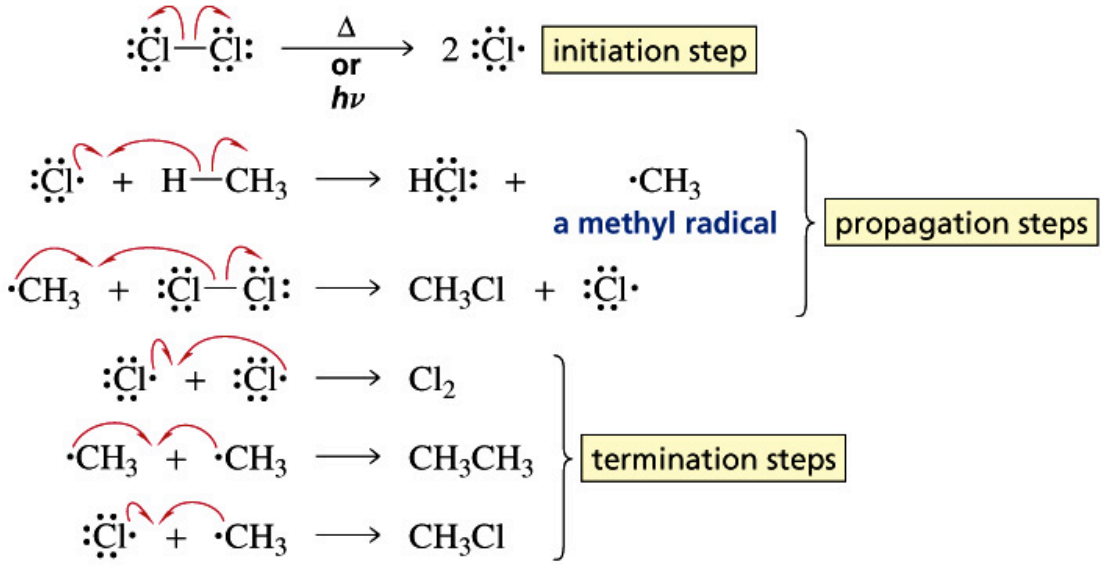
Mechanism of halogenation of CH_4:

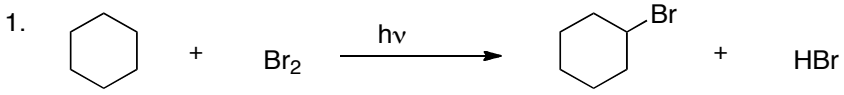
$$CH_4 + X_2 \xrightarrow{h\upsilon} CH_3X + HX$$

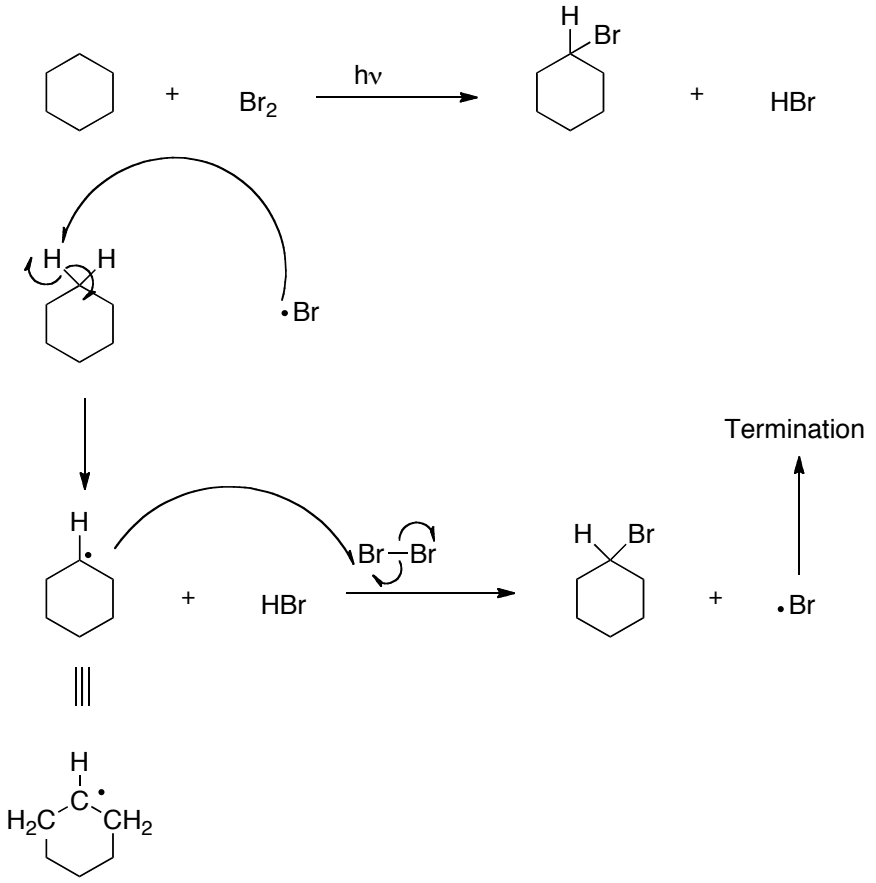
X = F, Cl, Br



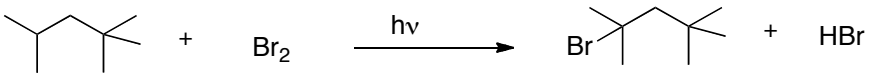
Note: above mechanism applies to other halogens (F, Cl, Br)

Further examples -

1. 



2. "isooctane"



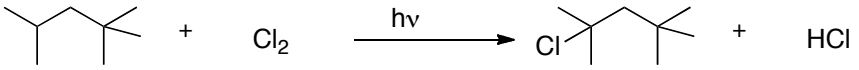
2,2,4-trimethylpentane

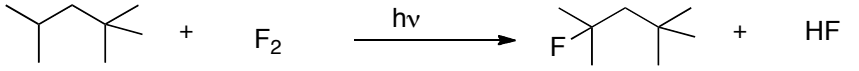
Stability of radicals:

Increases with alkyl substitution.
Alkyl groups are polarizable and donate electrons to electron deficient sites better than hydrogens. (This is called inductive effect.)

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

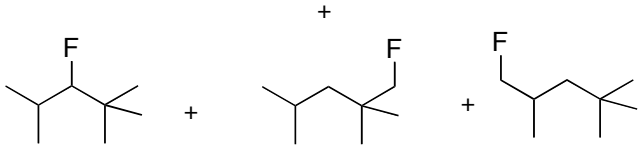
Further Examples

1. 

2. 

minor product

Note: F_2 very reactive

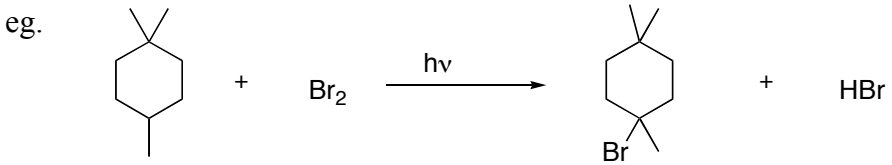


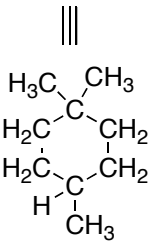
major product

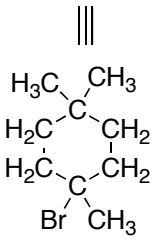
Stability of radicals:

Increases with alkyl substitution.
Alkyl groups are polarizable and donate electrons to electron deficient sites.
Inductive effect: through single bonds

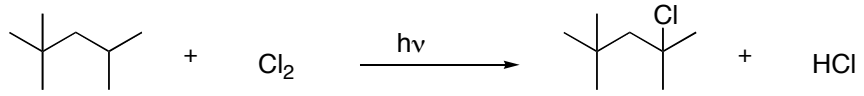
$\cdot CH_3$	<	$\cdot CH_2R$	<	$\cdot CHR_2$	<	$\cdot CR_3$
methyl radical (least stable)		primary radical		secondary radical		tertiary radical (most stable)

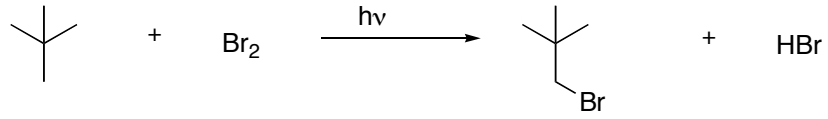
eg. 

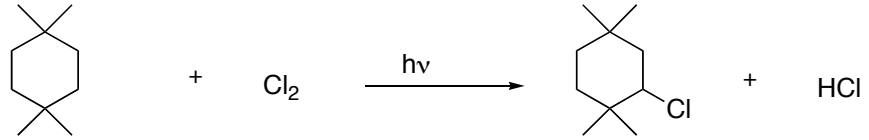


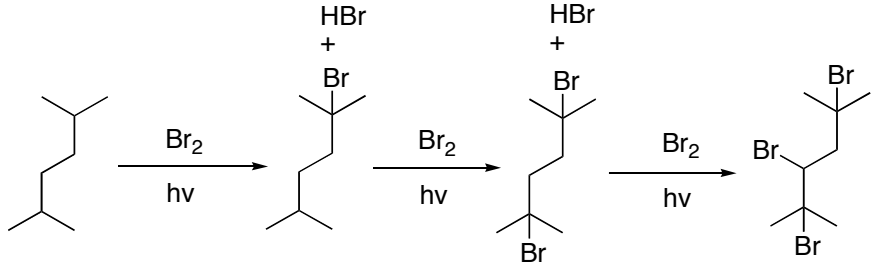


More examples:

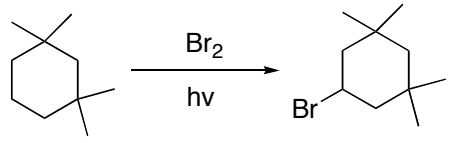
1. 

2. 

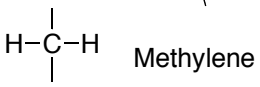
3. 



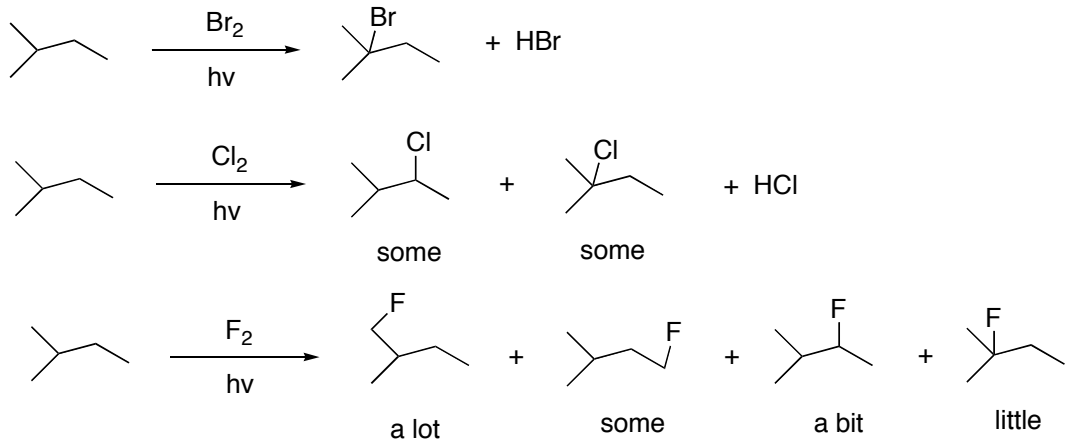
2, 5-dimethylhexane



Note that the bromine is furthest from the methyl groups due to destabilizing steric interactions.

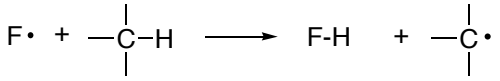


Reactivity



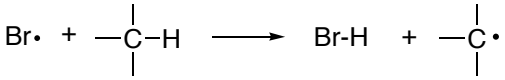
Reactivity

$F_2 > Cl_2 > Br_2 > I_2$



ΔH= -35kcal/mole

Exothermic



ΔH= +16kcal/mole

Endothermic

Br• > Cl• > F•

most selective — least selective

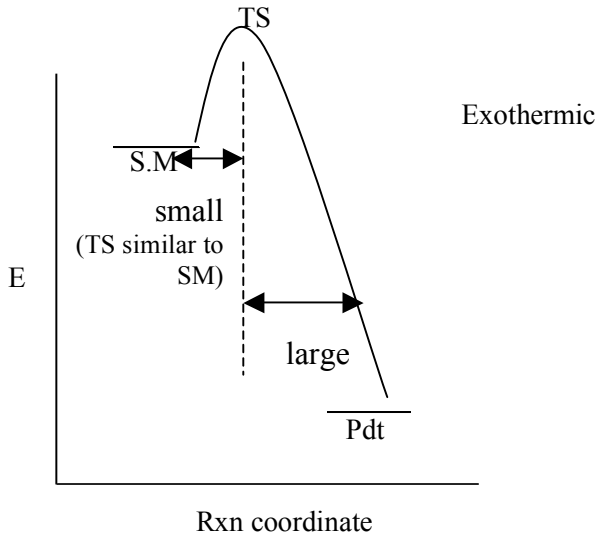
endothermic — exothermic

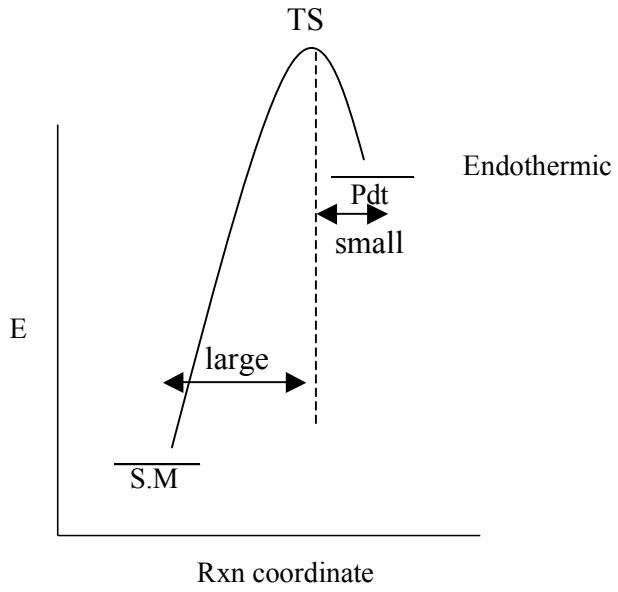
Hammond Postulate

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

Generally:

- More reactive radical →less selective radical
- less reactive radical →more selective radical

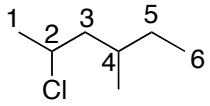




Alkyl Halides = haloalkanes

Structure and Nomenclature

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

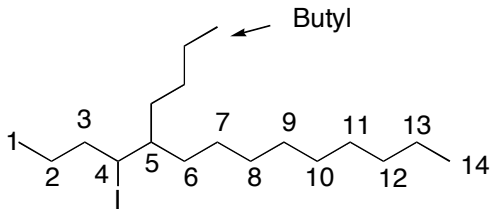


2 -chloro -4-methylhexane

Fluorocyclopropane

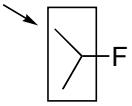
Cyclopropyl fluoride

look at atomic number



5-butyl-4-iodotetradecane

Isopropyl

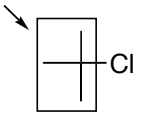


2-Fluoropropane

2-Propylfluoride

Isopropyl Fluoride

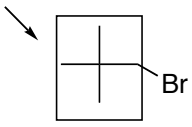
tert-Butyl



2-Chloro-2-methylpropane

tert-Butyl Chloride

Neopentyl



Neopentyl Bromide

1-Bromo-2,2-dimethylpropane