

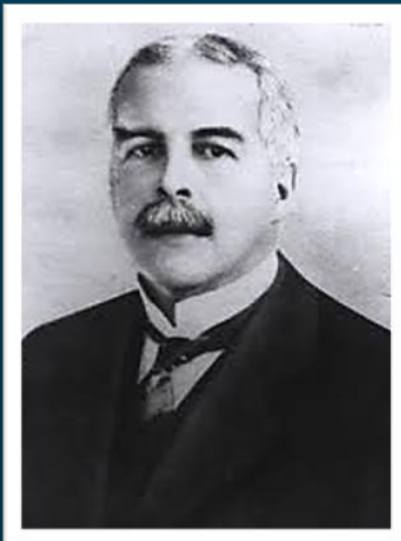
REACTION MECHANISM BASIC CONCEPT(S)

UNIT IV MODULE I

TOPICS: BOND FISSION



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Assistant Professor
Department of Chemistry



Gilbert Newton Lewis
(October 25, 1857–March 23, 1946)

Gilbert N Lewis was an American Physical Chemist known for the discovery of **COVALENT BOND** and his concept of electron pair; his Lewis dot structure and other contribution to Valence Bond Theory (VBT) had shaped modern theories of **CHEMICAL BONDING**.

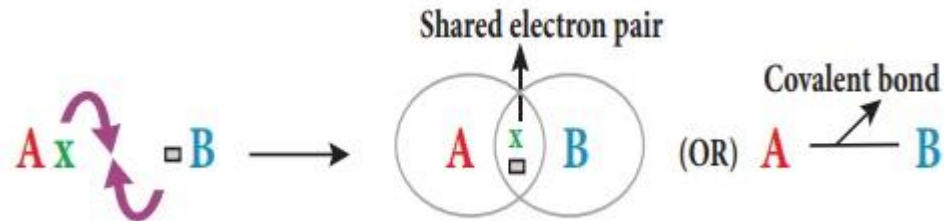
COVALENT BOND(s)

What is a covalent bond in chemistry?



A type of chemical where in two or more atom (s) share one or more electron pairs !

Illustration



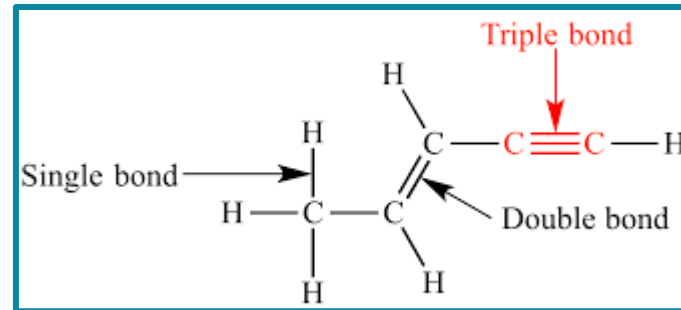
COVALENT BOND(s)

How many type of Covalent Bond is there ?



- ❖ Single Bond (s bond) formed by sharing of two electrons, depicted by a line between the two atoms.
- ❖ Double Bond (p bond) formed by sharing of four electrons, depicted by a double line between the two atoms.
- ❖ Triple Bond formed by sharing of Six electrons, depicted by a Triple line between the two atoms.

Illustration



COVALENT BOND(s)

Bond Fission

Bond fission is breaking of a Covalent Bond

A.

Heterolytic Fission

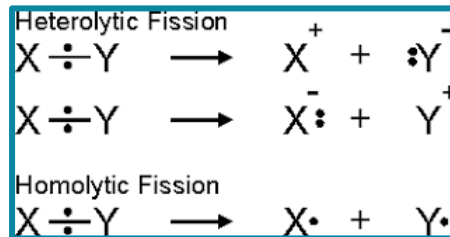
- a. Bond(s) break unevenly
- b. Both electron move to one atom
- c. Two different species are formed, an **Electrophile** and **Nucleophile**

B:

Homolytic

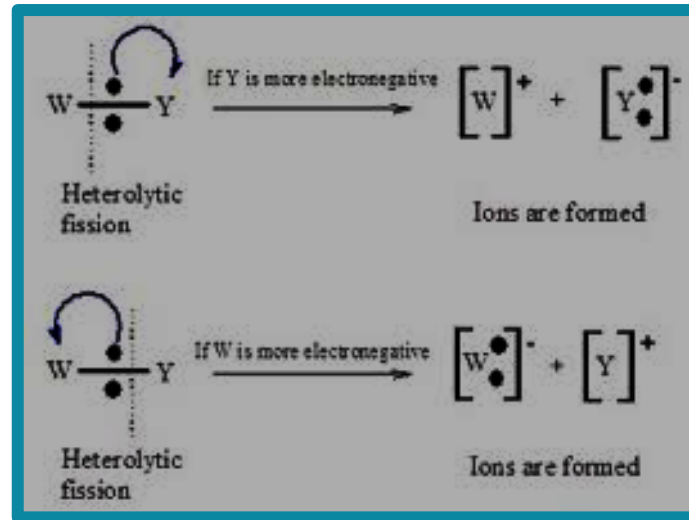
- a. Bond break evenly
- b. One electron move to one atom
- c. Form two free radicals

Illustration



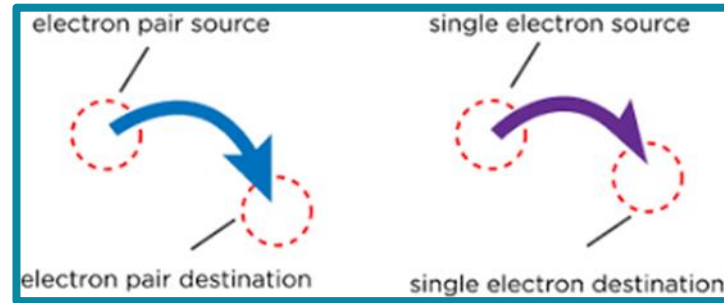
COVALENT BOND(s)

BOND FISSION



COVALENT BOND(s)

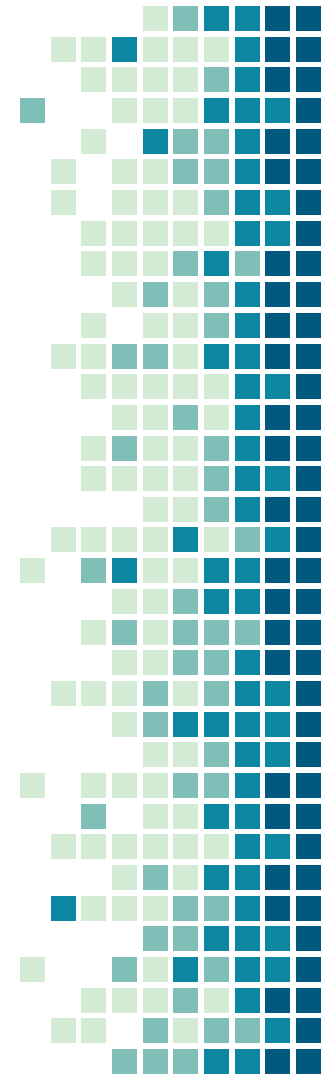
BOND FISSION



COVALENT BOND(s)

Reaction Intermediate (s)

1. Carbocations
2. Carbanions
3. Free Radicle



COVALENT BOND(s)

Reaction Intermediate (s)

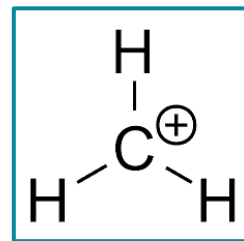
Carbocation (Carbonium Ion) :

Carbocation today is defined as any even-electron cation that possesses a significant positive charge on the carbon atom.

How carbocations are formed ?

Carbocations are most often formed in one of two ways:

- a. By ionization of an alkyl halide (or protonated alcohol)
- b. By the addition of an electrophile (E^+ ; frequently H^+) to an alkene, or other unsaturated species








COVALENT BOND(s)

Reaction Intermediate (s)

Type of Carbocation:

The **carbocation** can be termed as methyl, primary, secondary or tertiary based on how many carbon atoms are attached to it: Methyl **carbocation**: If no carbon is attached to the carbon with the positive charge it is simply called as methyl **carbocation**.

To distinguish carbocations, count the number of carbons connected to the carbon with the positive formal charge.

				
Methyl carbocation	Primary (1°) carbocation	Secondary (2°) carbocation	Tertiary (3°) carbocation	Quaternary (4°) carbocation
No carbons connected	One carbon connected	Two carbons connected	Three carbons connected	Cannot exist

COVALENT BOND(s)

Reaction Intermediate (s)

Stability of Carbocation:

There are three factor that stabilized the carbocation

1. Neighboring Carbon atom
2. Neighboring C-C multiple bond
3. Neighboring atom with loan pair

COVALENT BOND(s)

Reaction Intermediate (s)

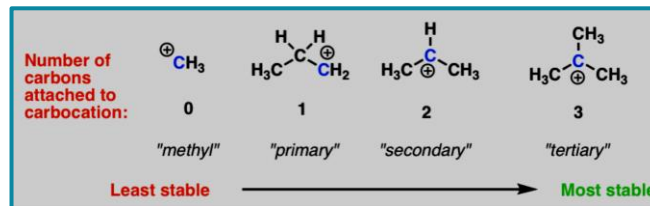
Stability of Carbocation:

1.

Neighboring Carbon atom:

The neighboring CARBON atom enhance the stability of Carbocations by the following effect(s)

- ❖ Inductive effect
- ❖ Hyperconjugative effect



* *This two effects will be discussed in detail later in this presentation.*

COVALENT BOND(s)

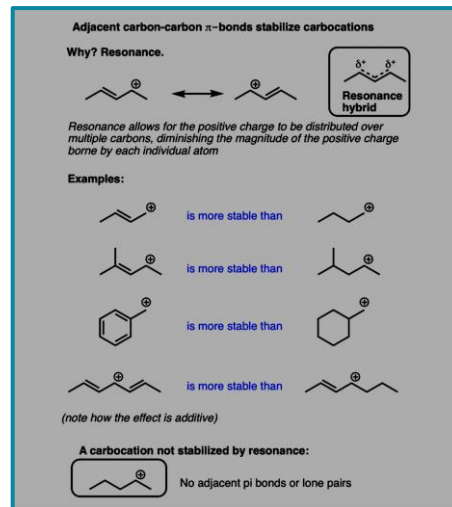
Reaction Intermediate (s)

Stability of Carbocation:

2.

Neighboring Carbon-Carbon multiple bond :

The neighboring CARBON-CARBON multiple bond (i.e. double bond or Triple bond) enhance the stability of Carbocations through **RESONANCE** effect.



COVALENT BOND(s)

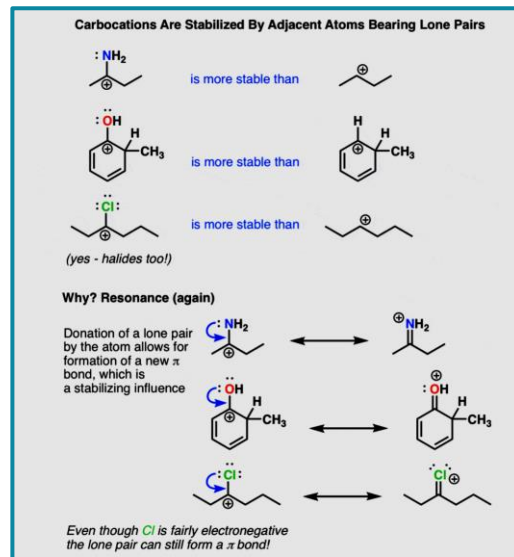
Reaction Intermediate (s)

Stability of Carbocation:

3.

Neighboring Hetero atom

The neighboring Hetero atom (i.e. O, N) bearing lone pairs enhance the stability of Carbocations through **RESONANCE** effect.

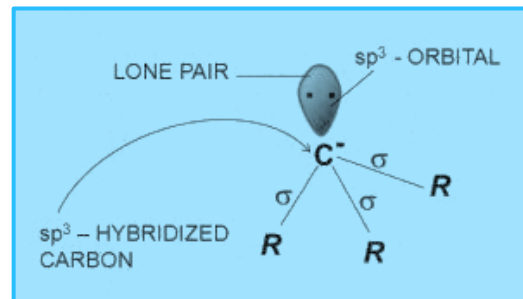


COVALENT BOND(s)

Reaction Intermediate (s)

CARBANION:

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. The carbanion exists in a trigonal pyramidal geometry.



** Similarly Carbanion is also primary, Secondary and Tertiary, based on the number of alkyl group linked to the negatively charged carbon atom(s)*

COVALENT BOND(s)

Reaction Intermediate (s)

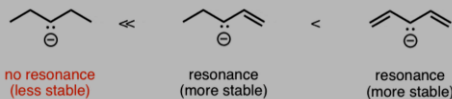
CARBANION:

Stability of Carbanion:

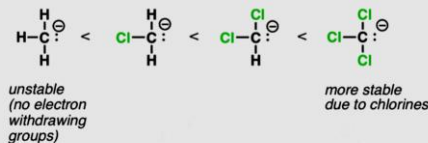
A carbanion is a nucleophile, which stability and reactivity determined by several factors like:

- Resonance stabilized the negative charge
- Inductive effect (EWG, enhance the stability of Carbanion)
- S-Character
- Aromaticity

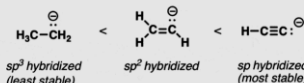
Negative charge is stabilized by resonance, which delocalizes charges



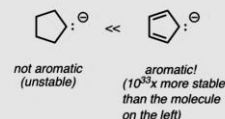
Negative charge is stabilized by adjacent electron withdrawing groups (inductive effects)



Negative charge is stabilized as the hybridization includes more s orbitals



Negative charge is especially stable if the electrons are part of an aromatic π -system



COVALENT BOND(s)

Reaction Intermediate (s)

Free Radicals:

The Organic Free Radical identified was Triphenylmethyl radicle obtained by the abstraction chlorine atom by Silver atom. These species was discovered by Moses Gomberg in 1900 at the University of Michigan USA.



(1866-1947)

Moses Gomberg
Professor of Chemistry
University of Michigan, USA

COVALENT BOND(s)

Reaction Intermediate (s)

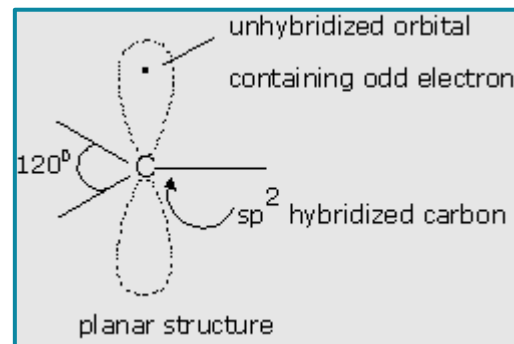
Free Radicals:

- ❖ A radical is a reactive intermediate with a single unpaired electron, having very short lifetime
- ❖ Radical reaction are non-ionic reactions judged by the frontier molecular orbital the approach.
- ❖ It is generated by homolysis of a covalent bond
- ❖ Radical is represented by atom with one dot
- ❖ Electronic movements involving radicals are represented using half headed fishhook arrows
- ❖ Carbon radical is a neutral carbon species with three single bonds and one unpaired electron.

COVALENT BOND(s)

Reaction Intermediate (s)

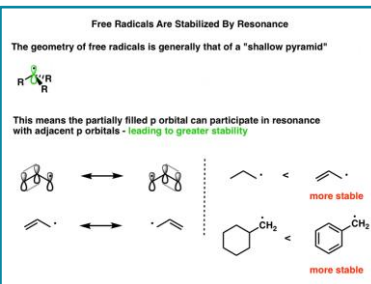
Structure of Free Radicals:



"Carbon radical is sp^2 hybridized with an unpaired single electron occupying an unhybridized p-orbital, having trigonal pyramidal or planar geometry possessing an angle of 120° ".

Factors That Stabilize Free Radicals:

1. Stability Of Free Radicals Increases In The Order Methyl < Primary < Secondary < Tertiary
2. Free Radicals Are Stabilized by Delocalization ("Resonance")
3. The Geometry Of Free Radicals Is That Of A "Shallow Pyramid", Which Allows For Overlap Of The Half-Filled p-Orbital With Adjacent Pi Bonds
4. The Same Factors Which Stabilize Carbocation Also Stabilize Free Radical



COVALENT BOND(s)

Inductive Effect

Inductive effect is an effect regarding the transmission of unequal sharing of the bonding electron through a chain of atoms in a molecule, leading to a permanent dipole in a bond.

Point to Remember:

- a. **An inductive effect** is an electronic effect due to the polarization of σ bonds within a molecule or ion.
- b. This is typically due to an electronegativity difference between the atoms at either end of the bond.
- c. The more electronegative atom pulls the electrons in the bond towards itself creating some bond polarity.
- d. Electrons in C-C bonds are more readily polarized than those in a C-H bond.
- e. Therefore, alkyl groups are better at stabilizing C⁺ than H atoms

COVALENT BOND(s)

Inductive Effect

Type of Inductive Effect

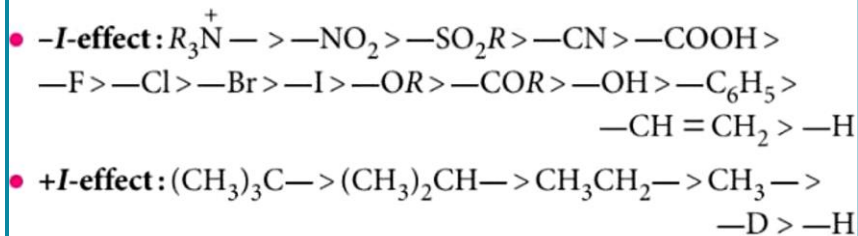
a: + I Effect (push the electron towards the central atom/flush electron right)

b: -I Effect (pull the electron from the central atom/flush the electron left)

*The inductive effect is a distance-dependent phenomenon:

For application of Inductive effect refer the hyper link below:

<https://youtu.be/J5J9Vzd0VTQ>



COVALENT BOND(s)

Electrometric Effect

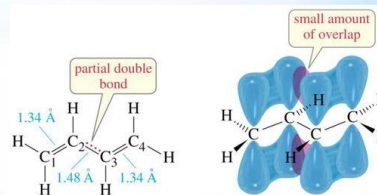
Mesomeric effect

If the displacement of the electron density takes place along π -bonds, **mesomeric effect (M)** takes place - conjugation effect

Conjugation - overlap of three or more adjacent p-orbitals - **energetically favorable**

Atoms capable of conjugation:

- atoms that are part of a double/triple bond
- atoms with lone pairs
- atoms with empty p orbitals (such as carbocations)
- atoms with half-filled orbitals (radicals)



Ref: t.ly/lxSG

COVALENT BOND(s)

Electrometric Effect

Mesomeric Effect (M-Effect)

- It refers to the polarity produced in a molecule as a result of interaction between two pi bonds or a pi bond and lone pair of electrons.
- The electron withdrawing or releasing effect attributed to a substituent through delocalization of π electrons, which can be visualized by drawing various canonical forms, is known as **mesomeric effect or resonance effect**. It is symbolized by M or R.

COVALENT BOND(s)

Electrometric Effect

Negative mesomeric effect (-M or -R):

- 2) The negative mesomeric effect (-R or -M) shown by cyanide group in acrylonitrile is illustrated below. The electron density on third carbon decreases due to delocalization of π electrons towards cyanide group.

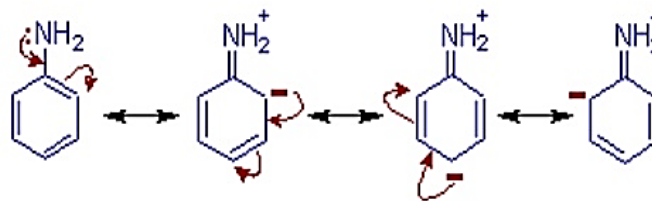


COVALENT BOND(s)

Electrometric Effect

Positive resonance or mesomeric effect (+M or +R):

- The -NH_2 group in aniline also exhibits +R effect. It releases electrons towards benzene ring through delocalization.



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COVALENT BOND(s)

Hyperconjugation Effect

Hyperconjugation: Definitions

Hyperconjugation is the donation of a sigma bond into an adjacent empty or partially filled p orbital, which results in an increased stability of the molecule.



Hyperconjugation contributes to the resonance stabilization of this tertiary carbocation, where electrons from the C-H sigma bonding orbital are donated to the empty p orbital of the cation.

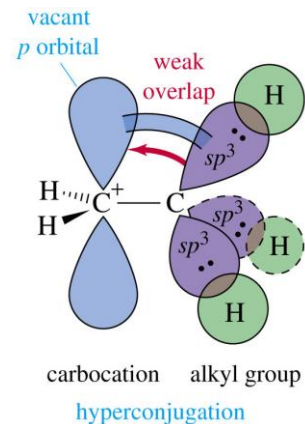
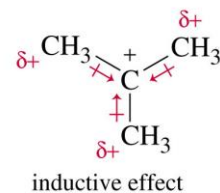
Hyperconjugation was first described by Baker and Nathan in 1935 to describe the “abnormal behavior” of alkyl-substituted compounds.¹

1. *J. Chem. Soc.*, **1935**, 1844-1847.

COVALENT BOND(s)

Hyperconjugation Effect

carbocation stability:
 $3^\circ > 2^\circ > 1^\circ > ^+\text{CH}_3$



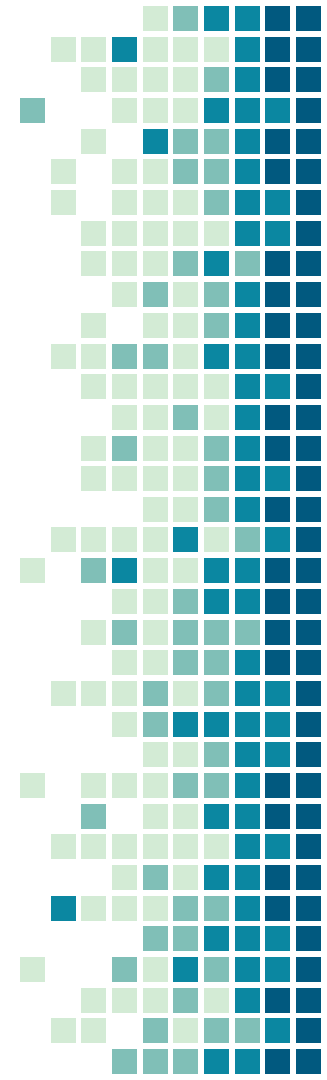
Ref: <https://socratic.org/questions/what-is-hyperconjugation-1>

COVALENT BOND(s)

Hyperconjugation Effect

For detail please follow the link below:

<https://youtu.be/5BSQG2sbrQw>

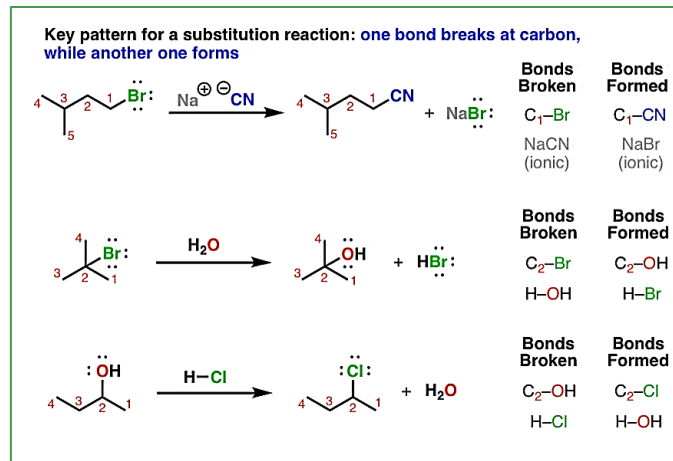


COVALENT BOND(s)

Substitution Reaction

In organic chemistry and inorganic chemistry, nucleophilic substitution is a fundamental class of reactions in which a leaving group is replaced by an electron rich compound (nucleophile). The whole molecular entity of which the electrophile and the leaving group are part is usually called the substrate.

Illustration



COVALENT BOND(s)

Substitution Reaction

Type of Nucleophilic Substitution Reaction:

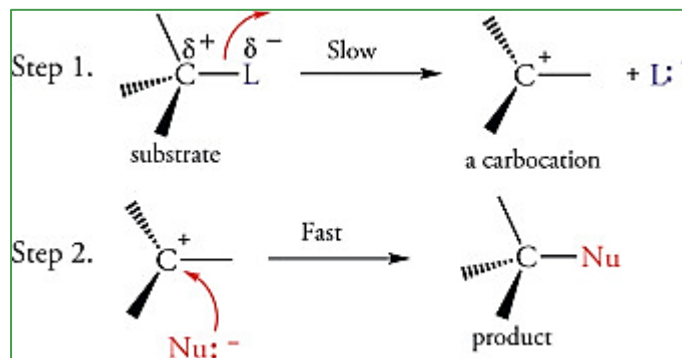
- ❖ SN1 (SN stand for Substitution Nucleophilic, 1 stands for order of reaction, Unimolecular)
- ❖ SN2 (SN stand for Substitution Nucleophilic, 2 stands for order of reaction, bimolecular)

COVALENT BOND(s)

Substitution Reaction

SN1 Reaction:

A nucleophilic substitution reaction that occurs by an SN1 mechanism proceeds in two steps. In the first step, the bond between the carbon atom and the leaving group breaks to produce a carbocation and, most commonly, an anionic leaving group. In the second step, the carbocation reacts with the nucleophile to form the substitution product.

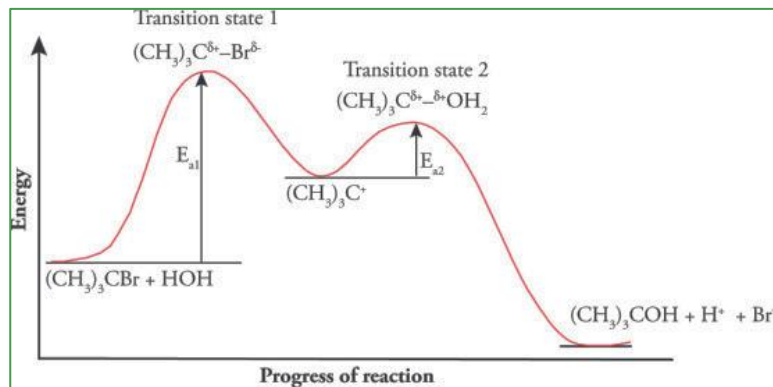


COVALENT BOND(s)

Substitution Reaction

SN1 Reaction:

- ❖ The formation of a carbocation is the slow, or rate-determining, step. The subsequent step, formation of a bond between the nucleophile and the carbocation, occurs very rapidly. Because the slow step of the reaction involves only the substrate, the reaction is unimolecular.
- ❖ Because only the substrate is present in the transition state, the rate of the reaction depends only on its concentration, and not on the concentration of the nucleophile.



COVALENT BOND(s)

Substitution Reaction

SN1 Reaction:

- ❖ The rates of SN1 reactions decrease in the order $3^\circ > 2^\circ > 1^\circ$, which is the reverse of the order observed in SN2 reactions.
- ❖ The relative reactivity of haloalkanes in SN1 reactions corresponds to the relative stability of carbocation intermediates that form during the reaction.
- ❖ The order of stability of carbocations is tertiary > secondary > primary.
- ❖ SN1 mechanisms are also favored by resonance-stabilized primary carbocations such as benzyl and allyl.

COVALENT BOND(s)

Substitution Reaction

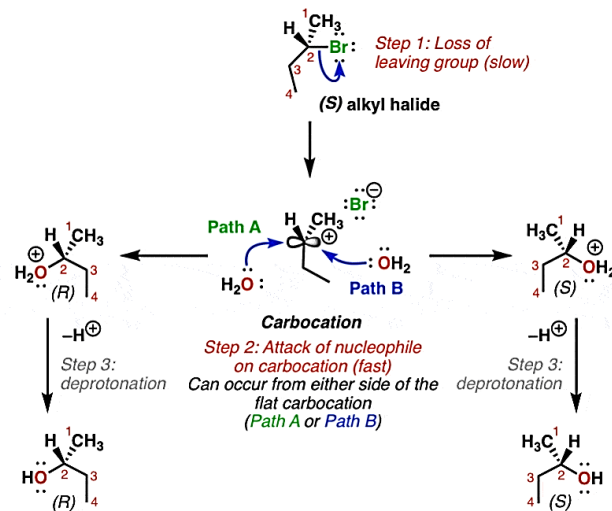
Stereochemistry of S_N1 reaction:

- ❖ S_N1 reaction gives a racemic mixture of enantiomers that has no optical rotation. For example, (S)-2-bromobutane reacts with water to give a racemic mixture of Butan-2-ol. The reaction occurs via an achiral carbocation intermediate with a plane of symmetry.

COVALENT BOND(s)

The "Stepwise" Reaction Mechanism Fits All The Data

- In the "stepwise" mechanism, the leaving group leaves, forming a carbocation. **This is the rate-determining step**
- In the second step the nucleophile attacks the carbocation (fast) to give the substitution product.
- Importantly, the nucleophile can attack either face of the flat carbocation



Path A gives inversion (R)

Path B gives retention (S)

- Explains unimolecular rate law (depends only on concentration of substrate)
- Explains why a mixture of retention and inversion obtained (attack can occur from either face of the carbocation)
- Explains sensitivity to substitution pattern ($3^\circ > 2^\circ > 1^\circ$ because tertiary carbocations are more stable).

This is called the **S_N1** mechanism (**S**ubstitution, **N**ucleophilic, **u**nimolecular)

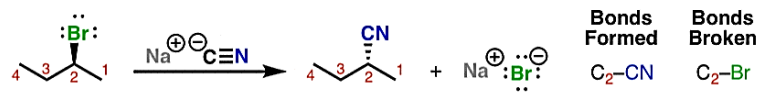
COVALENT BOND(s)

SN2 Reaction

SN2 reactions are bimolecular with simultaneous bond-making and bond-breaking steps.

- ❖ SN2 reactions do not proceed via an intermediate.
- ❖ SN2 reactions give inversion of stereochemistry at the reaction center.
- ❖ Steric effects are particularly important in SN2 reactions.
- ❖ SN2 Reaction Proceeds With Inversion of Configuration
- ❖ Rate Law Of The S_N2 Is Second Order Overall

Substitution occurs with inversion of configuration at chiral centers



One stereoisomer

One stereoisomer

inversion!

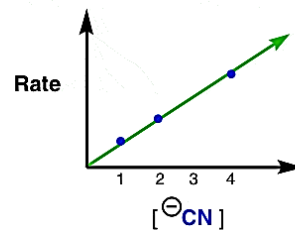
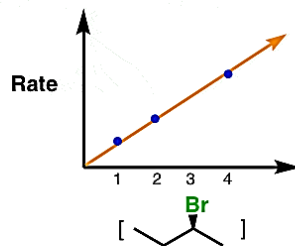
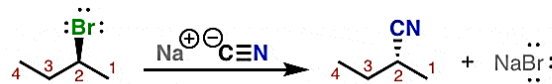
This substitution reaction results in an inversion of configuration at C_2

COVALENT BOND(s)

SN2 Reaction

Rate Law:

This substitution reaction is sensitive to the concentration of both nucleophile and substrate



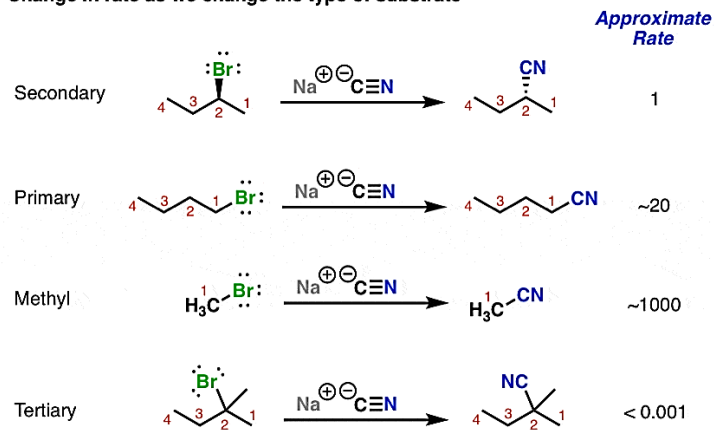
$$\text{Rate} = k [\text{R-Br}] [\text{CN}^-]$$

COVALENT BOND(s)

SN2 Reaction

The Reaction Rate Of The SN2 Reaction Is Fastest For Small Alkyl Halides (Methyl > Primary > Secondary >> Tertiary)

Change in rate as we change the type of substrate



What hypothesis fits best with the experimental results above?

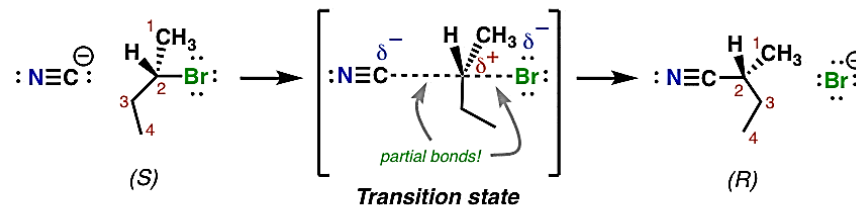
COVALENT BOND(s)

SN2 Reaction

The SN2 Mechanism Proceeds Through A Concerted Backside Attack Of The Nucleophile Upon The Alkyl Halide

The "backside attack" hypothesis fits all experimental data

In the "backside attack", the nucleophile attacks the substrate from the backside in a single step, resulting in inversion of configuration.



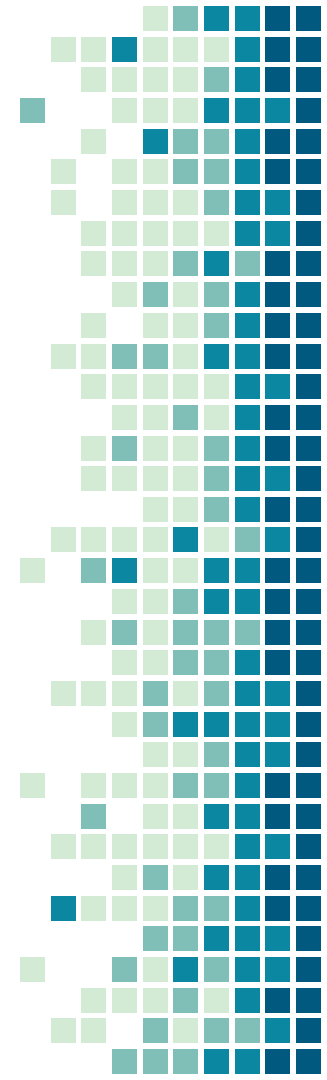
- Explains bimolecular rate law (depends on conc. of nucleophile and substrate)
- Explains inversion of stereochemistry
- Explains sensitivity to steric hindrance (bulky groups slow down backside attack)

This is called the $\text{S}_{\text{N}}2$ mechanism (Substitution, Nucleophilic, bimolecular)

COVALENT BOND(s)

SN1 vs SN2 reaction follow the video link below !

<https://youtu.be/boYgKqSBUaU>



THANKS!

Any questions?

You can find me at:

aks.vbspu@gmail.com

COVID-19 safety guideline's

<https://www.cdc.gov/coronavirus/2019-ncov/prevent-getting-sick/prevention.html>



“Details of the questioners based on each topics will be communicated in the next modules”