CHM 222: Organic Chemistry II
STEREOCHEMISTRY

- Stereoisomers
- Geometric isomers
- Optical isomers
- Chirality
- Relative and absolute configuration
STEROCHEMISTRY

Stereochemistry refers to chemistry in three dimensions (stereo – three-dimension).
ISOMERS
[Different compounds with Same molecular formula]

Constitutional isomers
[Isomers whose atoms have a different connectivity]

Stereoisomers
[Isomers that have the same connectivity but that differ in the arrangement of atoms in space]

Enantiomers
[Stereoisomers that are nonsuperimposable mirror image of each other]

Diastereomers
[Stereoisomers that are not mirror images of each other]

Geometric isomers
[Isomers that differ only in the spatial orientation of groups plane or direction]
Molecular formula | Constitutional isomers
---|---
C₄H₁₀ | CH₃CH₂CH₂CH₃ and CH₃CHCH₃
Butane | 2-methylpropane
C₃H₇Cl | CH₃CH₂CH₂Cl and Cl\[CH₃\]CHCH₃
1-chloropropane | 2-chloropropane
C₂H₆O | CH₃CH₂OH and CH₃OCH₃
Geometric isomers

- Geometric isomers (or cis–trans isomers) differ only in the spatial orientation of groups about a plane or direction.
- Two geometric isomers have the same molecular formula, the same functional groups, the same base chain or ring, and the same order of attachment of atoms; they differ in orientation either (1) around a double bond or (2) across the ring in a cyclic compound.
- If the larger groups are on opposite sides of the ring or the double bond, the designation trans appears in the name; if they are on the same side, the designation is cis.
cis-2-pentene

cis-1-bromo-3-chlorocyclobutane

cis-1,4-dimethylcyclohexane

trans-2-pentene

trans-1-bromo-3-chlorocyclobutane

trans-1,4-dimethylcyclohexane
Chirality centre (or chiral carbon or asymmetrical carbon/centre) is a tetrahedra atom bonded to four different groups.
Identify the chirality centre (if any) in the following compounds:

1. 2-Butanol
2. 2-Propanol
3. 2-Bromopentane
4. 3-Bromopentane
Identify the chirality centre (if any) in the cyclic compounds below:

1. 2-Cyclopentenol

2. 3-Cyclopentenol

3. 1,1,2-Trimethylcyclobutane

4. 1,1,3-trimethylcyclobutane.
Isomers with one Chiral carbon

2-bromobutane

Enantiomers
To draw the stereorepresentation for enantiomers:

(a) \( \text{CH}_3\text{CH}_2\text{CHCHCH}_3 \)

(b) \( \text{CH}_3\text{CH}_2\text{CHCH}_2\text{OH} \)
Step 1:
Locate the chiral carbon/centre;

\[
\text{CH}_3\text{CH}_2\text{CHCH}_3^*\]

Step 2:
Draw the four groups attached to the chiral carbon/centre;
Step 3:
Draw its mirror image

Exercise:
Draw the stereopresentation for compound (b) above
Molecules with Two or more Chiral Carbon

(A) Enantiomers and Diastereoisomers.

Compounds that contain two or more chiral carbons can exist in more than two optical isomers. The maximum number of optical isomers is $2^n$ (n = number of chiral carbons). E.g.

\[
\begin{array}{c}
  \text{CH}_2 \quad \text{*CH} \quad \text{*CH} \quad \text{CHO} \\
  \text{OH} \quad \text{OH} \quad \text{OH}
\end{array}
\]

2,3,4-Trihydroxybutanal

There are $2^2 = 4$ optical isomers
Diastereoisomer are optical isomers that are not mirror images of each other.

Enantiomers are optical isomers that are nonsuperimposable mirror images of each other.
(B) Meso compounds

A structure that contains two or more chiral carbons but is superimposable on its mirror image is called a meso compound.

The 3 optical isomers of tartaric acid. [(c) and (d) are superimposable]
Naming the Enantiomers by the R, S system

[The Cahn-Ingold-Prelog R-S notational system]

According to this nomenclature, one enantiomer in the pair is designated $S$, the other $R$. $R$ comes from the Latin *rectus* for right, and $S$ from the Latin *sinister* for left.

The $(R)$ and $(S)$ configurations are assigned on the basis of the following rules:
Identify the substituents at the chirality centre and assigned a *priority* or ranked them in order of decreasing/increasing atomic number (a,b,c,d or 1,2,3,4). If isotopes are involved, the isotope of greatest atomic mass has the highest priority.

If priority cannot be given based on the atoms directly attached to the stereocenter, the next set of atoms attached to the unassigned groups is examined. In other words, priority is assigned at the first point of difference. E.g. -Cl-H; -CH₂-OH; -CH₂-NH₂; -CH₂-CH₃; -CH₂-H
A double bond is considered to be bonded to an equivalent number of similar atoms by single bonds.

\[ \text{COH} \quad \text{is equivalent to} \quad \text{C}_2\text{O}_2\text{H} \]

\[ \text{CH} \quad \text{is equivalent to} \quad \text{CH}_2\text{O} \]
Orient the molecule so that the lowest ranked substituent points away from you. (this is the imaginary rotation of the molecule such that the group with lowest priority is directed away from the observer).

If the order of decreasing precedence of the three highest ranked substituents appears in a clockwise sense, the absolute configuration is R. If the order of decreasing precedence is counterclockwise, the absolute configuration is S.
Assign absolute configuration as R or S to each of the following compounds:
Indicate the configuration of each of the following structures:
Draw the perspective formulas for the following:

a) \((S)-2\text{-chlorobutane}\)

b) \((S)-1,2\text{-dibromobutane}\)
Absolute And Relative Configuration

The spatial arrangement of substituents at a chirality centre is its absolute configuration. 
**Relative configuration** compares the arrangement of atoms in space to some reference. 
**Absolute configuration** is an exact description of the arrangement of atoms in space.

Enantiomers of lactic acid
Exercise

Assign absolute configuration as R or S to each of the following compounds:

1. (+)-glyceraldehyde
Solution

1st: Rank the groups attached to the chiral carbon in order of priority. For (+)-glyceraldehyde, the order is

\[ \text{—OH} \quad \text{—CH} \quad \text{—CH}_2\text{OH} \quad \text{—H} \]

(1) (2) (3) (4)

2nd: Turn the molecule in space so that the group of lowest priority (—H) is away from you and the remaining three groups face you.

3rd: Draw an arrow from group of highest priority (—OH) to the group of 2nd-highest priority (—CHO) and then to the group of 3rd-highest priority (—CH\textsubscript{2}OH).
For (+)-glyceraldehyde, the arrow turns clockwise, and therefore the configuration of this enantiomer is \( \text{R} \).
**D and L configuration**

Another convention involving the use of letter D and L was proposed by Emil Fischer to deal with the absolute configuration of carbohydrates.

\[
\begin{align*}
\text{D-glyceraldehyde} & \quad \text{L-glyceraldehyde} \\
\text{The enantiomers of glyceraldehyde}
\end{align*}
\]
Fischer convention has been modified as follows;

D-glyceraldehyde  
(R-glyceraldehyde)  
L-glyceraldehyde  
(S-glyceraldehyde)
To determine the configuration of a compound drawn as a Fisher projection

✓ Rank the groups (or atoms) that are bonded to the asymmetric centre in order of priority.

✓ Draw an arrow from the group (or atom) with the highest priority (1) to the next highest priority (2). If the arrow points clockwise, the enantiomer has an R configuration; if it points counterclockwise, the enantiomers has the S configuration, provided the group with lowest priority (4) is on a vertical bond.

✓ If the group (or atom) with the lowest priority is on a horizontal bond, the naming will be opposite the correct answer.
D-glyceraldehyde and L-glyceraldehyde serve as reference points for the assignment of configuration to all other aldoses and ketoses.

Those that have the same configuration as D-glyceraldehyde about the chiral carbon farthest from the aldehyde or ketone are called D-monosaccharides;

those that have the same configuration as L-glyceraldehyde about the chiral carbon farthest from the aldehyde are called L-monosaccharide.
Naming isomers with more than one chirality centre.

a stereoisomer of 3-bromo-2-butanol
Determine each configuration separately

2S,3R-3-bromo-2-butanol
Configuration and conformation

✓ Changing the configuration of a molecule always means that bonds are broken.
✓ A different configuration is a different molecule
✓ Changing the conformation of a molecule means rotating about bonds, but not breaking them.
✓ Conformations of a molecule are readily interconvertible, and are all the same molecule.
Absolute And Relative Configuration

The spatial arrangement of substituents at a chirality centre is its absolute configuration. *Relative configuration* compares the arrangement of atoms in space to some reference. *Absolute configuration* is an exact description of the arrangement of atoms in space.

Enantiomers of lactic acid
Reactions of compounds with chiral centre

✓ When a compound containing chiral centre undergoes a reaction, the effect on the configuration of the chiral centre depends on the reaction.

✓ If the reaction does not break any of the four bonds to the chiral centre, then the relative positions of the groups bonded to the chiral centre will not change. i.e. reactant and products have the same relative configurations.
Same relative configurations

(S)-1-chloro-3-methylpentane → (S)-3-methyl-1-pentanol

Same relative configurations, but different absolute configurations

(S)-3-methylhexene → (R)-3-methylhexane
Racemic mixtures

- Mixtures containing equal quantities of enantiomers are called racemic mixtures.
- Racemic mixtures are optically inactive.
- Optical activity is the ability of a chiral substance to rotate the plane of plane-polarized light and is measured using an instrument called a polarimeter.
- To be optically active, the sample must contain a chiral substance and one enantiomer must be present in excess of the other.
- All achiral substances are optically inactive.
✓ Rotation of plane of polarized light in the clockwise sense is taken as positive (+) and rotation in the counterclockwise sense is taken as negative (-) rotation (formerly dextrorotatory & levorotatory respectively).

✓ Specific rotation \([\alpha]^T_{\lambda} = \frac{\alpha_{cl}}{c}\]

\([\alpha]\) unit = \(10^{-1}\) deg cm\(^2\) g\(^{-1}\)

where \(c\) is the concentration of the sample in gram/mL of solution, and \(l\) is the length of polarimeter tube in decimeter. \(T = \) Temperature (oC), \(\lambda = \) wavelength of the incident light.

✓ Specific rotation \([\alpha] = \frac{\alpha}{c}\) where \(c = g/mL\)
Specific rotation is a physical property (such as boiling point, melting point, density etc.) and is usually cited as

$$[\alpha]^{25}_D = +3.8^\circ$$

Where the temperature (°C) and the wavelength of light (when sodium D-line is used, \(\lambda\) is indicated as D) at which the measurement was made are indicated in the superscripts and subscripts respectively.
Exercise

1. Monosodium glutamate (MSG) is a flavour enhancer used in many foods. Some people have allergic reaction to MSG (headache, chest pain, etc). (S)-(+)(MSG) has a specific rotation of +24.
   (a) what is the specific rotation of (R)-(+)MSG?
   (b) what is the specific rotation of racemic mixture of MSG?

2. Cholesterol, when isolate from natural sources, is obtained as a single enantiomer. The observed rotation $\alpha$ of a 0.3g sample of cholesterol in 15mL of chloroform solution contained in a 10cm polarimeter tube is $-0.78^\circ$. Calculate the specific rotation of cholesterol.
Separation of enantiomers

✓ Enantiomers can not be separated by the usual separation techniques such as fractional distillation, crystallization etc: because of their identical boiling points and solubilities.

✓ Resolution of enantiomers can be done by;
  ✓ Manual separation with a pair of tweezers – Louis Pasteur method (few compounds form asymmetrical compounds).
  ✓ Chemically converting enantiomers to diastereomers, which can be separated because they have different physical properties. After separation, the individual diastereomers had to be chemically converted back to the original enantiomers (tedious and unreliable)

✓ Chromatography technique: Best method.
Chromatography method

✓ The mixture to be separated is dissolved in a solvent and the solution is passed through a column packed with a chiral material that tends to adsorb organic compounds.

✓ The two enantiomers can be expected to move through the column at different rates because they will have different affinities for the chiral material.

✓ Because of the ease of separation of enantiomers, many drugs are now being sold as a single enantiomeric rather than as racemic mixtures.

✓ The chiral material used in chromatography is an example of chiral probe, another example is polarimeter: capable of distinguishing between enantiomers.
ENERGY OF ACTIVATION AND FREE RADICAL SUBSTITUTION REACTION OF ALKANE

• The ultimate source of organic chemicals is petroleum. Petroleum is a mixture of paraffin-alkane, cyclic and aromatic hydrocarbons. Alkane undergoes substitution reaction due to its saturated nature. Alkane has no pi (Π)-bond, no expanded octet, neither is it nucleophilic or electrophilic in nature, hence it is less reactive at room temperature.

• Substitution of an H atom in alkane by a functional group to give a substituted product, which can be transformed into other organic compounds by reaction which occur at the site of the functional groups. For instance:
Even though the C-H of alkane is not polar (i.e. alkane does not react with nucleophilic or electrophilic acids or base), alkane can still undergo certain chemical reactions under certain reaction conditions suitable for the substitution of a H atom by a functional group.
CHLORINATION OF ALKANE

This is the oldest known substitution reaction of alkane. This reaction occur in the presence of ultra violet (UV) radiation or heat, 300°C; e.g.

$$R - H \xrightarrow{\text{heat or } 300^\circ C} R - Cl + H - Cl$$

R=alkane or benzene ring or cycloalkane, cyclopentane, cyclohexane

Halogens such as Cl and Br2 substitute H in compounds containing $\alpha_{sp3-s}$ C—H bonds. These reactions are initiated either thermally (action of heat) or upon irradiation with UV light. Fluorinations also occur with alkane but such substitution must be initiated by light at low temperature. At room temperature or above room temperature, reactions are explosive. Alkane does not react with I$_2$ to give a substituted product.
• The relative order of reactivities of Halogens is $F_2 > Cl_2 > Br_2 > I_2$

• Compounds formed when alkane reacts with halogen are referred to as alkyl halides; $RX$, represented by the general formular $C_nH_{2n+1}X$, where $X$ is the substituted halogen atom. Thus:
TYPES OF HYDROGEN OR DIFFERENT KINDS OF HYDROGEN IN ALKANE AND RATE OF SUBSTITUTION

• It is important to note that substitution reactions of alkane occur via free radical chain reaction mechanism, involving three steps: chain initiation (step 1), chain propagation (step 2) and chain termination (step 3). Free radicals are species formed via homolytic bond cleavage of covalent bonds. They are highly reactive and unstable species. They contain unpaired electrons.
\[
\text{CH}_4 + \text{Cl}_2 \quad \xrightarrow{UV} \quad \text{CH}_3\text{Cl} + \text{HCl}
\]

**Step 1:**

\[
\text{Cl}_2 \quad \rightarrow \quad \text{Cl} . + \text{Cl} . \quad \text{Cl} . = \text{chlorine radical}
\]

**Step 2:**

\[
\text{Cl} . + \text{H} \rightarrow \text{CH}_3 \quad \rightarrow \quad \text{H} \rightarrow \text{Cl} + \text{CH}_3 .
\]

\[
\text{CH}_3 . + \text{Cl} \rightleftharpoons \text{Cl} \rightarrow \text{CH}_3 \quad \rightarrow \text{Cl} + \text{Cl} .
\]

**Step 3:**

\[
\text{Cl} . + \text{Cl} . \quad \rightarrow \quad \text{Cl}_2
\]

\[
\text{CH}_3 . + \text{CH}_3 . \quad \rightarrow \quad \text{CH}_3 \rightarrow \text{CH}_3
\]
• Iodination is not feasible under the reaction conditions above since I—I bond cannot be splitted into radical at low temperature of the reaction, due to low electronegativity of iodine.

Since each H is subject to substitution by a halogen, all possible isomeric products (monohalides) can be obtained in the halogenations reaction, e.g.
1. CH₃CH₂CH₂CH₃ + F₂ $\xrightarrow{-80°C/UV\ light}$ CH₃CH₂CH₂CH₂ + CH₃CH₂CHCH₃
   - 2-fluorobutane (55%)
   - 1-fluorobutane (45%)

2. CH₃CH₂CH₃ + Cl₂ $\rightarrow$ CH₃CH₂CH₂ + CH₃CHCH₃
   - 1-chloropropane (50%)
   - 2-chloropropane (45%)
   - b.pt=47°C

3. H₃C $\xrightarrow{C-C}$ CH₃ + Br₂ $\rightarrow$ H₃C $\xrightarrow{C-C}$ C $\xrightarrow{C}$ Br + 2,2,3-trimethylbutane
   - 2-bromo-2,3,3-trimethylbutane
• The number of isomeric alkyl halides obtained depends on the type of H on the alkane moiety. There are 3 types of Hydrogen positions, primary, secondary and tertiary hydrogen.
• Isomeric halides can be separated using fractional distillation.
• However, ratio of isomeric halides does not often correspond to the number and kind of chemically equivalent hydrogen at each chemically equivalent position. For example, propane has 2 kinds of hydrogen, \( \text{CH}_3^*\text{CH}_2^*\text{CH}_3^* \), where * represents primary and ** represent secondary hydrogen. Hence only two monosubstituted products /halides can be obtained if propane reacts with halogen, given the necessary conditions. Propane has 8 eight hydrogen, six equivalent hydrogen are primary while 2 equivalent hydrogen are secondary. Hence, only two substituted alkyl halide will be produced, assuming the substitution is statistical.
• Likewise, n-butane has the ratio of primary to secondary hydrogen as 3:2, by this statistical argument, we would expect chlorination of butane at 300°C to give 60% 1-chlorobutane and 40% 2-chlorobutane in a statistical ratio of 3:2.
Chlorination of isobutene at 300°C shows similar result e.g.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + \text{Cl}_2 & \xrightarrow{300^\circ\text{C}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{CH}_3\text{CHCH}_2\text{CH}_3 \\
1\text{-chloropropane} & \text{predicted}=60\% \quad \text{observed}=33\% \\
2\text{-chloropropane} & \text{predicted}=40\% \quad \text{observed}=67\%
\end{align*}
\]

Chlorination of isobutene at 300°C shows similar result e.g.

\[
\begin{align*}
\text{CH}_3 & \quad \text{C} \quad \text{H} \\ 
\text{CH}_3 & \quad \bigg| \quad \text{CH}_3 \\
9\text{-1}^\circ\text{ Hydrogen} & \quad 1\text{-3}^\circ\text{ Hydrogen} \\
\text{H}_2\text{C} & \quad \text{C} \quad \text{H} \\
\text{CH}_3 & \quad \bigg| \quad \text{CH}_3 \\
isobutylchloride & \text{predicted}=90\% \quad \text{observed}=67\% \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{Cl} \\
\text{CH}_3 & \quad \bigg| \quad \text{CH}_3 \\
\text{tert-butylchloride} & \text{predicted}=10\% \quad \text{observed}=33\%
\end{align*}
\]
RELATIVE REACTIVITIES IN THE HALOGENATION OF ALKANE

- Halogenation of alkane does not give the isomeric primary, secondary and tertiary monohalides in statistical yields. The observed ratio of product indicates a difference in the reactivity at primary, secondary and tertiary positions. The relative reactivity at each position can then be calculated for each position, e.g.

\[
\text{CH}_3\text{CH}_2\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3\text{Cl} + \text{CH}_3\text{CH} (\text{Cl})\text{CH}_3
\]

- Relative reactivity at 2º position over 1º position is calculated thus:
\[
\frac{(% 2\text{-chloropropane})_{\text{obs}}}{(% 2\text{-chloropropane})_{\text{pred}}} \times 100
\]

\[
\frac{(% 1\text{-chloropropane})_{\text{obs}}}{(% 1\text{-chloropropane})_{\text{pred}}}
\]

Key:

obs= observed yields, pred = predicted yields

= 50%/25% = 3.0

= 50%/75%
• The relative reactivity of 3.0 indicates that hydrogen on 2° position is three times more reactive than hydrogen on 1° position towards chlorination at 300°C. Similarly, H on a 3° position is 4.5 times more reactive towards chlorination at 300°C than are H on primary position.

• In summary, the relative order of chemical reactivity at different hydrogen position follows the rate and type of radical formed at each stage. Note that free radical reaction mechanism has been proposed for the mechanism of halogenations, it stems clearly that 1°, 2° and 3° radicals reacts at different rate.
FREE RADICAL REACTION

• Just like carbonium ions, free radicals have different reactivity and stability. The order of stability and relative reactivities of free radicals is in the order:

• Methyl radical < ethyl radical($1^\circ$) < propyl radical ($2^\circ$) < tert-butyl ($3^\circ$) radical < H$_2$C=CH-CH$_2$. (vinyl radical) < phenyl radical ($C_6H_5.$) < triphenyl radical ($C_6H_5.$)$_3$. 
• The relative stability of radical species can be explained on the basis of the electron-releasing tendency of alkyl group which stabilize the radical. The more the alkyl groups, the higher the stability of the radical. The positive inductive effects of alkyl group accounts for this tendency.

• Again, the number of canonical structure dictates relative stability of radical.

• Free radicals unlike free carbonium ions are incapable of exhibiting optical activity. Free radicals

• Are neither acidic nor basic in the Bronsted-Lowry or Lewis sense, and do not react with other paramagnetic substances. However, due to unpaired electron in free radical, they are paramagnetic and can react with species (nucleophiles) such as oxygen. They abstract atoms from covalent molecules and can add on to unsaturated compounds. The major reactions are shown thus:
\[
\text{CH}_3. + \text{O}_2 \rightarrow \text{H}_3C - \cdot\cdot\cdot - \cdot\cdot\text{methylperoxy radical}
\]

\[
\text{CH}_3. + \text{CH}_3. \rightarrow \text{CH}_3 \cdot - \cdot\cdot\cdot - \cdot\cdot\text{ethane}
\]

\[
\text{CH}_3. + \text{A} \rightarrow \text{B} \rightarrow \text{CH}_3 \cdot \rightarrow \text{A} + \text{B}. \text{ATOM ABSTRACTION}
\]

\[
\text{CH}_3. + \text{H}_2\text{C} = \text{CH}_2 \rightarrow \text{CH}_2\text{CH}_2\text{CH}_3. \text{n-propyl radical} + \text{B}. \text{RADICAL ADDITION}
\]
BOND DISSOCIATION ENERGY (BDE)

- In homolytic bond cleavage of covalent bond, such as \( \text{CH}_3-\text{H} \rightarrow \text{CH}_3. + \text{H}. \), energy required for the homolytic cleavage (measured in KJ/mol) is known as the bond dissociation energy. The lower the BDE, the less the energy required for homolytic cleavage, e.g. less energy is required to cleave a Br—Br bond (46 KCal/mol) than a Cl—Cl bond (58 KCal/mol), etc. Various values of BDE for different bonds are in literature.

- The BDE allows an easy estimation of the reasonableness of the pathway by which certain reactions occur. It allows us to predict the covalent bond preferably broken or cleaved preferentially.

- BDE allows one to predict the probability of a subsequent process and in the process allows an easy calculation of the enthalpy (heat) of a reaction (\( \Delta H \)).

\[ \Delta H = \sum (\text{BDE}_{\text{bond broken}} - \text{BDE}_{\text{bond formed}}) \].
• Calculation based on bond dissociation energy (BDE)

• Q1 Given the BDE data as $\text{C}_6\text{H}_5\text{—H} = 103\text{kCal/mol}$, $\text{Br—Br} = 46\text{kCal/mol}$, $\text{H—Br} = 87.5\text{ kCal/mol}$, $\text{C}_6\text{H}_5\text{—Br} = 1311.5\text{ kCal/mol}$, calculate $\Delta H$ for the reaction below:
• Solution:
• \( \Delta H = \Sigma (\text{BDE}_{\text{bond broken}} - \text{BDE}_{\text{bond formed}}) \)
• Bond broken = \( \text{C}_6\text{H}_5—\text{H}, \text{ Br—Br bonds} \)
• Bond formed = \( \text{C}_6\text{H}_5—\text{Br}, \text{ H—Br bonds} \).
• \( \Delta H = [(103+ 46)-(1311.5-87.5)] \text{ kCal/mol} \)
• \( = [149-1399.0] \text{ kCal/mol} \)
• \( = -1250 \text{ kCal/mol} \).
• Thus BDE can be used to predict the probability of a reaction occurring, since \( \Delta H \) can be used to predict the feasibility of a reaction.
FREE RADICAL REACTION OF HBr – effect of peroxide

• In the absence of light and peroxides, addition of HBr to an alkene gives a product in line with Markovnikov rule, often called Markovnikov addition, e.g

• \( \text{CH}_3\text{CH}=\text{CH}_2 + \text{HBr} \)

• However, free radical addition in the presence of light, occur via anti Markovnikov addition.

• \( \text{CH}_3\text{CH}=\text{CH}_2 + \text{HBr} \)
• Peroxides such as di-tertiary butyl peroxides i.e. \((\text{CH}_3)_3\text{O} - \text{O} - (\text{CH}_3)_3\) undergoes homolytic cleavage of the oxygen-oxygen bonds at temperature below 100\(^\circ\)C to give alkoxy radical, e.g.

\[
\text{R} - \ddot{\text{O}} \quad \ddot{\text{O}} \quad \text{R} \quad \xrightarrow{\text{heat or light}} \quad \text{2R} - \ddot{\text{O}}.
\]

where \(\text{R} = (\text{CH}_3)_3\text{C}\)

• Alkoxy radicals produced through homolytic cleavage of peroxides abstracts H from HBr. The resulting bromine atom adds to the C—C double bonds to form the more stable free radical. The carbon radical subsequently abstracts H from H—Br to continue the chain reaction process.
CHAIN INITIATION

\[ R - \dot{O} - \dot{O} - R \xrightarrow{\text{heat or light}} 2R - \cdot \dot{O} \cdot \] where \( R = (\text{CH}_3)_3\text{C} \)

\[ 2R - \cdot \dot{O} \cdot + \text{H} \xrightarrow{} \text{Br} \xrightarrow{} R - \dot{O} - \text{H} + \text{Br}. \]

HOMOLYTIC CLEAVAGE OF COVALENT BOND

CHAIN PROPAGATION

\[ \text{Br} + \text{H}_2\text{C} = \text{CHCH}_3 \xrightarrow{} \text{Br} - \text{CH}_2 - \cdot \text{CHCH}_3 \]

\[ \text{BrCH}_2 - \cdot \text{CHCH}_3 + \text{HBr} \xrightarrow{} \text{Br} - \text{CH}_2\text{CH}_2\text{CH}_3 + \text{Br}. \]

Formation of more stable free radical