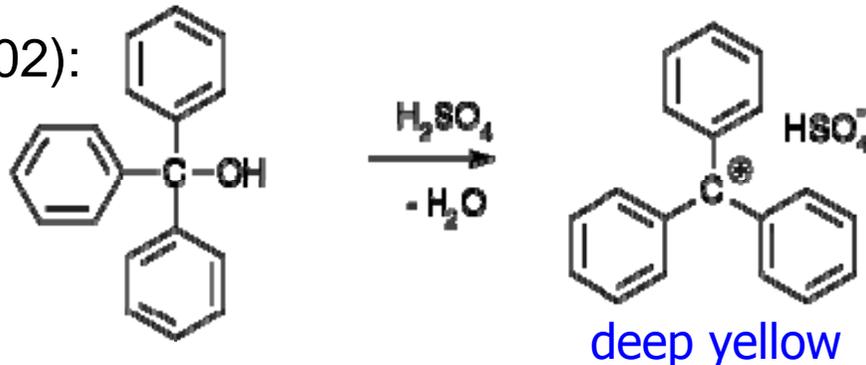
In 1962 Olah directly observed the *tert*-butyl carbocation by NMR as a stable species on dissolving tert-butyl fluoride in magic acid.

I. STRUCTURE AND STABILITY

In solution, the carbocation may be free (this is more likely in polar solvents, in which it is solvated) or it may exist as an ion pair. Ion pairs are more likely in nonpolar solvents.

A. Simple alkyl carbocations

Stability: tertiary > secondary > primary
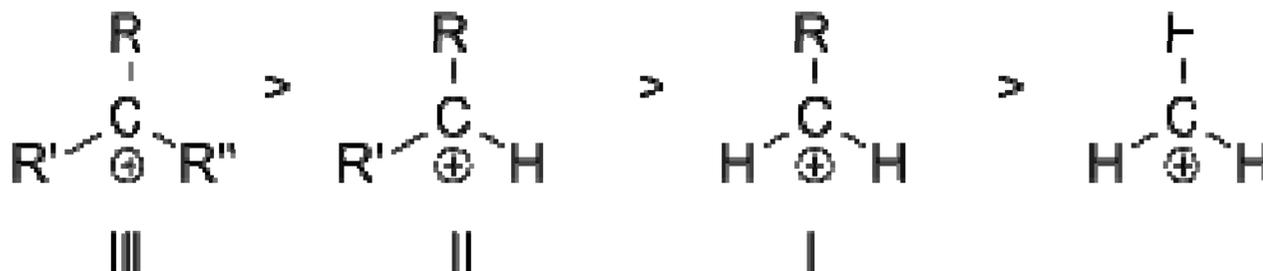
The most stable of all alkyl cations is the *tert*-butyl cation. Methane, ethane, and propane, treated with superacid, also yield *tert*-butyl cation as the main product.

No matter how they are generated, study of the simple alkyl cations has provided dramatic evidence for the stability. Both propyl fluorides gave the isopropyl cation; all four butyl fluorides gave the *tert*-butyl cation. Butane, in superacid, gave only the *tert*-butyl cation.

$$ROH \xrightarrow[\text{SO}_2]{\text{superacid}} R^+ \xleftarrow[\substack{\text{SO}_2 \text{ or} \\ \text{SO}_2\text{ClF}}]{\text{HF-SbF}_5} R'CH=CH_2$$

$$\underset{\text{(isobutane)}}{Me_3C\text{-}H} \xrightarrow[\text{SO}_3]{\text{HF-SbF}_5} Me_3C^+SbF_5FSO_3^- + H_2$$

$$CH_3CH_3CH_2F \longrightarrow CH_3\overset{+}{C}HCH_3 \longleftarrow (CH_3)_2CHF$$

$$C_4H_9F \longrightarrow \underset{\underset{CH_3}{|}}{CH_3\overset{+}{C}CH_3} \xleftarrow{\text{superacid}} \text{Butane}$$
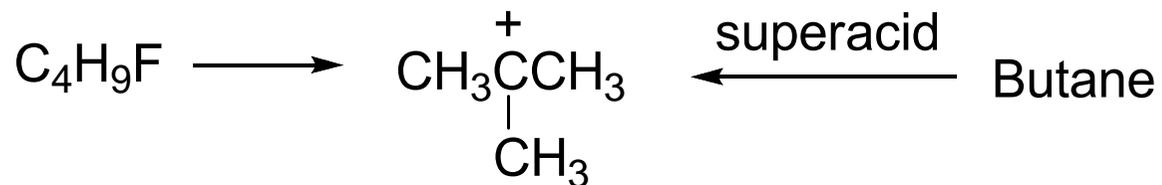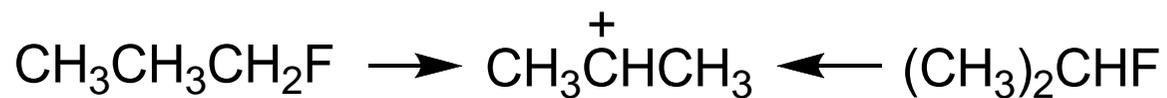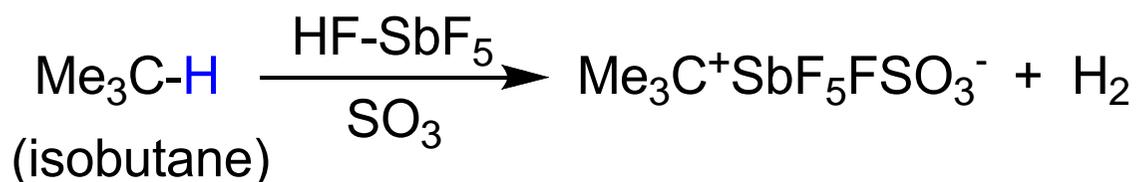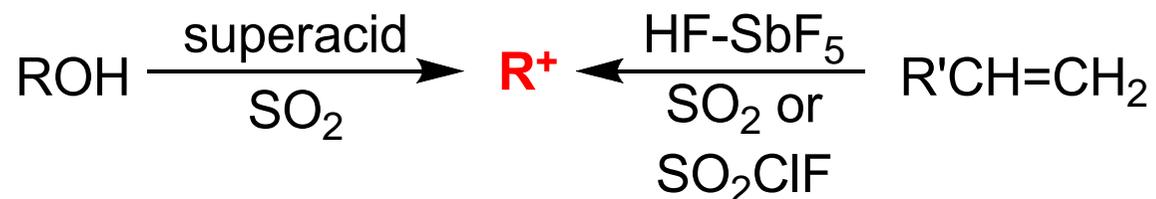
To date, no primary cation has survived long enough for detection.

$$CH_3^+ \ ?$$

$$CH_3F \ + \ SbF_5\text{-}SO_2 \ \longrightarrow \ (CH_3OSO)^+SbF_6^-$$

$$\left[\begin{array}{c} O{=}S{=}O \\ CH_3^+SbF_6^- \end{array} \right]$$
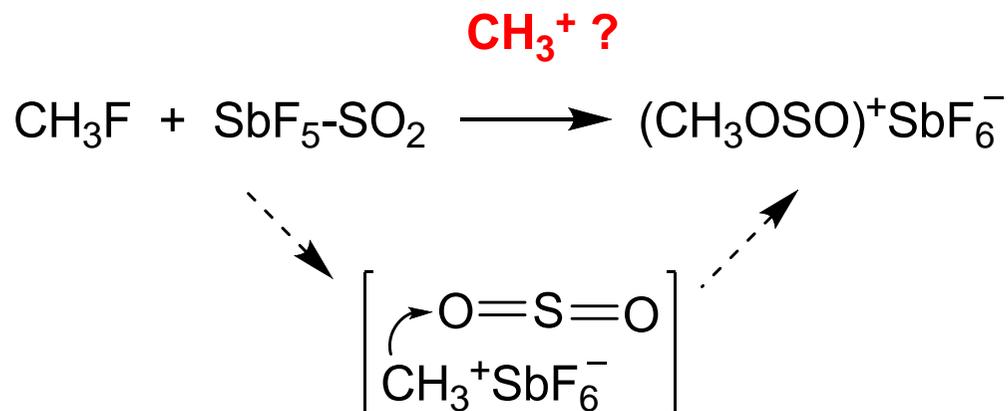
♦ **The field effect.** The electron-donating effect of alkyl groups increases the electron density at the charge-bearing carbon, reducing the net charge on the carbon, and in effect spreading the charge over the α carbons.

♦ **Hyperconjugation.** Tertiary carbocations are more stable (and form more readily) than secondary carbocations; primary carbocations are highly unstable because, while ionized higher-order carbons are stabilized by **hyperconjugation**, unsubstituted (primary) carbons are not.

$$(CD_3)_3C^+ + (CH_3)_3CH \;\underset{}{\overset{K}{\rightleftharpoons}}\; (CH_3)_3C^+ + (CD_3)_3CH$$

(1)   (2)
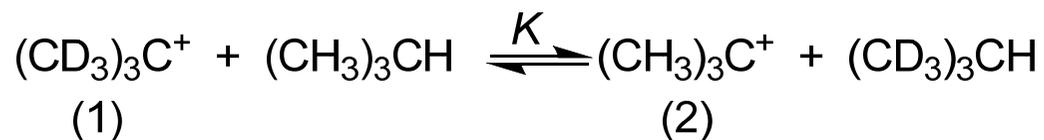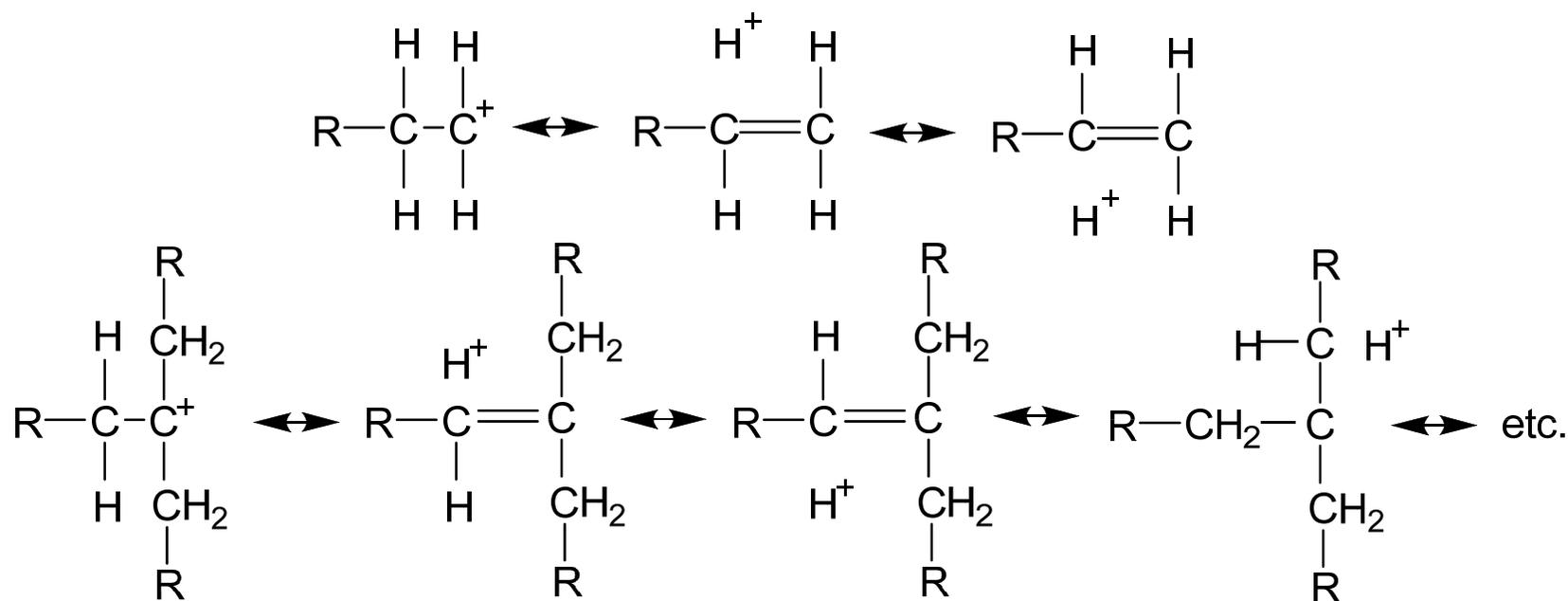
$$K_{298} = 1.97 \pm 0.20$$

K is 1.97, showing that <u>2</u> is more stable than <u>1</u>. This is a secondary isotopic effect; there is less hyperconjugation in <u>1</u> than <u>2</u>.

It is a general rule that the more concentrated any charge is, the less stable the species bearing it will be.

STABLE ALLYLIC-TYPE CATIONS

Allyl cation and benzyl cation are more stable than most other carbocations. Molecules which can form allyl or benzyl carbocations are especially reactive. Stable allylic cations have been obtained by the reaction between alkyl halides, alcohols, or alkenes (by hydride extraction) and SbF_5 in SO_2 or SO_2ClF.
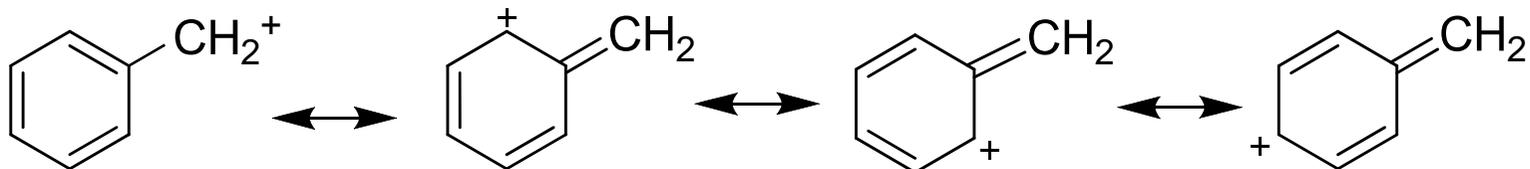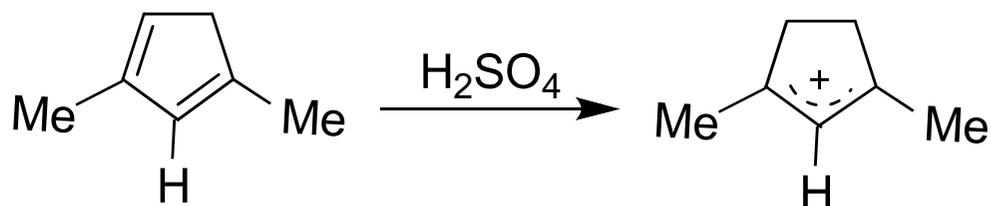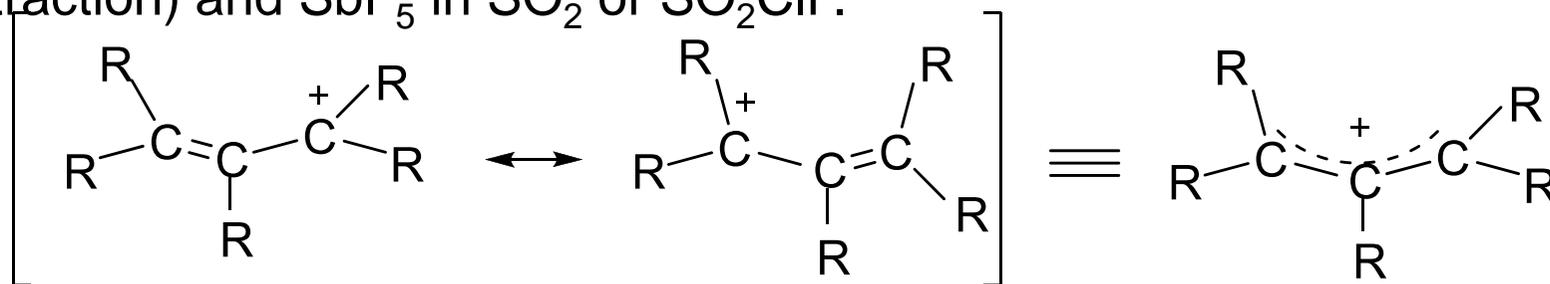
CYCLOPROPYLMETHYL CATIONS

Cyclopropylmethyl cation are even more stable than the benzyl type. Compound (c) has been prepared by solution of the corresponding alcohol in H_2SO_4. Compounds *a, b,* and similar ions have been prepared by solution of the alcohols in FSO_3H-SO_2-SbF_5.

NMR spectrum of a dimethyl derivative (a), identical signals are found for the two methyl groups.

J. Am. Chem. Soc. 1970, 92, 3234–3235
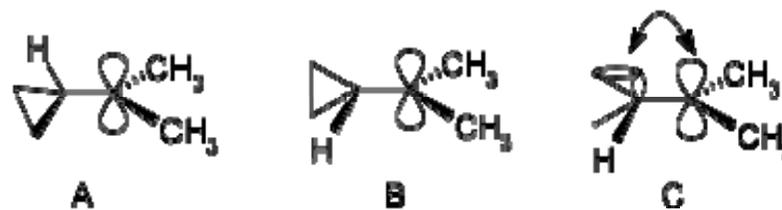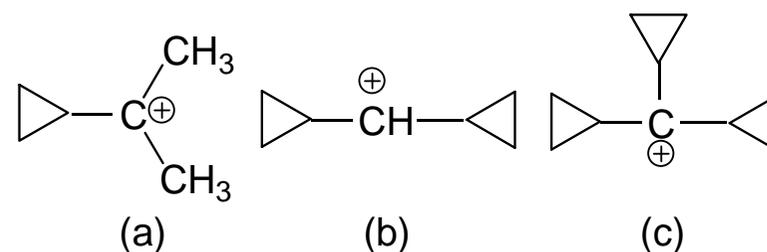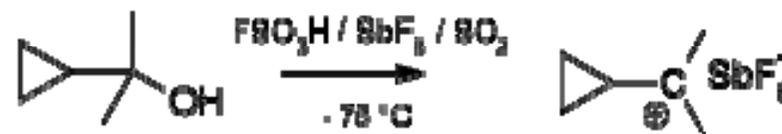
Another structural feature that increases carbocation stability is the presence, adjacent to the cationic center, of a heteroatom bearing an unshared pair.

$$R-\overset{R}{\underset{\oplus}{C}}-\overset{..}{\underset{..}{O}}-CH_3 \longleftrightarrow R-\overset{R}{C}=\overset{..}{\underset{\oplus}{O}}-CH_3$$

(I)   (II)
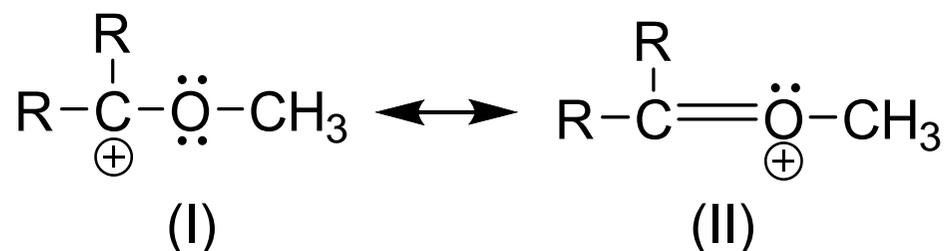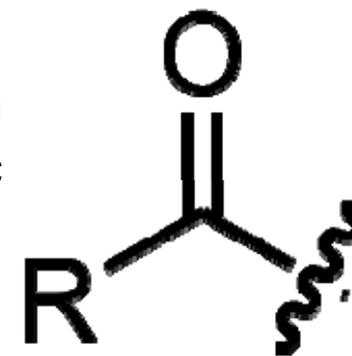
◆ Simple acyl cations (RCO⁺) have been prepared in solution and the gas state. The acetyl (CH₃CO⁺) is about as stable as the *tert*-butyl cation. The 2,4,6-trimethylbenzoyl cations are especially stable (for steric reasons) and are easily formed in 96% H_2SO_4.

$$R-\overset{\oplus}{C}=\overset{..}{\underset{..}{O}} \longleftrightarrow R-\!\!\!\equiv\!\!\overset{\oplus}{\underset{..}{O}}$$

(III)   (IV)
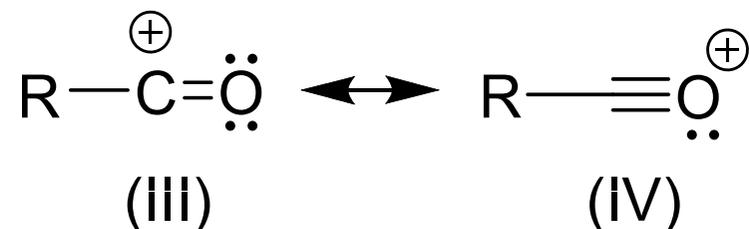
◆ Friedel-Crafts acylation


Mechanism:

Haworth reaction:
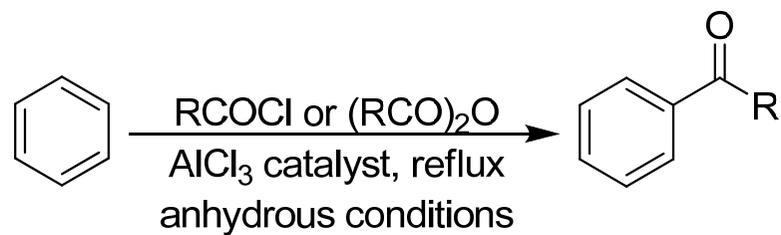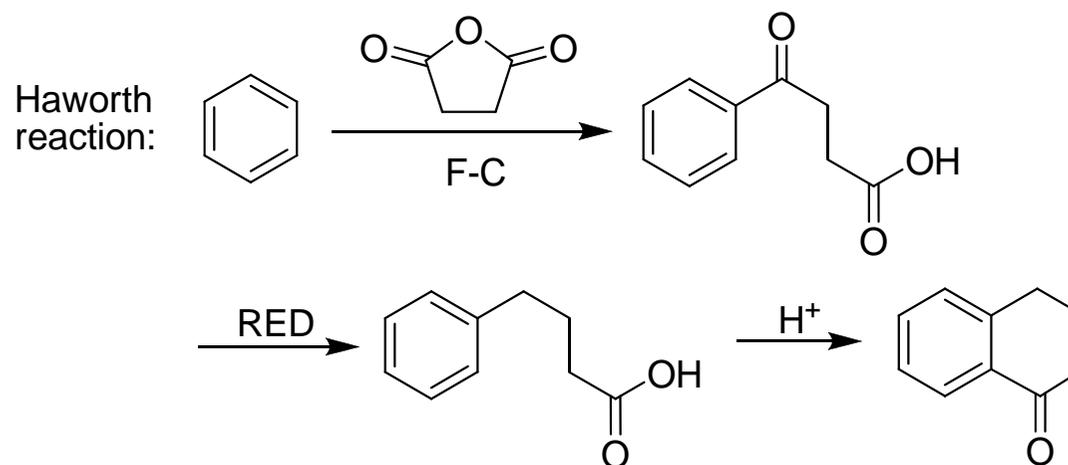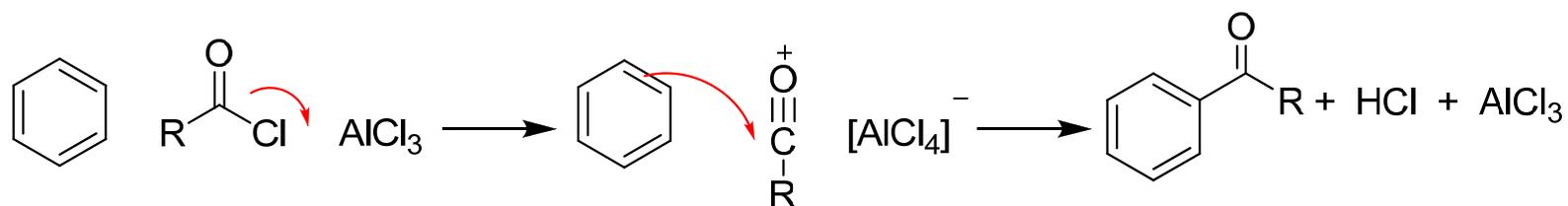
**CARBOCATION STRUCTURES:** PLANAR SP^2 HYBRID

2p$_z$
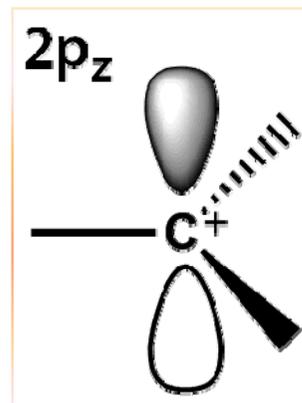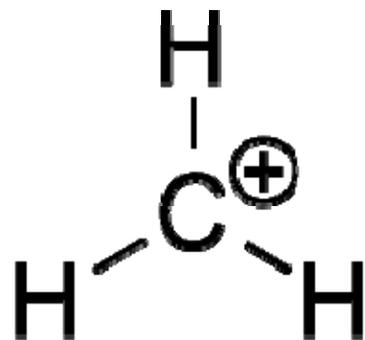
tert-butyl cation
demonstrating planar geometry
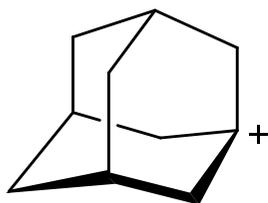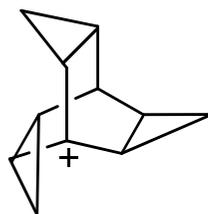
adamentyl 1-trishomobarrelyl triphenylmethyl
propeller-shaped
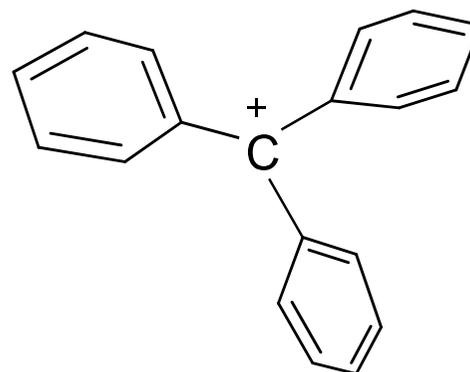
◆ An important tool for the investigation of carbocation structure is measurement of the ^{13}C NMR chemical shift of the carbon atom bearing the positive charge. *This shift approximately correlates with electron density on the carbon*.

TABLE 1. The ^{13}C chemical shift values for the charged carbon atom of some carbocations in SO_2ClF-SbF_5, SO_2-FSO_3H-SbF_6, or SO_2-SbF_5.

Ion	Chemical shift (ppm)	Temp (^oC)	Ion	Chemical shift (ppm)	Temp (^oC)
Et_2MeC^+	-139.4	-20	$C(OH)_3^+$	+28.0	-50
Me_2EtC^+	-139.2	-60	$PhMe_2C^+$	-61.1	-60
Me_3C^+	-135.4	-20	$PhMeCH^+$	-40	
Me_2CH^+	-125.0	-20	Ph_2CH^+	-5.6	-60
Me_2COH^+	-55.7	-50	Ph_3C^+	-18.1	-60
$MeC(OH)_2^+$	-1.6	-30	$Me_2(cyclopropyl)C^+$	-86.8	-60
$HC(OH)_2^+$	+17.0	-30			

II. THE GENERATION AND FATE OF CARBOCATIONS

Two general ways to form carbocations:

i. A direct ionization:

$$R - X \longrightarrow R^+ + X^- \text{ (may be reversible)}$$
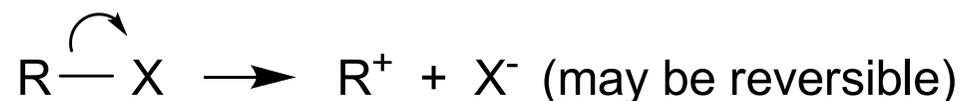
ii. Addition of a positive species toan unsaturateraed system:

$$\diagdown{=}Z + H^+ \longrightarrow -\overset{+}{C}-Z-H$$
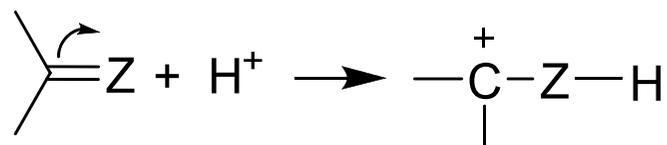
The reaction of carbocations:

i. Combination with a species possessing an electron pair.

$$R^+ + X^- \longrightarrow R-X$$
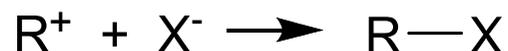
ii. The carbocation may lose a proton from the adjacent atom.

$$-\overset{+}{C}-Z-H \longrightarrow \diagdown{=}Z + H^+$$
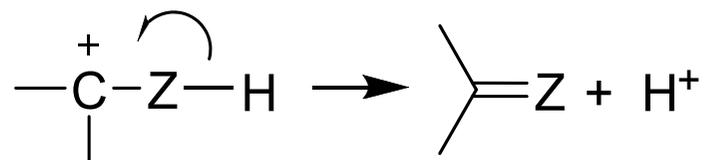
iii. Rearrangement
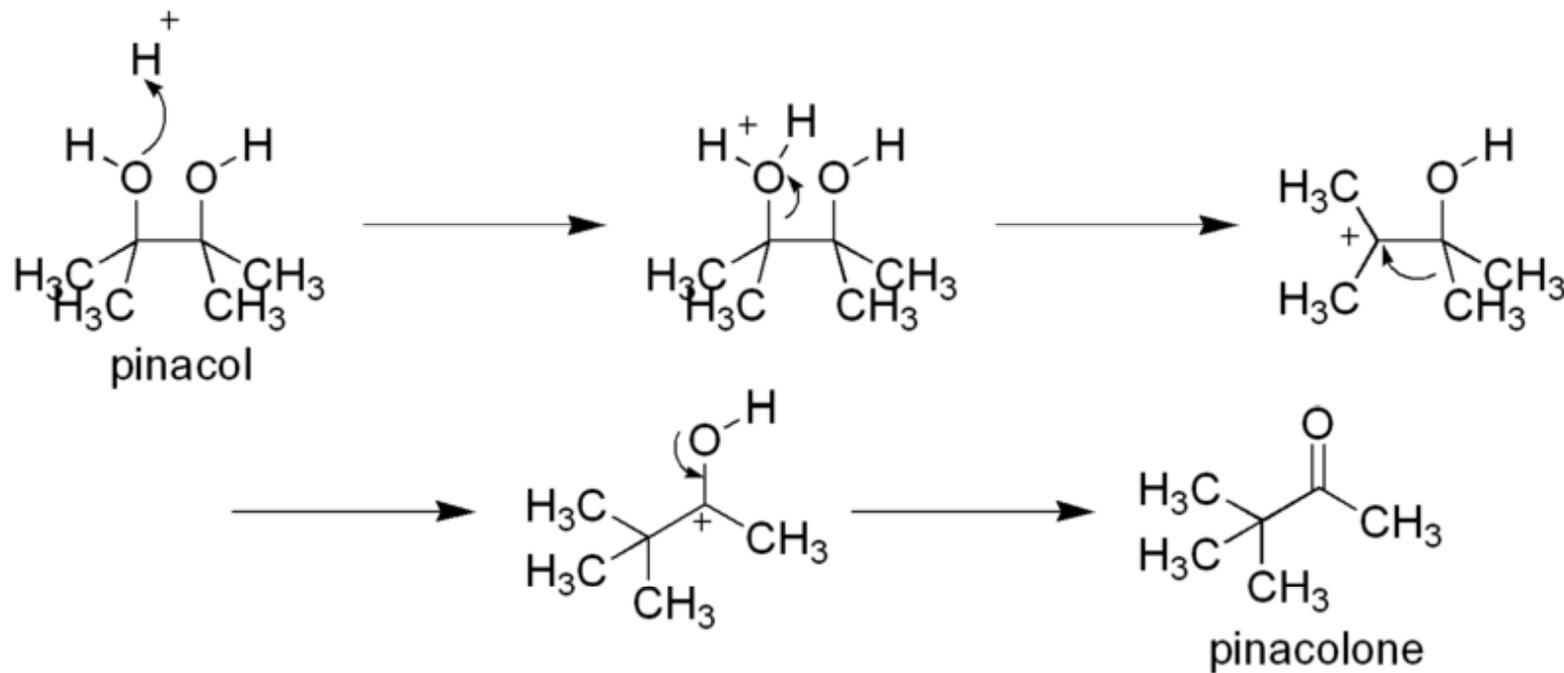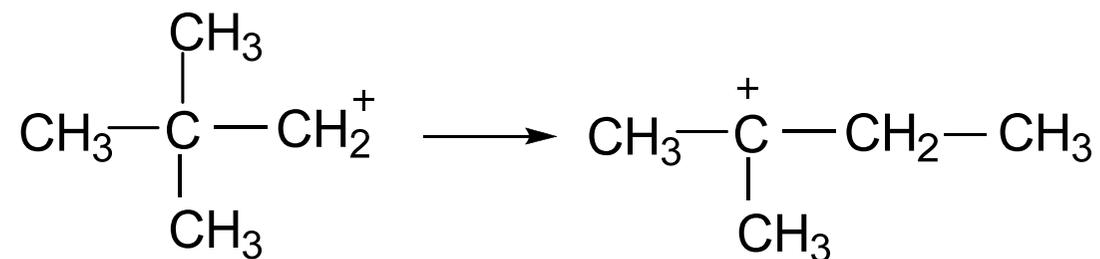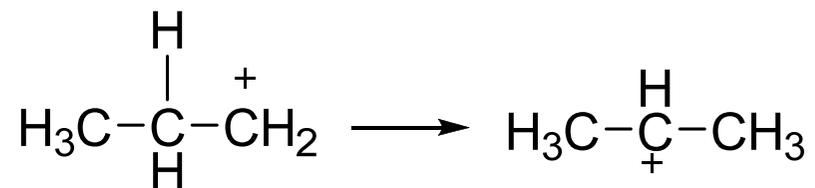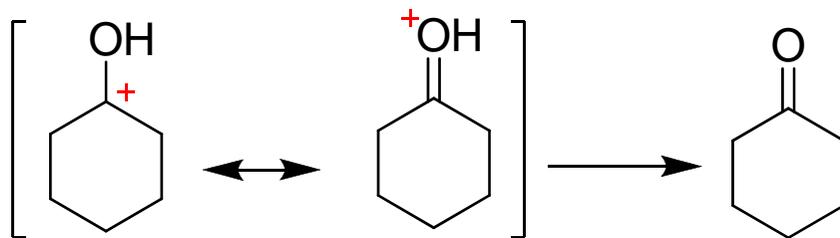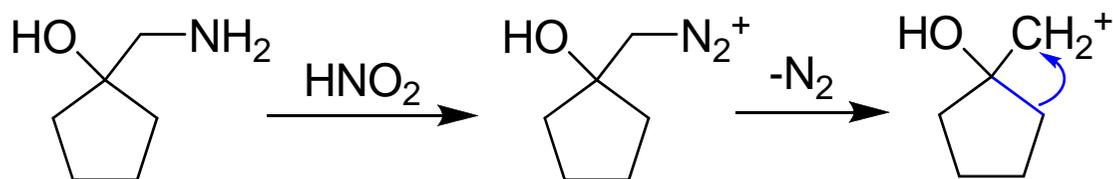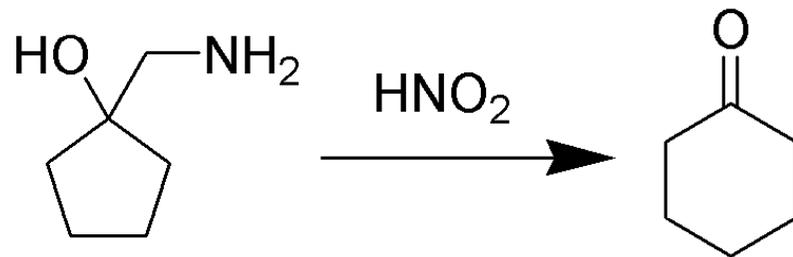
iv.
Addition
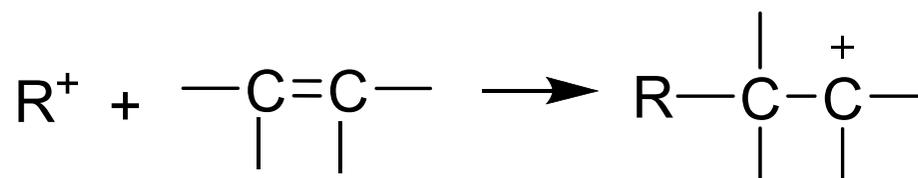
ii The Cyclopropylmethyl System

48%   17%   5%

homoally alcohol
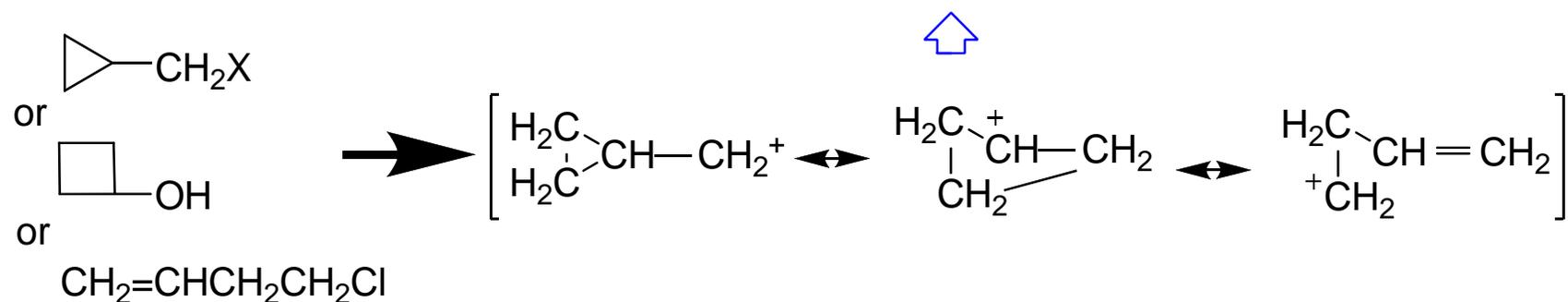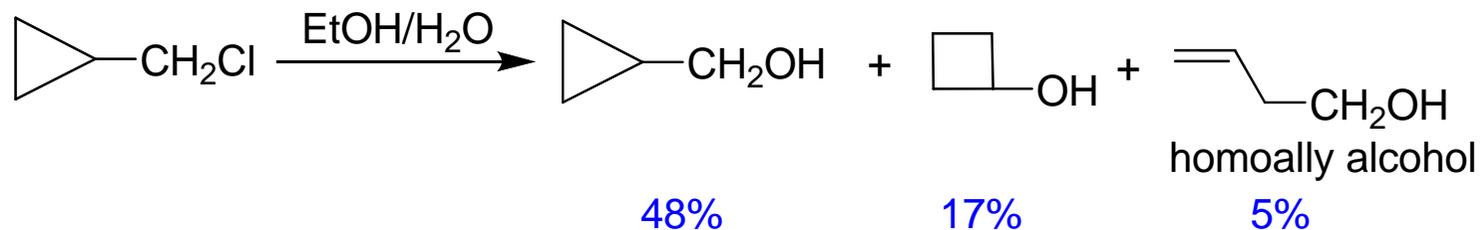
The carbocationic intermidate is delocalised onto many different carbons through a reversible ring opening.

iii. Methyl or Hydrogen as Neighboring Group

Neopentyltosylate

(a)

CH$_3$CH$_2$CDCD$_3$ (with OTs), deuterated sec-butyl tosylate $\xrightarrow{CF_3COOH}$ CH$_3$CH$_2$CDCD$_3$ (with OOCCF$_3$) (a) + CH$_3$CHCDHCD$_3$ (with OOCCF$_3$) (b)   CH$_3$CHDCHCD$_3$ (with OOCCF$_3$) (c)   CH$_3$CDCH$_2$CD$_3$ (with OOCCF$_3$) (d)

an equimolar mixture

were not found

$$\overset{\oplus}{CH_3CH_2CDCD_3} \rightleftharpoons \overset{\oplus}{CH_3CHCDHCD_3} \rightleftharpoons \overset{\oplus}{CH_3CHDCHCD_3} \rightleftharpoons \overset{\oplus}{CH_3CDCH_2CD_3}$$

open cations
in equilibrium

no NGP by hydrogen

Ts = H₃C—⟨benzene⟩—S— (with =O above and =O below)

NGP by hydrogen

(e)
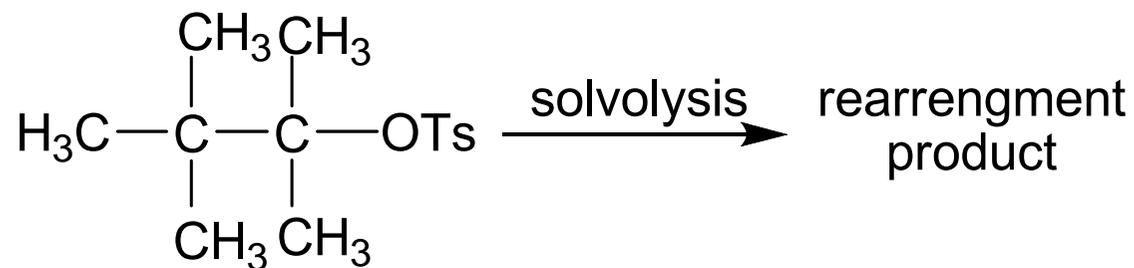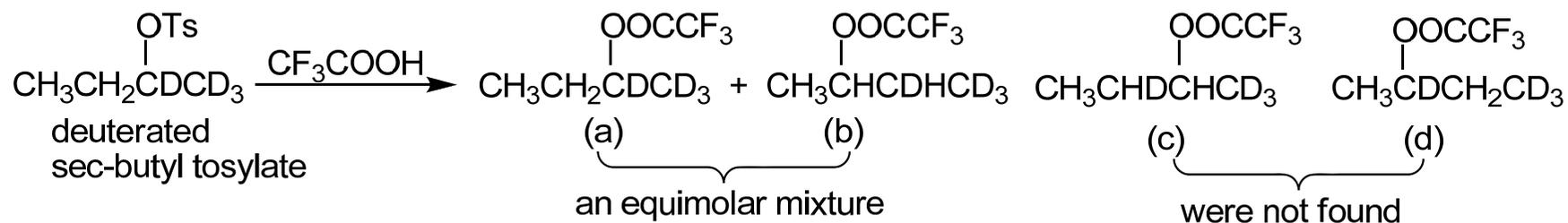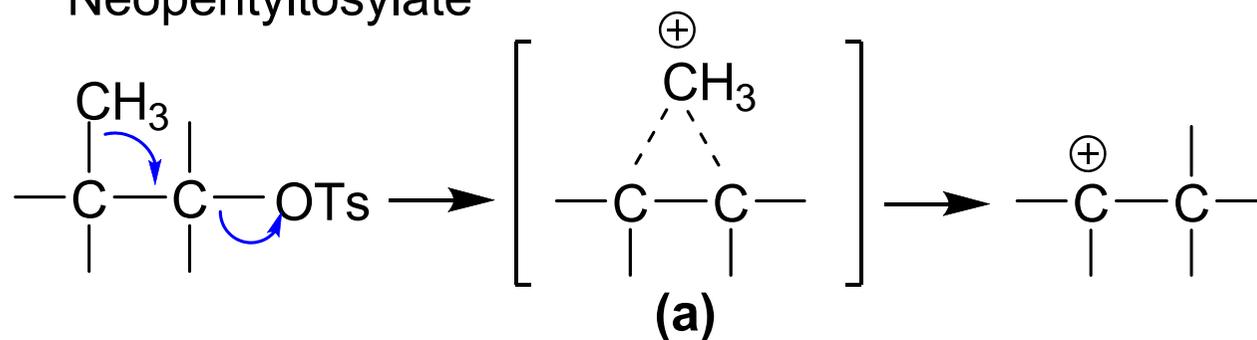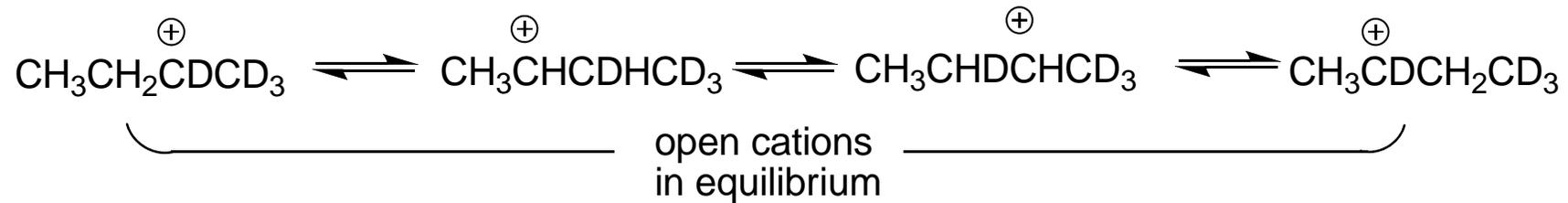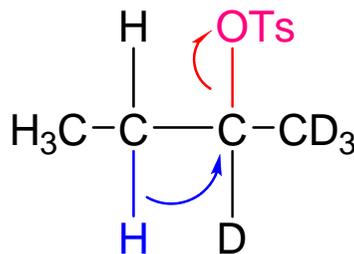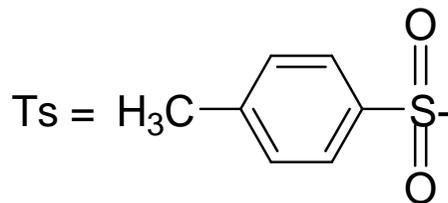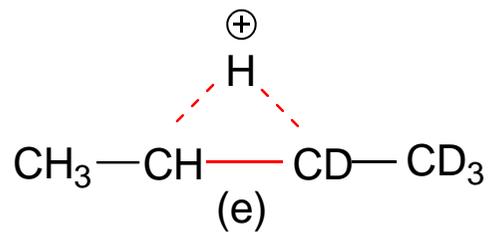
4.2 CARBANIONS

A **carbanion** is an anion in which carbon has an unshared pair of electrons and bears a negative charge usually with three substituents for a total of eight valence electrons.

Formally a carbanion is the conjugate base of a **carbon acid**.

$$R-\overset{|}{\underset{|}{C}}-H \;\rightleftharpoons\; R-\overset{|}{\underset{|}{C}}\!:^{-} \;+\; H^{+}$$
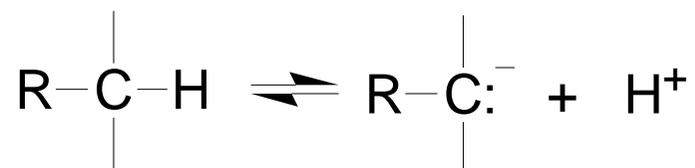
Stable carbanions do however exist although in most cases they are reactive.

Olmstead
(1984):

propelled at 31.2°

n-BuLi THF   12-crown-4

Li⁺.THF

145pm

precipitated at -20°C
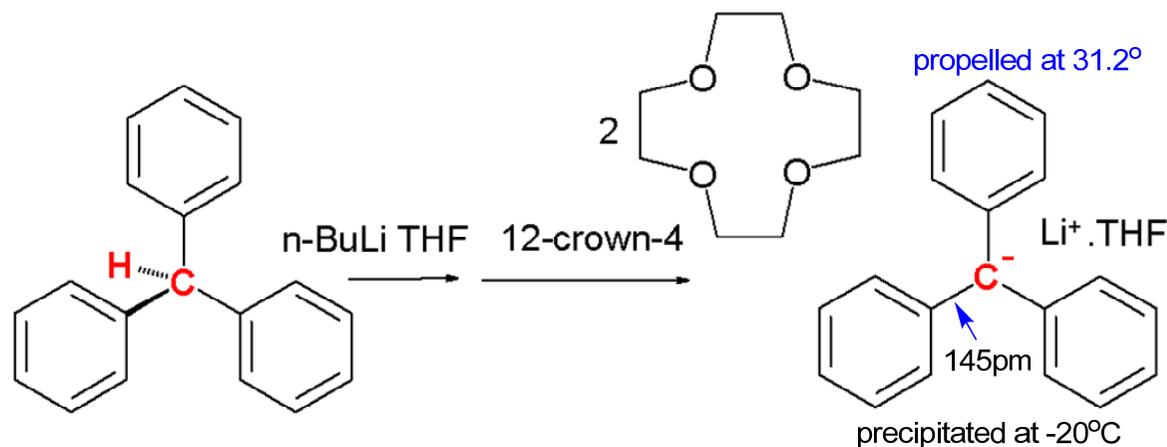
I. STABILITY AND STRUCTURE

The stability of the carbanion is directly related to the strength of the conjugate acid. The weaker is the acid, the greater is the base strength and the lower is the stability of the carbanion.

Factors determining the stability and reactivity of a carbanion:

o The inductive effect. Electronegative atoms adjacent to the charge will stabilize the charge;

o Hybridization of the charge-bearing atom. The greater the *s*-character of the charge-bearing atom, the more stable the anion;

o The extent of conjugation of the anion. Resonance effects can stabilize the anion. This is especially true when the anion is stabilized as a result of aromaticity.

RELATIVELY STABLE CARBANIONS WITH CERTAIN STRUCTURAL FEATURES

Conjugation of the unshared pair of electrons with an unsaturated bond

$$Y=C-C: \longleftrightarrow :Y-C=C \quad (Y=C, O \text{ or } N)$$

$$R-C=CH-CH_2: \longleftrightarrow R-C=CH=CH_2$$
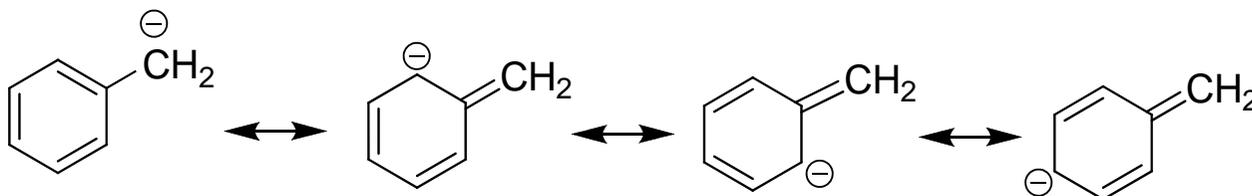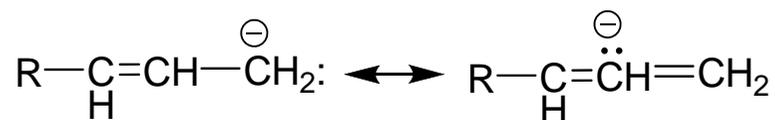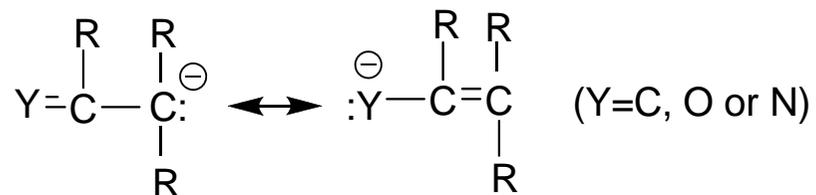
Carbanions increase in stability with an increase in the amount of *s* character at the carbanionic carbon.

Stability:

$$RC{\equiv}C^- > R_2=CH^- \approx Ar^- > RCH_2^-$$

○ Stabilization by sulfur or phosphorus.
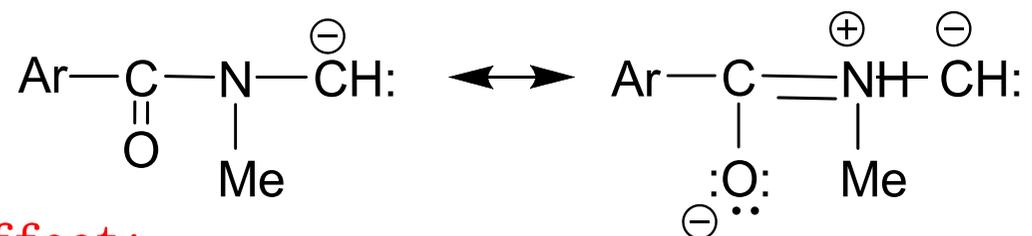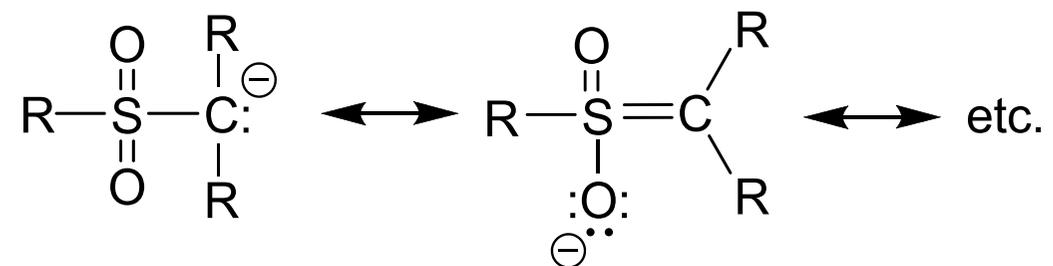
○ Field effect:

➢ Ylides are more stable than the corresponding simple carbanions.

➢ Carbanions are stabilized by a field effect if there is any hetero atom (O, N or S) connected to the carbanionic carbon, provided that the hetero atom bears a positive charge in at least one important canonical form.
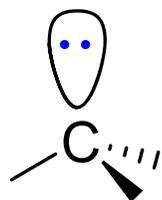
trigonal pyramid

Question:
Whether or not carbanions
can display chirality?

1 phosphate

0.9 eq. n-BuLi
TEMEDA

Et$_2$O - 78°C - 0°C

2 (S)

phosphate-
phosphorane
rearrangement

AcOH

3
phosphorane
(R)

4 (R)
70% yield
98% ee
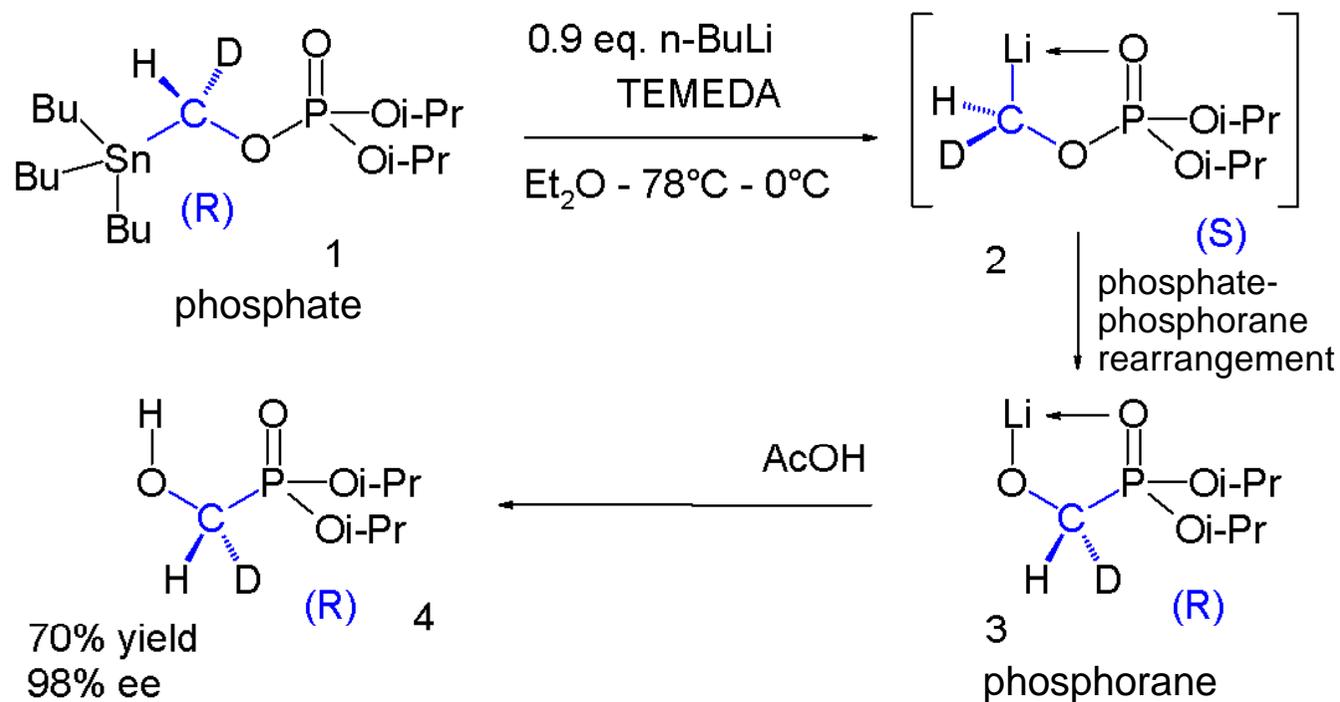
In the range of -78 to 0°C the chirality is preserved in this reaction sequence.

II. THE GENERATION AND FATE OF CARBANIONS

a) A group attached to a carbon leaves without its electron pair.

$$R-H \longrightarrow R:^{\ominus} + H^+$$

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{..}{\underset{..}{O}}:^{\ominus} \longrightarrow R:^{\ominus} + CO_2$$
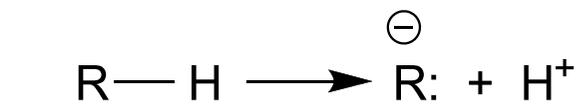
b) A negative ion adds to a carbon-carbon double or triple bond.

$$\overset{}{\underset{}{C}}=\overset{}{\underset{}{C} \quad + \quad Y^{\ominus} \longrightarrow \quad -\overset{..}{\underset{}{C}}^{\ominus}-\overset{}{\underset{}{C}}-Y}$$

Reactions:

$$R:^{\ominus} + Y^{\oplus} \longrightarrow R-Y$$

$$R:^{\ominus} \cdots\rightarrow \overset{}{\underset{}{C}}-X \longrightarrow R-\overset{}{\underset{}{C}} + X:^{\ominus}$$

$$R:^{\ominus} + \overset{}{\underset{\overset{\|}{O}}{C}} \longrightarrow -\overset{\overset{\displaystyle R}{|}}{\underset{\underset{..}{\overset{..}{O}:^{\ominus}}}{C}}-$$

$$Ph_3C\overset{..}{C}H_2:^{\ominus} \longrightarrow Ph_2\overset{..}{C}CH_2Ph$$
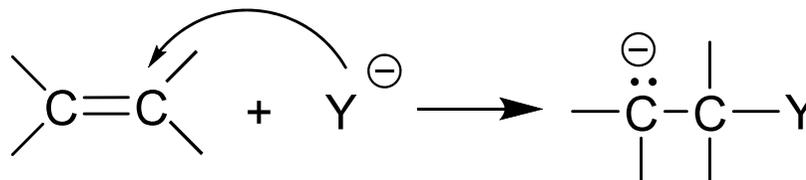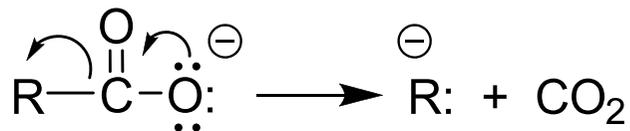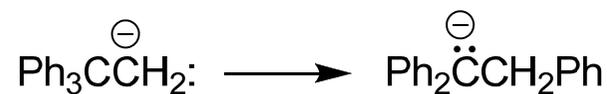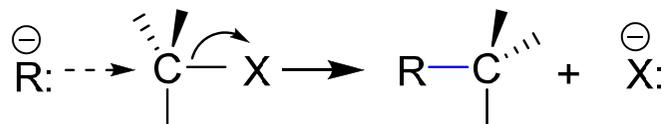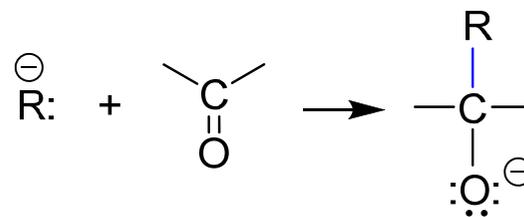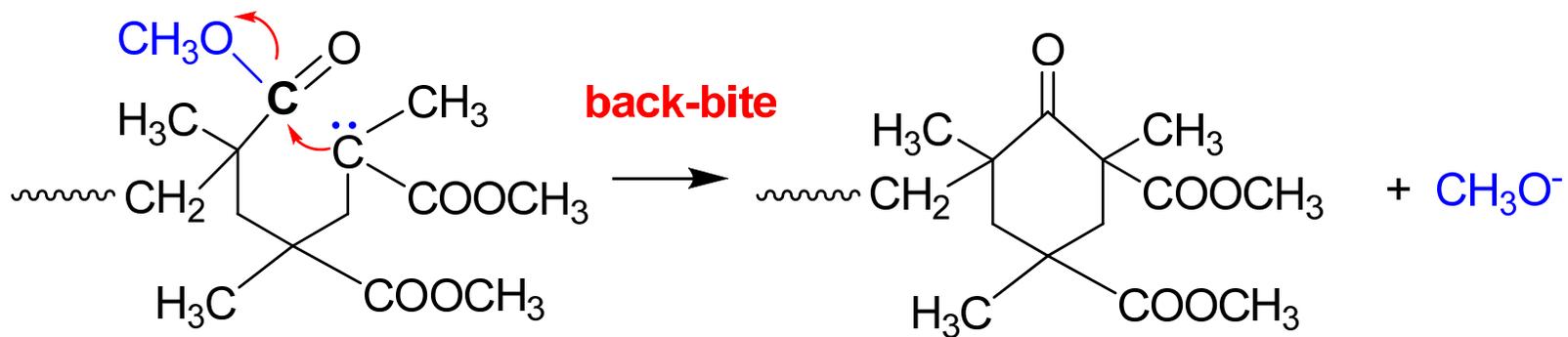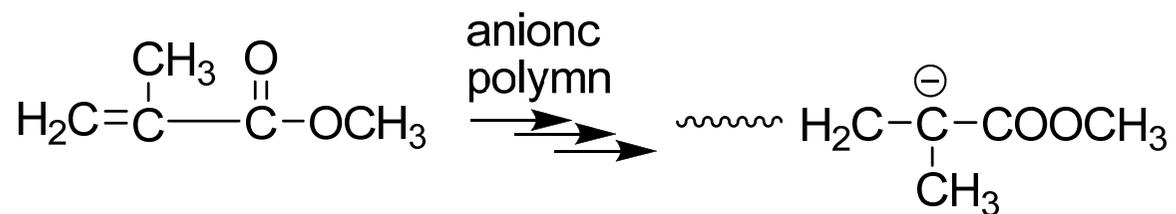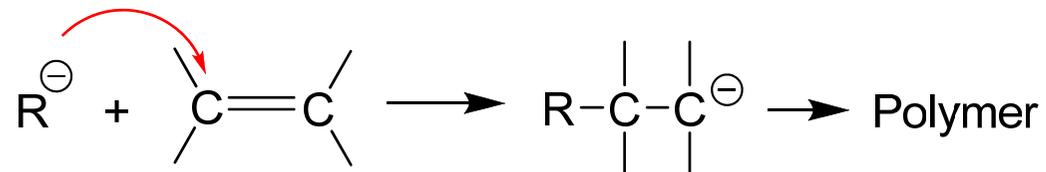
4.3 FREE RADICALS

- A free radical may be defined as a species that contains one or more unpaired electrons.

- Radicals play an important role in *combustion*, *atmospheric chemistry*, *polymerization*, *plasma chemistry*, *biochemistry*, and many other chemical processes, including human physiology.

- The first organic free radical identified was triphenylmethyl radical, by Moses Gomberg (the founder of radical chemistry) in 1900.

Ag

yellow

In benzene the concentration of the radical is 2%.

1

2

4

3

The ^{1}H NMR (ppm)
25 aromatic protons: 6.8 - 7.4
4 olefinic protons: 5.8 - 6.4
a single aliphatic proton: 5
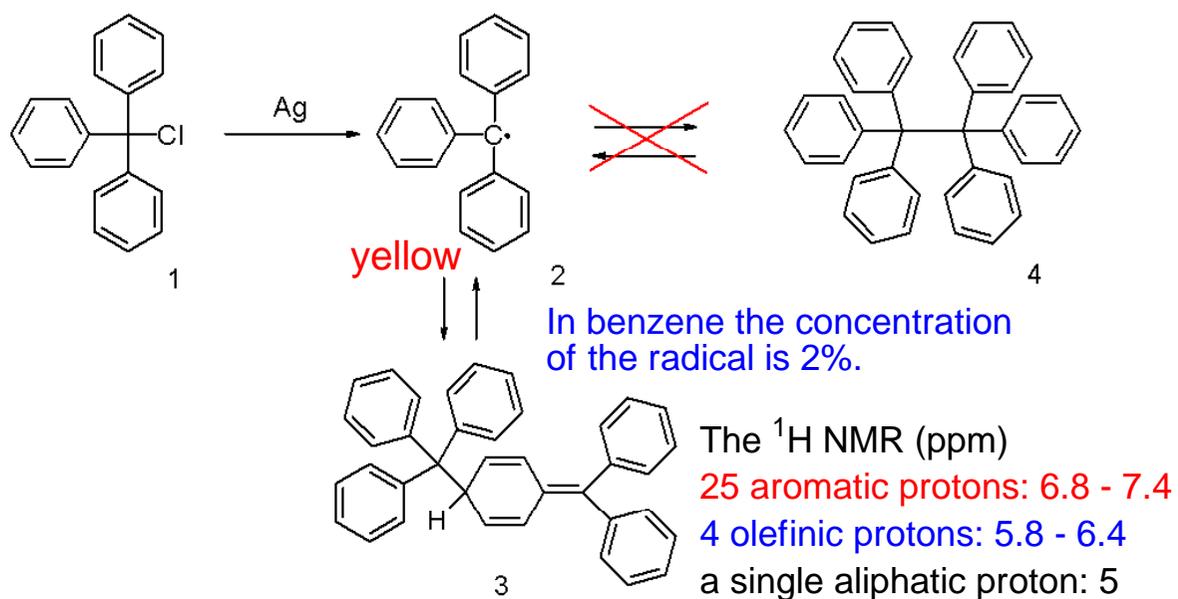
I. Stability and Structure

○ Alkyl radical intermediates are stabilized by similar criteria as carbocations: *the more substituted the radical center is, the more stable it is.*

The stability order for radical: tertiary > secondary > primary

Hyperconjugation:

$$R-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}\cdot \;\longleftrightarrow\; R-\underset{\underset{H}{|}}{\overset{\overset{H\cdot}{|}}{C}}=\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} \;\longleftrightarrow\; R-\underset{\underset{H\cdot}{|}}{\overset{\overset{H}{|}}{C}}=\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}$$
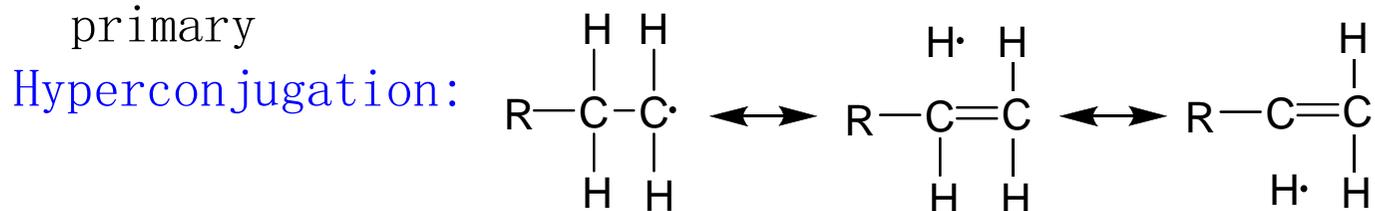
TABLE. The D_{298} values for R–H bonds					
R	D (kJ/mol)	R	D (kJ/mol)	R	D (kJ/mol)
Ph	464	Et	419	Me_3C	401
CF_3	446	Me_3CCH_2	418	Cyclohexyl	400
$CH_2{=}CH$	444	Pr	417	$PhCH_2$	368
Cyclopropyl	444	Cl_3C	401	HCO	364
Me	438	Me_2CH	401	$CH_2{=}CH{-}CH_2$	361
Free radical stability is in reverse order.					

♦ Radicals next to functional groups, such as carbonyl, nitrile, and ether are even more stable than tertiary alkyl radicals.

$$R-\overset{\displaystyle \cdot}{\underset{\underset{\displaystyle \ddot{N}R'_2}{|}}{C}}-C\equiv N: \longleftrightarrow R-\overset{\displaystyle \ominus}{\underset{\underset{\displaystyle \overset{\cdot +}{N}R'_2}{|}}{\ddot{C}}}-C\equiv N: \longleftrightarrow R-\underset{\underset{\displaystyle \overset{\cdot +}{N}R'_2}{|}}{C}=C=\overset{\displaystyle \ominus}{\ddot{N}}:$$

$$\longleftrightarrow R-\underset{\underset{\displaystyle \ddot{N}R'_2}{|}}{C}=C=\overset{\displaystyle \cdot}{\ddot{N}}: \longleftrightarrow R-\underset{\underset{\displaystyle \oplus NR'_2}{\|}}{\overset{\displaystyle \cdot}{C}}-H\overset{\displaystyle \ominus}{\ddot{C}}=\ddot{N}:$$

PUSH-PULL EFFECT

♦ Organic radicals can be long lived if they occur in a conjugated π system.

The radical derived from *alpha*-tocopherol

♦ **PERSISTENT RADICAL** COMPOUNDS ARE THOSE WHOSE LONGEVITY IS DUE TO STERIC CROWDING AROUND THE RADICAL CENTER AND MAKES   I   T PHYSICALLY DIFFICULT FOR THE RADICAL TO REACT WITH ANOTHER MOLECULE.

Examples: Gomberg's triphenylmethyl radical

2,2-Diphenyl-1-picrylhydrazyl (DPPH)

2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO)
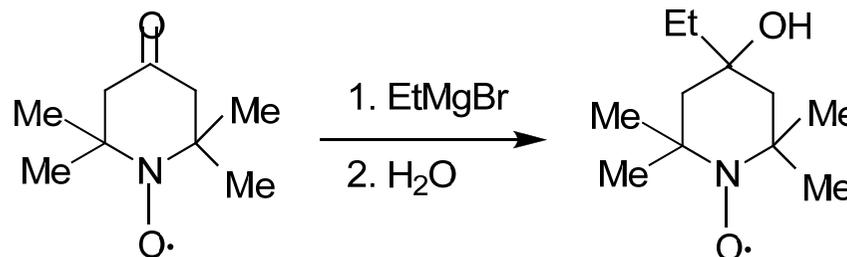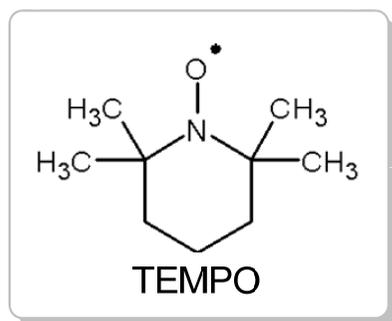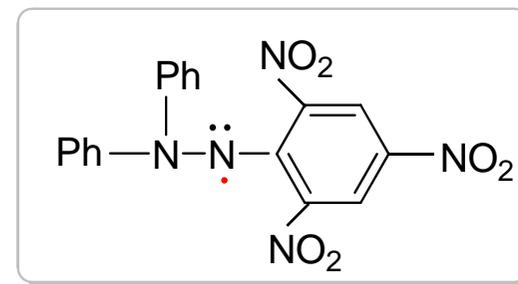
Application of TEMPO: as a radical trap, as a structural probe for biological systems in conjunction with electron spin resonance spectroscopy, as a reagent in organic synthesis, and as a mediator in controlled free radical polymerization.
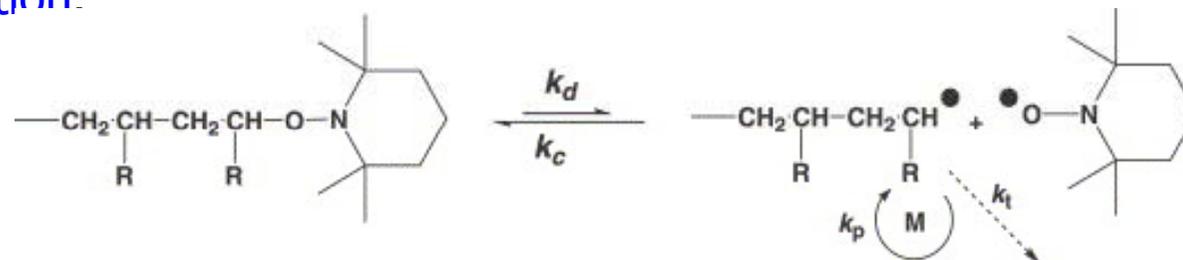
THE GENERATION AND FATE OF FREE RADICALS

- The formation of radicals may involve breaking of covalent bonds homolytically, a process that requires significant amounts of energy.
- Homolytic bond cleavage most often happens between two atoms of similar electronegativity.

$$R-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-R \xrightarrow{\text{heat}} 2\ R-\overset{\overset{O}{\|}}{C}-O\cdot$$

$$R-N=N-R \xrightarrow{\text{heat}} 2\ R^{\cdot} + N_2$$

$$Cl_2 \xrightarrow{h\nu} 2\ Cl\cdot$$

$$R-\overset{\overset{O}{\|}}{C}-R \xrightarrow[\substack{\text{vapor}\\\text{phase}}]{h\nu} R-\overset{\overset{O}{\|}}{C}^{\cdot} + R\cdot$$

$$Ph-\overset{\overset{O}{\|}}{C}-O\cdot \longrightarrow Ph\cdot + CO_2$$
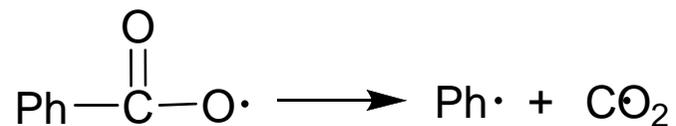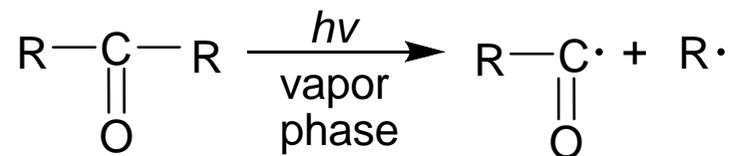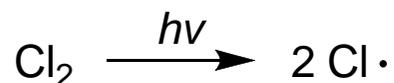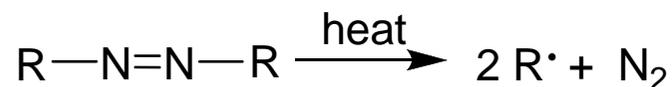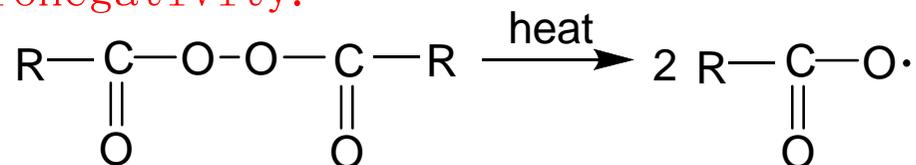
- Free radicals take part in radical addition and radical substitution as reactive intermediates.
- Chain reactions involving free radicals can usually be divided into three distinct processes: *initiation*, *propagation*, and *termination*.

Termination reactions → stable products

$$\text{(i)} \quad R^{\cdot} \; + \; R'^{\cdot} \rightarrow R\!\!-\!\!R$$

$$\text{(ii)} \quad 2CH_3CH_2{}^{\cdot} \rightarrow CH_3CH_3 + CH_2{=}CH_2$$

Propagation reactions → other radicals (which usually react further)

(iii) abstraction of another atom or group, usually a hydrogen atom:

$$R^{\cdot} + R'\!\!-\!\!H \rightarrow R'^{\cdot} + RH$$
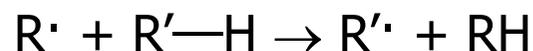
(iv) addition to a multiple bond:

$$R^{\cdot} + \;\diagup\!\!\!\!\!\overset{\displaystyle \diagdown}{C}{=}\overset{\displaystyle \diagup}{C}\!\!\!\!\!\diagdown \; \longrightarrow \; R\!\!-\!\!\overset{|}{\underset{|}{C}}\!\!-\!\!\overset{|}{\underset{|}{C}}{\cdot}$$
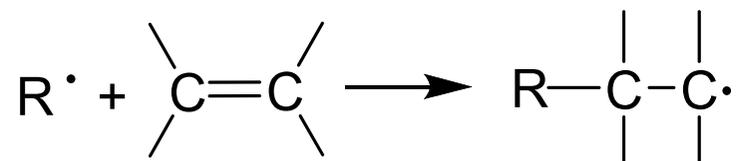
- Refrigerants: Freon. Freon-11 is trichlorofluoromrthane, while Freon-12 is dichlorodifluoromethane. Freon-113 (1,1,2-Trichloro-1,2,2-trifluoroethane).

- $CFCl_3 + h\nu \rightarrow CFCl_2 + Cl\bullet$
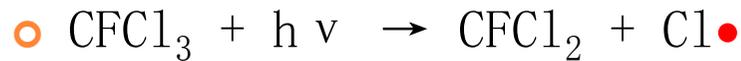
These free radicals then react with ozone in a catalytic chain reaction which destroys the ozone:

- $Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$
- $ClO\bullet + O_3 \rightarrow Cl\bullet + 2\ O_2$

Sources of stratospheric chlorine

15% CH3Cl
3% HCl
Natural
3% HCFC-22
6% CFC-113
10% CH$_3$CCl$_3$
12% CCl$_4$
23% CFC-11
Antropogenic
28% CFC-12
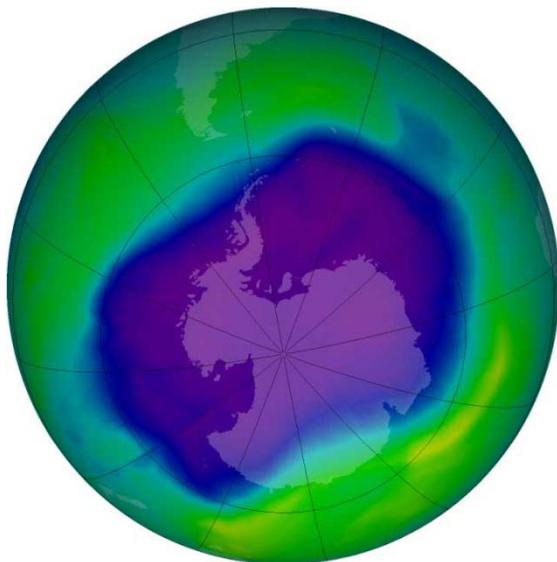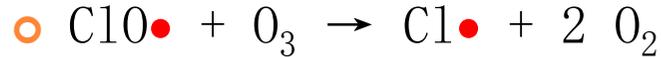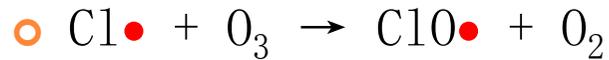
Image of the largest Antarctic ozone hole ever recorded (September 2006)
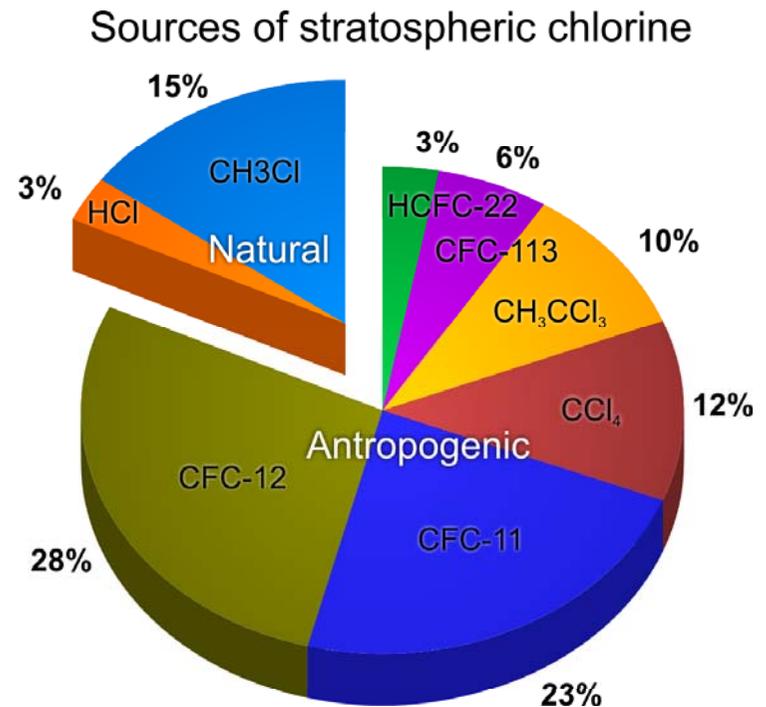
RADICAL IONS

- A radical ion is a free radical species that carries a charge.
- Many aromatic compounds can undergo *one-electron reduction* by alkali metals.

Sodium naphthalenide: the reaction of naphthalene with sodium in an aprotic solvent.

a dark green solution

a red solution

Polystyrene
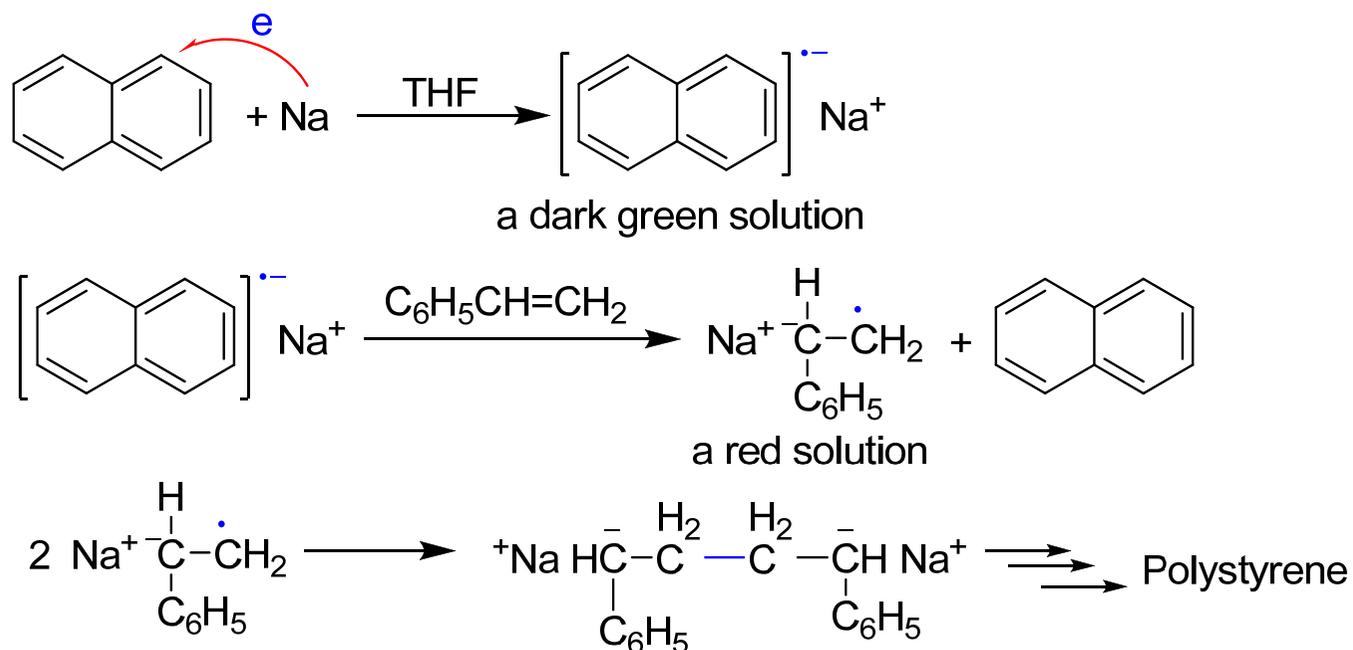
KETYL

○ A `ketyl` group is an anion radical with the general structure C–O· in which an oxygen radical is bonded directly to carbon.
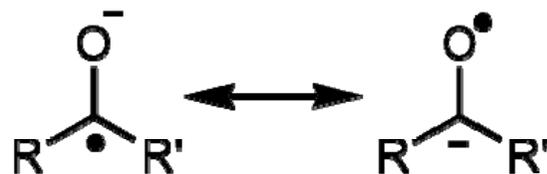
Benzophenone radical anion

Sodium reduces benzophenone to the soluble ketyl radical, which reacts quickly with the water and oxygen dissolved in the solvent. The deep blue coloration qualitatively indicates dry, oxygen-free conditions.

$$Na + Ph_2CO \rightarrow Na^+ + Ph_2CO^{\cdot -}$$
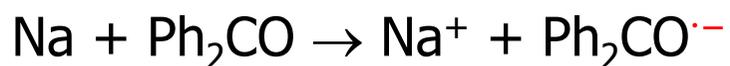
The intense blue coloration due to the benzophenone ketyl radical shows that the toluene is considered free of air and moisture.

RADICAL CATIONS

○ Cationic radical species are much less stable. They appear prominently in mass spectroscopy (MS). When a gas-phase molecule is subjected to electron ionization, one electron is abstracted by an electron in the electron beam to create a radical cation $M^{+\cdot}$. *This species represents the molecular ion or parent ion and will tell the precise molecular weight.*

• Examples:

$$CH_3OH \xrightarrow{-e} [CH_3OH]^{\bullet+} \longrightarrow CH_3^+ + \overset{\bullet}{O}H$$

parent ion
(M)

$$\xrightarrow{-e} C_{10}H_8^{\bullet+} \longrightarrow C_{10}H_9^+ + C_{10}H_7^{\bullet}$$

(M)   (M+1) (M-1)

Sample → Ion Source → Mass Analyzer → Detector → Data Analysis
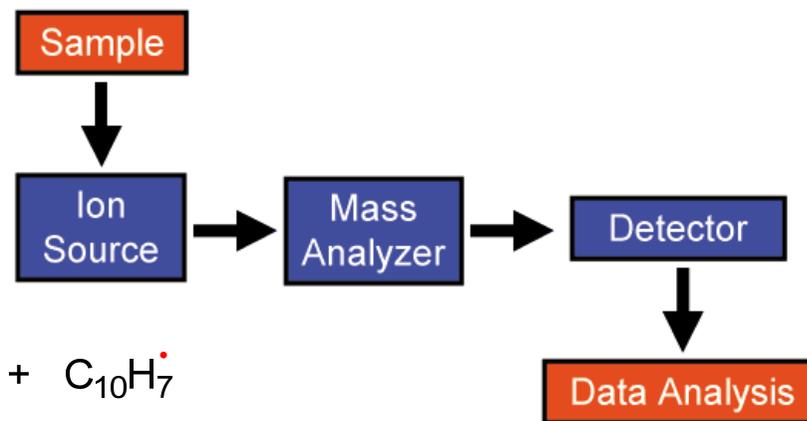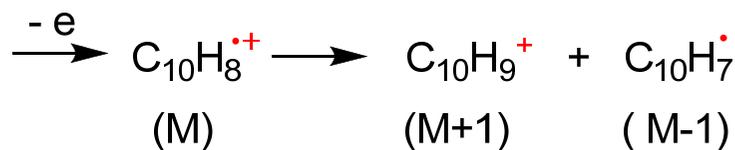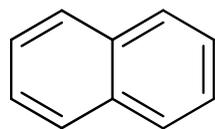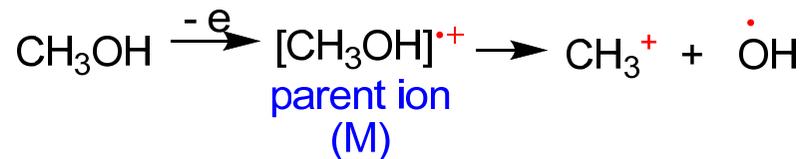
CARBENES

○ A carbene is a **highly reactive species** containing a carbon atom with six valence electrons and having the general formula RR′ C:, practically all having lifetimes considerably under 1 sec.

i. Structure and bonding

125-140°

singlet

the total spin=0
bond angle = 102°
for single methylene
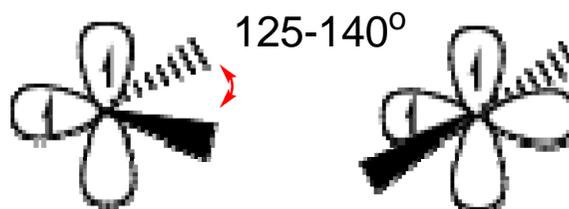
triplet

the total spin=1;
paramagnetic, may be
observed by
electron spin resonance
spectroscopy

triplet

Triplet carbenes are generally stable in the gaseous state, while singlet carbenes occur more often in aqueous media.

○ Singlet and triplet carbenes exhibit divergent reactivity. Singlet carbenes generally participate in cheletropic reactions. Singlet carbenes with unfilled p-orbital should be electrophilic. Triplet carbenes can be considered to be diradicals, and participate in stepwise radical additions.

Addition to C=C:

cheletropic reaction
stereospecific
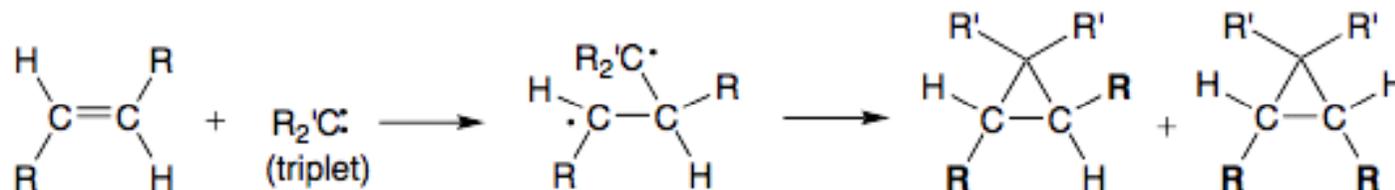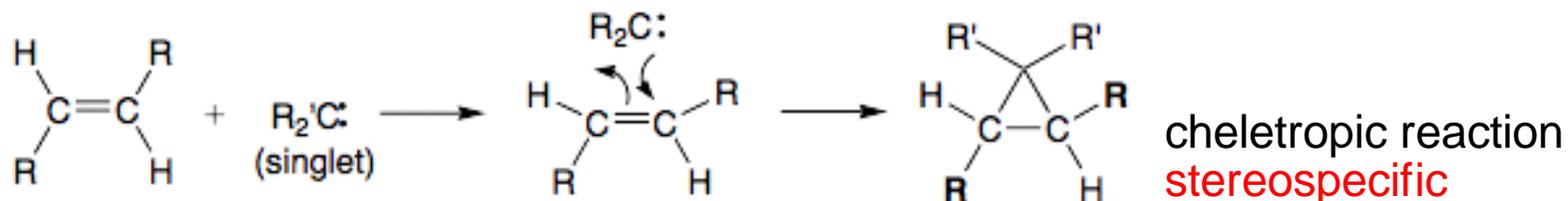
stepwise radical addition, may be stereoselective

INSERTION REACTION

(one step insertion)   **3**   :   **1**
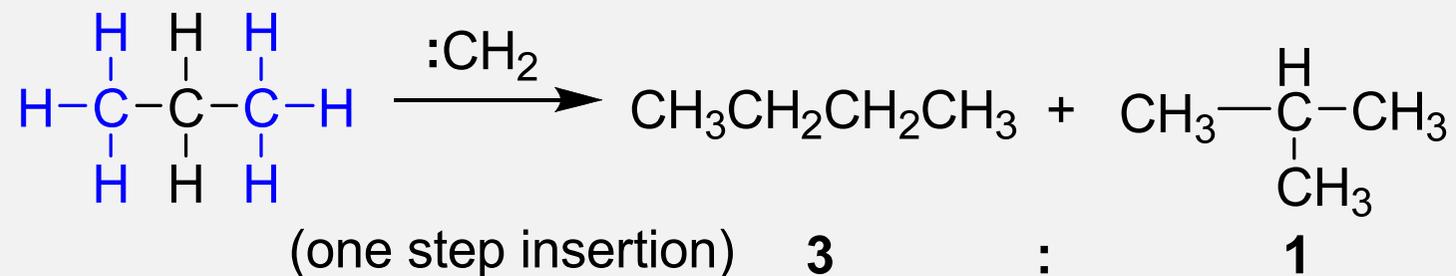
- The order of preference: X–H (where X is not carbon) > C–H > C–C
  Insertions may or may not occur in single step.

- When an intramolecular insertion is possible, no intermolecular insertions are seen. *In flexible structures, five-membered ring formation is preferred to six-membered ring formation.*

51

(intermolecular insertion of carbene)
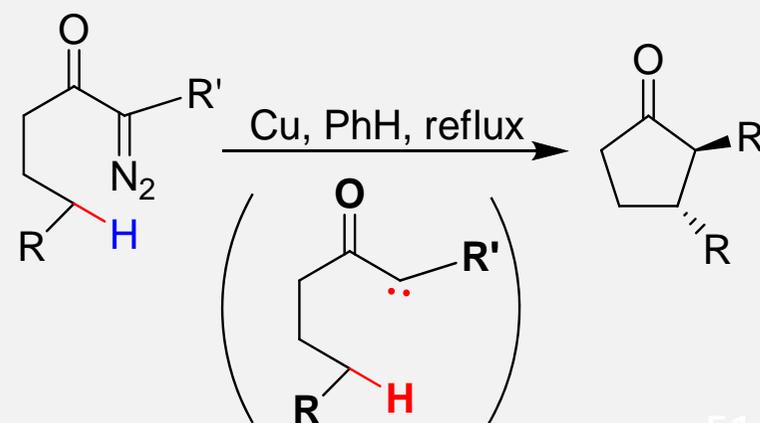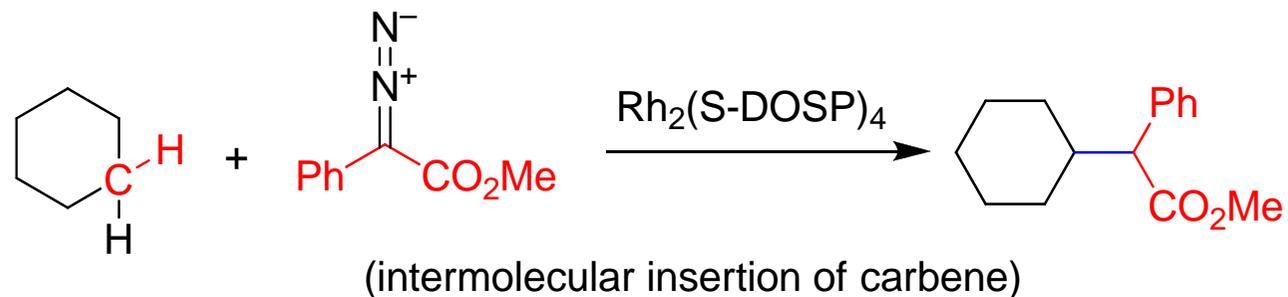
○ Alkylidene carbenes are alluring in that they offer formation of cyclopentene moieties. To generate an alkylidene carbene a ketone can be exposed to trimethylsilyl diazomethane.

An alkylidene carbene
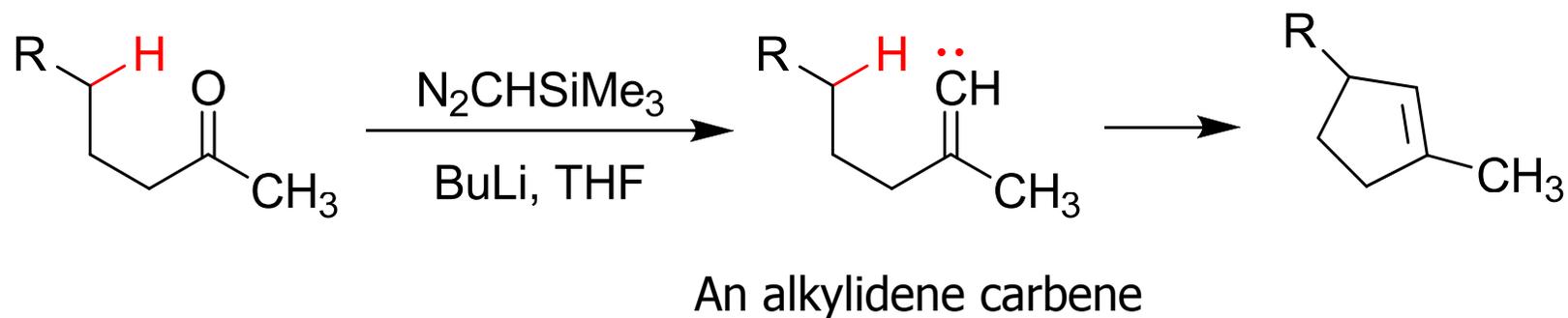
- **Disintegration of** diazoalkanes and their analogs, via photolytic, thermal, or transition metal (Rh, Cu)-catalyzed routes.

$$H_2C=N^+=N^- \xrightarrow[\text{pyrolysis}]{h\nu} \ddot{C}H_2 \; + \; :N\equiv N:$$

$$H_2C=C=\ddot{O}: \xrightarrow[\text{pyrolysis}]{h\nu} \ddot{C}H_2 \; + \; :C\equiv O:$$

$$R_2C\underset{\ddot{N}}{\overset{\ddot{N}}{\diagdown \diagup}} \longrightarrow \ddot{C}R_2 \; + \; :N\equiv N:$$

$$+ \quad H_3C-O-\overset{\displaystyle O}{\overset{\|}{C}}-CH=N^+=N^- \xrightarrow{\text{CuCN}}$$

$$\left(H\ddot{C}\overset{\displaystyle O}{\overset{\|}{-C}}-O-CH_3 \right)$$

○ Base-induced α-elimination

$$R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}-Cl \xrightarrow{-H^+} R-\overset{\overset{\displaystyle \ominus}{\ddot{C}}}{\underset{\underset{\displaystyle R}{|}}{C}}-Cl \xrightarrow{-Cl^{\ominus}} R-\overset{\displaystyle \ddot{C}}{\underset{\underset{\displaystyle R}{|}}{}}$$

$$Cl_3C-COO^- \longrightarrow :CCl_2 + CO_2 + Cl^-$$

 $\longrightarrow$ $+$ $:CH_2$
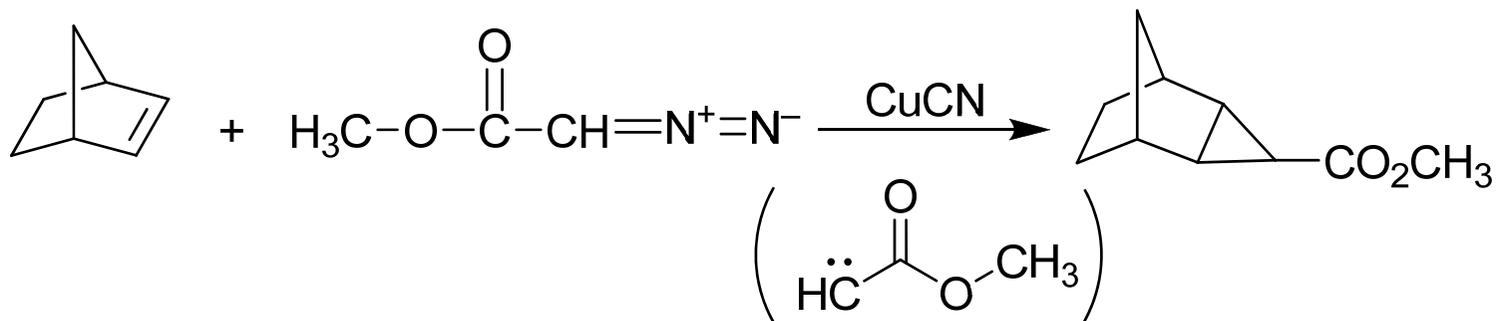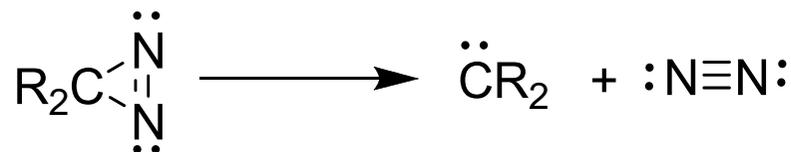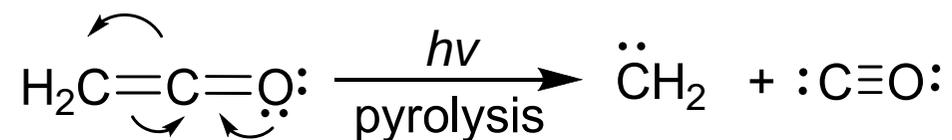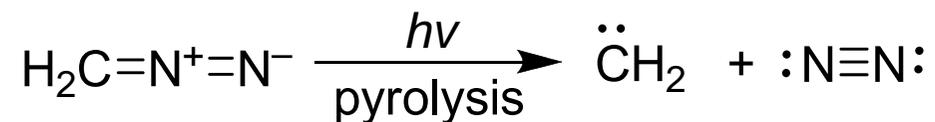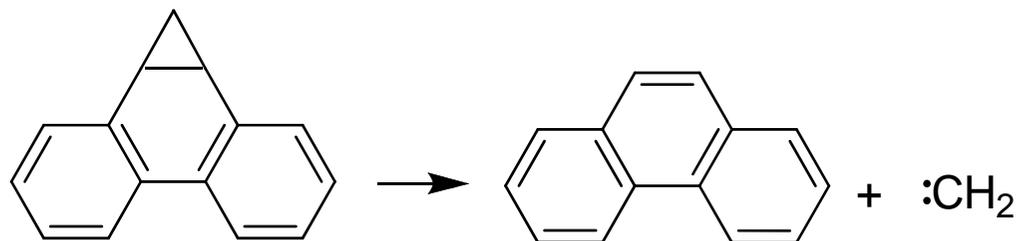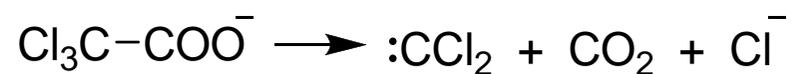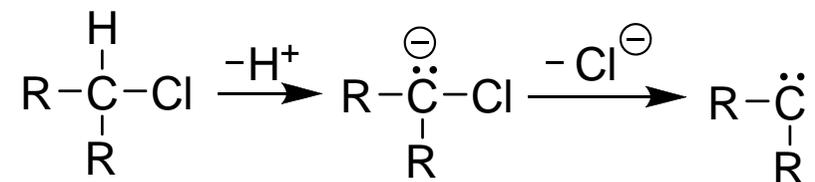
• Carbenes are intermediates in the *Wolff rearrangement*.
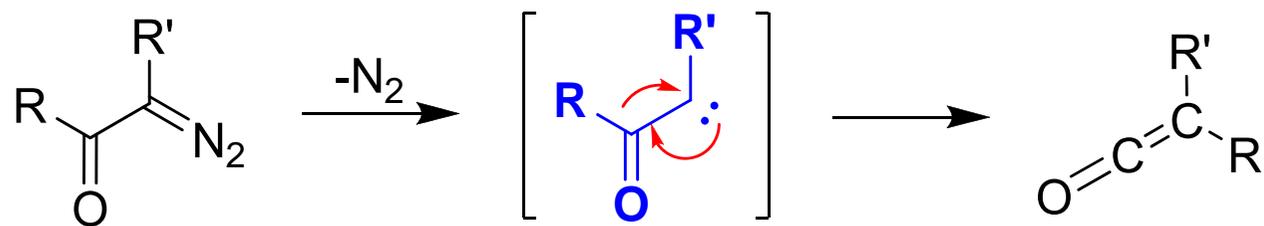
APPLICATIONS OF CARBENES

o A large scale application of carbenes is the industrial production of tetrafluoroethylene. Tetrafluoroethylene is generated via the intermediacy of difluorocarbene:

$$CHCl_3 + 2\ HF \rightarrow CHClF_2 + 2\ HCl$$

$$CHClF_2 \rightarrow :CF_2 + HCl$$

$$2\ :CF_2 \rightarrow F_2C=CF_2$$

• Polytetrafluoroethylene (PTFE, mp **327°C** the DuPont brand name **Teflon**) is a synthetic fluoropolymer of tetrafluoroethylene which finds numerous applications: used as a non-stick coating for pans and other cookware.
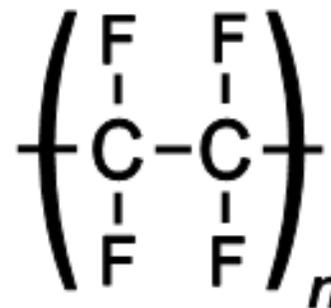
NITRENES

○ A **nitrene** (R–N:) is the nitrogen analogue of a carbene. The nitrogen atom has only 6 electrons available and is therefore considered an electrophile. A nitrene is a reactive intermediate and is involved in many chemical reactions.

$$R \text{———} \overset{..}{N}:$$

The structure of a typical nitrene group

- Formation of nitrenes
➤ from <u>thermolysis</u> or photolysis of <u>azides</u>.
➤ from <u>isocyanates</u>, with expulsion of CO.

tosyl azide

$$R-N=C=O \xrightarrow{- CO} R-\overset{..}{\underset{.}{N}}:$$
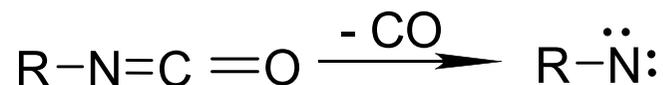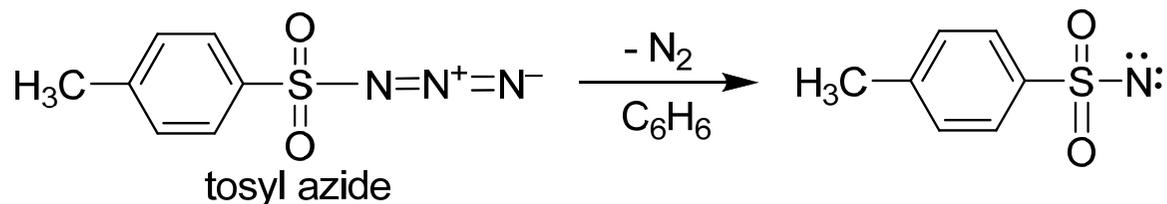
o **Nitrene C-H insertion.** A nitrene can easily insert into a C–H bond yielding an amine or amide.

Org. Lett. **9**, 981(2007)
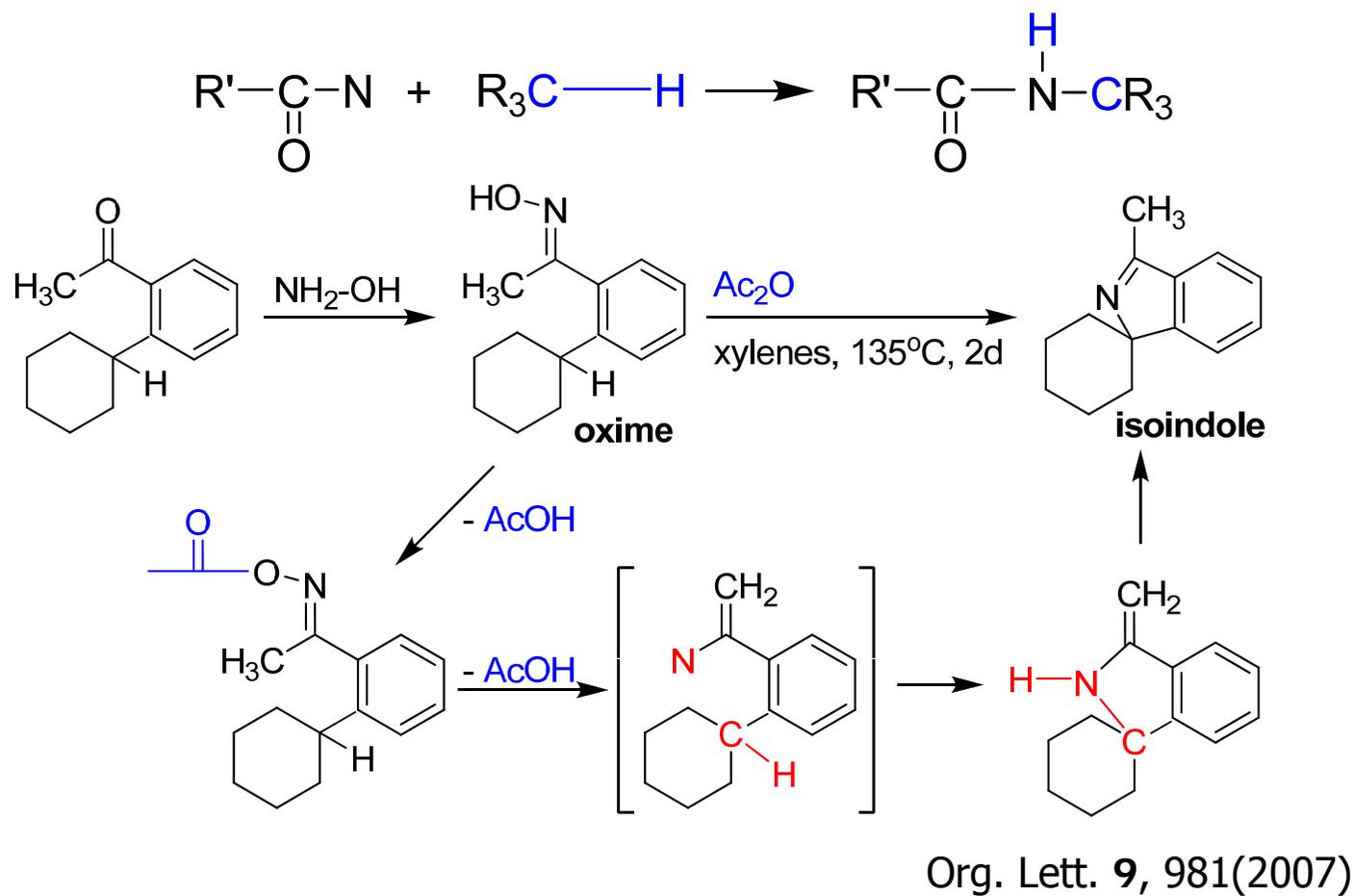
- **Nitrene cycloaddition.** With alkenes, nitrenes react to aziridines.

$$R-N + \ \ ^{}C=C^{} \longrightarrow \text{aziridines}$$

Ex. 1

stilbene

Cu(acac)$_2$, acetonitril

A precursor of nitrene

J. Org. Chem. **71**, 5876(2006)

Ex. 2

(N-sulfonyloxy precursor)

ethoxycarbonylnitrene
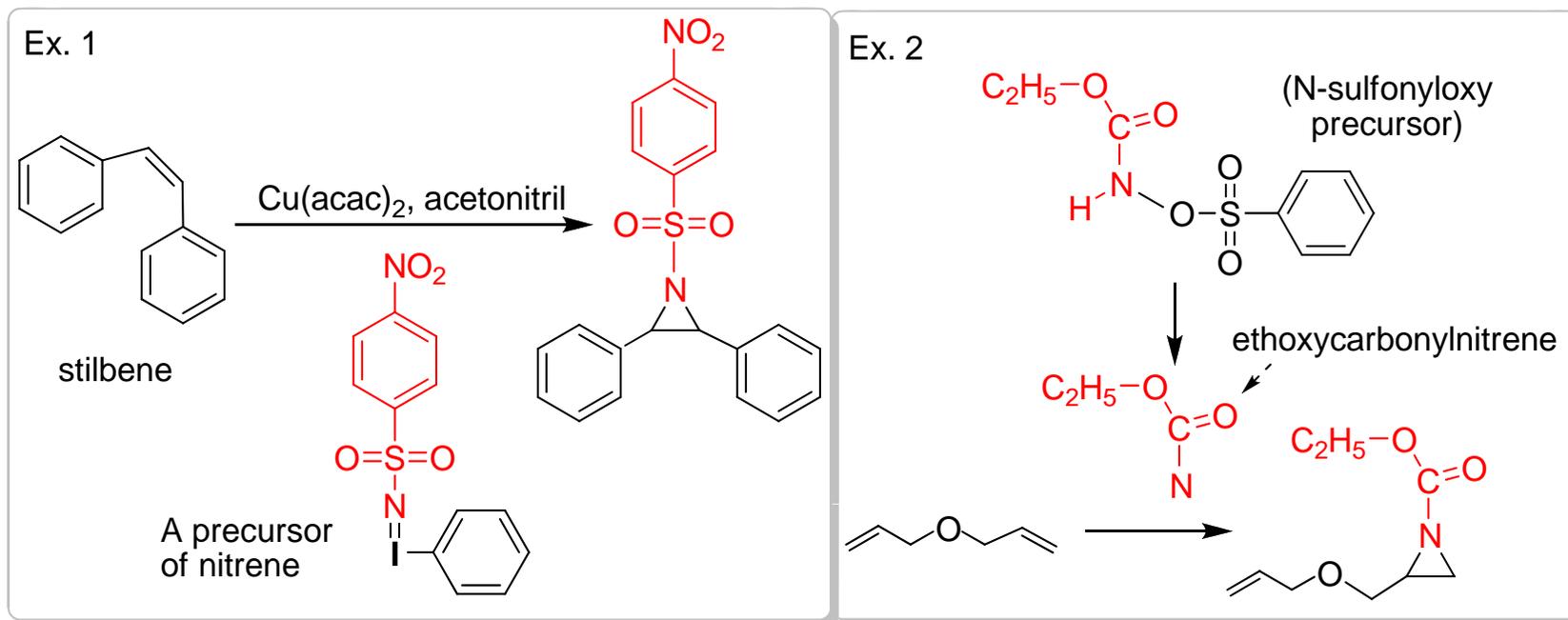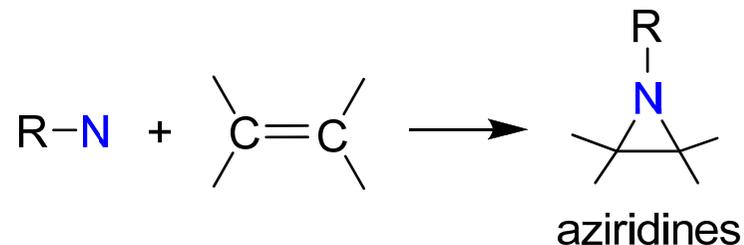
Tetrahedron Letters, **25**, 4271(1984)

Determining Reaction Mechanisms

1. Identification of reaction products
2. Determination of Intermediates

$\rightarrow$ Determining no. of steps
(a one step reaction, with reactant $\rightarrow$ Transition State $\rightarrow$ product, is   an elementary reaction)

if more than one elementary steps, an intermediate is involved

$$\text{reactant} \xrightarrow{k_1} \text{intermediate} \xrightarrow{k_2} \text{product}$$

depending on the magnitude of k_1, k_2, the concentration of intermediate can be high or low
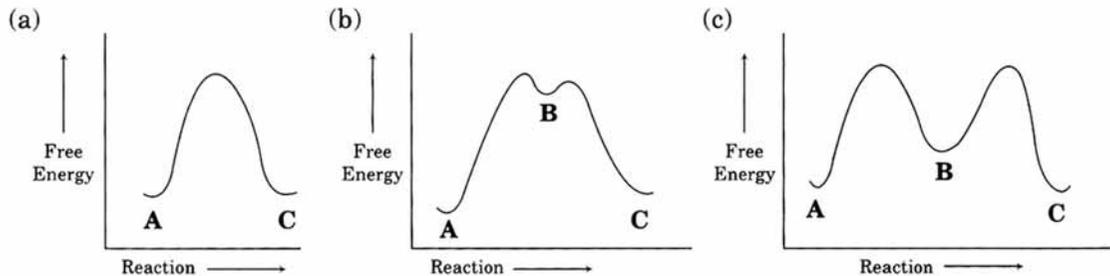
$\rightarrow$ Isolating intermediate
quench the reaction (by cooling, by diluting, by removing catalyst,…..)

$\rightarrow$ Spectroscopic characterization
UV-VIS, IR, NMR, ESR……

If not isolable, not spectroscopically observable,
$\rightarrow$ trap the intermediate by a trapping agent

R· + C₆H₅–N=O (Spin trap) → C₆H₅–N(–O·)–R less reactive

(alkene) $\xrightarrow[CCl_4]{Br_2}$ (dibromide product)

(alkene) $\xrightarrow[\substack{CCl_4 \\ CH_3OH}]{Br_2}$ (dibromide) + (bromo-methoxy product) indicate carbocation mechanism
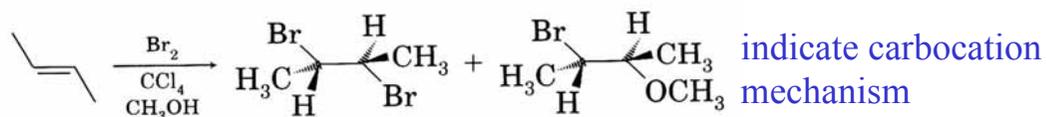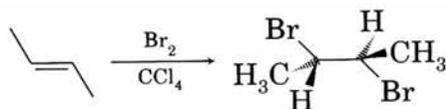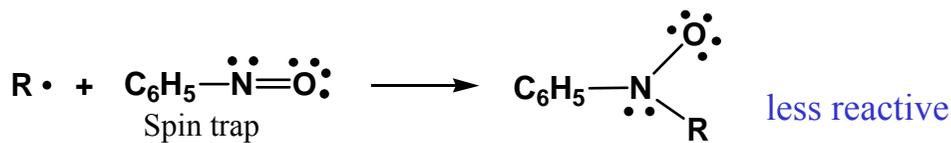
→ Disprove an intermediate
  synthesize a proposed intermediate and compare the
  reaction properties…

→ Crossover Experiment
  To differentiate intra-molecular or inter-molecular
                                    (inter fragmental)

?
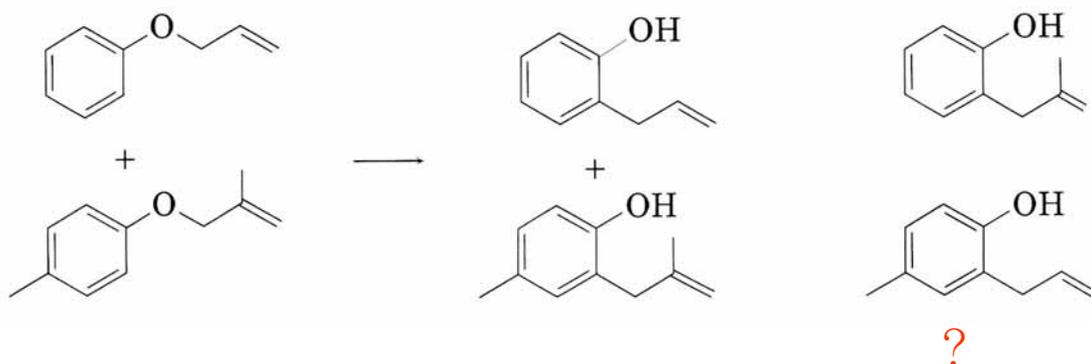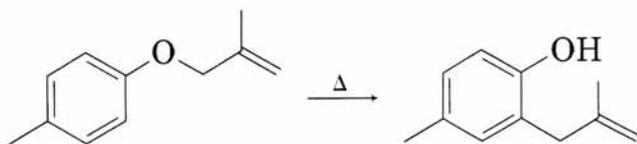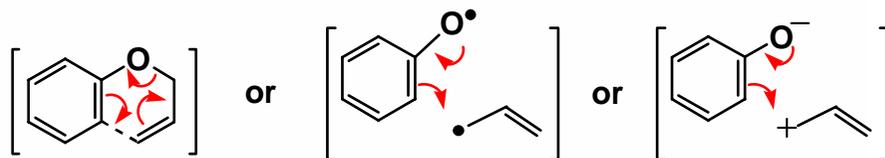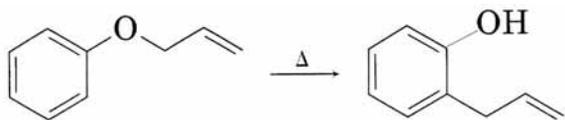
→ Isotope labeling

the least perturbation to a system is by isotope replacement

* = ^{14}C ONLY   Not Observed   3,3-sigmatopic

dissociative radical mech.

* = ^{14}C
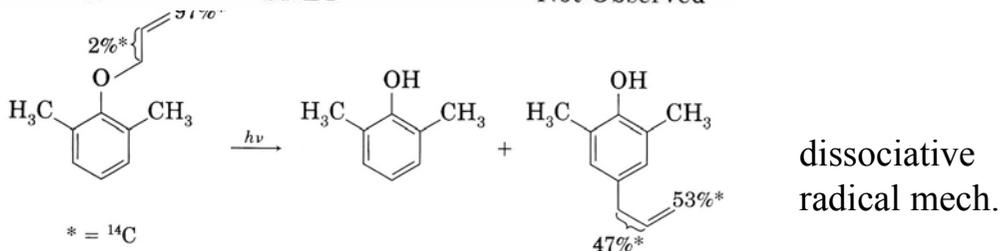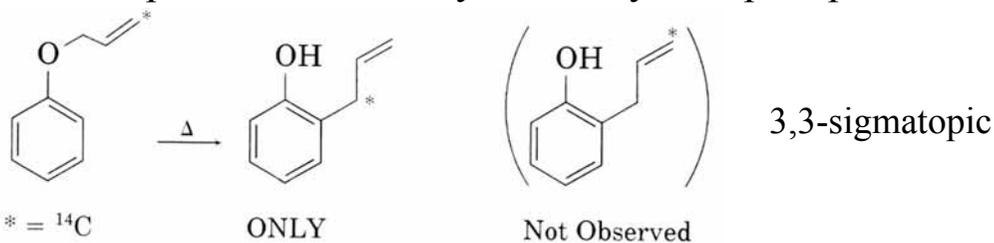
→ Stereochemical Studies

suggest inversion of reaction center

(S)   (R)

(R)

(R)

(S) suggest an achiral reaction center

Br_2 rule out
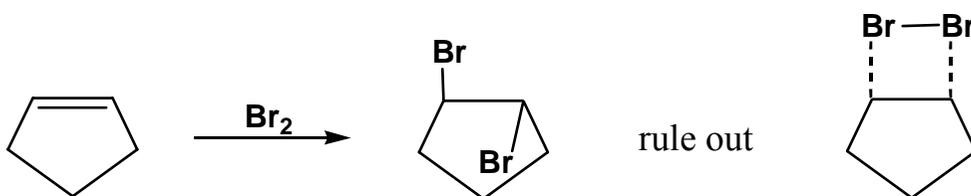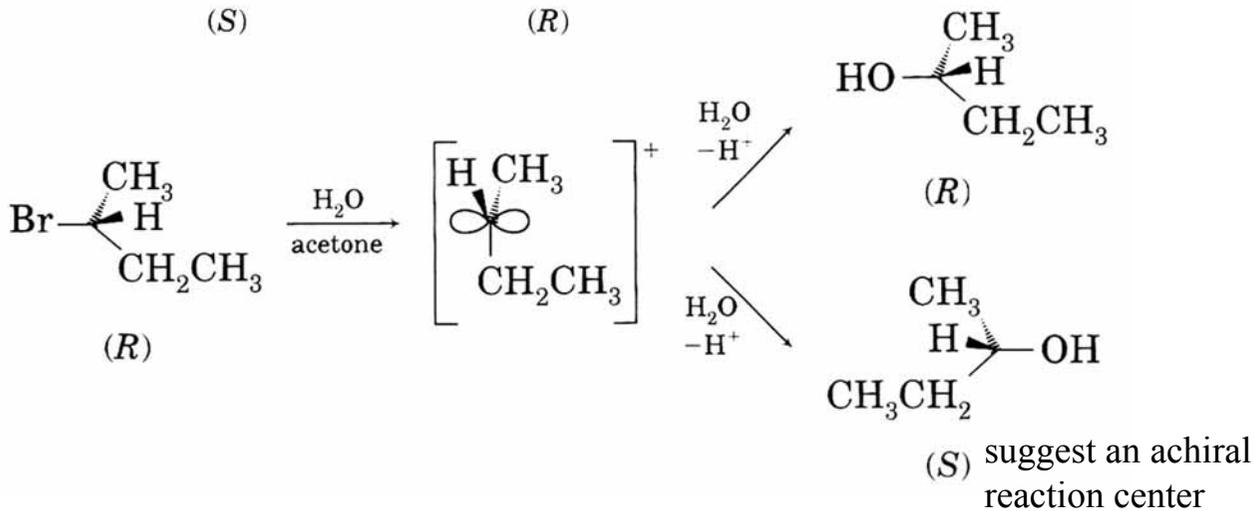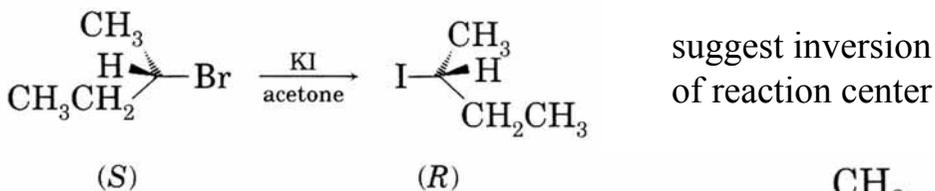
→ **Solvent Effect**

Solvent affects reaction rate through relative stabilization of reactants / transition →deduce T.S. structure

e.g

S_{N1} $(CH_3)_3C\text{-}Cl \overset{\delta^+ \quad \delta^-}{\longrightarrow} (CH_3)_3\overset{\delta^+}{C}\cdots\overset{\delta^-}{Cl} \xrightarrow{Nu^-} (CH_3)_3C\text{-}Nu + X^-$

the rate increases with increasing solvent polarity.
→ more ionic character in T.S. than the reactant

S_{N2} $OH^- + CH_3\text{-}Br \longrightarrow [\ \overset{\delta^-}{HO}\cdots CH_3 \cdots \overset{\delta^+}{Br}\ ] \longrightarrow CH_3OH + Br^-$

The rate decreases with increasing solvent polarity
→ less ionic character in T.S. than starting material

Measurement of solvent polarity：

μ：dipole moment (a molecular property)

+ e   -e $+e = 4.8\times10^{-10}$ esu, for $r = 1\times10^{-8}$ cm
$\underbrace{}_{r}$ $\mu = e \cdot r = 4.8\times10^{-18}$ esu $\cdot$ cm
                         $= 4.8$ D

ε：dielectric constant, effect of substance on the E-field between an capacitor, relating to polarity and polarizability

$$E = \frac{E_0}{\varepsilon}$$
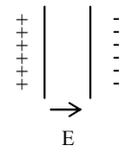
Hexane	1.89	H_2O	78.4
CCl_4	2.23	MeOH	32.7
$CHCl_3$	4.8	EtOH	24.5
		n-PrOH	20.4

Z：Kosower scale
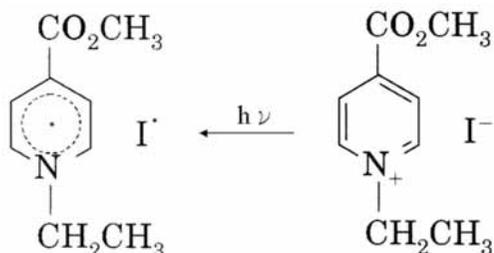
the charge-transfer band is sensitive to solvent

the transition energy：$Z = E_T$

$E_T(30)$

charge-transfer band
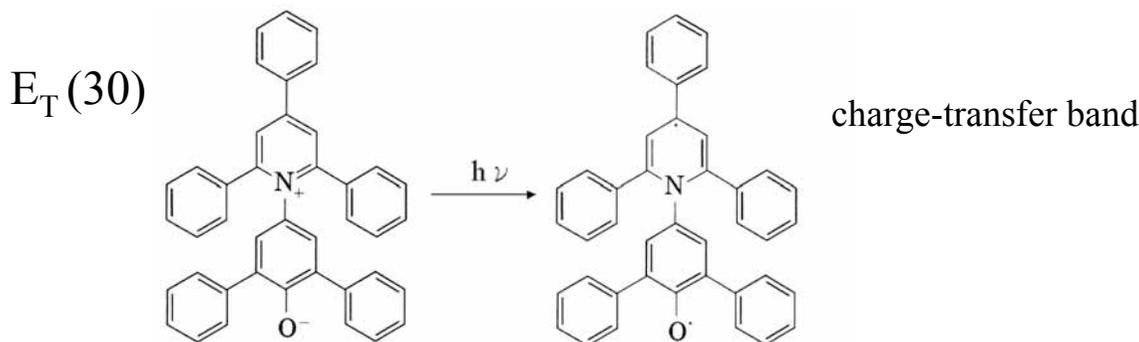
α：acidity as H-bonding Donor (the ability of the solvent to donate a proton in solvent-solute H-bond)

β：basicity as H-bonded Acceptor

Table 6.1 Solvent parameters.

Solvent	ϵ^a	$\mu(D)^a$	Z^b	$E_T(30)^c$	π^*	β	α^f
Formamide	111.0	3.37	83.3	56.6	0.97	0.48[g]	0.71
Water	78.4	1.8	94.6	63.1	1.09	0.47[g]	1.17
Formic acid	58.5	1.82		54.3	0.65[g]	0.38[g]	1.23[g]
Dimethyl sulfoxide	46.5	4.06	71.1	45.1	1.00	0.76	0.00
N,N-Dimethylformamide	36.7	3.24	68.5	43.8	1.00[g]	0.76[g]	0.00
Nitromethane	35.9	3.56		46.3	0.85	0.06[g]	0.22
Acetonitrile	35.9	3.53	71.3	45.6	0.75	0.40[g]	0.19
Methanol	32.7	2.87	83.6	55.4	0.60	0.66[g]	0.93
Hexamethylphosphoramide	29.3	4.31	62.8[d]	40.9	0.87[g]	1.05[g]	0.00
Ethanol	24.5	1.66	79.6	51.9	0.54	0.75[g]	0.83
1-Propanol	20.4	3.09	78.3	50.7	0.52	0.90[g]	0.84[g]
1-Butanol	17.5	1.75	77.7	50.2	0.47	0.84[g]	0.84[g]
Acetone	20.6	2.69	65.7	42.2	0.71	0.43[g]	0.08
2-Propanol	19.9	1.66	76.3	48.4	0.48	0.84[g]	0.76
Pyridine	12.9	2.37	64.0	40.5	0.87	0.64	0.00
t-Butyl alcohol	12.5	1.66	71.3	43.3	0.41	0.93[g]	0.42[b]
Methylene chloride	8.9	1.14	64.2	40.7	0.82	0.10[g]	0.13[g]
Tetrahydrofuran	7.58	1.75		37.4	0.58	0.55	0.00
1,2-Dimethoxyethane	7.20	1.71	62.1[d]	38.2	0.53	0.41	0.00
Acetic acid	6.17	1.68	79.2	51.7	0.64	0.45[g]	1.12
Ethyl acetate	6.02	1.82		38.1	0.55	0.45	0.00
Chloroform	4.80	1.15	63.2[e]	39.1	0.58	0.10[g]	0.20[g]
Diethyl ether	4.2	1.15		34.5	0.27	0.47	0.00
Benzene	2.27	0	54.0[d]	34.3	0.59	0.10	0.00
Carbon tetrachloride	2.23	0		32.4	0.28	0.10[g]	0.00
n-Hexane	1.89	0.085		31.0	−0.04[g]	0.00	0.00

[a]Data from the compilation in reference 34. [b]Data from reference 38. [c]Data from the compilation in reference 39, pp. 365–371. [d]Data from the compilation in reference 35, p. 301. [e](0.13 M EtOH). [f]Values for π^*, β, and α from reference 40. [g]Data from the compilation in reference 42.

Application of Kinetics in Studying Rxn   Mechanism

reaction rate：rate of change of concentration of reactant or product

For a reaction

$$n_A A + n_B B + n_C C \rightarrow n_P P$$
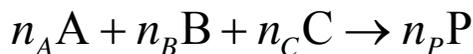
$$\text{rate} = -\frac{1}{n_A}\frac{dA}{dt} = -\frac{1}{n_B}\frac{dB}{dt} = -\frac{1}{n_C}\frac{dC}{dt} = \frac{1}{n_P}\frac{dP}{dt}$$

$$= k_r [A]^a [B]^b [C]^c$$

overall reaction order = a + b + c. ← determined by experiment
not by stoichiometry

(For elementary reaction

the order of the reaction = the no. of reacting molecule
= molecularity   )

Pseudo order：if one reactant doesn't change its concentration significantly, e.g. [C] ≒ const

rate = $k'[A]^a[B]^b$, reaction order = a + b

e.g.   ROTs $\xrightarrow{\text{aq EtOH}}$ R-OEt   pseudo first order

zero order

$$A \xrightarrow{\ k\ } \text{product}$$
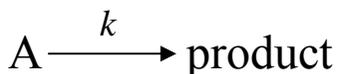
$$\text{rate} = -\frac{dA}{dt} = k \qquad \int -dA = \int k dt$$
Differential rate equation

$$A - A_0 = -kt$$ Integration rate equation
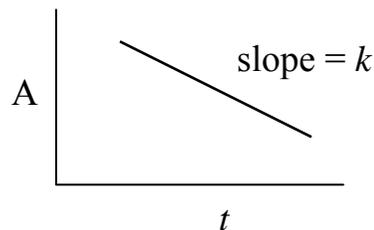
e.g.   Saturation reaction on the surface of a metal

half life $t^{1/2}$ = the time for $A = \dfrac{A_0}{2}$

$$\frac{A_0}{2} - A_0 = -kt^{1/2}, \qquad t^{1/2} = \frac{A_0}{2k}$$

(graph: A vs t, straight line with slope = k)

First order reaction

$$A \xrightarrow{\quad k \quad} P$$
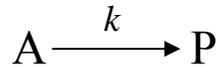
$$-\frac{d[A]}{dt} = k[A], \qquad \int \frac{d[A]}{[A]} = -\int k\,dt$$

$$ln\frac{[A]}{[A]_0} = -kt, \qquad [A] = [A]_0 e^{-kt}, \qquad t_{1/2} = \frac{ln2}{k} = \frac{0.693}{k}$$

plot $\quad ln[A] \quad$ v.s $\quad t \quad \rightarrow$ straigh line, slope $= -k$

Second order reaction

type 1 $\qquad\qquad 2A \xrightarrow{\quad k \quad} P$

$$\frac{d[P]}{dt} = -\frac{d[A]}{2dt} = k[A]^2,$$

$$\frac{d[A]}{2[A]^2} = -kdt, \qquad \int \frac{d[A]}{[A]^2} = -\int 2kdt, \qquad \frac{1}{[A]} - \frac{1}{[A]_0} = 2kt$$

plot $\quad \dfrac{1}{[A]} \quad$ v.s $\quad t \quad \rightarrow$ straigh line slope $= 2k$

$t_{1/2}$: $\qquad \dfrac{2}{[A]_0} - \dfrac{1}{[A]_0} = 2kt_{1/2} \qquad t_{1/2} = \dfrac{1}{2k[A]_0}$

type 2 $\qquad\qquad A + B \xrightarrow{\quad k_2 \quad} P$

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k_2[A][B],$$

$$ln\frac{[A]}{[B]} + ln\frac{[B]_0}{[A]_0} = ([A]_0 - [B]_0)k_2 t,$$

plot $\quad ln\dfrac{[A]}{[B]} \quad$ v.s $\quad t \quad \rightarrow$ straigh line slope $= ([A]_0 - [B]_0)k_2$

Reversible reaction

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

$$-\frac{dA}{dt} = \frac{dB}{dt} = k_1 A - k_{-1} B \quad , \qquad A_0 + B_0 = A + B$$

$$-\frac{dA}{dt} = k_1 - k_{-1}(A_0 + B_0 - A)$$
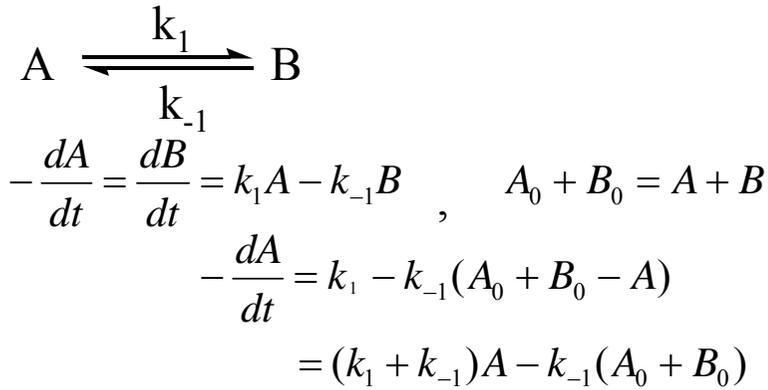
$$= (k_1 + k_{-1})A - k_{-1}(A_0 + B_0)$$

$$\int \frac{dA}{(k_1 + k_{-1})A - k_{-1}(A_0 + B_0)} = \int - dt \quad \because \int \frac{dx}{a+bx} = \frac{1}{b}\ln(a+bx)$$

$$\frac{1}{k_1 + k_{-1}}\ln[(k_1 + k_{-1})A - k_{-1}(A_0 + B_0)] = -t + const.$$

at $t = 0$

$$const. = \frac{1}{k_1 + k_{-1}}\ln[(k_1 + k_{-1})A_0 - k_{-1}(A_0 + B_0)]$$

subst. into above eq.

$$\ln\frac{(k_1 + k_{-1})A_0 + k_{-1}(A_0 + B_0)}{(k_1 + k_{-1})A - k_{-1}(A_0 + B_0)} = (k_1 + k_{-1})t$$

$$\ln\left(\frac{k_1 A_0 + k_{-1} B_0}{k_1 A + k_{-1}A - k_{-1}A_0 - k_{-1}B_0}\right) = (k_1 + k_{-1})t$$

at $t = \infty$ $A = A_\infty$, $B = B_\infty$ $\qquad k_{eq} = \frac{B_\infty}{A_\infty} = \frac{k_1}{k_{-1}} \qquad k_1 = k_{-1}\frac{B_\infty}{A_\infty}$

$$\ln\frac{k_{-1}\dfrac{A_0}{A_\infty} B_\infty - k_{-1}B_0}{k_{-1}\dfrac{B_\infty}{A_\infty} A - k_{-1}B} = (k_1 + k_{-1})t$$

$$\ln\left(\frac{A_0 B_\infty - A_\infty B_0}{B_\infty A - BA_\infty}\right) = (k_1 + k_{-1})t$$

plot left hand side v.s. t → slop = $k_1 + k_{-1}$

→ k_1, k_{-1} from $k_1 = k_{-1}\dfrac{B_\infty}{A_\infty}$

more common simplification : Pseudo first order

$$A + B \longrightarrow P \quad \text{let } [B] >> [A] \text{ so that } [B] \text{ is relatively constant}$$

$$-\frac{d[A]}{dt} = k'[A] \qquad \text{where } k' = k_2[B]$$

$$\Rightarrow \ln \frac{[A]}{[A_0]} = -k't$$

third order reaction

$$3A \longrightarrow \text{product}$$

$$rate = -\frac{d[A]}{3dt} = k[A]^3$$

$$2A + B \longrightarrow \text{product}$$
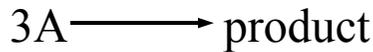
$$rate = -\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A]^2[B]$$

$$A + B + C \xrightarrow{\quad k \quad} \text{product}$$

$$rate = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = -\frac{d[C]}{dt} = k[A][B][C]$$

For consecutive and irreversible reaction

$$A \xrightarrow{\quad k_1 \quad} B \xrightarrow{\quad k_2 \quad} C$$

$$rate = \frac{d[C]}{dt} = k_2[B]$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B], \qquad -\frac{d[A]}{dt} = k_1[A], \qquad [A] = [A]_0 e^{-k_1 t}$$

$$\Rightarrow C = A_0 - A_0 e^{-k_1 t} - \frac{k_1 A_0}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t})$$

Experimental methods for determination of reaction orders

(1) method of integration

$$-\frac{dA}{dt} = k[A]^a[B]^b[C]^c \quad \text{evaluation of a, b, c by integration plot}$$

(2) method of half life

$t_{1/2} \propto A_0{}^{1-n}$, n is the order

determine the relationship between $t_{1/2}$ and $A_0 \Rightarrow$ order

(3) method of isolation --------Pseudo orders

$$-\frac{dA}{dt} = k[A]^a[B]^b[C]^c$$

make the concentration of B and C extremely large

so that they don't change with progress of rxn.

(4) Differential method
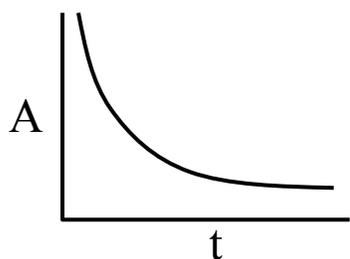
monitor the conc. of A v.s. t

$$-\frac{dA}{dt} \approx \frac{\Delta A}{\Delta t}$$

$\text{if } -\frac{dA}{dt} = kA^n \quad \log(-\frac{dA}{dt}) = \log k + n\log A$

determine several $-\frac{dA}{dt}$, plot $\log(-\frac{dA}{dt})$ v.s. $\log A$

the slope is the order of A

no matter what the order is,

$\log(-\frac{dA}{dt})$ v.s. $\log A$ is always a straight line, with slope n

Kinetic Isotope Effect
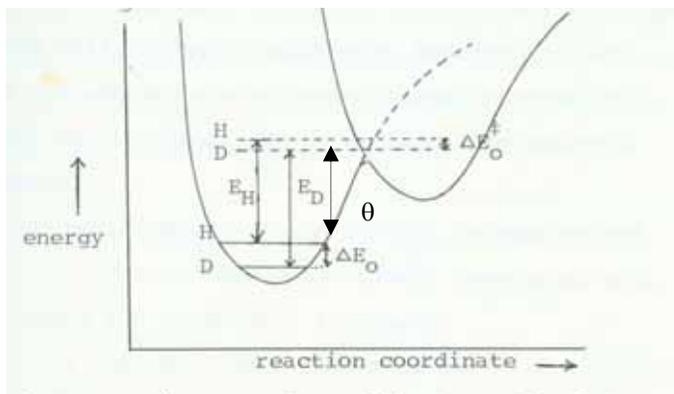
the KIE results from the zero point energy difference for H- or D- substituted species

$$E_D - E_H = (\theta + \Delta E_o) - (\theta + \Delta E^{\ddagger}_o) = \Delta E_o - \Delta E^{\ddagger}_o$$

due to anharmonicity

zero point energy $E_0 = \dfrac{1}{2}h\nu_0$

$$\nu_0 = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{\mu}}$$

force const.

reduced mass

e.g. for a C-H bond, $\nu_{C-H} \sim 3000 cm^{-1}$

replaced by D, $\nu_{C-D} \sim 2100 cm^{-1}$

In ground state, the zero point energy differs by ΔE_0, in transition state, zpe differs by $\Delta E_0^{\ddagger}$, (usually $\Delta E_0^{\ddagger} < \Delta E_0$) depend on the extent of C-H bond breakage, k_H/k_D may very.

$$k_H/k_D = \exp\{(\Delta E_0 - \Delta E_0^{\ddagger})/RT\}$$

for C-H k_H/k_D maximum value at room temp. ~7 for primary KIE

depend on the ext. of bond cleavage, $1 < k_H/k_D < 7$

Information provided by primary KIE：

1. $k_H/k_D > 2 \rightarrow$ strong evidence that the C-H bond is broken in T.S.

2. the magnitude of k_H/k_D provides qualitative indication of where the T.S. lies relative to S.M. or Product

$C-H\cdots A$	$C\cdots H\cdots A$	$C\cdots H-A$
	symmetric	
k_H/k_D small	large	small

early transition state   late transition state
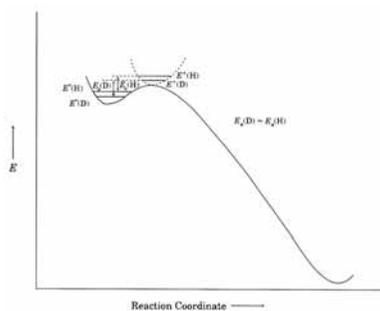
$k_H/k_D \sim 1$

C-H (or C-D) bond is
slightly broken in the T.S.
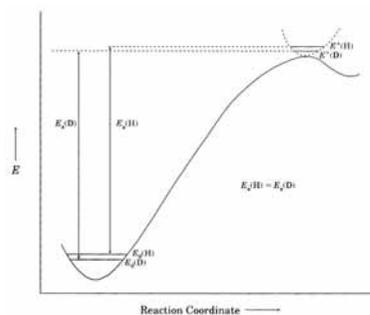
$k_H/k_D \sim 1$ (small)

C-H (or C-D) is nearly fully
broken away from S.M., but
nearly fully from in product.
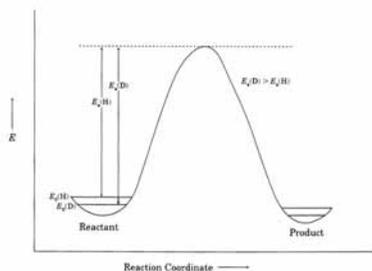
Symmetric T.S
C-H (or C-D) is half-broken → large k_H/k_D

[Transition State Theory Description :]

$\longrightarrow$ $\longleftarrow$ $\longrightarrow$ $\longleftarrow$ $\longrightarrow$
$B\cdots H \cdots A$ $B\cdots H \cdots A$

contribute to Zero
Point energy in T.S.

asymmetric stretching   symmetric stretching
(reaction coordinate)

                                        $+$ $-$ $+$
$B\cdots H \cdots A$ $B\cdots H \cdots A$
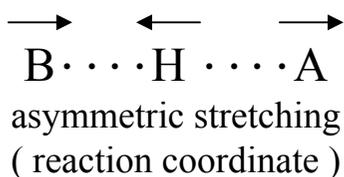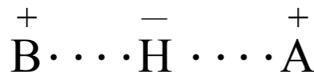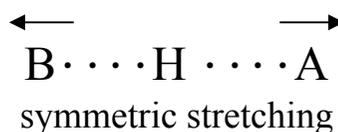
in plane bending   out-of-plane bending

of low energy & cancel similar bending in S.M.

                                EtO⁻
e.g. $\phi CH_2CH_2\text{-}X$ $\xrightarrow[\text{EtOH, 30}°]{}$ $\phi CH=CH_2$
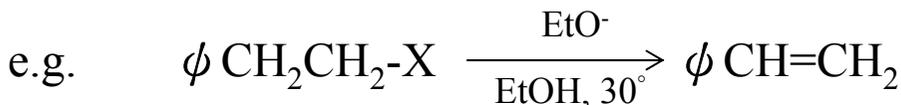
X =   Br   OTs   SMe$_2$ NMe$_3$ for non-linear T.S. KIE
k_H/k_D 7.11   5.67   5.07   2.98   is also smaller

k_H/k_D ~7

50% H-transfer

s
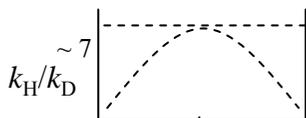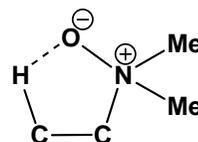
What is lattice enthalpy?

There are two different ways of defining lattice enthalpy which directly contradict each other, and you will find both in common use. In fact, there is a simple way of sorting this out, but many sources don't use it.

Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the lattice enthalpy, the stronger the forces.

Those forces are only completely broken when the ions are present as gaseous ions, scattered so far apart that there is negligible attraction between them. For sodium chloride, the solid is more stable than the gaseous ions by 787 kJ mol^{-1}, and that is a measure of the strength of the attractions between the ions in the solid. Remember that energy (in this case heat energy) is given out when bonds are made, and is needed to break bonds.

So lattice enthalpy could be described in either of two ways.

- You could describe it as the enthalpy change when 1 mole of sodium chloride (or whatever) was formed from its scattered gaseous ions.

  In the sodium chloride case, that would be -787 kJ mol$^-$ Or, you could describe it as the enthalpy change when 1 mole of sodium chloride (or whatever) is broken up to form its scattered gaseous ions. In the sodium chloride case, that would be +787 kJ mol-

So . . .

The lattice dissociation enthalpy is the enthalpy change needed to convert 1 mole of solid crystal into its scattered gaseous ions. Lattice dissociation enthalpies are always positive.

The lattice formation enthalpy is the enthalpy change when 1 mole of solid crystal is formed from its scattered gaseous ions. Lattice formation enthalpies are always negative.

Factors affecting lattice enthalpy

The two main factors affecting lattice enthalpy are the charges on the ions and the ionic radii (which affects the distance between the ions).

The charges on the ions

Sodium chloride and magnesium oxide have exactly the same arrangements of ions in the crystal lattice, but the lattice enthalpies are very different.

lattice enthalpy of magnesium oxide is much greater than that of sodium chloride. That's because in magnesium oxide, 2+ ions are attracting 2- ions; in sodium chloride, the attraction is only between 1+ and 1- ions

The radius of the ions

The lattice enthalpy of magnesium oxide is also increased relative to sodium chloride because magnesium ions are smaller than sodium ions, and oxide ions are smaller than chloride ions.

That means that the ions are closer together in the lattice, and that increases the strength of the attractions.

You can also see this effect of ion size on lattice enthalpy as you go down a Group in the Periodic Table.

For example, as you go down Group 7 of the Periodic Table from fluorine to iodine, you would expect the lattice enthalpies of their sodium salts to fall as the negative ions get bigger - and that is the case:
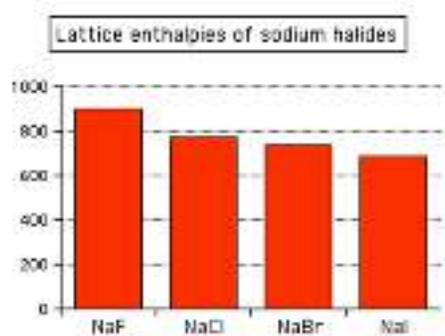
Attractions are governed by the distances between the centres of the oppositely charged ions, and that distance is obviously greater as the negative ion gets bigger.

Calculating lattice enthalpy

It is impossible to measure the enthalpy change starting from a solid crystal and converting it into its scattered gaseous ions. It is even more difficult to imagine how you could do the reverse - start with scattered gaseous ions and measure the enthalpy change when these convert to a solid crystal.

Instead, lattice enthalpies always have to be calculated, and there are two entirely different ways in which this can be done   You can can use a Hess's Law cycle (in this case called a Born-Haber cycle) involving enthalpy changes which *can* be measured. Lattice enthalpies calculated in this way are described as experimental values.

Or you can do physics-style calculations working out how much energy would be released, for example, when ions considered as point charges come together to make a lattice. These are described as theoretical values. In fact, in this case, what you are actually calculating are properly described as lattice *energies*.

Experimental values - Born-Haber cycles

Standard atomisation enthalpies

Before we start talking about Born-Haber cycles, there is an extra term which we need to define. That is ***atomisation enthalpy***, ΔH°_a.

> The standard atomisation enthalpy is the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state. Enthalpy change of atomisation is always positive.

You are always going to have to supply energy to break an element into its separate gaseous atoms.

All of the following equations represent changes involving atomisation enthalpy:

$$\tfrac{1}{2}Cl_2 \longrightarrow Cl \quad \Delta H_a = +122 \text{ kJ mol}^{-1}$$

$$\tfrac{1}{4}S_8 \longrightarrow S \quad \Delta H_a = +179 \text{ kJ mol}^{-1}$$

$$Na \longrightarrow Na \quad \Delta H_a = +107 \text{ kJ mol}^{-1}$$

Notice particularly that the "mol⁻¹" is per mole of atoms formed - NOT per mole of element that you start with. You will quite commonly have to write fractions into the left-hand side of the equation. Getting this wrong is a common mistake.

Born-Haber cycles

I am going to start by drawing a Born-Haber cycle for sodium chloride, and then talk it through carefully afterwards. You will see that I have arbitrarily decided to draw this for lattice formation enthalpy. If you wanted to draw it for lattice dissociation enthalpy, the red arrow would be reversed - pointing upwards.

Enthalpy

$Na^+_{(g)} + e^- + Cl_{(g)}$

$Na^+_{(g)} + e^- + \frac{1}{2}Cl_{2(g)}$ +122

-349

$Na^+_{(g)} + Cl^-_{(g)}$

+496

$Na_{(g)} + \frac{1}{2}Cl_{2(g)}$

$Na_{(s)} + \frac{1}{2}Cl_{2(g)}$ +107

lattice formation enthalpy

411

$NaCl_{(s)}$
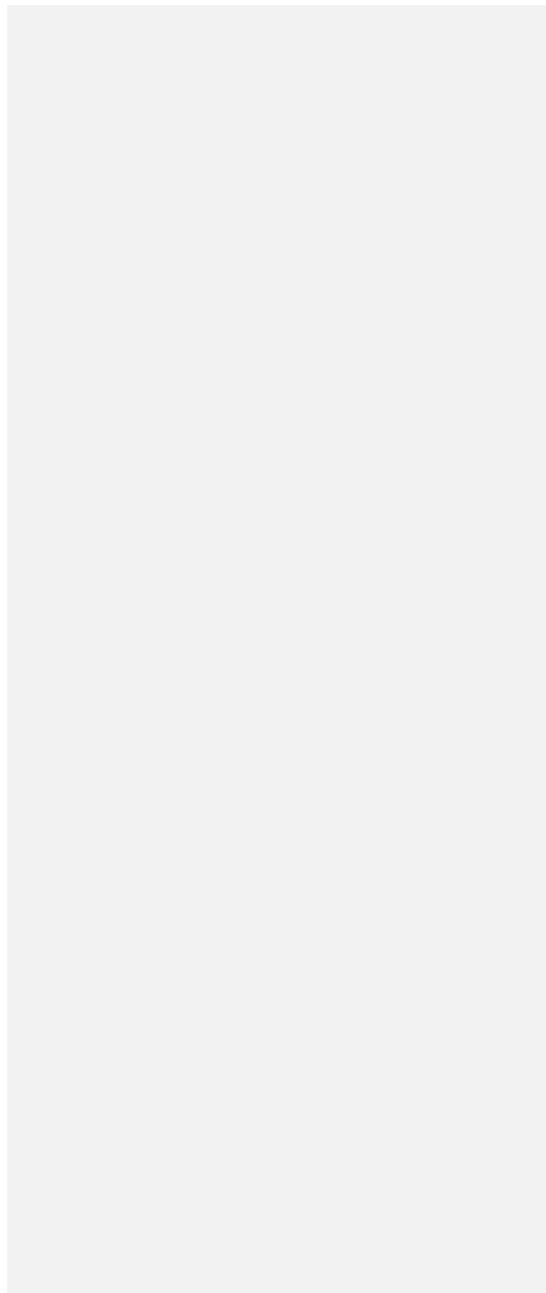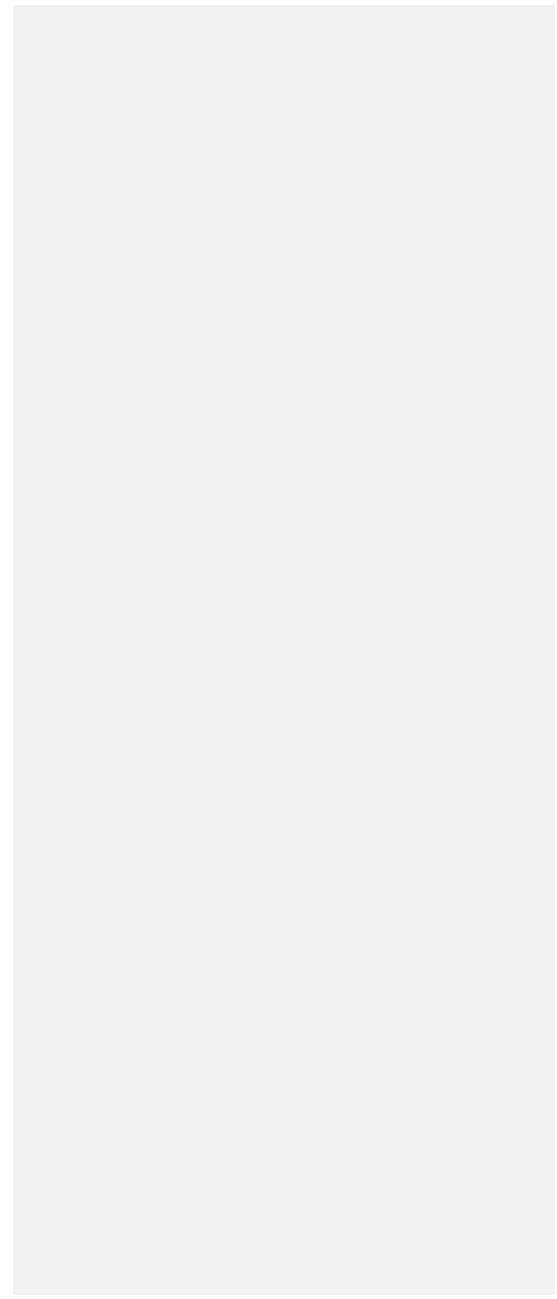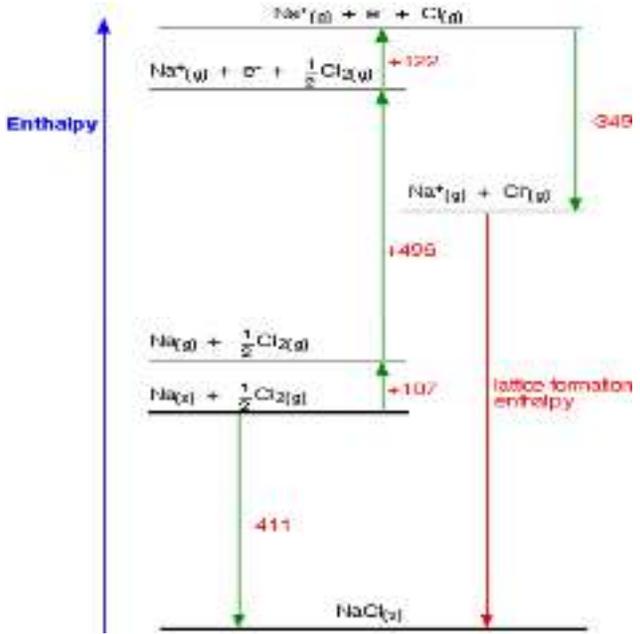
Focus to start with on the higher of the two thicker horizontal lines. We are starting here with the elements sodium and chlorine in their standard states. Notice that we only need half a mole of chlorine gas in order to end up with 1 mole of NaCl.

The arrow pointing down from this to the lower thick line represents the enthalpy change of formation of sodium chloride.

The Born-Haber cycle now imagines this formation of sodium chloride as happening in a whole set of small changes, most of which we know the enthalpy changes for - except, of course, for the lattice enthalpy that we want to calculate.

- The +107 is the atomisation enthalpy of sodium. We have to produce gaseous atoms so that we can use the next stage in the cycle.
- The +496 is the first ionisation energy of sodium. Remember that first ionisation energies go from gaseous atoms to gaseous singly charged positive ions.
- The +122 is the atomisation enthalpy of chlorine. Again, we have to produce gaseous atoms so that we can use the next stage in the cycle.
- The -349 is the first electron affinity of chlorine. Remember that first electron affinities go from gaseous atoms to gaseous singly charged negative ions.
- And finally, we have the positive and negative gaseous ions that we can convert into the solid sodium chloride using the lattice formation enthalpy.

Now we can use Hess's Law and find two different routes around the diagram which we can equate.

As I have drawn it, the two routes are obvious. The diagram is set up to provide two different routes between the thick lines.So, here is the cycle again, with the calculation directly underneath it . . .

Enthalpy

$Na^+_{(g)} + e^- + Cl_{(g)}$

$Na^+_{(g)} + e^- + \frac{1}{2}Cl_{2(g)}$ +122

-349

$Na^+_{(g)} + Cl^-_{(g)}$

+496

$Na_{(g)} + \frac{1}{2}Cl_{2(g)}$

$Na_{(s)} + \frac{1}{2}Cl_{2(g)}$ +107

lattice formation enthalpy

-411

$NaCl_{(s)}$
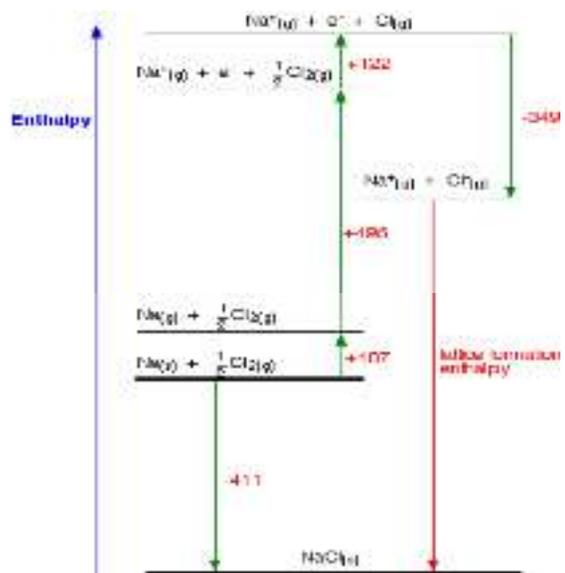
-411 = +107 + 496 + 122 - 349 + LE

LE = -411 - 107 - 496 - 122 + 349

LE = -787 kJ mol^{-1}

How would this be different if you had drawn a lattice dissociation enthalpy in your diagram?

Your diagram would now look like this:

The only difference in the diagram is the direction the lattice enthalpy arrow is pointing. It does, of course, mean that you have to find two new routes. You can't use the original one, because that would go against the flow of the lattice enthalpy arrow.

This time both routes would start from the elements in their standard states, and finish at the gaseous ions.

-411 + LE = +107 + 496 + 122 - 349

LE = +107 + 496 + 122 - 349 + 411

LE = +787 kJ mol^{-1}

Once again, the cycle sorts out the sign of the lattice enthalpy for you.
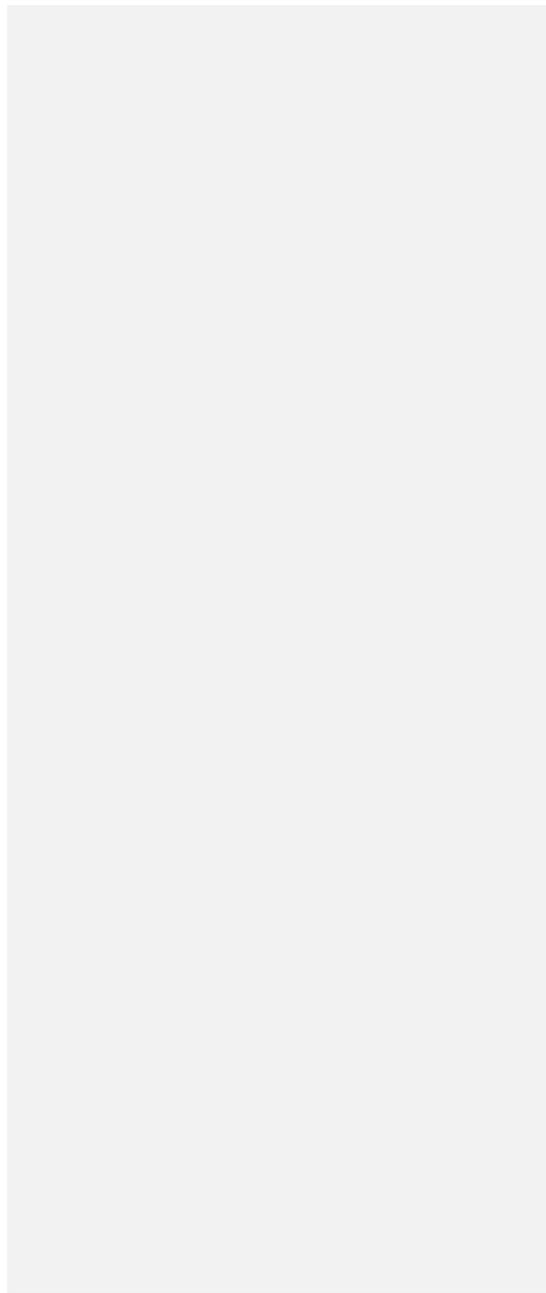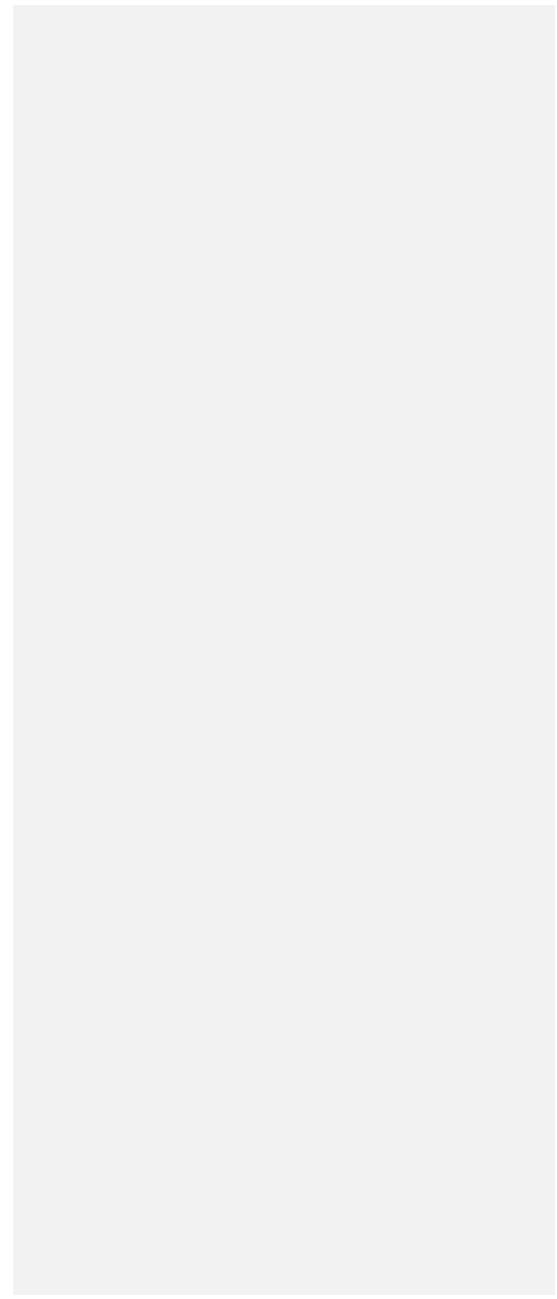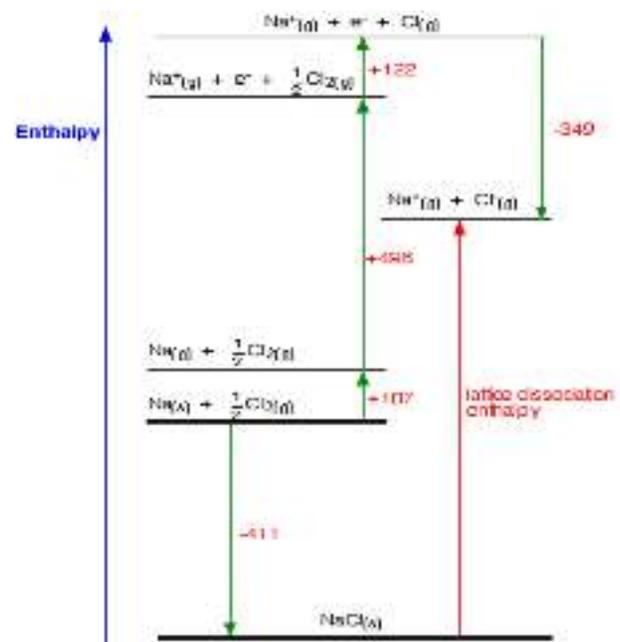
Lattie energy and solubility

When a salt, such as NaCl dissolves in water, the crystals disappear on the macroscopic scale. On the atomic scale, the Na^+ and Cl^- ions in the crystal are released into solution.

$$NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq)$$
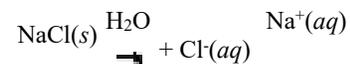
The lattice energy of a salt therefore gives a rough indication of the solubility of the salt in water because it reflects the energy needed to separate the positive and negative ions in a salt.

Sodium and potassium salts are soluble in water because they have relatively small lattice energies. Magnesium and aluminum salts are often much less soluble because it takes more energy to separate the positive and negative ions in these salts. NaOH, for example, is very soluble in water (420 g/L), but $Mg(OH)_2$ dissolves in water only to the extent of 0.009 g/L, and $Al(OH)_3$ is essentially insoluble in water

The Radius Ratio Rule.

If we consider an array of anions present in the form of cubic close packing, the tetrahedral holes and the octahedral holes will vary in the sizes. Therefore, the cations will occupy the voids only if they are enough space to accommodate them. This prediction of whether the ions will be able to hold the cations can be done on the basis of Radius Ratio.

Ionic Crystals comprises many cations and anions. We know that anions are larger in size and surround the smaller cations. They are arranged in space such that anions and cations touch each other and produce maximum stability.

This stability of the ionic crystals can be explained on the basis of radius ratio. Therefore, radius ratio is the ratio of cation to the ratio of an anion. Here, Ratio of cation= r, Ratio of anion = R. Thus, Radius ratio = (r/R). Limiting radius ratio helps in expressing the range of radius ratio.

Definition of the Radius Ratio Rule

Radius Ratio refers to as the ration of smaller ionic radius (cation) by the ratio of larger ionic radius (anion). Hence, Radius ration $\rho = r_s/r_l$.

Importance of the Radius Ratio Rule

This rule helps in the determination of arrangement of ions in various types of crystal structures. It also helps to determine the stability of an ionic crystal structure. For instance, larger cations will fill the larger voids like cubic sites whereas smaller cations will fill the smaller voids such as tetrahedral sites.

It is also possible to predict the coordination number of any compound. Hence, the radius ratio rule helps in determining the structure of ionic solids.

Examples of Radius Ratio Rule

The ratio of radii of the ions can affect the arrangement of ions in a crystal. Moreover, the limiting ratio has to be greater than 0.414, (radius ratio greater than 0.414) to fit an octahedral arrangement of anions. In this formation, cations will be able to accommodate 6 anions.

However, radius ration in between 0.225 to 0.414 will be able to fit into tetrahedral voids in the crystal lattice thereby preferring tetrahedral coordination and above 0.414 will prefer octahedral coordination. For example, if we consider an ion zinc sulfide, the radius ration will be

$$\frac{r_{Zn^{2+}}}{r_{S^{2-}}} = \frac{74}{184} = 0.40$$
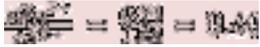
Therefore, zinc ion will favour tetrahedral voids in the closely arranged lattice of sulfide ions. However, in case of larger cations such as caesium, the radius ratio is larger than the limit of the coordination number of 6. Hence, the caesium ions will fit cubic sites so the coordination number SSwill increase to 8 in the chloride ions lattice.

$$\left(\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{169}{181} = 0.93 \right)$$

Below Table demonstrates the relationship between radius ratio (limiting ratio) and coordination number.

Radius Ratio	Coordination number	Type of void	Example
< 0.155	2	Linear	
0.155 - 0.225	3	Triangular Planar	B_2O_3
0.225 - 0.414	4	Tetrahedral	ZnS, CuCl
0.414 - 0.732	6	Octahedral	NaCl, MgO
0.732 - 1.000	8	Cubic	CsCl, NH_4Br
1	12	Close packing (ccp and hcp)	metals

Relationship between Radius Ratio and Coordination Number

Effect of Difference in Size of Ions on Arrangement

Below are the three diagrams which explain how the different sizes of ions will affect the arrangement as well as the stability of the ions.

Figure 1- Size of M⁺ Just Right

Figure 2- Size of M⁺ Very small

Figure 3- Size of M⁺ Too Large
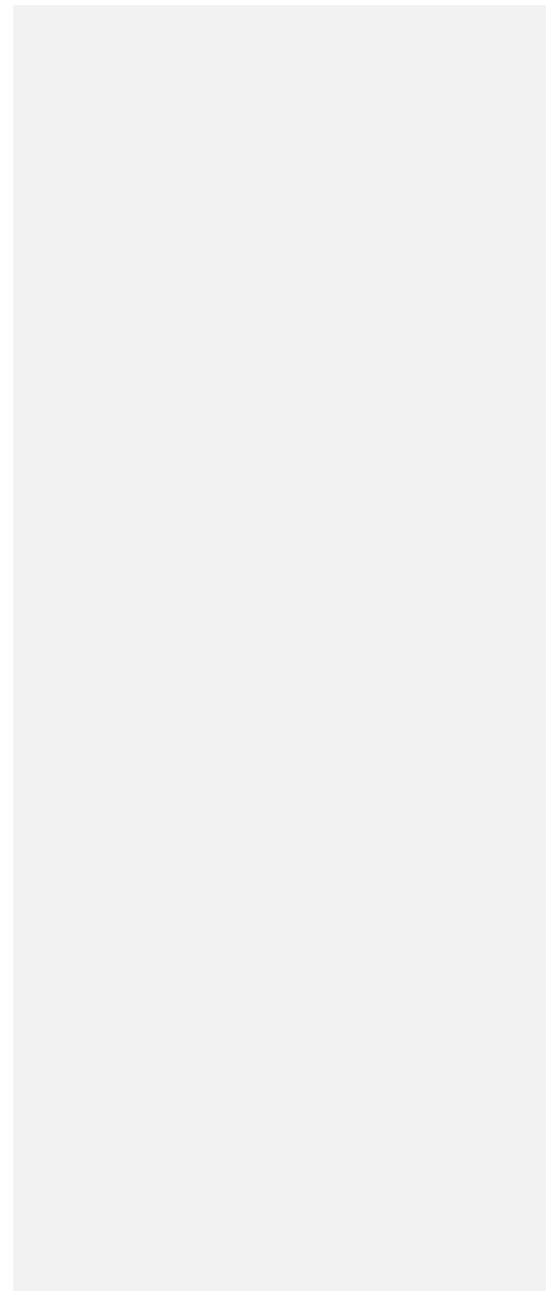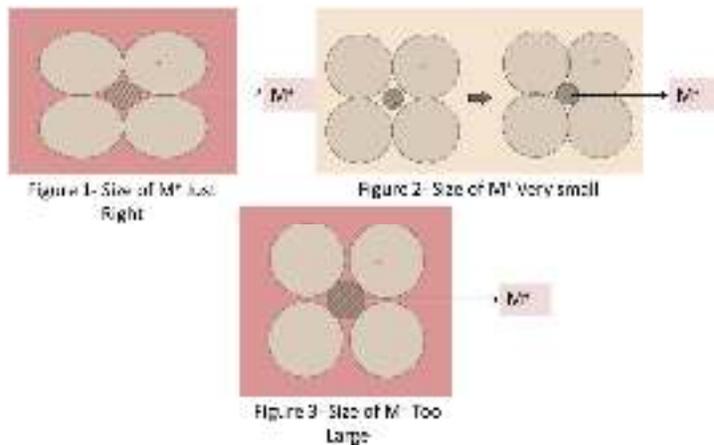
Figure 1 represents M$^+$ ion in contact with X$^-$ ions and the fit of the first layer are "just correct." However, Figure 2 the M$^+$ ion in contact with X$^-$ ions is smaller. Thus, the fit of the first layer of arrangement is poor. Moreover, if the cations move closer to the anion, the crowding of the arrangement will increase which in turn would lead to repulsion among each other.

This will further increase the energy of the system. Furthermore, if the ions try to hold each other apart then it will not be near to the opposite M$^+$ ion. Figure 3 represents the arrangement of M$^+$ ion and X$^-$ ions where M$^+$ ion is too large. Therefore, the X$^-$ will be far away and not feel the X$^-$ – X$^-$ repulsion.

Therefore, in the case similar to figure 2 and figure 3, the crystal packing of MX will be different. Thus, if we take the example of compounds, then consider figure 1 as the lattice of NaCl. We ca relate figure 3 to the structure of CsCl where the M$^+$ ion is large and it can accommodate more X$^-$ ions.

Similarly, in Figure 2 M$^+$ ion is very small so it can accommodate only four negative ions and compounds such as ZnS can be the example of such a case.

Solved Example

Question: If a solid "A^+B^-" has a structure similar to NaCl. Consider the radius of anion as 250 pm. Find the ideal radius of the cation in the structure. Is it possible to fit a cation C^+ of radius 180 pm in the tetrahedral site of the structure "A^+B^-"? Explain your answer

Solution: If the A^+B^- structure is similar to Na^+Cl^- ion then we know that six Cl^-ions will surround Na^+ and vice versa. Therefore, Na^+ ion fits into the octahedral void. Therefore the limiting ratio for an octahedral site is 0.414

Thus, limiting radius ratio= r/R= 0.414
From the question, R=250 pm
Therefore, r=0.414R= 0.414 × 250pm
Hence, r= 103.5pm
So the ideal radius ration of cation will be 103.5pm or A^+ = 103.5 pm

From the above table, we know r/R for a tetrahedral site is 0.225
Therefore, r/R= 0.225
Or, r= 0.225R = 0.225 × 250pm = 56.25 pm

Thus, the ideal radius for the cation in the given structure will be 56.25 pm for a tetrahedral site. However, we know the radius of C^+ is 180 pm. This means that the radius of C^+ is much larger than 56.25 pm. Therefore, it is not possible to fit cation C^+ in a tetrahedral site.

*

What is hybridization?

The phenomena of intermixing of atomic orbitals of individual atoms to give orbitals of equivalent energy is called hybridization. The new orbitals thus formed are known as **hybrid orbitals which have better overlap power and higly directional character.**

Key Features of Hybridization

- Atomic orbitals with equal energies undergo hybridization.
- The number of hybrid orbitals formed is equal to the number of atomic orbitals mixing.
- It is not necessary that all the half-filled orbitals must participate in hybridization. Even completely filled orbitals with slightly different energies can also participate.
- The shape of the molecule can be predicted if hybridization of the molecule is known.

Types of Hybridization

Based on the types of orbitals involved in mixing, the hybridization can be classified as sp3, sp2, sp, sp3d, sp3d2, sp3d3. Let us now discuss the various types of hybridization along with their examples.

sp Hybridization

sp hybridization is observed when one s and one p orbital in the same main shell of an atom mix to form two new equivalent orbitals. The new orbitals formed are called **sp hybridized orbitals.** It forms linear molecules with an angle of 180°

- This type of hybridization involves the mixing of one 's' orbital and one 'p' orbital of equal energy to give a new hybrid orbital known as an sp hybridized orbital.
- sp hybridization is also called diagonal hybridization.
- Each sp hybridized orbital has an equal amount of s and p character, i.e., 50% s and p character.
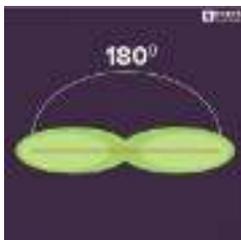
Examples of sp Hybridization:

- All compounds of beryllium like BeF_2, BeH_2, $BeCl_2$
- All compounds of carbon-containing triple Bond like C_2H_2.

sp² Hybridization

sp² hybridisation is observed when one s and two p orbitals of the same shell of an atom mix to form 3 equivalent orbital. The new orbitals formed are called **sp² hybrid orbitals.**

- sp² hybridization is also called trigonal hybridization.
- It involves mixing of one 's' orbital and two 'p' orbital's of equal energy to give a new hybrid orbital known as sp^2.
- A mixture of s and p orbital formed in trigonal symmetry and is maintained at 120^0.
- All the three hybrid orbitals remain in one plane and make an angle of 120° with one another. Each of the hybrid orbitals formed has 33.33% s character and 66.66% 'p' character.
- The molecules in which the central atom is linked to 3 atoms and is sp2 hybridized have a triangular planar shape.
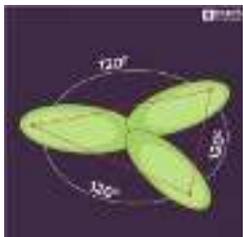
Examples of sp² Hybridization

- All the compounds of Boron i.e. BF_3, BH_3
- All the compounds of carbon containing a carbon-carbon double bond, Ethylene (C_2H_4)

sp³ Hybridization

When one 's' orbital and 3 'p' orbitals belonging to the same shell of an atom mix together to form four new equivalent orbital, the type of hybridization is called a **tetrahedral hybridization or sp³**. The new orbitals formed are called **sp³ hybrid orbitals.**

- These are directed towards the four corners of a regular tetrahedron and make an angle of 109°28' with one another.
- The angle between the sp3 hybrid orbitals is 109.28^0
- Each sp³ hybrid orbital has 25% s character and 75% p character.
- Example of sp³ hybridization: ethane (C_2H_6), methane.
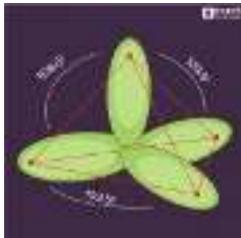
sp³d Hybridization

sp³d hybridization involves the mixing of 3p orbitals and 1d orbital to form 5 sp3d hybridized orbitals of equal energy. They have trigonal bipyramidal geometry.

- The mixture of s, p and d orbital forms trigonal bipyramidal symmetry.
- Three hybrid orbitals lie in the horizontal plane inclined at an angle of 120° to each other known as the equatorial orbitals.
- The remaining two orbitals lie in the vertical plane at 90 degrees plane of the equatorial orbitals known as axial orbitals.
- **Example:** Hybridization in Phosphorus pentachloride (PCl_5)

sp^{3}d^2 Hybridization

- sp3d2 hybridization has 1s, 3p and 2d orbitals, that undergo intermixing to form 6 identical sp3d2 hybrid orbitals.
- These 6 orbitals are directed towards the corners of an octahedron.
- They are inclined at an angle of 90 degrees to one another.

Key Features of Hybridization

- Atomic orbitals with equal energies undergo hybridization.
- The number of hybrid orbitals formed is equal to the number of atomic orbitals mixing.
- It is not necessary that all the half-filled orbitals must participate in hybridization. Even completely filled orbitals with slightly different energies can also participate.
- Hybridization happens only during the bond formation and not in an isolated gaseous atom.
- The shape of the molecule can be predicted if hybridization of the molecule is known.
- The bigger lobe of the hybrid orbital always has a positive sign while the smaller lobe on the opposite side has a negative sign.

The VSEPR Model

Commented [acs1]:

The VSEPR model can predict the structure of nearly any molecule or polyatomic ion in which the central atom is a nonmetal, as well as the structures of many molecules and polyatomic ions with a central metal atom. The premise of the VSEPR theory is that electron pairs located in bonds and lone pairs repel each other and will therefore adopt the geometry that places electron pairs as far apart from each other as possible. This theory is very simplistic and does not account for the subtleties of orbital interactions that influence molecular shapes; however, the simple VSEPR counting procedure accurately predicts the three-dimensional structures of a large number of compounds, which cannot be predicted using the Lewis electron-pair approach.
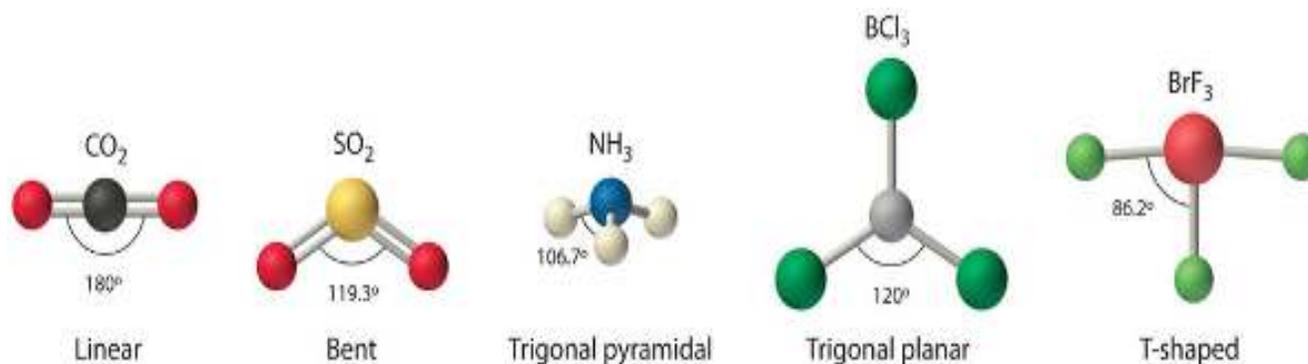
Figure 10.2.110.2.1: Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms

We can use the VSEPR model to predict the geometry of most polyatomic molecules and ions by focusing only on the number of electron pairs around the *central atom*, ignoring all other valence electrons present. According to this model, valence electrons in the Lewis structure form *groups*, which may consist of a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron, which in the VSEPR model is counted as a lone pair. Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsions. Groups are positioned around the central atom in a way that produces the molecular structure with the lowest energy, as illustrated in Figures 10.2.110.2.1 and 10.2.210.2.2.

Electron Groups	2	3	4	5	6
Geometry	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
Predicted Bond Angles	$180°$	$120°$	$109.5°$	$90°, 120°$	$90°$

***Figure** 10.2.210.2.2: Electron Geometries for Species with Two to Six Electron Groups. Groups are placed around the central atom in a way that produces a molecular structure with the lowest energy, that is, the one that minimizes repulsions.*

In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and m and n are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the bond angles. Using this information, we can describe the molecular geometry, the arrangement of the *bonded atoms* in a molecule or polyatomic ion.

VESPR PRODUCE TO PREDICT MOLECULAR GEOMETRY

This VESPR procedure is summarized as follows:

1. Draw the Lewis electron structure of the molecule or polyatomic ion.
2. Determine the electron group arrangement around the central atom that minimizes repulsions.

3. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations from ideal bond angles.

4. Describe the molecular geometry.

We will illustrate the use of this procedure with several examples, beginning with atoms with two electron groups. In our discussion we will refer to Figure 10.2.210.2.2 and Figure 10.2.310.2.3, which summarize the common molecular geometries and idealized bond angles of molecules and ions with two to six electron groups.

AX_mE_n Notation	AX_2	AX_2E	AX_3	AX_3E
Geometry	Linear	Bent (V-shaped)	Trigonal planar	Trigonal pyramidal
	X—A—X			
Idealized Bond Angles	180°	<180°	120°	<120°
AX_mE_n Notation	AX_4E_2	AX_4	AX_5	AX_6
Geometry	Square planar	Tetrahedral	Trigonal bipyramidal	Octahedral
Idealized Bond Angles	90°	109.5°	90°, 120°	90°
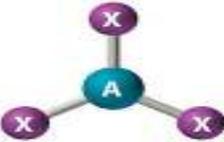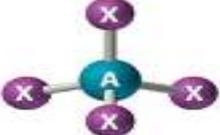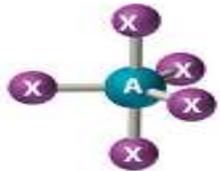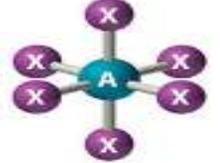
Figure 10.2.310.2.3*: Common Molecular Geometries for Species with Two to Six Electron Groups. Lone pairs are shown using a dashed line.*

Two Electron Groups

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, BeH2BeH2.
AX$_2$ MOLECULES: BEH$_2$

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is

$$H:Be:H \quad or \quad H—Be—H$$

Lewis structure

2. There are two electron groups around the central atom. We see from Figure 10.2.210.2.2 that the arrangement that minimizes repulsions places the groups 180° apart.

3. Both groups around the central atom are bonding pairs (BP). Thus BeH$_2$ is designated as AX$_2$.

4. From Figure 10.2.310.2.3 we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH$_2$ is *linear*.
AX$_2$ MOLECULES: CO$_2$

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is

$$:O::C::O:$$

2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like BeH$_2$, the arrangement that minimizes repulsions places the groups 180° apart.

3. Once again, both groups around the central atom are bonding pairs (BP), so CO$_2$ is designated as AX$_2$.

4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of CO$_2$ is linear (Figure 10.2.310.2.3). The structure of CO2CO2 is shown in Figure 10.2.110.2.1.

Three Electron Groups

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is
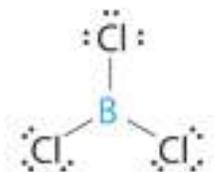
Lewis structure

2. There are three electron groups around the central atom. To minimize repulsions, the groups are placed 120° apart (Figure 10.2.210.2.2).

3. All electron groups are bonding pairs (BP), so the structure is designated as AX$_3$.

4. From Figure 10.2.310.2.3 we see that with three bonding pairs around the central atom, the molecular geometry of BCl$_3$ is *trigonal planar*, as shown in Figure 10.2.210.2.2.

1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. As you learned previously, the Lewis electron structure of one of three resonance forms is represented as
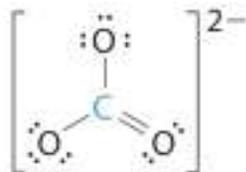
Lewis structure

2. The structure of CO_3^{2-} is a resonance hybrid. It has three identical bonds, each with a bond order of 113113. We minimize repulsions by placing the three groups 120° apart (Figure 10.2.210.2.2).

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as AX_3.

4. We see from Figure 10.2.310.2.3 that the molecular geometry of CO_3^{2-} is trigonal planar with bond angles of 120°.

Molecular geometry
(trigonal planar)
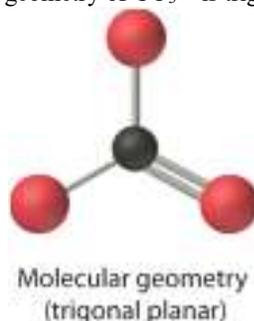
In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

AX_2E MOLECULES: SO_2

1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.
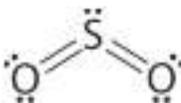
2. There are three electron groups around the central atom, two double bonds and one lone pair. We initially place the groups in a trigonal planar arrangement to minimize repulsions (Figure 10.2.210.2.2).
3. There are two bonding pairs and one lone pair, so the structure is designated as AX_2E. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (Figure 10.2.410.2.4). Thus bonding pairs and lone pairs repel each other electrostatically in the order BP–BP < LP–BP < LP–LP. In SO_2, we have one BP–BP interaction and two LP–BP interactions.
4. The molecular geometry is described only by the positions of the nuclei, *not* by the positions of the lone pairs. Thus with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement with a missing vertex

(Figures 10.2.210.2.2 and 10.2.310.2.3). The O-S-O bond angle is expected to be *less than* 120° because of the extra space taken up by the lone pair.
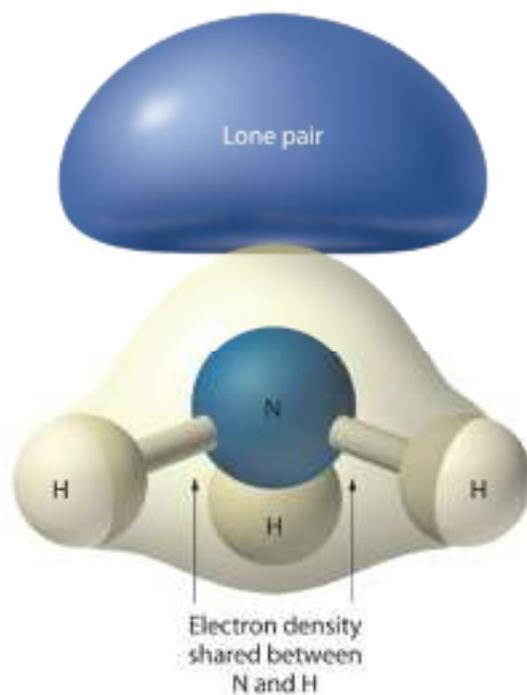
***Figure** 10.2.410.2.4: The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair*

As with SO_2, this composite model of electron distribution and negative electrostatic potential in ammonia shows that a lone pair of electrons occupies a larger region of space around the nitrogen atom than does a bonding pair of electrons that is shared with a hydrogen atom.

Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond, which can cause other bond angles to be somewhat smaller than expected. This is because a multiple bond has a higher electron density than a single bond, so its

electrons occupy more space than those of a single bond. For example, in a molecule such as CH_2O (AX_3), whose structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an H–C–H bond angle of 116.5° rather than 120°).

116.5°
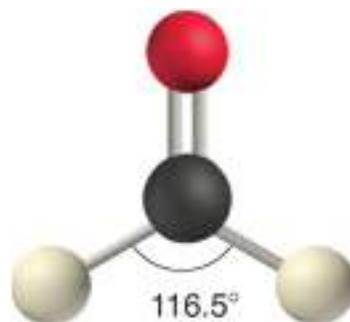
Four Electron Groups

One of the limitations of Lewis structures is that they depict molecules and ions in only two dimensions. With four electron groups, we must learn to show molecules and ions in three dimensions.

AX_4 MOLECULES: CH_4

1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is

Lewis structure
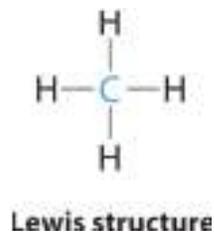
2. There are four electron groups around the central atom. As shown in Figure 10.2.210.2.2, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

3. All electron groups are bonding pairs, so the structure is designated as AX_4.

4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure 10.2.310.2.3).
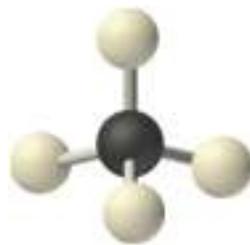
Molecular geometry
(tetrahedral)

AX₃E MOLECULES: NH₃

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure
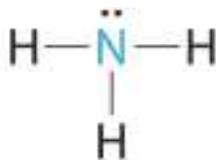
Lewis structure

2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

3. With three bonding pairs and one lone pair, the structure is designated as AX_3E. This designation has a total of four electron pairs, three X and one E. We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing (Figure 10.2.310.2.3). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions (Figure 10.2.310.2.3 and Figure 10.2.410.2.4).

AX_2E_2 MOLECULES: H_2O

1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure
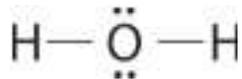
2. There are four groups around the central oxygen atom, two bonding pairs and two lone pairs. Repulsions are minimized by directing the bonding pairs and the lone pairs to the corners of a tetrahedron Figure 10.2.210.2.2.

3. With two bonding pairs and two lone pairs, the structure is designated as AX_2E_2 with a total of four electron pairs. Due to LP–LP, LP–BP, and BP–BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H–O–H angle that is even less than the H–N–H angles in NH_3, as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one. This molecular shape is essentially a tetrahedron with two missing vertices.

104.5°
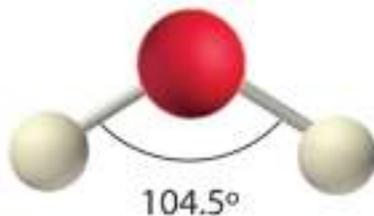
Five Electron Groups

In previous examples it did not matter where we placed the electron groups because all positions were equivalent. In some cases, however, the positions are not equivalent. We encounter this situation for the first time with five electron groups.

AX$_5$ MOLECULES: PCL$_5$

1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl$_5$ is
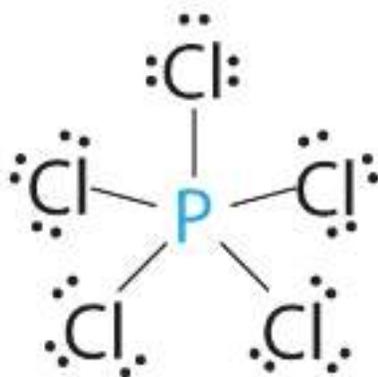
2. There are five bonding groups around phosphorus, the central atom. The structure that minimizes repulsions is a *trigonal bipyramid*, which consists of two trigonal pyramids that share a base (Figure 10.2.210.2.2):

3. All electron groups are bonding pairs, so the structure is designated as AX$_5$. There are no lone pair interactions.

4. The molecular geometry of PCl$_5$ is *trigonal bipyramidal*, as shown in Figure 10.2.310.2.3. The molecule has three atoms in a plane in *equatorial* positions and two atoms above and below the plane in *axial* positions. The three equatorial positions are separated by 120° from one another, and the two axial positions are at 90° to the equatorial plane. The axial and equatorial positions are not chemically equivalent, as we will see in our next example.

PCl$_5$
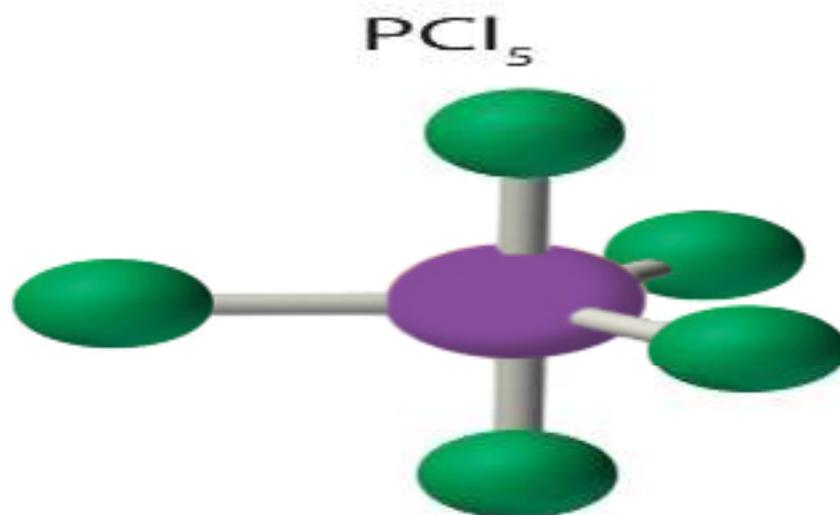
AX$_4$E MOLECULES: SF$_4$

1. The sulfur atom has six valence electrons and each fluorine has seven valence electrons, so the Lewis electron structure is

Lewis structure
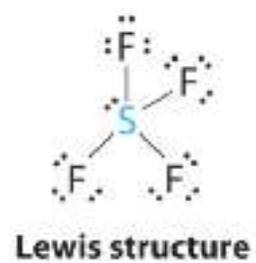
With an expanded valence, this species is an exception to the octet rule.

2. There are five groups around sulfur, four bonding pairs and one lone pair. With five electron groups, the lowest energy arrangement is a trigonal bipyramid, as shown in Figure 10.2.210.2.2.

3. We designate SF_4 as AX_4E; it has a total of five electron pairs. However, because the axial and equatorial positions are not chemically equivalent, where do we place the lone pair? If we place the lone pair in the axial position, we have three LP–BP repulsions at 90°. If we place it in the equatorial position, we have two 90° LP–BP repulsions at 90°. With fewer 90° LP–BP repulsions, we can predict that the structure with the lone pair of electrons in the *equatorial position is more stable than the one with the lone pair in the axial position*. We also expect a deviation from ideal geometry because a lone pair of electrons occupies more space than a bonding pair.
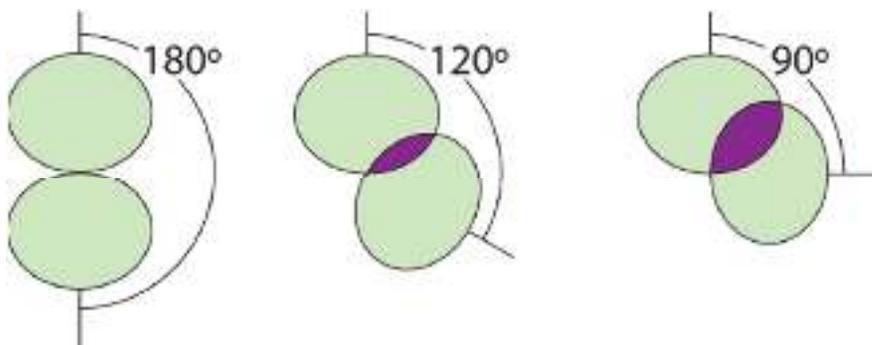
Figure 10.2.510.2.5*: Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them*

At 90°, the two electron pairs share a relatively large region of space, which leads to strong repulsive electron–electron interactions.

4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The F_{axial}–S–F_{axial} angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.
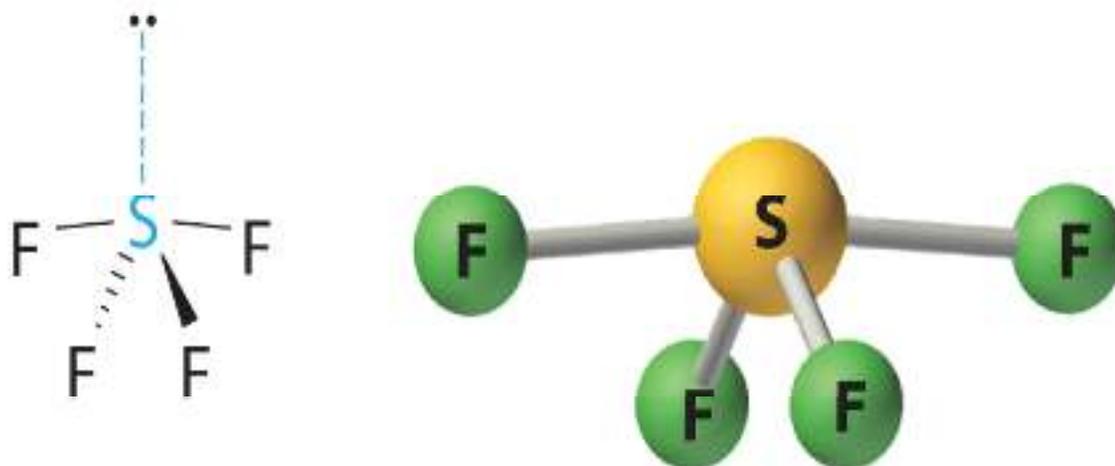
Molecular geometry (seesaw)

AX$_3$E$_2$ MOLECULES: BROMINE TRIFLUORIDE

1. The bromine atom has seven valence electrons, and each fluorine has seven valence electrons, so the Lewis electron structure is
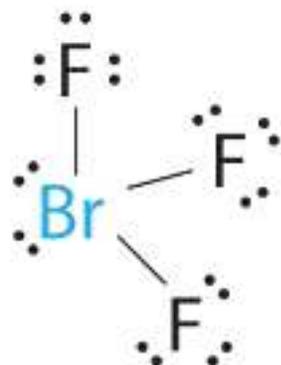
Lewis structure

Once again, we have a compound that is an exception to the octet rule.

2. There are five groups around the central atom, three bonding pairs and two lone pairs. We again direct the groups toward the vertices of a trigonal bipyramid.

3. With three bonding pairs and two lone pairs, the structural designation is AX_3E_2 with a total of five electron pairs. Because the axial and equatorial positions are not equivalent, we must decide how to arrange the groups to minimize repulsions. If we place both lone pairs in the axial positions, we have six LP–BP repulsions at 90°. If both are in the equatorial positions, we have four LP–BP repulsions at 90°. If one lone pair is axial and the other equatorial, we have one LP–LP repulsion at 90° and three LP–BP repulsions at 90°:
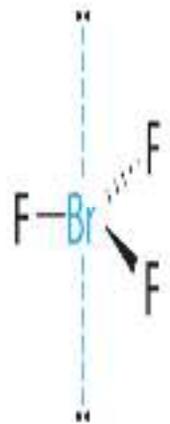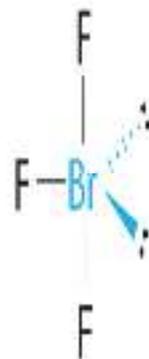
	Lone pairs axial	Lone pairs equatorial	Lone pairs axial and equatorial
	(a)	(b)	(c)
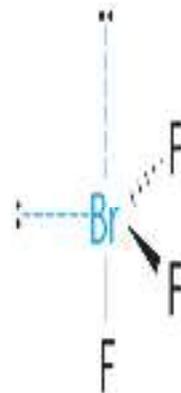
Interactions

90° LP–LP	0	0	1
90° LP–BP	6	4	3
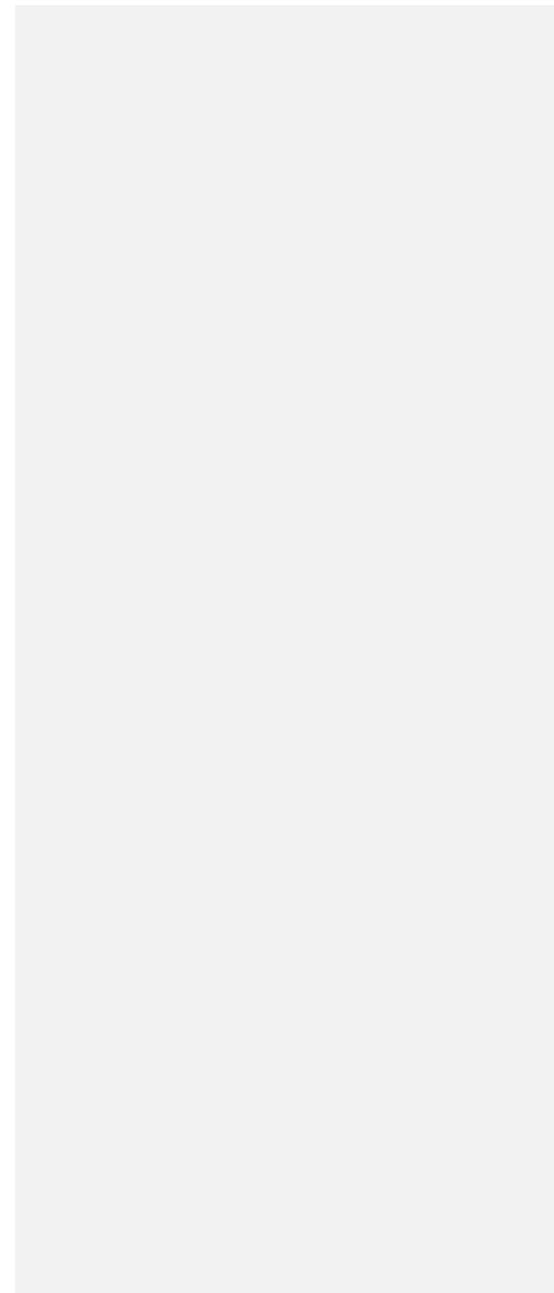
Structure (c) can be eliminated because it has a LP–LP interaction at 90°. Structure (b), with fewer LP–BP repulsions at 90° than (a), is lower in energy. However, we predict a deviation in bond angles because of the presence of the two lone pairs of electrons.

4. The three nuclei in BrF_3 determine its molecular structure, which is described as *T shaped*. This is essentially a trigonal bipyramid that is missing two equatorial vertices. The F_{axial}–Br–F_{axial} angle is 172°, less than 180° because of LP–BP repulsions (Figure 10.2.210.2.2.1).

Because lone pairs occupy more space around the central atom than bonding pairs, electrostatic repulsions are more important for lone pairs than for bonding pairs.

AX_2E_3 MOLECULES: I_3^-

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is

2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

3. With two bonding pairs and three lone pairs, I_3^- has a total of five electron pairs and is designated as AX_2E_3. We must now decide how to arrange the lone pairs of electrons in a trigonal bipyramid in a way that minimizes repulsions. Placing them in the axial positions eliminates 90° LP–LP repulsions and minimizes the number of 90° LP–BP repulsions.
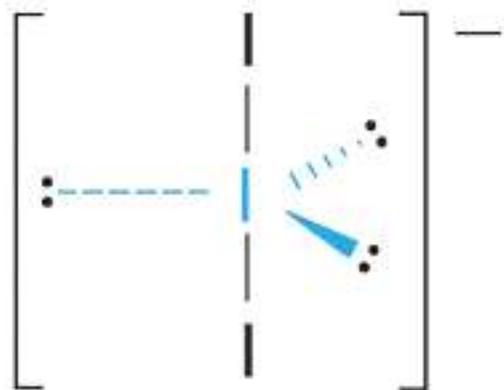
The three lone pairs of electrons have equivalent interactions with the three iodine atoms, so we do not expect any deviations in bonding angles.

4. With three nuclei and three lone pairs of electrons, the molecular geometry of I_3^- is linear. This can be described as a trigonal bipyramid with three equatorial vertices missing. The ion has an I–I–I angle of 180°, as expected.

$$I_3^-$$
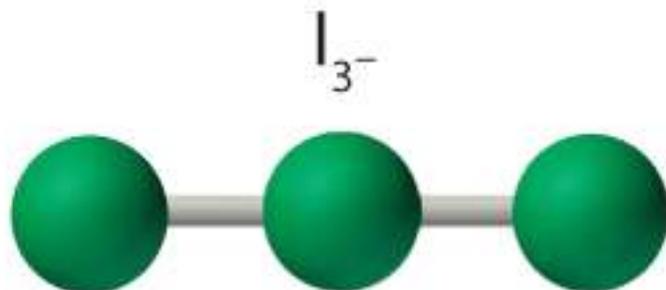
Six Electron Groups

Six electron groups form an *octahedron*, a polyhedron made of identical equilateral triangles and six identical vertices (Figure $10.2.210.2.2.$)

AX$_6$ MOLECULES: SF$_6$

1. The central atom, sulfur, contributes six valence electrons, and each fluorine atom has seven valence electrons, so the Lewis electron structure is
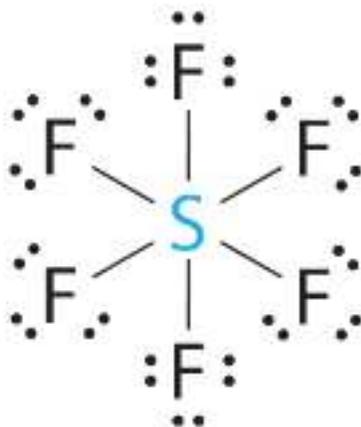
Lewis structure

With an expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the central atom, each a bonding pair. We see from Figure $10.2.210.2.2$ that the geometry that minimizes repulsions is *octahedral*.

3. With only bonding pairs, SF$_6$ is designated as AX$_6$. All positions are chemically equivalent, so all electronic interactions are equivalent.

4. There are six nuclei, so the molecular geometry of SF_6 is octahedral.
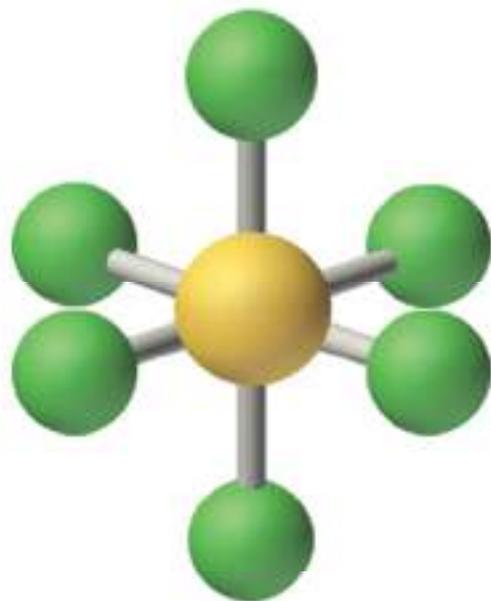
Molecular geometry
(octahedral)

AX₅E MOLECULES: BRF₅

1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is
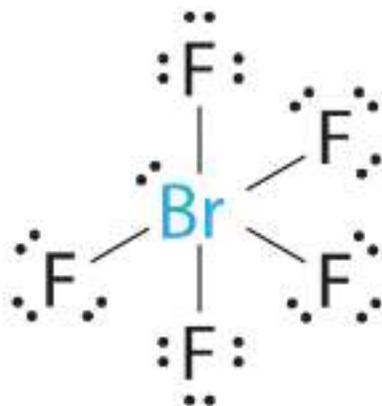

Lewis structure

With its expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the Br, five bonding pairs and one lone pair. Placing five F atoms around Br while minimizing BP–BP and LP–BP repulsions gives the following structure:
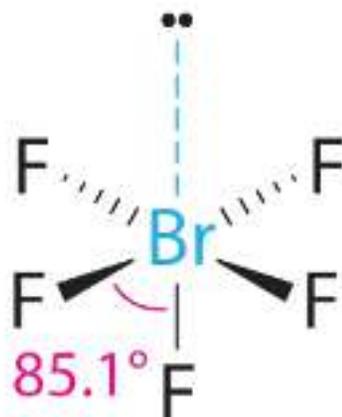
3. With five bonding pairs and one lone pair, BrF_5 is designated as AX_5E; it has a total of six electron pairs. The BrF_5 structure has four fluorine atoms in a plane in an equatorial position and one fluorine atom and the lone pair of electrons in the axial positions. We expect all F_{axial}–Br–$F_{equatorial}$ angles to be less than 90° because of the lone pair of electrons, which occupies more space than the bonding electron pairs.

4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.

Molecular geometry
(square pyramidal)
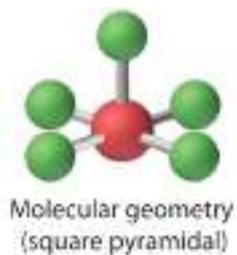
AX$_4$E$_2$ MOLECULES: ICL$_4^-$

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is
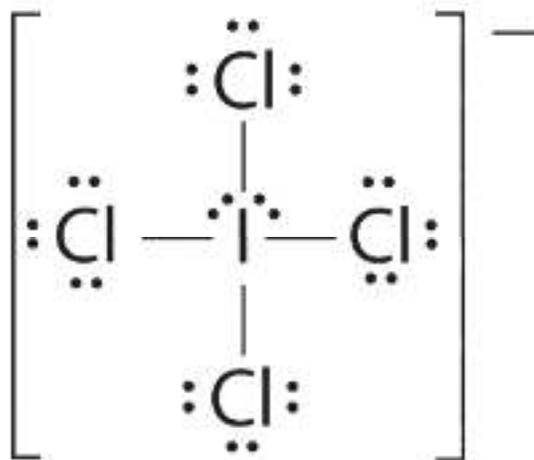
2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is
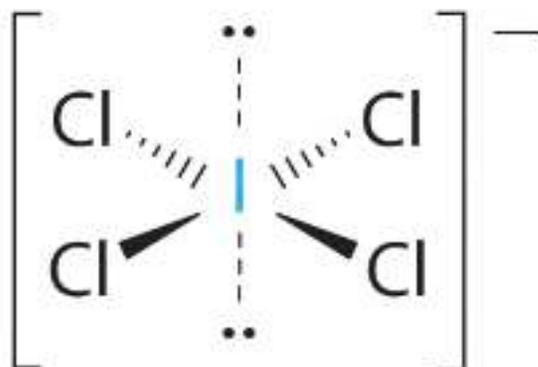
3. ICl_4^- is designated as AX_4E_2 and has a total of six electron pairs. Although there are lone pairs of electrons, with four bonding electron pairs in the equatorial plane and the lone pairs of electrons in the axial positions, all LP–BP repulsions are the same. Therefore, we do not expect any deviation in the Cl–I–Cl bond angles.

4. With five nuclei, the $ICl4^-$ ion forms a molecular structure that is *square planar*, an octahedron with two opposite vertices missing.
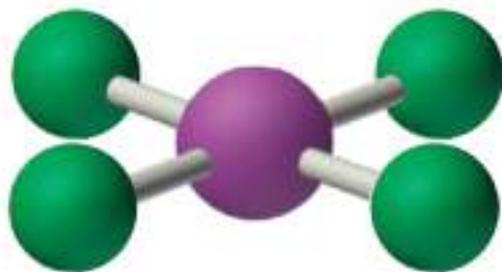
The relationship between the number of electron groups around a central atom, the number of lone pairs of electrons, and the molecular geometry is summarized in Figure 10.2.610.2.

Figure 10.2.610.2.6*: Overview of Molecular Geometries*

EXAMPLE 10.2.110.2.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

1. PF_5 (phosphorus pentafluoride, a catalyst used in certain organic reactions)
2. H_3O^+ (hydronium ion)

Given: two chemical species

Asked for: molecular geometry

Strategy:

A. Draw the Lewis electron structure of the molecule or polyatomic ion.
B. Determine the electron group arrangement around the central atom that minimizes repulsions.
C. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations in bond angles.
D. Describe the molecular geometry.

Solution:

1. **A** The central atom, P, has five valence electrons and each fluorine has seven valence electrons, so the Lewis structure of PF_5 is
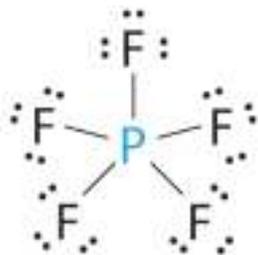
B There are five bonding groups about phosphorus. The structure that minimizes repulsions is a trigonal bipyramid (Figure 10.2.610.2.6).

C All electron groups are bonding pairs, so PF_5 is designated as AX_5. Notice that this gives a total of five electron pairs. With no lone pair repulsions, we do not expect any bond angles to deviate from the ideal.

D The PF$_5$ molecule has five nuclei and no lone pairs of electrons, so its molecular geometry is trigonal bipyramidal.
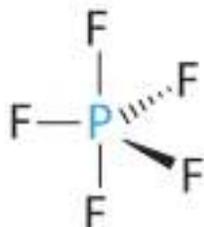

2. **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is
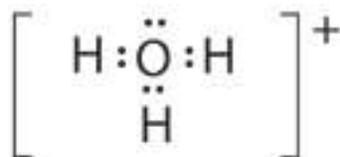
B There are four electron groups around oxygen, three bonding pairs and one lone pair. Like NH$_3$, repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

C With three bonding pairs and one lone pair, the structure is designated as AX$_3$E and has a total of four electron pairs (three X and one E). We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

D There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*, in essence a tetrahedron missing a vertex. However, the H–O–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions:

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

    a. XeO_3
    b. PF_6^-
    c. NO_2^+

Answer a
Answer b
Answer c

EXAMPLE 10.2.210.2.2

Predict the molecular geometry of each molecule.

    1. XeF_2
    2. $SnCl_2$

Given: two chemical compounds

Asked for: molecular geometry

Strategy:

Use the strategy given in Example10.2.110.2.1.

Solution:

1. **A** Xenon contributes eight electrons and each fluorine seven valence electrons, so the Lewis electron structure is

$$:\ddot{F}-\overset{.}{\underset{..}{X}e}-\ddot{F}:$$
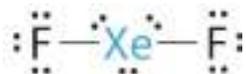
B There are five electron groups around the central atom, two bonding pairs and three lone pairs. Repulsions are minimized by placing the groups in the corners of a trigonal bipyramid.

C From B, XeF_2 is designated as AX_2E_3 and has a total of five electron pairs (two X and three E). With three lone pairs about the central atom, we can arrange the two F atoms in three possible ways: both F atoms can be axial, one can be axial and one equatorial, or both can be equatorial:


(a)	(b)	(c)
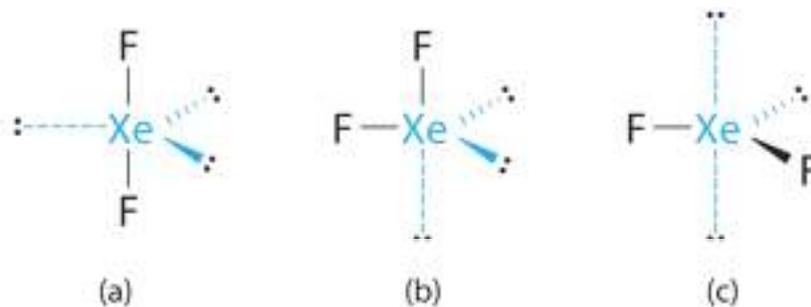
Interactions

90 LP–LP	0	2	2

The structure with the lowest energy is the one that minimizes LP–LP repulsions. Both (b) and (c) have two 90° LP–LP interactions, whereas structure (a) has none. Thus both F atoms are in the axial positions, like the two iodine atoms around the central iodine in I_3^-. All LP–BP interactions are equivalent, so we do not expect a deviation from an ideal 180° in the F–Xe–F bond angle.

D With two nuclei about the central atom, the molecular geometry of XeF_2 is linear. It is a trigonal bipyramid with three missing equatorial vertices.

2. **A** The tin atom donates 4 valence electrons and each chlorine atom donates 7 valence electrons. With 18 valence electrons, the Lewis electron structure is
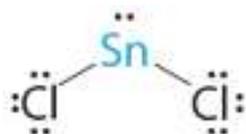
B There are three electron groups around the central atom, two bonding groups and one lone pair of electrons. To minimize repulsions the three groups are initially placed at 120° angles from each other.

C From B we designate $SnCl_2$ as AX_2E. It has a total of three electron pairs, two X and one E. Because the lone pair of electrons occupies more space than the bonding pairs, we expect a decrease in the Cl–Sn–Cl bond angle due to increased LP–BP repulsions.

D With two nuclei around the central atom and one lone pair of electrons, the molecular geometry of $SnCl_2$ is bent, like SO_2, but with a Cl–Sn–Cl bond angle of 95°. The molecular geometry can be described as a trigonal planar arrangement with one vertex missing.

Calculation of Percentage Ionic Character

Several empirical equations have been proposed to calculate the percentage ionic character in the bond. It is important to note that no bond (even ionic) in chemistry is 100% ionic. The following methods have been proposed for this purpose:

1. Pauling's Electronegativity Difference Method
According to Pauling, when the electronegativity difference between two elements is 1.7, percentage of ionic character is 50% i.e.

1.7 ΔE.N. produces 50% ionic character

x ΔE.N. produces $\dfrac{x\ \Delta E.N.}{1.7}$ x 50 ionic character

% Ionic character $= \dfrac{\Delta E.N.}{1.7}$ x 50

For example; in HF, the electronegativity difference between H and F is 1.9. Therefore, % ionic character is computed to be 56%.

% Ionic character $= \dfrac{1.9.}{1.7}$ x 50 = 56%

The relation between electronegativity difference and percentage ionic character of compounds is summarized as:

(i). When ΔE.N. = 1.7,	the bond has 50% ionic and 50% covalent character.
(ii). When ΔE.N. < 1.7,	the bond has ionic character less than 50% and covalent character more than 50% i.e. the bond is more covalent than ionic in character.
(iii). When ΔE.N. > 1.7,	the bond has ionic character more than 50% and covalent character less than 50% i.e. the bond is more ionic than covalent in character.

2.Pauling's Alternative Electronegativity Difference Method

Pauling suggested the following alternative equation for calculating the % ionic character in the bond:

$$\% \text{ Ionic character} = \left[18 \, (\Delta E.N.)^{1.4} \right] \%$$

For example; the percentage of ionic character in HF molecule having $\Delta E.N. = 4.0 - 2.1 = 1.9$ is found to be $= \left| 18 \, (1.9)^{1.4} \right| \% - 44.12\%$. This value (44.12%) is quite close to that (45%) obtained by Pauling from dipole moment of HF molecule.

3. Hannay and Smith Electronegativity Difference Method

These two chemists proposed the following equation called Hannay-Smith's Equation for calculating the % ionic character in the bond:

$$\% \text{ Ionic character} = \left[16 \, (\Delta E.N.) + 3.5 \, (\Delta E.N.)^2\right]\%$$

For example; in HF ($\Delta E.N. = 1.9$), HCl ($\Delta E.N. = 0.9$), HBr ($\Delta E.N. = 0.7$) and HI ($\Delta E.N. = 0.4$), the percentage of ionic character by Hannay-Smith's Equation is calculated to be:

$$\% \text{ Ionic character in HF} = \left|16 \, (1.9) + 3.5 \, (1.9)^2\right| = 43.04\%$$
$$\% \text{ Ionic character in HCl} = \left|16 \, (0.9) + 3.5 \, (0.9)^2\right| = 17.24\%$$
$$\% \text{ Ionic character in HBr} = \left|16 \, (0.7) + 3.5 \, (0.7)^2\right| = 12.92\%$$
$$\% \text{ Ionic character in HI} = \left|16 \, (0.4) - 3.5 \, (0.4)^2\right| = 6.96\%$$

Fajan's Rule

Although atomic bond in a compound like M^+X^- is considered to be 100% ionic, actually it also has some covalent character. An explanation for the partial covalent character of an ionic bond has been given by Fajan. According to Fajan, if two oppositely charged ions are brought together, the nature of the bond between them depends upon the effect of one ion on the other.

When two oppositely charged ions (say A^+ and B^-) approach each other the positive ion attracts electrons on the outermost shell of the anion and repels its positively charged nucleus. This results in the distortion, deformation or polarization of the anion. If the polarization is quite small, an ionic bond is formed, while if the degree of polarization is large, a covalent bond results.

Thus the power of an ion (cation) to distort the other ion is known as its **polarization power** and the tendency of the ion(anion) to get polarized by the other ion is known as its **polarisability**. Greater the polarization power or polarisability of an ion, greater will be its tendency to form a covalent bond.

The polarising power, or polarisability and hence formation of covalent bond is favoured by the following factors:

- **Small Positive Ion (Cation):** Due to greater concentration of positive charge on a small area, the smaller cation has high polarising power. This explains why LiCl is more covalent than KCl.
- **Large Negative Ion (Anion):** The larger the anion, the greater is its polarisability, i.e. susceptibility to get polarised. It is due to the fact that the outer electrons of a large anion are loosely held and hence can be more easily pulled out by the cation. This explains why iodides, among halides, are most covalent in nature.
- **Large Charge on Either of the Two Ions:** As the charge on the ion increases, the electrostatic attraction of the cation for the outer electrons of the anion also increases, with the result its ability for forming the covalent bond increases. Thus covalency increases in the order : Na^+Cl^-, $Mg^{2+}(Cl_2)^{2-}$, $Al^{3+}(Cl_3)^{3-}$
- **Electronic Configuration of the Cation :** For the two ions of the same size and charge, one with a pseudo noble gas configuration (i.e., 18 electrons in outer-most shell) than a cation with noble gas configuration (i.e. 8 electrons in outermost shell) will be more polarising. Thus copper (I) chloride is more covalent than sodium chloride although Cu^+ ion (0.96A°) and Na+ ion (0.95A°) have same size and charge.

The orbital overlapping involved in covalency reduces, the charge on each ion and so weakens the electrovalent forces throughout the solid, as is evident from the melting point of lithium halides.

LiF = 870°C   LiCl = 613°C

LiBr = 547°C   LiI = 446°C

From the above discussion, we find that **greater the possibility of polarisation, lower is the melting point and heat of sublimation and greater is the solubility in non-polar solvents.**

Example: The melting point of KCl is higher than that of AgCl though the crystal radii of Ag^+ and K^+ ions are almost the same.

Solution : Now whenever any comparison is asked about the melting point of the compounds which are fully ionic from the electron transfer concept it means that the compound having lower melting point has got lesser amount of ionic character than the other one. To analyse such a question first find out the difference between the 2 given compounds. Here in both the compounds the anion is the same. So the deciding factor would be the cation. Now if the anion is different, then the answer should be from the variation of the anion. Now in the above example, the difference of the cation is their electronic configuration. $K^+ = [Ar]$; $Ag^+ = [Kr] 4d^{10}$. This is now a comparison between a noble gas core and pseudo noble gas core,

the   analysis   of   which   we   have   already   done.   So   try   to   finish   off   this   answer.

Percentage of Ionic Character

Every ionic compound having some percentage of covalent character according to Fajan's rule. The percentage of ionic character in a compound having some covalent character can be calculated by the following equation.

The percent ionic character = Observed dipole moment/Calculated dipole moment assuming 100% ionic bond × 100

Example: Dipole moment of KCl is $3.336 × 10^{-29}$ coulomb metre which indicates that it is highly polar molecule. The interatomic distance between k^+ and Cl^- is $2.6 ×10^{-10}$ m. Calculate the dipole moment of KCl molecule if there were opposite charges of one fundamental unit located at each nucleus. Calculate the percentage ionic character of KCl.

Solution: Dipole moment $μ = e × d$ coulomb metre

For KCl d = $2.6 × 10^{-10}$ m

For complete separation of unit charge

e = $1.602 × 10^{-19}$ C
Hence $μ = 1.602 × 10^{-19} × 2.6 × 10^{-10} = 4.1652 × 10^{-29}$ Cm
$μ_{KCl} = 3.336 × 10^{-29}$ Cm
∴ % ionic character of KCl = $3.336×10^{-29}/4.165×10^{-29}$ = 80.09%

Example. Calculate the % of ionic character of a bond having length = 0.83 Å and 1.82 D as it's observed dipole moment.

Solution: Tocalculate $μ$ considering 100% ionic bond
 = $4.8 × 10^{-10} × 0.83 × 10^{-8}$ esu cm
= $4.8 × 0.83 × 10^{-18}$ esu cm = 3.984 D

∴ % ionic character = 1.82/3.984 × 100 = 45.68

The example given above is of a very familiar compound called HF. The % ionic character is nearly 43.25%, so the % covalent character is (100 – 43.25) = 56.75%. But from the octet rule HF should have been a purely covalent compound but actually it has some amount of ionic character in it, which is due to the electronegativity difference of H and F. Similarly knowing the bond length and observed dipole moment of HCl, the % ionic character can be known. It was found that HCl

has 17% ionic character. Thus it can be clearly seen that although we call HCl and HF as covalent compounds but it has got appreciable amount of ionic character. So from now onwards we should call a compound having more of ionic less of covalent and vice versa rather than fully ionic or covalent

Q.9. A diatomic molecule has a dipole moment equal to 1.2 D and bond length is 1.0 Å, the fraction of electronic charge 'e' existing on each atom is :

(A) 25%

(B) 30%

(C) 35%

(D) none of these

Solution:

We have, δ = Dipole moment / d = $(1.2 \times 10^{-18}$ esu cm$)/(1.0 \times 10^{-8})$ cm \

= 1.2×10^{-10} esu

Therefore, fraction of electronic charge on each end = $(1.2 \times 10^{-10})/(4.8 \times 10^{-10})$

   = 0.25 = 25%   **(A)[Ans.]**

Q.10. The dipole moment of LiH is 1.964×10^{-29} cm and the intermolecular distance between Li and H in this molecule is 1.596 Å. The percentage ionic character in molecule is :

(A) 75%

(B) 76%

(C) 76.82%

(D) 77%

Solution:

We have, $\mu_{molecule} = \delta \times d$

Or, $1.964 \times 10^{-29} = \delta \times 1.596 \times 10^{-10}$

Therefore, $\delta = 1.2306 \times 10^{-19}$ C

Therefore,   % of ionic nature $= (1.2306 \times 10^{-19})/(1.602 \times 10^{-19}) \times 100$ %

= 76.82%   **(C)[Ans.]**

Molecular Orbital Theory

For almost every covalent molecule that exists, we can now draw the Lewis structure, predict the electron-pair geometry, predict the molecular geometry, and come close to predicting bond angles. However, one of the most important molecules we know, the oxygen molecule O_2, presents a problem with respect to its Lewis structure. We would write the following Lewis structure for O_2:
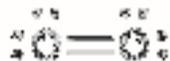
This electronic structure adheres to all the rules governing Lewis theory. There is an O=O double bond, and each oxygen atom has eight electrons around it. However, this picture is at odds with the magnetic behavior of oxygen. By itself, O_2 is not magnetic, but it is attracted to magnetic fields. Thus, when we pour liquid oxygen past a strong magnet, it collects between the poles of the magnet and Such attraction to a magnetic field is called **paramagnetism**, and it arises in

molecules that have unpaired electrons. And yet, the Lewis structure of O_2 indicates that all electrons are paired. How do we account for this discrepancy?

Experiments show that each O_2 molecule has two unpaired electrons. The Lewis-structure model does not predict the presence of these two unpaired electrons. Unlike oxygen, the apparent weight of most molecules decreases slightly in the presence of an inhomogeneous magnetic field. Materials in which all of the electrons are paired are **diamagnetic** and weakly repel a magnetic field. Paramagnetic and diamagnetic materials do not act as permanent magnets. Only in the presence of an applied magnetic field do they demonstrate attraction or repulsion.

Molecular orbital theory (MO theory) provides an explanation of chemical bonding that accounts for the paramagnetism of the oxygen molecule. It also explains the bonding in a number of other molecules, such as violations of the octet rule and more molecules with more complicated bonding (beyond the scope of this text) that are difficult to describe with Lewis structures. Additionally, it provides a model for describing the energies of electrons in a molecule and the probable location of these electrons. Unlike valence bond theory, which uses hybrid orbitals that are assigned to one specific atom, MO theory uses the combination of atomic orbitals to yield molecular orbitals that are *delocalized* over the entire molecule rather than being localized on its constituent atoms.

Molecular orbital theory describes the distribution of electrons in molecules in much the same way that the distribution of electrons in atoms is described using atomic orbitals. Using quantum mechanics, the behavior of an electron in a molecule is still described by a wave function, Ψ, analogous to the behavior in an atom. Just like electrons around isolated atoms, electrons around atoms in molecules are limited to discrete (quantized) energies. The region of space in which a valence electron in a molecule is likely to be found is called a **molecular orbital (Ψ^2)**. Like an atomic orbital, a molecular orbital is full when it contains two electrons with opposite spin.

We will consider the molecular orbitals in molecules composed of two identical atoms (H_2 or Cl_2, for example). Such molecules are called **homonuclear diatomic molecules**. In these diatomic molecules, several types of molecular orbitals occur.

The mathematical process of combining atomic orbitals to generate molecular orbitals is called the **linear combination of atomic orbitals (LCAO)**. The wave function describes the wavelike properties of an electron. Molecular orbitals are combinations of atomic orbital wave functions. Combining waves can lead to constructive interference, in which peaks line up with peaks, or destructive interference, in which peaks line up with trough.In orbitals, the waves are three dimensional,

and they combine with in-phase waves producing regions with a higher probability of electron density and out-of-phase waves producing nodes, or regions of no electron density.

There are two types of molecular orbitals that can form from the overlap of two atomic *s*orbitals on adjacent atoms. The two types are illustrated in Figure 3. The in-phase combination produces a lower energy **σ_s molecular orbital** (read as "sigma-s") in which most of the electron density is directly between the nuclei. The out-of-phase addition (which can also be thought of as subtracting the wave functions) produces a higher energy ⬚**molecular orbital**(read as "sigma-s-star") molecular orbital in which there is a node between the nuclei. The asterisk signifies that the orbital is an antibonding orbital. Electrons in a σ_s orbital are attracted by both nuclei at the same time and are more stable (of lower energy) than they would be in the isolated atoms. Adding electrons to these orbitals creates a force that holds the two nuclei together, so we call these orbitals **bonding orbitals**. Electrons in the ⬚ orbitals are located well away from the region between the two nuclei. The attractive force between the nuclei and these electrons pulls the two nuclei apart. Hence, these orbitals are called **antibonding orbitals**. Electrons fill the lower-energy bonding orbital before the higher-energy antibonding orbital, just as they fill lower-energy atomic orbitals before they fill higher-energy atomic orbitals.
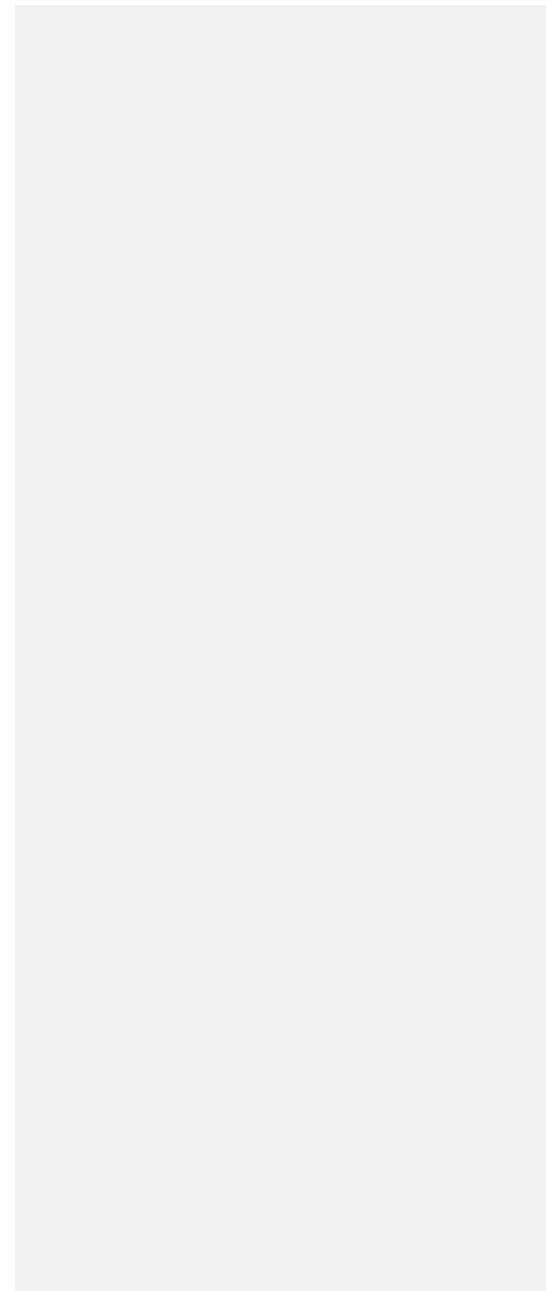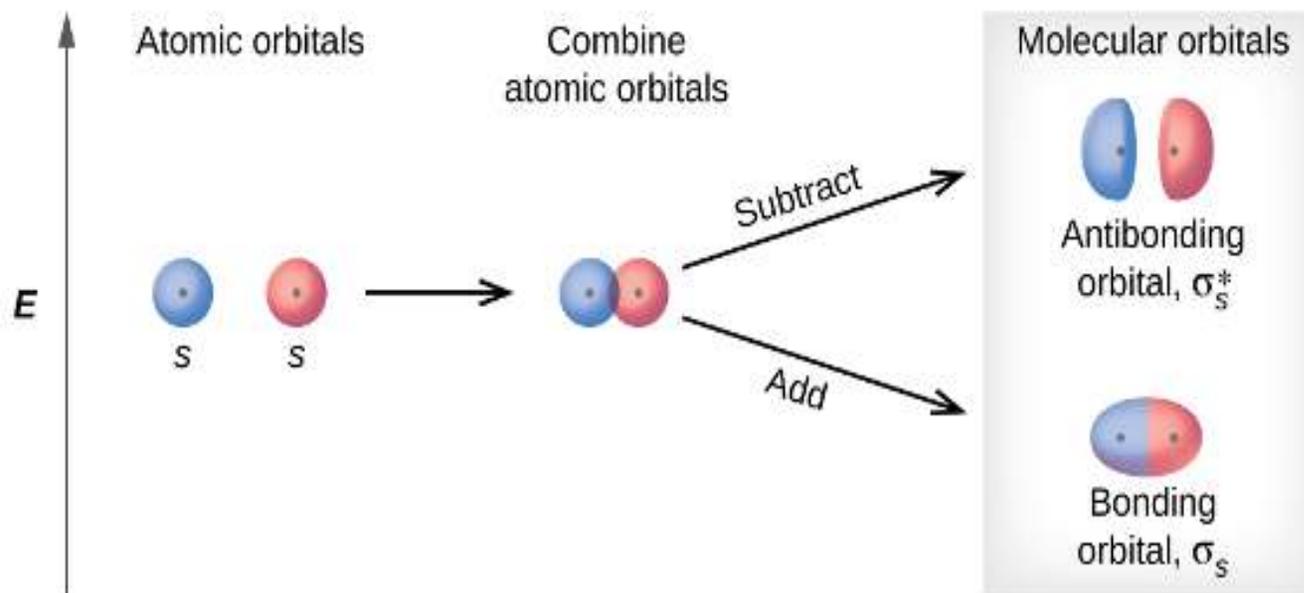
Figure 3. Sigma (σ) and sigma-star (σ*) molecular orbitals are formed by the combination of two s atomic orbitals.
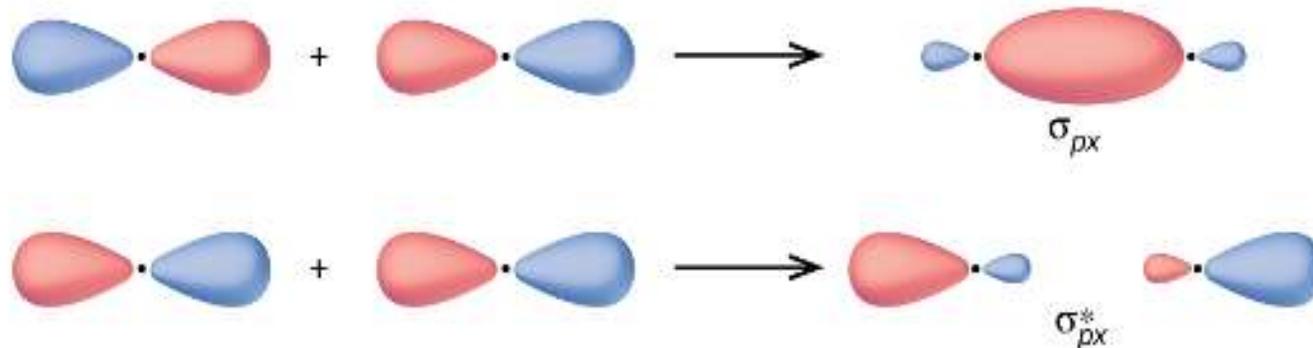
We indicate the phases by shading the orbital lobes different colors. When orbital lobes of the same phase overlap, constructive wave interference increases the electron density. When regions of opposite phase overlap, the destructive wave interference decreases electron density and creates nodes. When p orbitals overlap end to end, they create σ and σ* orbitals (Figure 4). If two atoms are located along the x-axis in a Cartesian coordinate system, the two p_x orbitals overlap end to end and form σ_{px} (bonding) and (antibonding) (read as "sigma-p-x" and "sigma-p-x star," respectively). Just as with s-orbital overlap, the asterisk indicates the orbital with a node between the nuclei, which is a higher-energy, antibonding orbital.

Figure 4. Combining wave functions of two p atomic orbitals along the internuclear axis creates two molecular orbitals, σ_p and $\sigma*_p$.

The side-by-side overlap of two p orbitals gives rise to a **pi (π) bonding molecular orbital** and a **π* antibonding molecular orbital**, as shown in Figure 5. In valence bond theory, we describe π bonds as containing a nodal plane containing the internuclear axis and perpendicular to the lobes of the p orbitals, with electron density on either side of the node. In molecular orbital theory, we describe the π orbital by this same shape, and a π bond exists when this orbital contains electrons. Electrons in this orbital interact with both nuclei and help hold the two atoms together, making it a bonding orbital. For the out-of-phase combination, there are two nodal planes created, one along the internuclear axis and a perpendicular one between the nuclei.
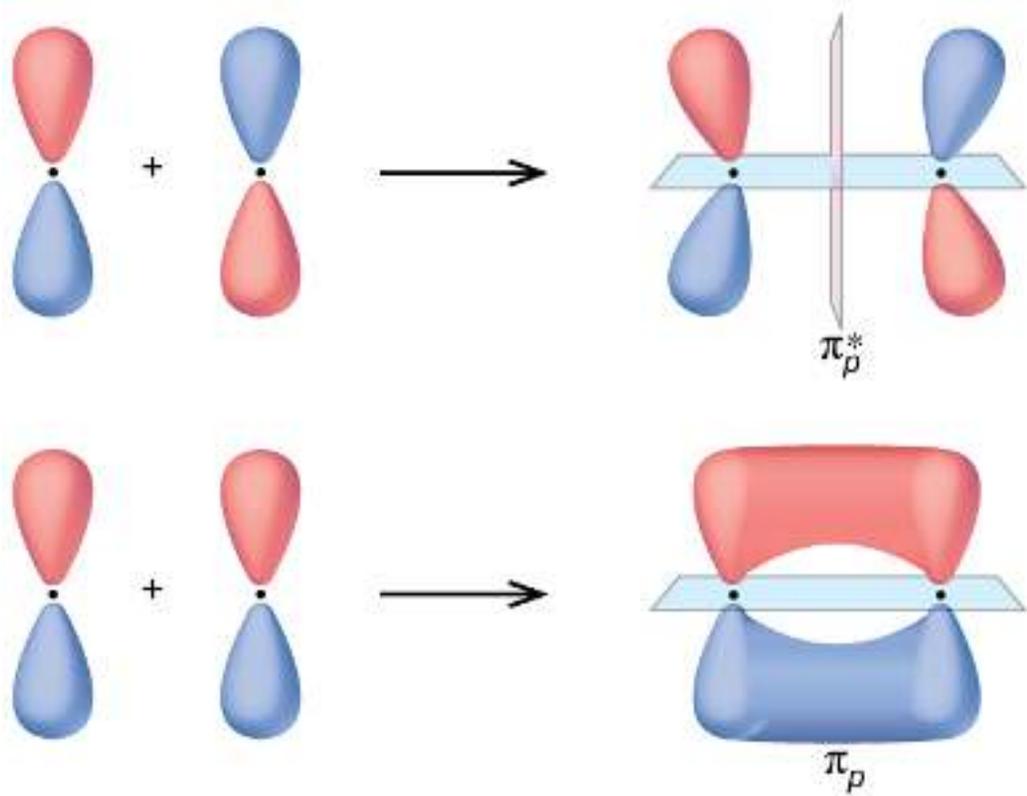
Figure 5. Side-by-side overlap of each two *p* orbitals results in the formation of two π molecular orbitals. Combining the out-of-phase orbitals results in an antibonding molecular orbital with two nodes. One contains the internuclear axis, and one is perpendicular to the axis. Combining the in-phase orbitals results in a bonding orbital. There is a node (blue) containing the internuclear axis with the two lobes of the orbital located above and below this node.

In the molecular orbitals of diatomic molecules, each atom also has two sets of p orbitals oriented side by side (p_y and p_z), so these four atomic orbitals combine pairwise to create two π orbitals and two π^* orbitals. The π_{py} and π_{py}^* orbitals are oriented at right angles to the π_{pz} and π_{pz}^* orbitals. Except for their orientation, the π_{py} and π_{pz} orbitals are identical and have the same energy; they are **degenerate orbitals**. The π_{py}^* and π_{pz}^* antibonding orbitals are also degenerate and identical except for their orientation. A total of six molecular orbitals results from the combination of the six atomic p orbitals in two atoms: σ_{px} and σ_{px}^*, π_{py} and π_{py}^*, π_{pz} and π_{pz}^*.

Example 1

Molecular Orbitals

Predict what type (if any) of molecular orbital would result from adding the wave functions so each pair of orbitals shown overlap. The orbitals are all similar in energy.


$3p_x$ and $3p_x$

(a)

$3p_x$ and $3p_y$

(b)

$3p_y$ and $3p_y$

(c)
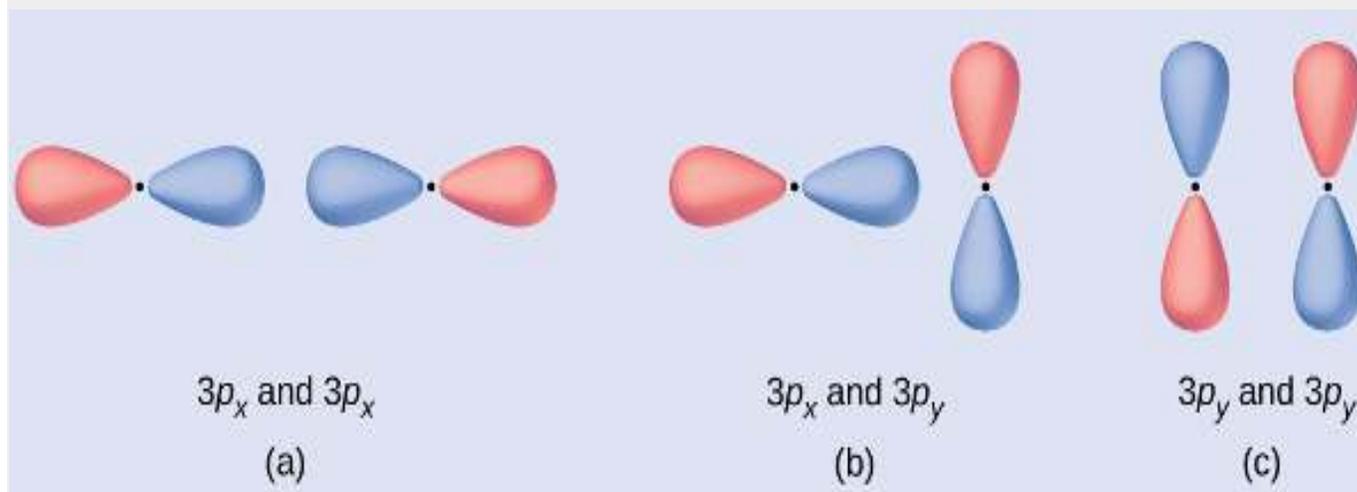
Solution

(a) is an in-phase combination, resulting in a σ_{3p} orbital

(b) will not result in a new orbital because the in-phase component (bottom) and out-of-phase component (top) cancel out. Only orbitals with the correct alignment can combine.

(c) is an out-of-phase combination, resulting in a orbital.

Label the molecular orbital shown as σ or π, bonding or antibonding and indicate where the node occurs.
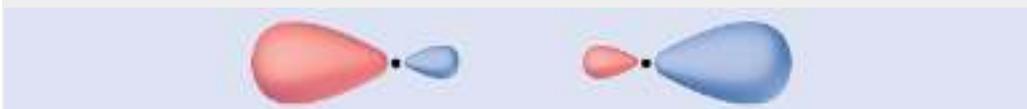
Answer:

   The orbital is located along the internuclear axis, so it is a σ orbital. There is a node bisecting the internuclear axis, so it is an antibonding orbital.

.

Molecular Orbital Energy Diagrams

 For a diatomic molecule, the atomic orbitals of one atom are shown on the left, and those of the other atom are shown on the right. Each horizontal line represents one orbital that can hold two electrons. The molecular orbitals formed by the combination of the atomic orbitals are shown in the center. Dashed lines show which of the atomic orbitals combine to form the molecular orbitals. For each pair of atomic orbitals that combine, one lower-energy (bonding) molecular orbital and one higher-energy (antibonding) orbital result. Thus we can see that combining the six $2p$ atomic orbitals results in three bonding orbitals (one σ and two π) and three antibonding orbitals (one σ* and two π*).

We predict the distribution of electrons in these molecular orbitals by filling the orbitals in the same way that we fill atomic orbitals, by the Aufbau principle. Lower-energy orbitals fill first, electrons spread out among degenerate orbitals before pairing, and each

orbital can hold a maximum of two electrons with opposite spins ([Figure 8](#)). Just as we write electron configurations for atoms, we can write the molecular electronic configuration by listing the orbitals with superscripts indicating the number of electrons present. For clarity, we place parentheses around molecular orbitals with the same energy. In this case, each orbital is at a different energy, so parentheses separate each orbital. Thus we would expect a diatomic molecule or ion containing seven electrons (such as Be_2^+) would have the molecular electron configuration $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^1 (\sigma_{2p}^*)^2$. It is common to omit the core electrons from molecular orbital diagrams and configurations and include only the valence electrons.

Figure 8. This is the molecular orbital diagram for the homonuclear diatomic Be_2^+, showing the molecular orbitals of the valence shell only. The molecular orbitals are filled in the same manner as atomic orbitals, using the Aufbau principle and Hund's rule.

Bond Order

The filled molecular orbital diagram shows the number of electrons in both bonding and antibonding molecular orbitals. The net contribution of the electrons to the bond strength of a molecule is identified by determining the **bond order** that results from the filling of the molecular orbitals by electrons.

When using Lewis structures to describe the distribution of electrons in molecules, we define bond order as the number of bonding pairs of electrons between two atoms. Thus a single bond has a bond order of 1, a double bond has a bond order of 2, and a triple bond has a bond order of 3. We define bond order differently when we use the molecular orbital description of the distribution of electrons, but the resulting bond order is usually the same. The MO technique is more accurate and can handle cases when the Lewis structure method fails, but both methods describe the same phenomenon.

In the molecular orbital model, an electron contributes to a bonding interaction if it occupies a bonding orbital and it contributes to an antibonding interaction if it occupies an antibonding orbital. The bond order is calculated by subtracting the destabilizing (antibonding) electrons from the stabilizing (bonding) electrons. Since a bond consists of two electrons, we divide by two to get the bond order. We can determine bond order with the following equation:

$$\text{bond order} = \frac{(\text{number of bonding electrons}) - (\text{number of antibonding electrons})}{2}$$

The order of a covalent bond is a guide to its strength; a bond between two given atoms becomes stronger as the bond order increases. If the distribution of electrons in the molecular orbitals between two atoms is such that the resulting bond would have a bond order of zero, a stable bond does not form. We next look at some specific examples of MO diagrams and bond orders.

Bonding in Diatomic Molecules

A dihydrogen molecule (H_2) forms from two hydrogen atoms. When the atomic orbitals of the two atoms combine, the electrons occupy the molecular orbital of lowest energy, the σ_{1s}bonding orbital. A dihydrogen molecule, H_2, readily forms because the energy of a H_2molecule is lower than that of two H atoms. The σ_{1s} orbital that contains both electrons is lower in energy than either of the two $1s$ atomic orbitals.

A molecular orbital can hold two electrons, so both electrons in the H_2 molecule are in the σ_{1s}bonding orbital; the electron configuration is ⸤⸥⸤⸥. We represent this configuration by a molecular orbital energy diagram (Figure 9) in which a single upward arrow indicates one electron in an orbital, and two (upward and downward) arrows indicate two electrons of opposite spin.
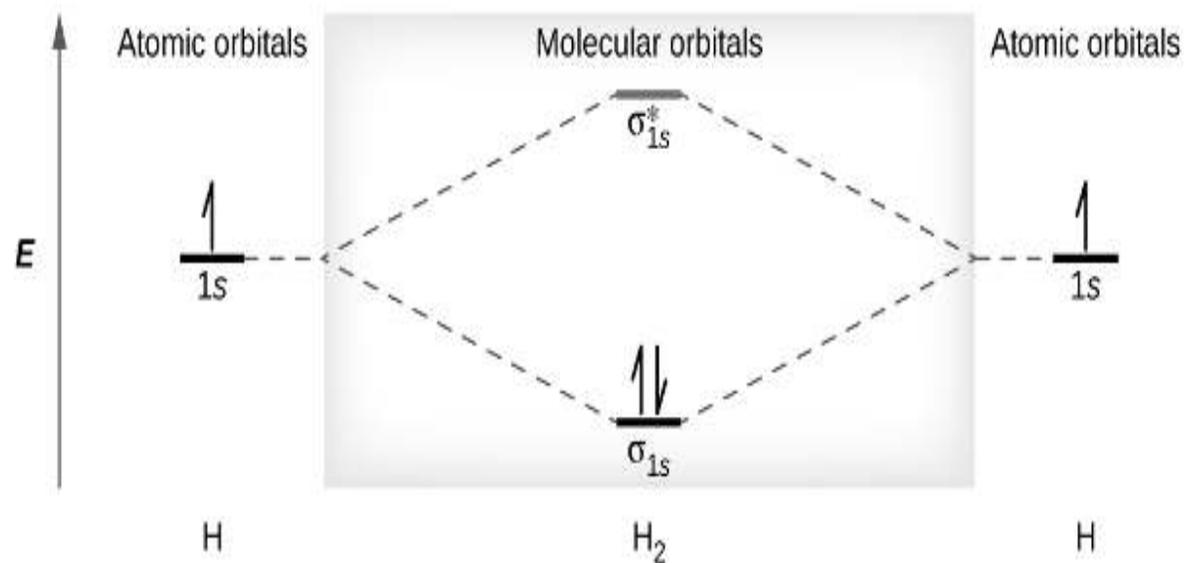

Figure 9. The molecular orbital energy diagram predicts that H_2 will be a stable molecule with lower energy than the separated atoms.

A dihydrogen molecule contains two bonding electrons and no antibonding electrons so we have

$$\text{bond order in } H_2 = \frac{(2-0)}{2} = 1$$

Because the bond order for the H–H bond is equal to 1, the bond is a single bond.

A helium atom has two electrons, both of which are in its $1s$ orbital. Two helium atoms do not combine to form a dihelium molecule, He_2, with four electrons, because the stabilizing effect of the two electrons in the lower-energy bonding orbital would be offset by the destabilizing effect of the two electrons in the higher-energy antibonding molecular orbital. We would write the hypothetical electron configuration of He_2 as $(\sigma_{1s})^2(\sigma^*_{1s})^2$ as in Figure 10. The net energy change would be zero, so there is no driving force for helium atoms to form the diatomic molecule. In fact, helium exists as discrete atoms rather than as diatomic molecules. The bond order in a hypothetical dihelium molecule would be zero.

$$\text{bond order in } He_2 = \frac{(2-2)}{2} = 0$$

A bond order of zero indicates that no bond is formed between two atoms.
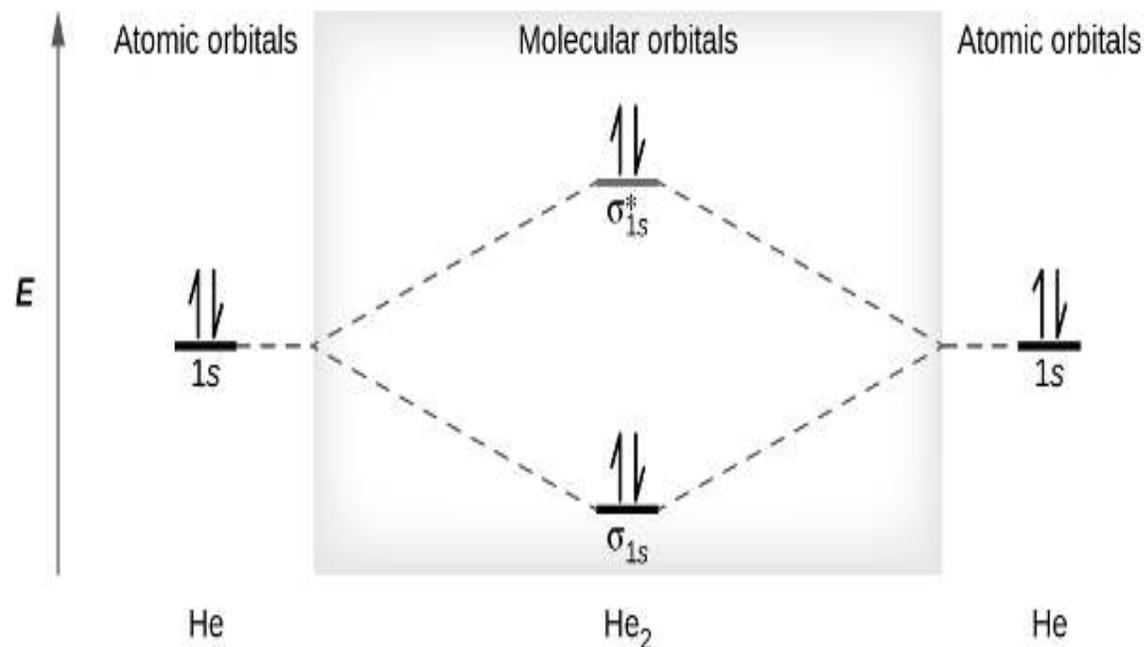
Figure 10. The molecular orbital energy diagram predicts that He_2 will not be a stable molecule, since it has equal numbers of bonding and antibonding electrons.

The Diatomic Molecules of the Second Period

Eight possible homonuclear diatomic molecules might be formed by the atoms of the second period of the periodic table: Li_2, Be_2, B_2, C_2, N_2, O_2, F_2, and Ne_2. However, we can predict that the Be_2 molecule and the Ne_2 molecule would not be stable. We can see this by a consideration of the molecular electron configurations (Table 3).

We predict valence molecular orbital electron configurations just as we predict electron configurations of atoms. Valence electrons are assigned to valence molecular orbitals with the lowest possible energies. Consistent with Hund's rule, whenever there are two or more degenerate molecular orbitals, electrons fill each orbital of that type singly before any pairing of electrons takes place.

As we saw in valence bond theory, σ bonds are generally more stable than π bonds formed from degenerate atomic orbitals. Similarly, in molecular orbital theory, σ orbitals are usually more stable than π orbitals. However, this is not always the case. The MOs for the valence orbitals of the second period are shown in Figure 11. Looking at Ne_2 molecular orbitals, we see that the order is consistent with the generic diagram shown in the previous section. However, for atoms with three or fewer electrons in the p orbitals (Li through N) we observe a different pattern, in which the σ_p orbital is higher in energy than the π_p set. Obtain the molecular orbital diagram for a homonuclear diatomic ion by adding or subtracting electrons from the diagram for the neutral molecule.
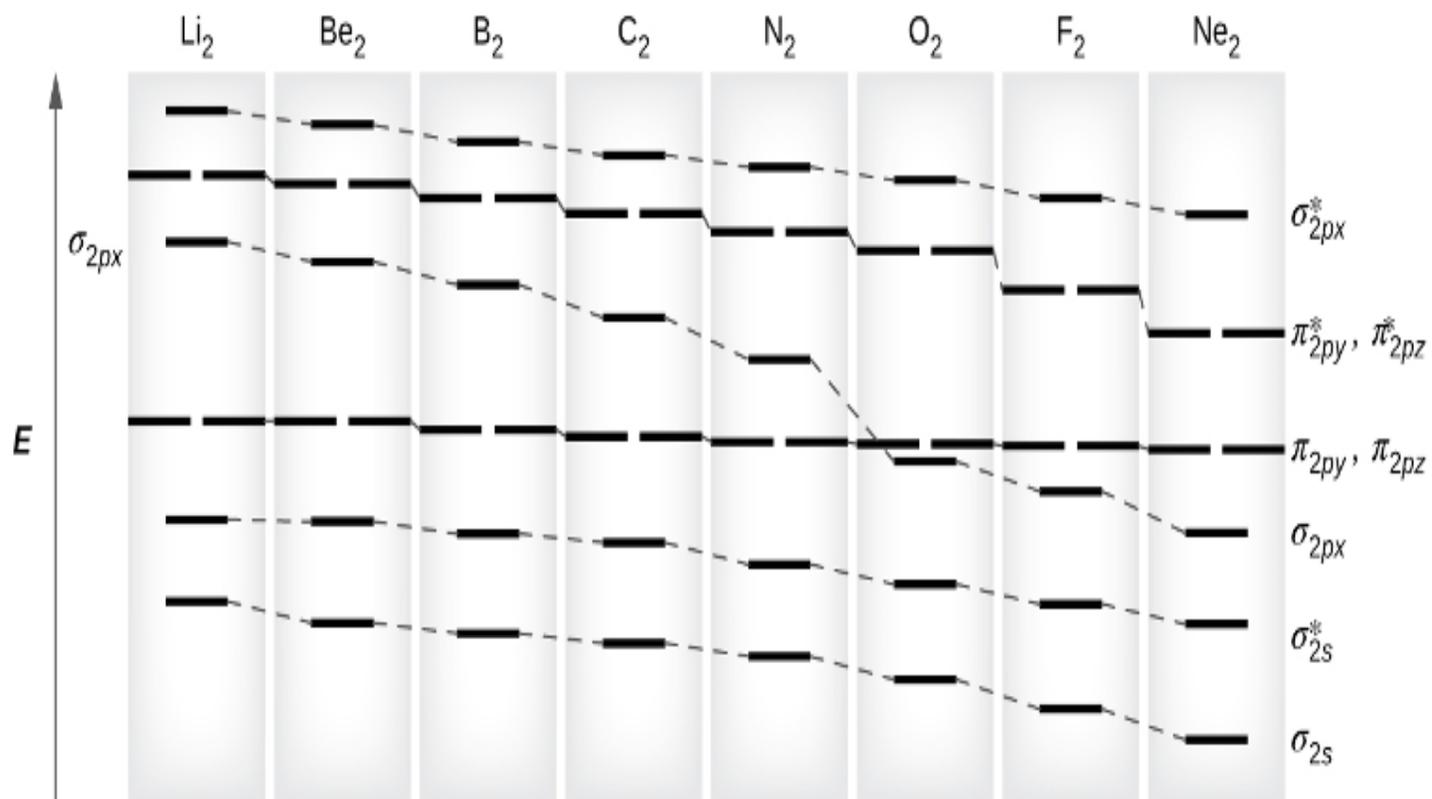
Figure 11. This shows the MO diagrams for each homonuclear diatomic molecule in the second period. The orbital energies decrease across the period as the effective nuclear charge increases and atomic radius decreases. Between N_2 and O_2, the order of the orbitals changes.

This switch in orbital ordering occurs because of a phenomenon called **s-p mixing**. s-p mixing does not create new orbitals; it merely influences the energies of the existing molecular orbitals. The σ_s wavefunction mathematically combines with the σ_p wavefunction, with the result that the σ_s orbital becomes more stable, and the σ_p orbital becomes less stable (Figure 12). Similarly, the antibonding orbitals also undergo s-p mixing, with the σ_{s*} becoming more stable and the σ_{p*} becoming less stable.
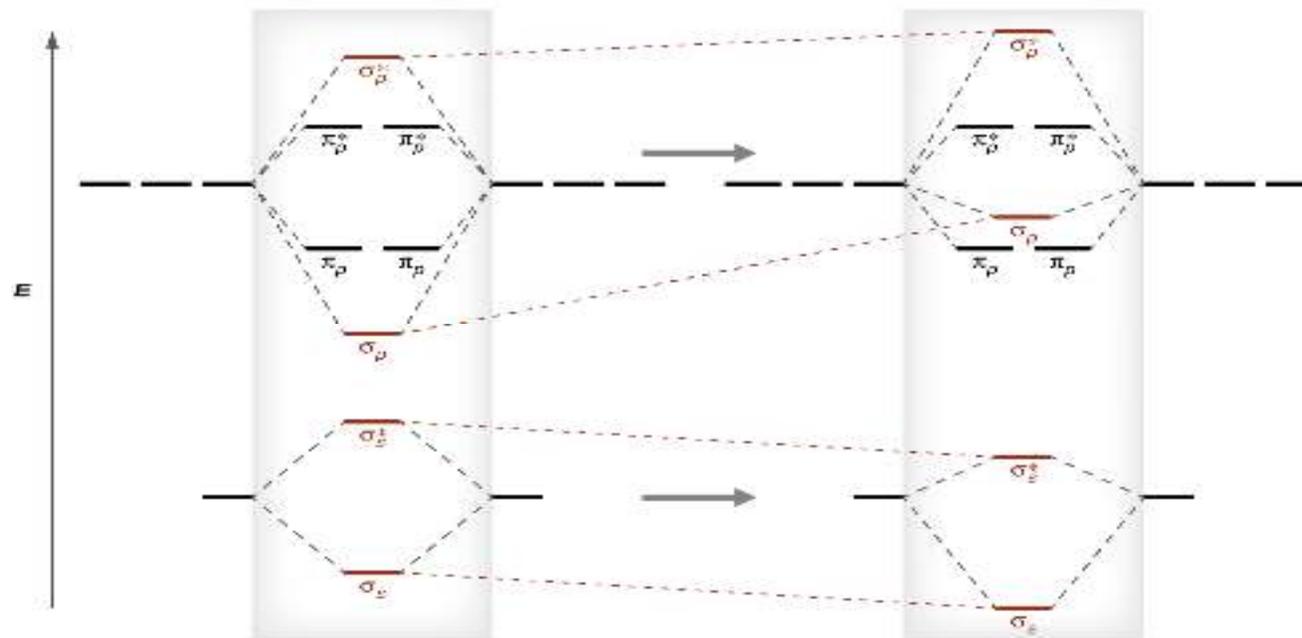
Figure 12. Without mixing, the MO pattern occurs as expected, with the σ_p orbital lower in energy than the σ_p orbitals. When s-p mixing occurs, the orbitals shift as shown, with the σ_p orbital higher in energy than the π_p orbitals.

s-p mixing occurs when the *s* and *p* orbitals have similar energies. When a single *p* orbital contains a pair of electrons, the act of pairing the electrons raises the energy of the orbital. Thus the *2p* orbitals for O, F, and Ne are higher in energy than the *2p* orbitals for Li, Be, B, C, and N. Because of this, O_2, F_2, and N_2 only have negligible s-p mixing (not sufficient to change the energy ordering), and their MO diagrams follow the normal pattern, as shown in Figure 11. All of the other period 2 diatomic molecules do have s-p mixing, which leads to the pattern where the σ_p orbital is raised above the π_p set.

Using the MO diagrams shown in [Figure 11](#), we can add in the electrons and determine the molecular electron configuration and bond order for each of the diatomic molecules. As shown in [Table 3](#), Be_2 and Ne_2 molecules would have a bond order of 0, and these molecules do not exist.

Molecule	Electron Configuration	Bond Order
Li_2	*(illegible)*	1
Be_2 (unstable)	*(illegible)*	0
B_2	*(illegible)*	1
C_2	*(illegible)*	2
N_2	*(illegible)*	3

Molecule	Electron Configuration	Bond Order
O_2		2
F_2		1
Ne_2 (unstable)		0

Table 3. Electron Configuration and Bond Order for Molecular Orbitals in Homonuclear Diatomic Molecules of Period Two Elements

The combination of two lithium atoms to form a lithium molecule, Li_2, is analogous to the formation of H_2, but the atomic orbitals involved are the valence $2s$ orbitals. Each of the two lithium atoms has one valence electron. Hence, we have two valence electrons available for the σ_{2s} bonding molecular orbital. Because both valence electrons would be in a bonding orbital, we would predict the Li_2 molecule to be stable. The molecule is, in fact, present in appreciable concentration in lithium vapor at temperatures near the boiling point of the element. All of the other molecules in Table 3 with a bond order greater than zero are also known.

The O_2 molecule has enough electrons to half fill the ($\pi^*_{2p_y}$, $\pi^*_{2p_z}$) level. We expect the two electrons that occupy these two degenerate orbitals to be unpaired, and this molecular electronic configuration for O_2 is in accord with the fact that the oxygen molecule has two unpaired electrons (Figure 14). The presence of two unpaired electrons has proved to be difficult to explain using Lewis structures, but

the molecular orbital theory explains it quite well. In fact, the unpaired electrons of the oxygen molecule provide a strong piece of support for the molecular orbital theory.

Slater's Rules

The general principle behind Slater's Rule is that the actual charge felt by an electron is equal to what you'd expect the charge to be from a certain number of protons, but minus a certain amount of charge from other electrons. Slater's rules allow you to estimate the effective nuclear charge Z_{eff}Zeff from the real number of protons in the nucleus and the effective shielding of electrons in each orbital "shell" (e.g., to compare the effective nuclear charge and shielding 3d and 4s in transition metals). Slater's rules are fairly simple and produce fairly accurate predictions of things like the electron configurations and ionization energies.

SLATER'S RULES

- **Step 1**: Write the electron configuration of the atom in the following form:

$$(1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p) \ldots$$

- **Step 2**: Identify the electron of interest, and ignore all electrons in higher groups (to the right in the list from Step 1). These do not shield electrons in lower groups
- **Step 3**: Slater's Rules is now broken into two cases:
  - the shielding experienced by an s- or p- electron,
    - electrons within same group shield **0.35**, except the 1s which shield **0.30**
    - electrons within the n-1 group shield **0.85**
    - electrons within the n-2 or lower groups shield **1.00**
  - the shielding experienced by nd or nf valence electrons
    - electrons within same group shield **0.35**
    - electrons within the lower groups shield **1.00**

These rules are summarized in Figure $2.6.12.6.1$ and Table $2.6.12.6.1$.
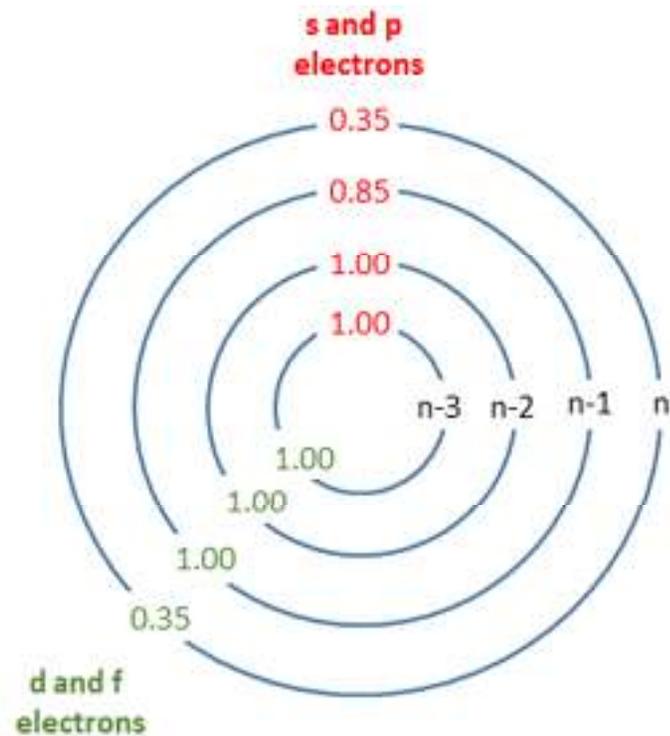
Figure 2.6.12.6.1: *Graphical depiction of Slater's rules with shielding constants indicated.*

Shielding happens when electrons in lower valence shells (or the same valence shell) provide a repulsive force to valence electrons, thereby "negating" some of the attractive force from the positive nucleus. Electrons really close to the atom (n-2 or lower) pretty much just look like protons, so they completely negate. As electrons get closer to the electron of interest, some more complex interactions happen that reduce this shielding. T

Group	Other electrons in the same group	Electrons in group(s) with principal quantum number n and azimuthal quantum number < l	Electrons in group(s) with principal quantum number n-1	Electrons in all group(s) with principal quantum number < n-1
		Table 2.6.12.6.1: Slater's Rules for calculating shieldings		
[1s]	0.30	-	-	-
[ns,np]	0.35	-	0.85	1
[nd] or [nf]	0.35	1	1	1

The shielding numbers in Table 2.6.12.6.1 were derived semi-empirically (i.e., derived from experiments) as opposed to theoretical calculations. This is because quantum mechanics makes calculating shielding effects quite difficult, which is outside the scope of this Module.

Calculating *S*

Sum together the contributions as described in the appropriate rule above to obtain an estimate of the shielding constant, *S*, which is found by totaling the screening by **all electrons** except the one in question.

$$S = \sum n_i S_i \quad (2.6.1)$$

where

- n_i is the number of electrons in a specific shell and subshell and
- S_i is the shielding of the electrions subject to Slater's rules

EXAMPLE 2.6.12.6.1: THE SHIELDING OF 3*P* ELECTRONS OF NITROGEN ATOMS

What is the shielding constant experienced by a 2*p* electron in the nitrogen atom?

Given: Nitrogen (N)

Asked for: S, the shielding constant, for a $2p$ electron

Strategy:

  A. Determine the electron configuration of nitrogen, then write it in the appropriate form.
  B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.

Solution A N: $1s^2\ 2s^2\ 2p^3$

N: $(1s^2)(2s^2,2p^3)$

Solution B $S[2p] = 1.00(0) + 0.85(2) + 0.35(4) = 3.10$

EXAMPLE 2.6.22.6.2: THE SHIELDING OF 3D ELECTRONS OF BROMINE ATOMS

What is the shielding constant experienced by a $3d$ electron in the bromine atom?

Given: Bromine (Br)

Asked for: S, the shielding constant, for a $3d$ electron

Strategy:

  A. Determine the electron configuration of bromine, then write it in the appropriate form.
  B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.

Solution A Br: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$

Br: $(1s^2)(2s^2,2p^6)(3s^2,3p^6)(3d^{10})(4s^2,4p^5)$

   Ignore the group to the right of the 3d electrons. These do not contribute to the shielding constant.

Solution B $S[3d] = 1.00(18) + 0.35(9) = 21.15$

Calculating Z$_{eff}$

 Zeff will be less than the actual nuclear charge (Z) because of the repulsive interaction between core and valence electrons. We can quantitatively represent this difference between Z and Zeff as follows:

S=Z−Zeff

Rearranging this formula to solve for Z_{eff} Zeff we obtain:
Zeff=Z−S

What is the effective nuclear charge experienced by a valence p- electron in boron?

Given: Boron (B)

Asked for: Zeff for a valence p- electron

Strategy:

A. Determine the electron configuration of boron and identify the electron of interest.
B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.
C. Use the Periodic Table to determine the actual nuclear charge for boron.
D. Determine the effective nuclear constant.

Solution:

A B: $1s^2\ 2s^2\ 2p^1$. The valence p- electron in boron resides in the $2p$ subshell.

B: $(1s^2)(2s^2,2p^1)$

B $S[2p] = 1.00(0) + 0.85(2) + 0.35(2) = 2.40$

C $Z = 5$

D Using Equation 2.6.3 2.6.3, $Z_{eff}=2.60$ Zeff=2.60

Anomalous behaviour of lithium with respect to other alkali metals:

• The melting point and boiling point of lithium are higher that than other alkali metals.
• The hardness of lithium is higher than other metals.
• The alkali metal chlorides do not have the capability to form hydrates but lithium chloride crystallizes to form a hydrate $LiCl_2.H_2O$
• Lithium nitrate decomposes to form an oxide whereas other metals on heating give nitrites.
• Compounds of lithium are partially soluble in water whereas the alkali metals are highly soluble in water.

Beryllium: The anomalous properties of beryllium is mainly due to its small size, high electronegativity, high ionization energy and high polarizing power compared to the other elements in the block. The anomalous properties of beryllium compared to other elements of the group is as mentioned below:

• The coordinate number of beryllium is not more than 4 whereas other alkali metals have coordinate number of 6.
• The melting point and boiling points are higher when compared to the other elements of the group.
• They form covalent bonds whereas the other members form of the group form ionic bonds.
• Be does not react with water like the other companions of the group.

These differences in properties with the subsequent rows are a result of:

• the smaller size of the atoms • an outer shell with a maximum of 8 electrons (2s and 2p) and an underlying shell with just 2 electrons • no acessible d-orbitals - energy too high for use in bonding.

Apart from the 2nd row (ignoring H/He 1st row) the later rows all end with inert gases but these do not have completed quantum levels. The 2nd row elements in general can only use the 2s and 2p electrons for bonding restricting the total number of bonds to 4. So N is not expected to have more than 4 bonds and 3 is common, while for P 5 and 6 bonded species are quite common. Reactivity of metals and metalloids For Lithium, compared to other alkali metals Reaction with water: Li reacts slowly with water at 25 °C Na reacts violently and K in flames 2M(s) + 2H2O(l) → 2M+ (aq) + 2OH- + H2(g) In general Li, Be, B, C, N, O, F are less reactive towards water than their heavier congeners. Reaction with oxygen: In conditions of excess oxygen, only Li forms a simple oxide, Li2O. Other metals form peroxides and superoxides Reaction with nitrogen: Li reacts directly with N2 to form Li3N 6Li(s) + N2 (g) → 2Li3N(s). No other alkali metal reacts with N2 Solubility: LiF, LiOH and Li2CO3 are less soluble than the corresponding Na and K compounds For Beryllium compared to the other alkaline earth metals: With water: All Group 2 metals except Be, react with water M(s) + 2H2O(l) → M2+(aq)+ 2OH- (aq) + H2 (g) With oxygen (air): Be only reacts with air above 600 °C if it is finely powdered. The BeO that is formed is amphoteric (other Group 2 oxides are basic). Of the Group 2 elements only Be reacts with NaOH or KOH to liberate H2 and form [Be(OH)4] 2- . Li and Be are metals but are less conducting than the higher members of Group 1 and 2 elements due to their high IEs (electrons are close to nucleus). Ionization of Boron to B3+ requires a large input of energy and B adopts a covalent polymeric structure with semi-metallic properties. The other elements of Group 14 become increasingly metallic as the group is descended due to the decrease in ionization energies. Crystalline Boron is chemically inert - unaffected by boiling HCl

and only slowly oxidized by hot concentrated HNO3 when finely powdered. Covalent character Li+ and Be2+ are small and have strong polarizing abilities. Their compounds are more covalent than those of the heavier elements in their groups. BeCl2 is covalent while MCl2 (M = Mg-Ba) are ionic. The conductivity of fused beryllium chloride is only 1/1000 that of sodium chloride under similar conditions.

Diagonal relationship between lithium and magnesium

The properties of lithium are quite different from the properties of other alkali metals. On the other hand, it shows greater resemblance with magnesium, which is diagonally opposite element to it.

The reason for resemblance of properties of lithium with magnesium is that these two elements have almost same polarizing power.

The following points illustrate the anomalous properties of lithium and its diagonal relationship with magnesium:

(a) The melting point and boiling point of lithium are comparatively high.

(b) Lithium is much harder than the other alkali metals. Magnesium is also hard metal.

(c) Lithium reacts with oxygen least readily to form normal oxide whereas other alkali metals form peroxides and superoxides.

(d) LiOH like Mg (OH)2 is weak base. Hydroxides of other alkali metals are strong bases.

(e) Due to their appreciable covalent nature, the halides and alkyls of lithum and magnesium are soluble in organic solvents.

(f) Unlike elements of group 1 but like magnesium. Lithium forms nitride with nitrogen.

$6Li + N2 \rightarrow 2Li3N$
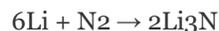
(g) LiCl is deliquescent and crystallizes as a hydrate, LiCI2H2O. Other alkali metals do not form hydrates. also forms hydrate, MgCI2.8H2O .

(h) Unlike other alkali metals lithium reacts directly with carbon to form an ionic carbide. Magnesium also forms a similar carbide.

(i) The carbonates, hydroxides and nitrates of lithium as well as magnesium decompose on heating.

$Li_2CO_3 \rightarrow Li_2O + CO_2$

$MgCO_3 \rightarrow MgO + CO_2$

$2LiOH \rightarrow Li_2O + H_2O$

$Mg(OH)_2 \rightarrow MgO + H_2O$

$4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$

$2Mg(NO_3)_2 \rightarrow 2Mg + 4NO_2 + O_2$
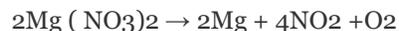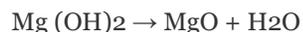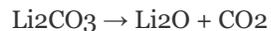
The corresponding salts of other alkali metals are stable towards heat.

(j) Lithium nitrate, on heating, decomposes to give lithium oxide, Li_2O whereas other alkali metals nitrate decomposes to give the corresponding nitrite.

$4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$

$2NaNO_3 \rightarrow 2NaNO_2 + O_2$

$2KNO_3 \rightarrow 2KNO_2 + O_2$
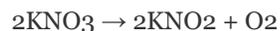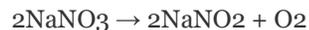
(k) Li_2CO_3, LiOH, LiF and Li_3PO_4 are the only alkali metal salts which are insoluble in water. The corresponding magnesium compounds are also insoluble in water.

(l) Hydrogen carbonates of both lithium and magnesium can not be isolated in solid state. Hydrogen carbonates of other alkali metals can be isolated in solid state.

Diagonal Relationship between Beryllium and Aluminium

The ionic radius of Be^{2+} is estimated to be 31 pm; the charge/radius ratio is nearly the same as that of the Al^{3+} ion. Hence beryllium resembles aluminium in some ways. Some of the similarities are: (i) Like aluminium, beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal. (ii) Beryllium hydroxide dissolves in excess of alkali to give a

beryllate ion, [Be(OH)4] 2– just as aluminium hydroxide gives aluminate ion, [Al(OH)4] – . (iii) The chlorides of both beryllium and aluminium have Cl– bridged chloride structure in vapour phase. Both the chlorides are soluble in organic solvents and are strong Lewis acids. They are used as Friedel Craft catalysts. (iv) Beryllium and aluminium ions have strong tendency to form complexes, BeF4 2–, AlF6 3–.

HYDRIDES CLASSIFICATION AND PROPERTIES

The term hydride is commonly named after binary compounds that hydrogen forms with other elements of the periodic table. Hydride compounds in general form with almost any element, except a few noble gases. The trends and properties vary according to the type of intermolecular force that bonds the elements together, the temperature, its molecular masses, and other components. Hydrides are classified into three major groups, depending on what elements the hydrogen bonds to. The three major groups are covalent, ionic, and metallic hydrides. Formally, hydride is known as the negative ion of a hydrogen, H⁻, also called a hydride ion. Because of this negative charge, hydrides have reducing, or basic properties. Its special characteristics will be further discussed.

Covalent Hydrides

The first major group is covalent hydrides, which is when a hydrogen atom and one or more non-metals form compounds. This occurs when hydrogen covalently bonds to a more electropositive element by sharing electron pairs. These hydrides can be volatile or non-volatile. Volatile simply means being readily able to be vaporized at low temperatures. One such example of a covalent hydride is when hydrogen bonds with chlorine and forms hydrochloric acid (HCl). Examples are listed below:

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \quad (1)$$

$$3H_2(g) + N_2(g) \rightarrow 2NH_3(g) \quad (2)$$
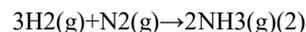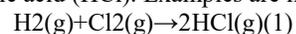
The hydrides of nonmetals on the periodic table become more electronegative as you move from group 13 to 17. This means that they are less capable of donating an electron, and want to keep them because their electron orbital becomes fuller. Instead of donating a H−H−, they would instead donate a H+ because they are more acidic. Examples are boron hydrides and nitrogen hydrides.

BORON HYDRIDES

Boron can form many different types of hydrides; one of them is borane (BH3), which reacts violently with air and is easily oxidized. Borane occurs as a gaseous substance, and can form B2H6 by two borane molecules combined with each other. Borane is not a stable compound because it does not follow a complete octet rule since it has only six valence electrons.

NITROGEN HYDRIDES

Ammonia is an important nitrogen hydride that is possible due to the synthesis of nitrogen and water which is called the Haber-Bosch process. The chemical equation for this reaction is:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad (1)$$
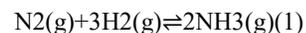
To yield ammonia, there needs to be a catalyst to speed up the reaction, a high temperature and a high pressure. Ammonia is a reagent used in many chemistry experiments and is used as fertilizer. Ammonia can react with sulfuric acid to produce ammonium sulfate, which is also an important fertilizer. In this reaction, ammonia acts as a base since it receives electrons while sulfuric acid gives off electrons.

$$2NH_3(aq) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq) \quad (2)$$
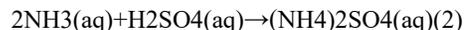
Other hydrides of nitrogen include ammonium chloride, hydrazine and hydroxylamine. Ammonium chloride is widely used in dry-cell batteries and clean metals.

Ionic Hydrides

The second category of hydrides are ionic hydrides (also known as saline hydrides or *pseudohalides*). These compounds form between hydrogen and the most active metals, especially with the alkali and alkaline-earth metals of group one and two elements. In this group, the hydrogen acts as the hydride ion ($H-H^-$). They bond with more electropositive metal atoms. Ionic hydrides are usually binary compounds (i.e., only two elements in the compound) and are also insoluble in solutions.

$$2A(s) + H_2(g) \rightarrow 2AH(s) \quad (3)$$
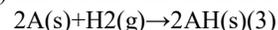
with A as any group 1 metal.

$$A(s) + H_2(g) \rightarrow AH_2(s) \quad (4)$$
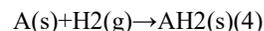
with A as any group 2 metal.

Ionic hydrides combine vigorously with water to produce hydrogen gas.

| EXAMPLE. |

As ionic hydrides, alkali metal hydrides contain the hydride ion H^- as well. They are all very reactive and readily react with various compounds. For example, when an alkali metal reacts with hydrogen gas under heat, an ionic hydride is produced. Alkali metal hydrides also react with water to produce hydrogen gas and a hydroxide salt:
$$MH(s) + H_2O(l) \rightarrow MOH(aq) + H_2(g)$$
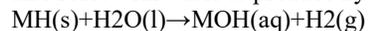
Metallic Hydrides

The third category of hydrides are metallic hydrides, also known as interstitial hydrides. Hydrogen bonds with transition metals. One interesting and unique characteristic of these hydrides are that they can be nonstoichiometric, meaning basically that the fraction of H atoms to the metals are not fixed. Nonstoichiometric compounds have a variable composition.

The idea and basis for this is that with metal and hydrogen bonding there is a crystal lattice that H atoms can and may fill in between the lattice while some might, and is not a definite ordered filling. Thus it is not a fixed ratio of H atoms to the metals. Even so, metallic hydrides consist of more basic stoichiometric compounds as well.