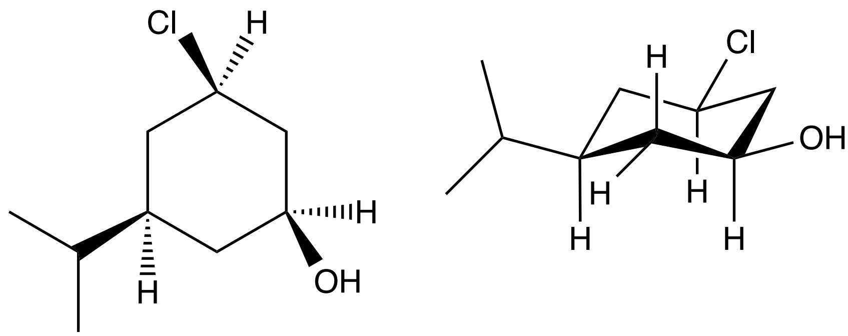
An additional example:



Reactions of alkanes: Two will be considered

1) **Combustion:**

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

R = any alkyl group

e.g. propane

$$CH_3CH_2CH_3 \quad + \quad 5O_2 \xrightarrow{\Delta} 3CO_2 \quad + \quad 4H_2O$$

2) **Halogenation of alkanes**

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

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 bromation.

Substitution reaction (via radicals) – Substitute H with X

e.g. Chlorination of methane

$$\underset{\text{methane}}{CH_4} + Cl_2 \xrightarrow{h\upsilon} \underset{\substack{\text{methyl chloride}\\ \text{chloromethane}}}{CH_3Cl} + HCl$$

light energy, E = hυ
h = Planck’s constant 6.6 x10^{-34} joules-sec
υ = frequency of light

$$CH_3Cl + Cl_2 \xrightarrow{h\upsilon} \underset{\substack{\text{methylene chloride}\\ \text{dichloromethane}}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\upsilon} \underset{\substack{\text{chloroform}\\ \text{trichloromethane}}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow{h\upsilon} \underset{\substack{\text{carbon tetrachloride}\\ \text{tetrachloromethane}}}{CCl_4} + HCl$$

Mechanism of reaction:

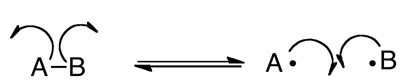
- Step by step description of a reaction process (hypothetical, educated guess of what happens; difficult to “prove”)

- The flow of electrons between atoms is depicted using arrows

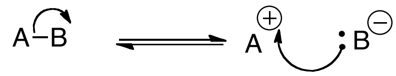
  - Full arrow heads being full to indicate the movement of a pair of electrons (2) or
  - Half of an arrow head to indicate the movement of one electron (1)

<u>Two kinds of mechanism</u>

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



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

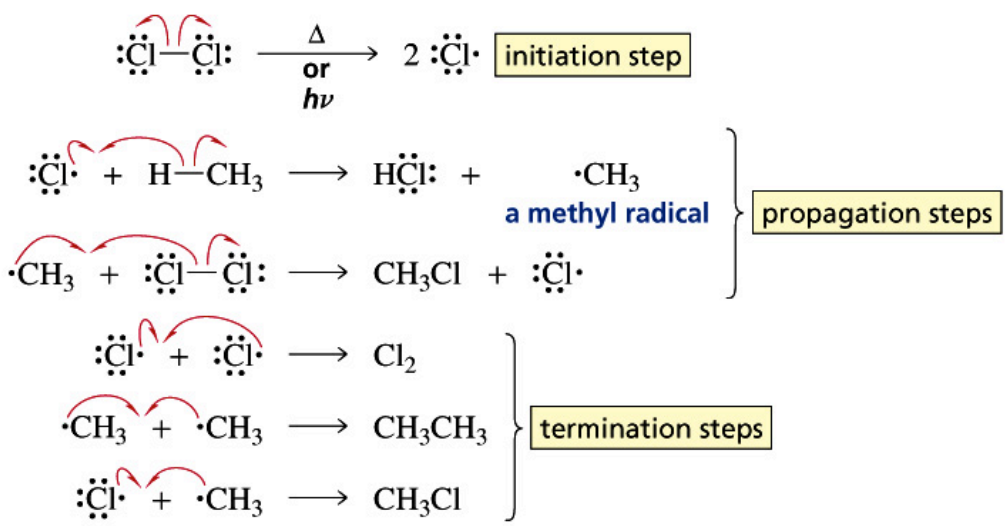


Homolytic reactions are less common than heterolytic reactions

- Initiated by heat (Δ) or by light (hυ)

Mechanism of halogenation of CH_4:

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



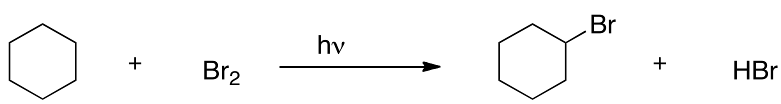
of radicals and is quite rare during the progress of the reaction.

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

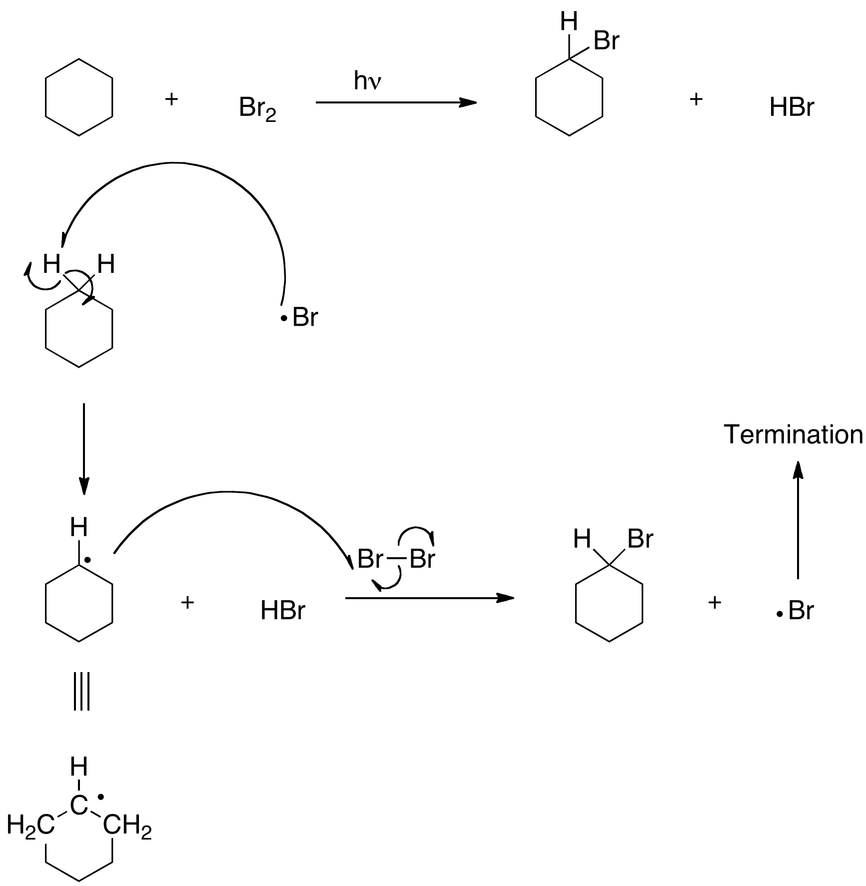
<u>Further examples</u>

1. Cyclohexane

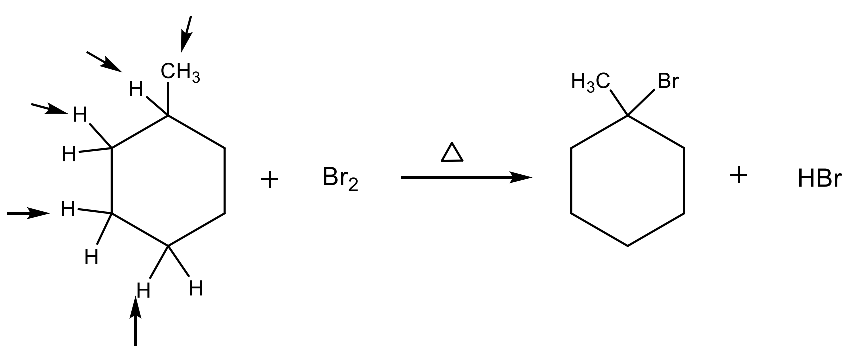
1.



C_6H_{12}



2. Methylcyclohexane



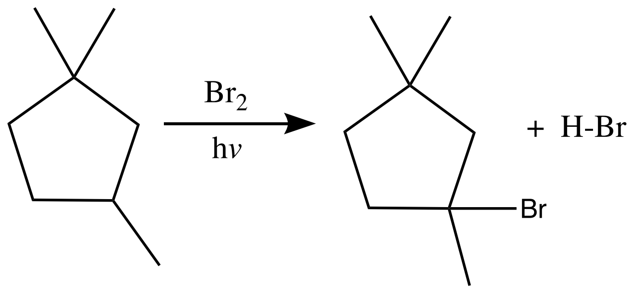
- Different types of hydrogen can be pulled from a methylcyclohexane in a radical halogenation reaction to give various products. However, just one main product is obtained. This is explained in terms of the stability of the radical formed during the reaction process.

Stability of radicals:

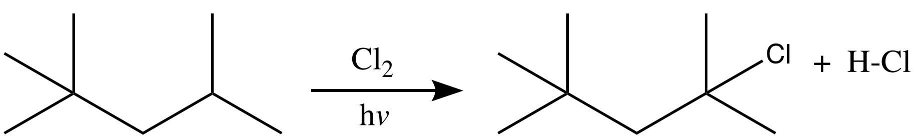
- Stability increases with alkyl substitution
- Alkyl groups are polarizable and donate electron density (negative charge) to electron deficient sites better than the hydrogens around the ring
- Inductive effect: through single bonds

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

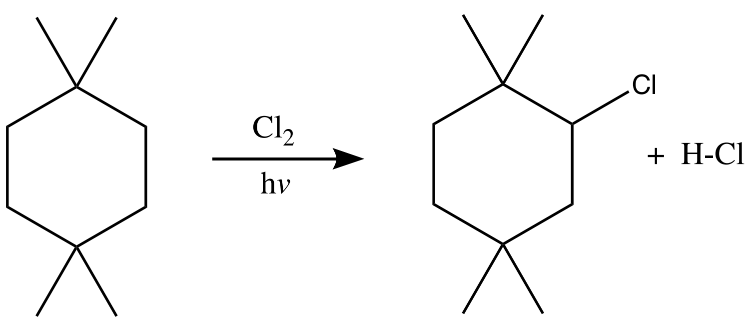
Examples



1,1,3-trimethylcyclohexane

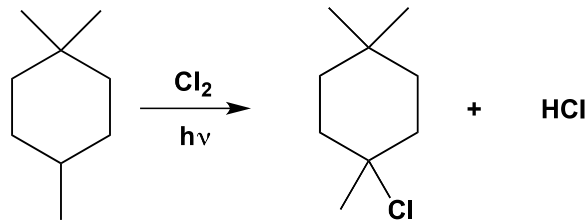


2,2,4-trimethylpentane

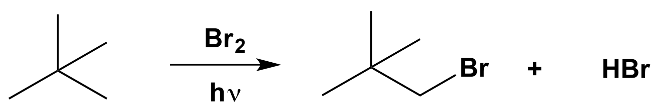


1,1,4,4-tetramethylcyclohexane

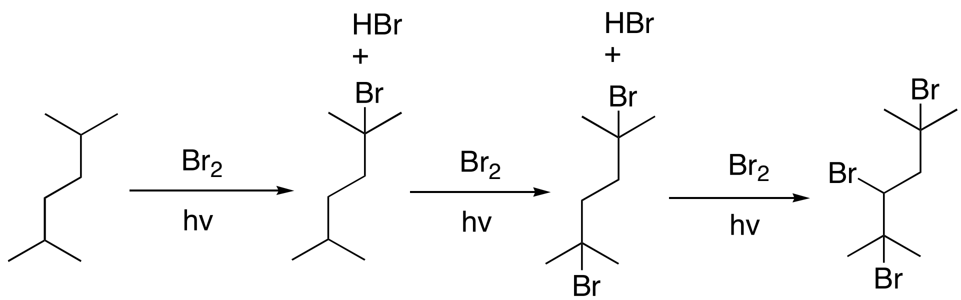
Additional examples for your reference:



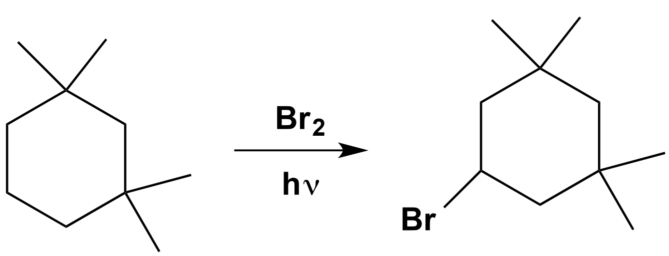
1,1,4-trimethylcyclohexane



Neopentane
(2,2-dimethylpropane)



2, 5-dimethylhexane



Note that the bromine is furthest from the methyl groups due to destabilizing steric interactions. Out of the methylene groups available, this one is the easiest for the bromine to access.

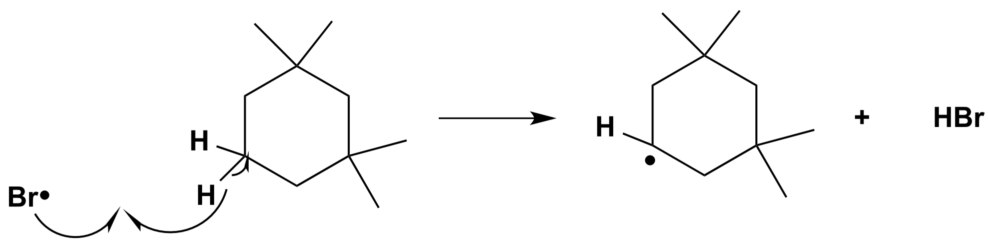
1,1,3,3-tetramethylcyclohexane

Mechanism of reaction between 1,1,3,3-tetramethylcyclohexane and Br_2

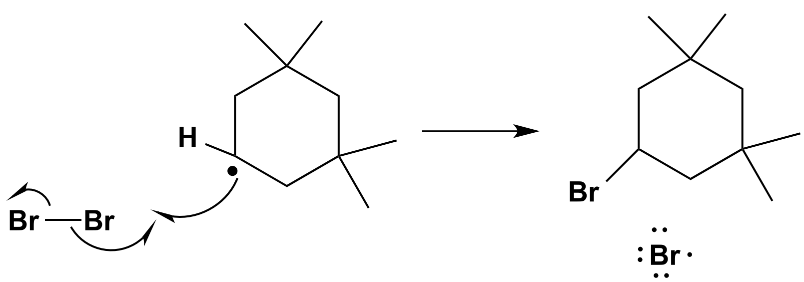
Initiation

$$Br_2 \xrightarrow{h\nu} :\ddot{\underset{..}{Br}}\cdot \quad \cdot\ddot{\underset{..}{Br}}:$$

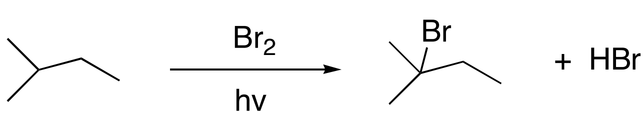
1st propagation step

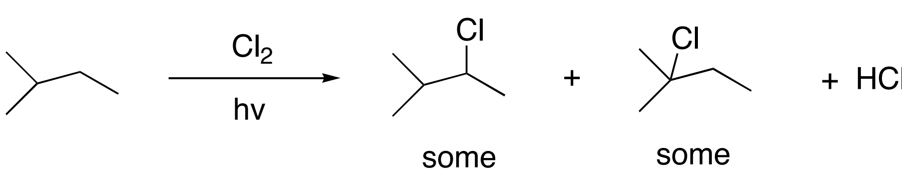


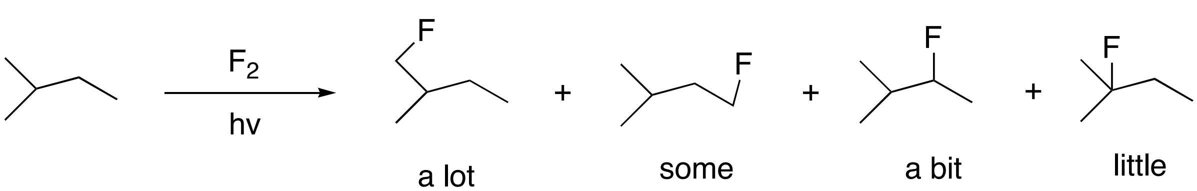
2nd propagation step



Reactivity and Selectivity (Hammond Postulate)

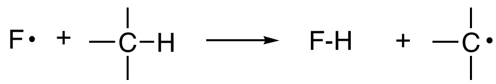




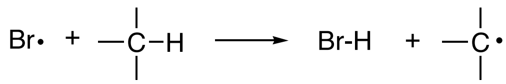


Reactivity

$F_2 > Cl_2 > Br_2 > I_2$ Iodine does not react



ΔH = -35 kcal/mole
Exothermic



ΔH = +16 kcal/mole
Endothermic

Br• > Cl• > F•

most selective — least selective

endothermic — exothermic

Bromine atom "searches" the molecule to create the most stable radical
Fluorine atom is small and feels the loss of an electron much more than bromine

- Fluorine is less precise and reacts immediately

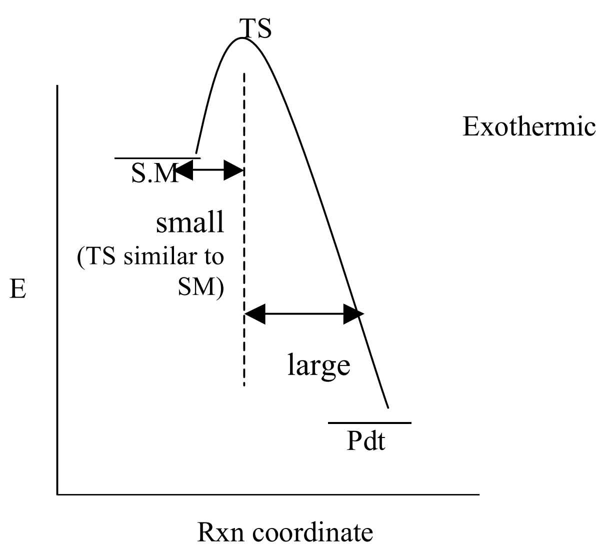
<u>Hammond Postulate</u>

- The more exothermic a reaction is, the more the transition state (TS) resembles the starting materials.
- The more endothermic a reaction is, the more the TS resembles the product.

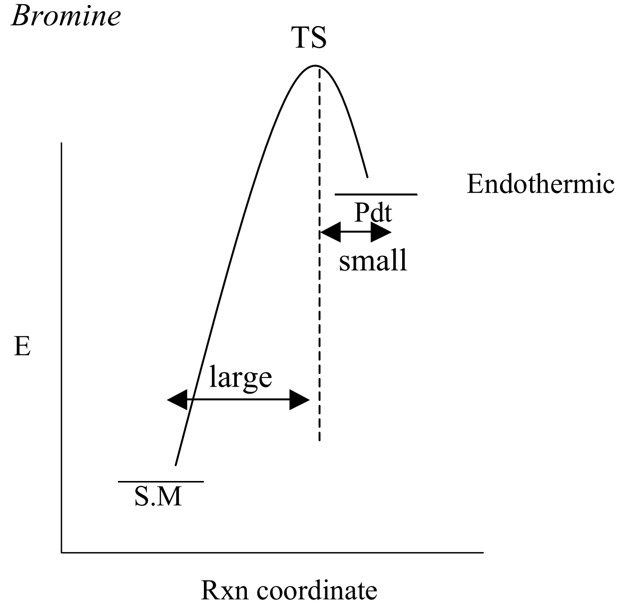
Generally:

- More reactive radical → Less selective
- Less reactive radical → More selective

Fluorine



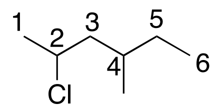
Bromine



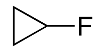
Alkyl Halides = Haloalkanes

<u>Structure and Nomenclature</u>

1) Find longest chain with largest number of branches
2) Number from end so as to give 1st branch the lowest number
3) Name prefix with "halo" (chloro, bromo, iodo, fluoro) OR name alkyl and add halide (chloride, bromide, iodide, fluoride) as the suffix



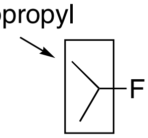
2 -chloro -4-methylhexane



Fluorocyclopropane

Cyclopropyl fluoride

Isopropyl

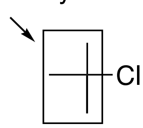


2-Fluoropropane

2-Propylfluoride

Isopropyl Fluoride

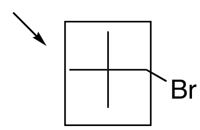
tert-Butyl



2-Chloro-2-methylpropane

tert-Butyl Chloride

Neopentyl



Neopentyl Bromide

1-Bromo-2,2-dimethylpropane

<u>Physical Properties of Alkyl Halides:</u>

- Governed primarily by dipole-dipole interactions.
- "Non-polar", but more polar than hydrocarbons.
- High MP and BP relative to hydrocarbons of similar molecular weight
- Good solvents for organic compounds e.g. Methylene chloride (CH_2Cl_2) and chloroform ($CHCl_3$) are very common.
- Density = ρ (rho) = 1.0 g/cm^3 for water
- If % composition > 65% halogen by weight, then more dense than water (ρ > 1.0)
- Immiscible (insoluble) in H_2O, which floats on top of the halide.