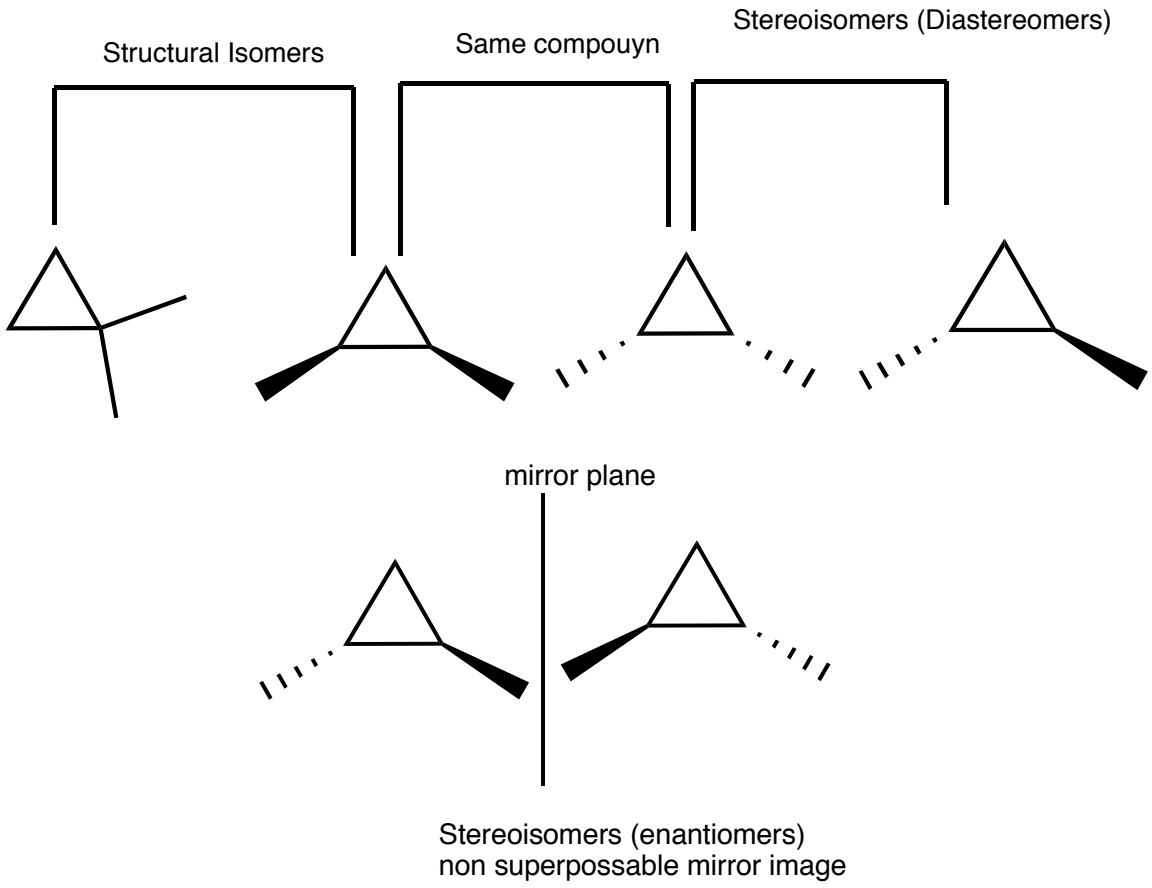
Review from last time:



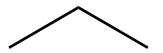
Reactions of alkanes: Two will be considered

1) **Combustion:**

$$R\text{-}H + O_2 \xrightarrow{\Delta=\textbf{heat}} CO_2 + H_2O$$

R = any alkyl group

e.g. propane



$CH_3CH_2CH_3$

$$5O_2 \xrightarrow{\Delta} 3CO_2 + 4H_2O$$

2) Halogenation of alkanes

$$R\text{-}H + X_2 \xrightarrow{h\upsilon = \text{light}} R\text{-}X + HX$$

R = any alkyl group, R-X = alkyl halide / haloalkane (X= Cl, Br, F); F_2 is the most reactive and I_2 fails to react.

In this course, we will be focused on chlorination and bromination.

Substitution reaction (via radicals) – Substitute H with X

e.g. Chlorination of methane

$$CH_4 + Cl_2 \xrightarrow{h\upsilon} CH_3Cl + HCl$$

methane → methyl chloride, chloromethane

light energy, $E = h\upsilon$

h = Planck's constant 6.6×10^{-34} joules-sec

υ = frequency of light

$$CH_3Cl + Cl_2 \xrightarrow{h\upsilon} CH_2Cl_2 + HCl$$

methylene chloride, dichloromethane

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\upsilon} CHCl_3 + HCl$$

chloroform, trichloromethane

$$CHCl_3 + Cl_2 \xrightarrow{h\upsilon} CCl_4 + HCl$$

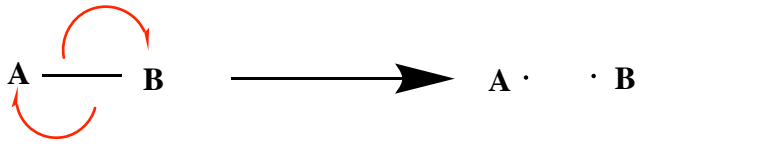
carbon tetrachloride, tetrachloromethane

Mechanism of reaction:

- Step by step description (proposal) of a reaction process (hypothetical and difficult to "prove")

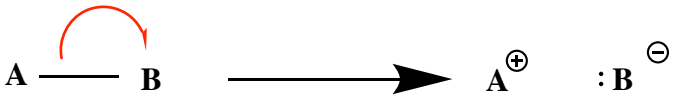
Two kinds of mechanism

1. **Homolytic** (radical): One electron goes to each atom once the bond in broken. e.g. Free radical halogenation of alkanes



radicals, very reactive

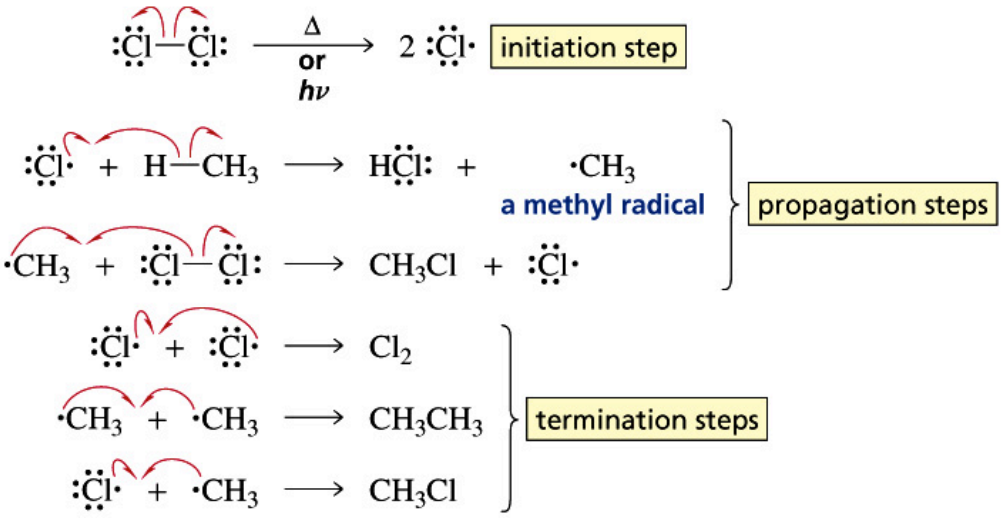
2. **Heterolytic** (polar rxns): The electron pair goes to one of the atoms once the bond is broken. e.g. Addition reactions of alkenes; elimination reactions



Homolytic reactions are less common than heterolytic reactions
- Initiated by heat (Δ) or by light (hυ)

Mechanism of halogenation of CH_4:

$CH_4 + X_2 \xrightarrow{h\upsilon} CH_3X + HX$



of radicals and is quite rare during the progress of the reaction.

Note: The above mechanism also applies to other halogens (F, Cl, Br; not I)

Example: Ethane

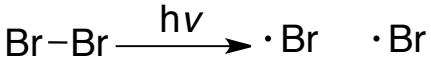
$$H_3C - CH_3 \xrightarrow[h_\nu]{Cl_2} CH_3\text{-}CH_2\text{-}Cl + HCl$$

$$CH_3 - CH_3 \xrightarrow[h_\nu]{Br_2} CH_3\text{-}CH_2\text{-}Br + HBr$$

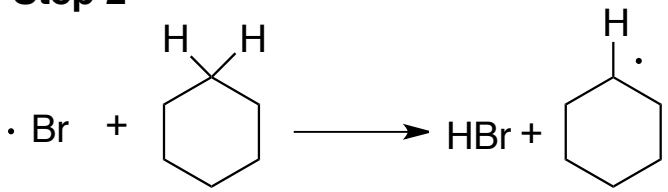
Further examples

1. Cyclohexane

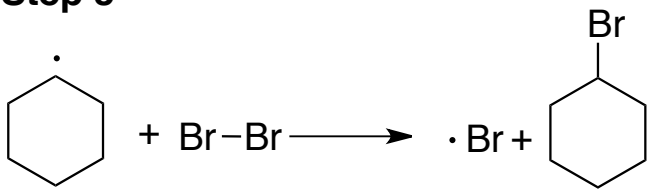
Step 1



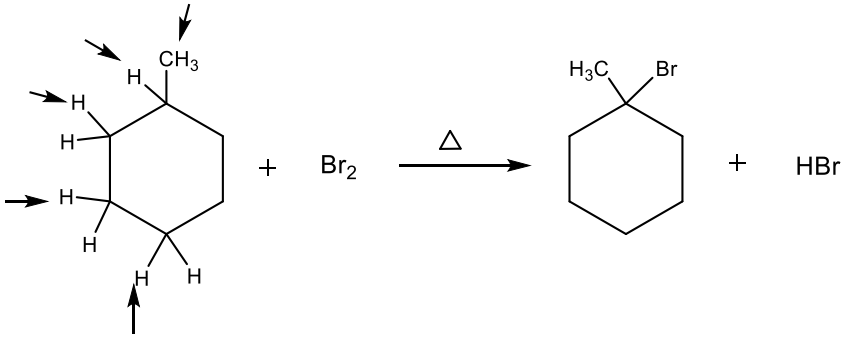
Step 2



Step 3



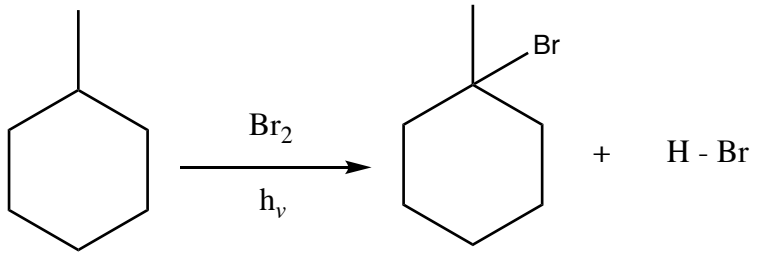
2. Methylcyclohexane

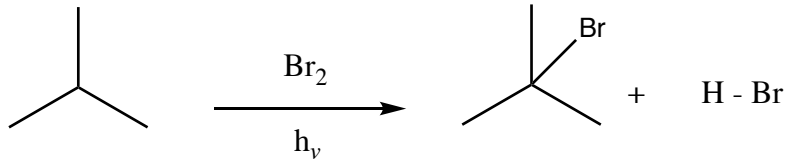


- The reaction can utilize either heat (Δ) or light (hν)

- Different types of hydrogen can be pull from a methylcyclohexane in a radical halogenation reaction to give various products. However, just one main product is obtained. This is explained in terms of the stability of the radical formed during the reaction process.

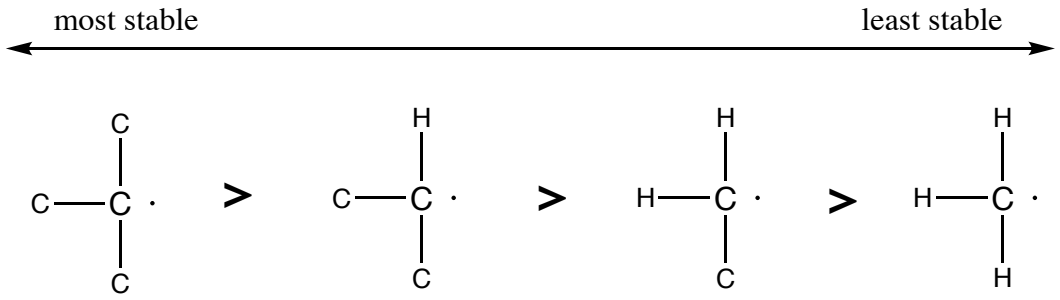
Other Examples:





Stability of radicals:

- Stability increases with alkyl substitution
- Alkyl groups are polarizable and donate electrons to electron deficient sites better than hydrogens (this is called **inductive effect** and occurs through sigma bonds)



tertiary (3°) radical

secondary (2°) radical

primary (1°) radical

methyl radical

Or it can also be summarized below from least to most stable radicals:

$\cdot CH_3$	<	$\cdot CH_2R$	<	$\cdot CHR_2$	<	$\cdot CR_3$
methyl radical (least stable)		primary (1°) radical		secondary (2°) radical		tertiary (3°) radical (most stable)