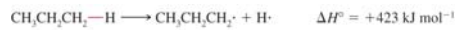


Relative stability of organic radicals

Compare the Bond Dissociation Energies for the primary and secondary hydrogens in propane



Propyl radical
(a 1° radical)

Diff = 10 kJ/mol

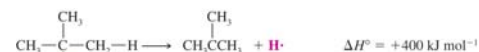


Isopropyl radical
(a 2° radical)

Since less energy is needed to form the isopropyl radical (from same starting material), the isopropyl radical must be more stable.

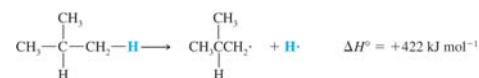
Relative Stability of organic radicals

Using the same table, the *tert*-butyl radical is more stable than the isobutyl radical



tert-Butyl radical
(a 3° radical)

Diff = 22 kJ/mol

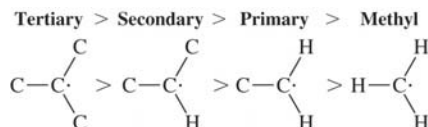


Isobutyl radical
(a 1° radical)

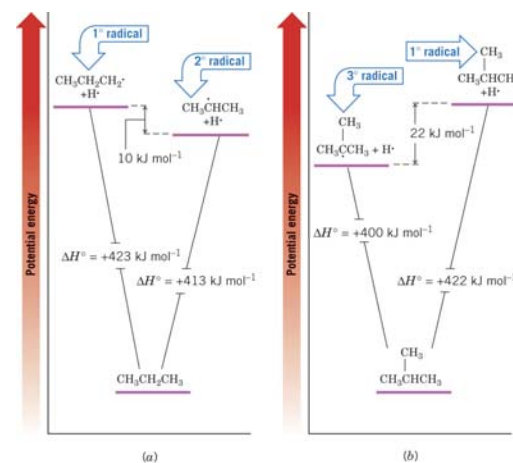
Relative Stability of Free Radicals

The relative stabilities of carbon radicals follows the same trend as for carbocations

- The more substituted radical is the more stable.
- Radicals are electron deficient, as are carbocations, and are therefore also stabilized by hyperconjugation.

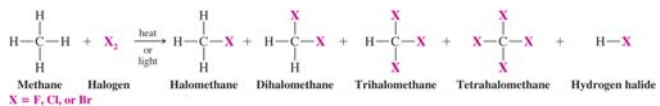


Energy diagrams for formation of radicals



The Reactions of Alkanes with Halogens

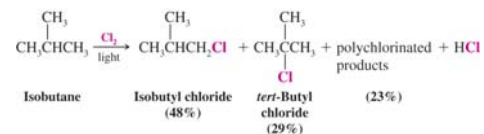
Alkanes undergo substitution reactions with halogens (fluorine, bromine and chlorine) initiated by heat or light



- Free radical halogenation can yield a mixture of halogenated compounds because all of the hydrogen atoms in an alkane are capable of substitution.
- Monosubstitution can be achieved by using a large excess of the alkane - so long as all hydrogens are equivalent.
- For example in CH₄, CH₃CH₃, cyclopentane
- (BUT NOT IN, for example, CH₃CH₂CH₃)

Chlorination

- Chlorination of higher alkanes leads to mixtures of monochlorinated product (and more substituted products)



Chlorine is relatively unselective and does not greatly distinguish between the type of hydrogen it replaces.

If there were no selectivity, the *t*-butyl chloride account for 1/9 of the product, whereas it is actually 2/3 meaning that there is a preference of about 5-fold.

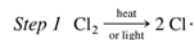
Mechanism of Chlorination: a Chain Reaction

- The reaction mechanism has three distinct aspects:
 - Initiation
 - Propagation
 - Termination

Initiation – Step 1

- Chlorine radicals form when the reaction mixture is subjected to heat or light.

Chain Initiation



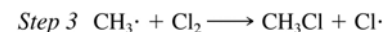
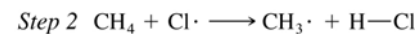
Recall that the Cl-Cl bond is relatively weak

Chlorination of Methane: Mechanism of Reaction

Propagation (2 steps which are repeated many times)

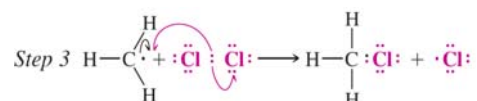
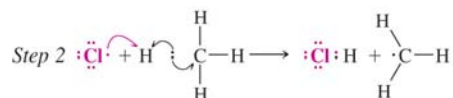
- A chlorine radical reacts with a molecule of methane to generate a methyl radical
- The methyl radical reacts with a molecule of chlorine to yield chloromethane and regenerates chlorine radical
- The new chlorine radical reacts with another methane molecule, continuing the chain reaction

Chain Propagation



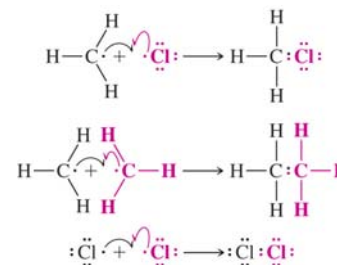
A single initiation step can lead to thousands of propagation steps, hence the term chain reaction

Electron flow in the mechanism



Termination

Occasionally, the reactive radical intermediates are quenched by reaction pathways that do not generate new radicals.



Therefore, the reaction of chlorine with methane requires constant irradiation to replace radicals quenched in chain-terminating steps.

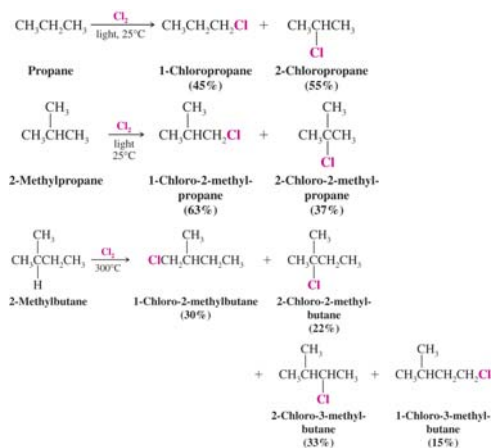
Reaction of Methane with Other Halogens

The order of reactivity of methane substitution with halogens is: **fluorine > chlorine > bromine >> iodine**

Halogenation of Higher Alkanes

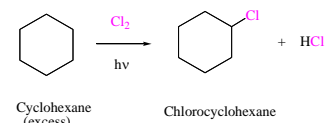
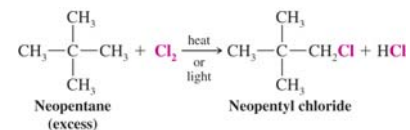
- ♦ Monochlorination of alkanes proceeds with **limited selectivity**.
 - Tertiary hydrogens are roughly 5 times more reactive than primary.
 - Secondary hydrogens are roughly 3.5 times more reactive than primary.

Chlorination occurs so rapidly it cannot distinguish well between types of hydrogen and so is not very selective.



Useful Chlorinations

Chlorination is synthetically useful only when molecular symmetry limits the number of possible substitution products.



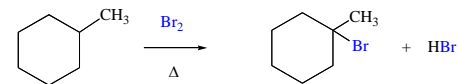
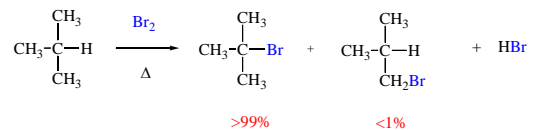
Is Fluorination Selective?

- ◆ Fluorine shows **almost no discrimination** in replacement of hydrogens because it is so reactive
- ◆ It is so reactive that only perfluoro compounds (all H replaced by F) are formed *via* direct fluorination.

Bromination

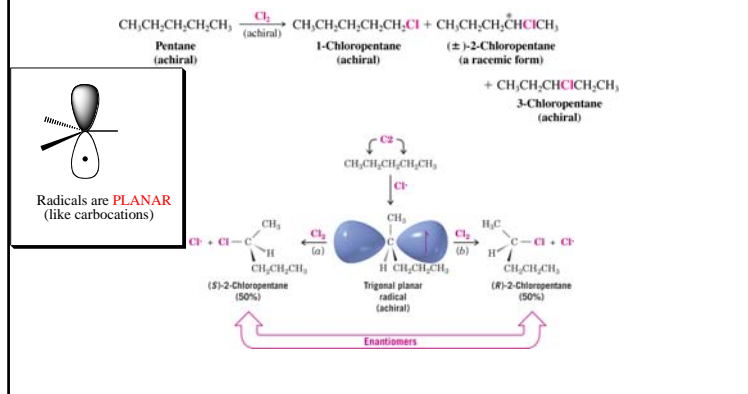
Bromination is the only halogenation that is **controllable and selective**.

Therefore, free radical bromination is the only practical method for halogenating alkanes.



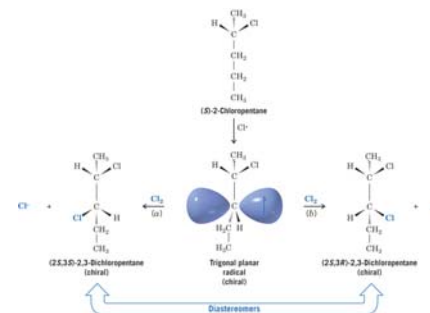
Reactions that Generate Tetrahedral Stereogenic Carbons

- ◆ A reaction of **achiral starting materials** which produces a product with a stereogenic carbon will produce a **racemic mixture**



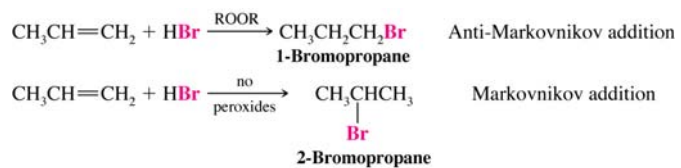
Generation of a Second Stereogenic Carbon

- ◆ When a molecule with one or more stereogenic carbons reacts to create another stereogenic carbon, **two diastereomeric products are produced**.
- The intermediate radical is chiral and reactions on the two faces of the radical lead to two diastereomers.



Anti-Markovnikov Addition of HBr to Alkenes

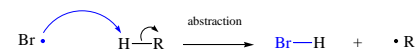
Addition of hydrogen bromide in the presence of peroxides gives anti-Markovnikov addition



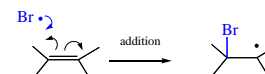
Works only for HBr: the other hydrogen halides do not give this type of anti-Markovnikov addition

A Second Way That Radicals React

Besides abstracting a hydrogen atom



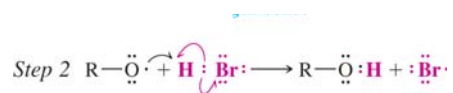
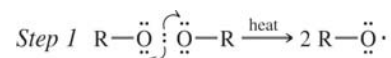
Radicals can add to the pi bond of an alkene



Mechanism for the Anti-Markovnikov Addition of HBr

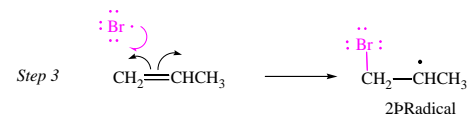
A free radical chain mechanism

Steps 1 and 2 of the mechanism are chain initiation steps which produce a bromine radical

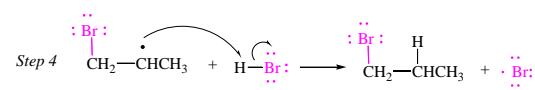


In **step 3**, the first step of propagation, a bromine radical adds to the double bond to give the most stable of the two possible carbon radicals (in this case, a 2° radical)

- Attack at the 1° carbon is also less sterically hindered



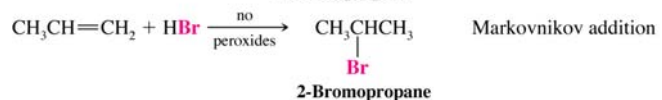
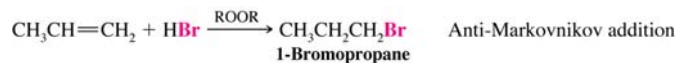
Step 4 regenerates a bromine radical



The new bromine radical reacts with another equivalent of alkene, and steps 3 and 4 repeat in a chain reaction

Controlling Addition of HBr to Alkenes

Early studies of HBr addition gave contradictory results – sometimes Markovnikov addition and sometime anti-Markovnikov



To favor “normal” addition, remove possible traces of peroxides from the alkene and use a polar, protic solvent

To favor anti-Mark, add peroxide and use non-polar solvent

Very useful for your synthetic tool box

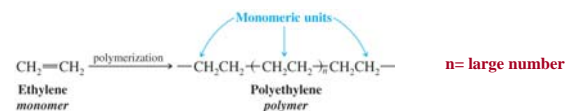
Radical Polymerization of Alkenes

Polymers are macromolecules made up of repeating subunits

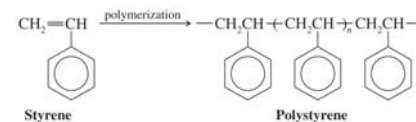
- The subunits used to synthesize polymers are called monomers

Polyethylene is made of repeating subunits derived from ethylene

- Polyethylene is called a chain-growth polymer or addition polymer



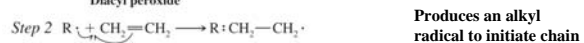
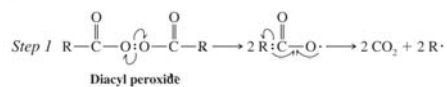
◆ Polystyrene is made in an analogous reaction using styrene as the monomer



Initiator used to start a chain reaction mechanism

A very small amount of a diacyl peroxide is added to initiate the reaction so that few, but very long polymer chains are obtained

Chain Initiation



The propagation step simply adds more ethylene molecules to a growing chain

Chain Propagation

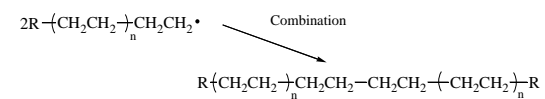


Chain termination

Chain growth can terminate by combination of two radicals.

Chain Termination

Step 4



Some other addition polymers from common alkenes

Monomer	Polymer	Names
$\text{CH}_2=\text{CHCH}_3$	$-(\text{CH}_2-\underset{\text{CH}_3}{\text{CH}})_n-$	Polypropylene
$\text{CH}_2=\text{CHCl}$	$-(\text{CH}_2-\underset{\text{Cl}}{\text{CH}})_n-$	Poly(vinyl chloride), PVC
$\text{CH}_2=\text{CHCN}$	$-(\text{CH}_2-\underset{\text{CN}}{\text{CH}})_n-$	Polyacrylonitrile, Orlon
$\text{CF}_2=\text{CF}_2$	$-(\text{CF}_2-\text{CF}_2)_n-$	Polytetrafluoroethene, Teflon
$\text{CH}_2=\underset{\text{CH}_3}{\text{C}}\text{CO}_2\text{CH}_3$	$-(\text{CH}_2-\underset{\text{CO}_2\text{CH}_3}{\text{C}}(\text{CH}_3))_n-$	Poly(methyl methacrylate), Lucite, Plexiglas, Perspex

Note the regular alternation of the X groups, since the addition step always produces the more stable radical

Superglue

- Some monomers can also be polymerized by nucleophiles

