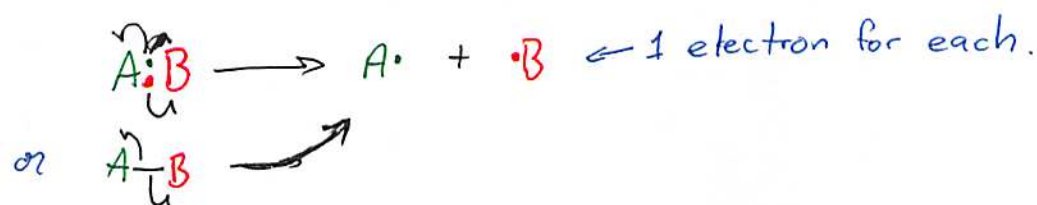


Reaction Mechanisms: An overall description of how a reaction occurs.

3 General Types:

- Radical \Rightarrow Homolytic process
 same cleave



- Polar \Rightarrow Heterolytic process
 different

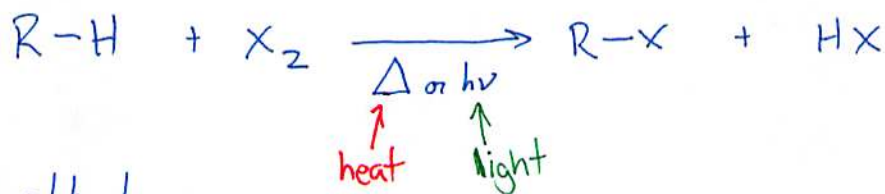


- Pericyclic \Rightarrow Not this semester :)

Radical-based Rxns: Example.

Halogenation of alkanes

General: This is an example of a substitution rxn.

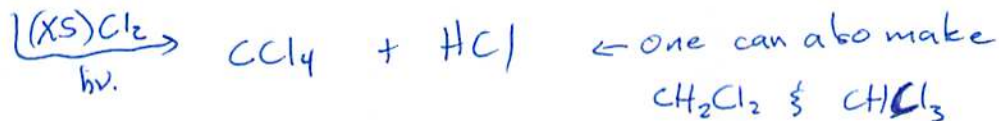
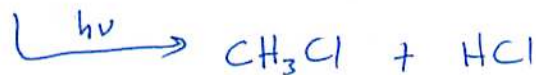


R = alkyl

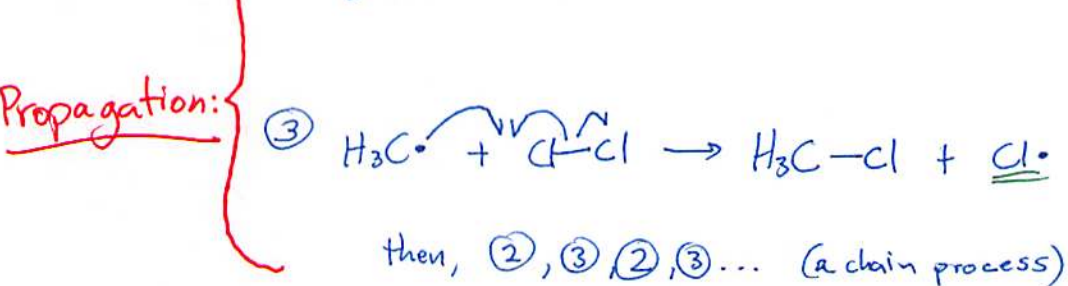
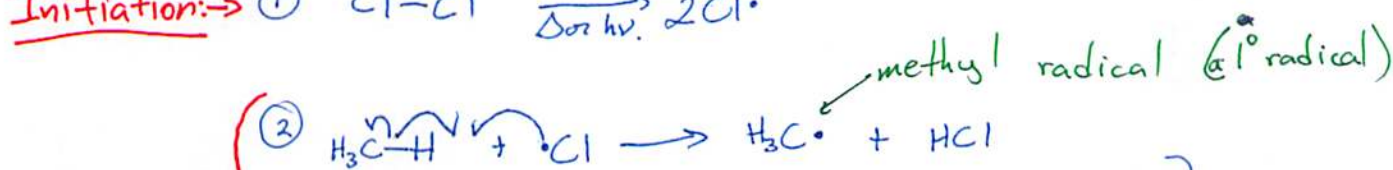
X = Cl or Br

No rxn without Δ or $h\nu$!!

This is what is observed experimentally:

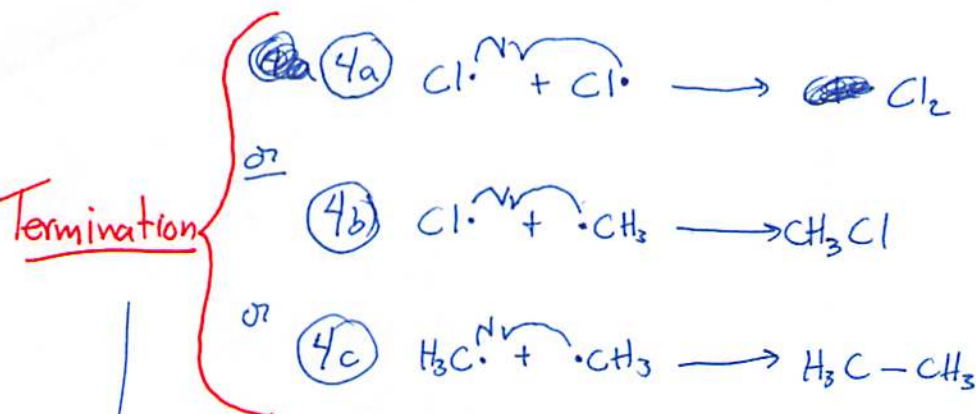


How? Mechanism.



- Radicals are continuously generated.
- Radicals are "reaction intermediates" (compounds that are short-lived during a rxn)

The rxn ends when:



→ All radicals are consumed

Why only Cl_2 & Br_2 , not I_2 ?

Consider Energy Diagrams.

- (BDE)
- Bond dissociation energy: The amount of energy to break a bond homolytically.
 - If a bond is broken: Endothermic (+)
 - " " " " made: Exothermic (-)

Generic Mechanism (excluding 2 terminating steps that yield products)

BDE's
if X = (Table 6.3)

①	$X-X$	$\xrightarrow{\Delta}$	$2 X\cdot$	ΔH (kcal/mol)
Cl	+58	-	-	+58 +58
Br	+46	-	-	+46 +46
I	+36	-	-	+36 +36

②	$X\cdot + H_3C-H$	\rightarrow	$HCl + \cdot CH_3$			} Rate Limiting Step!
Cl	- +105	-103	-	+2		
Br	- +105	-87	-	+18		
I	- +105	-71	-	+34		

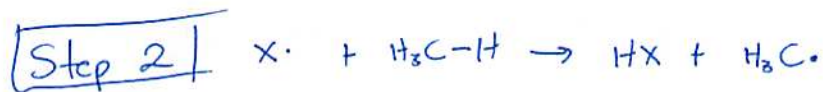
③	$H_3C\cdot + X-X$	\rightarrow	$H_3C-X + X\cdot$		
Cl	- +58	-84	-	-26	
Br	- +46	-70	-	-24	
I	- +36	-57	-	-21	

④	$2 X\cdot$	\rightarrow	$X-X$		
Cl	-	-58	-	-58	
Br	-	-46	-	-46	
I	-	-36	-	-36	

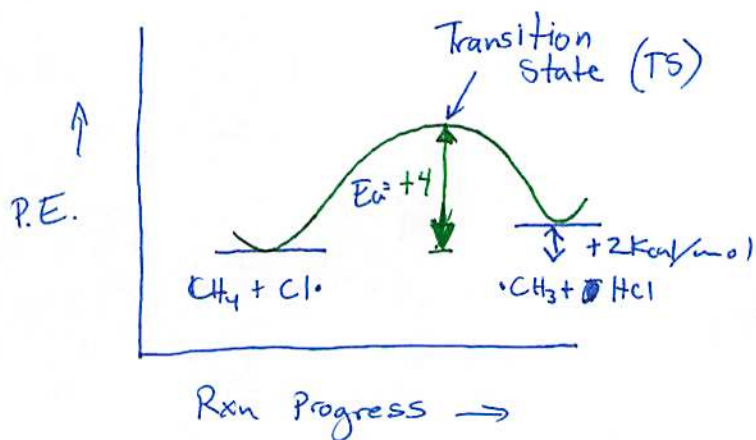
This trend explains reactivity.
- Good for Cl_2 & Br_2 not I_2

X =	ΔH_{rxn}
Cl	-24
Br	-6
I	+13 ← Endothermic

Free Energy Diagram of the Rate Limiting Step (RLS) or Rate Determining Step (RDS)*

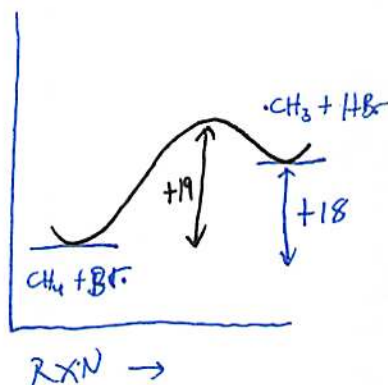


$X = Cl$



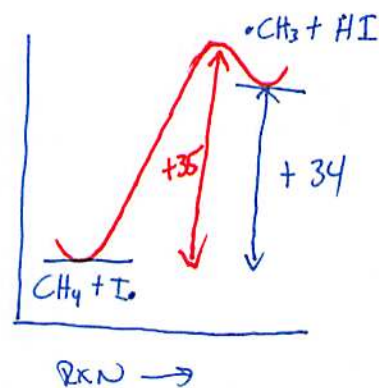
- slightly endothermic (+2)
- small Activation Energy (E_a)
- fast RXN

$X = Br$



- Larger E_a
- Slow RXN

$X = I$

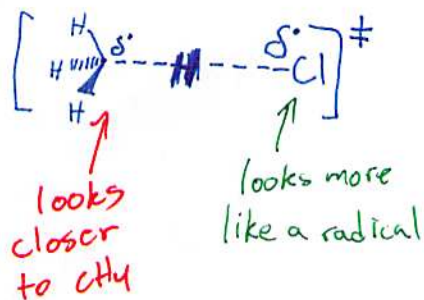


- Largest E_a
- N.R. !

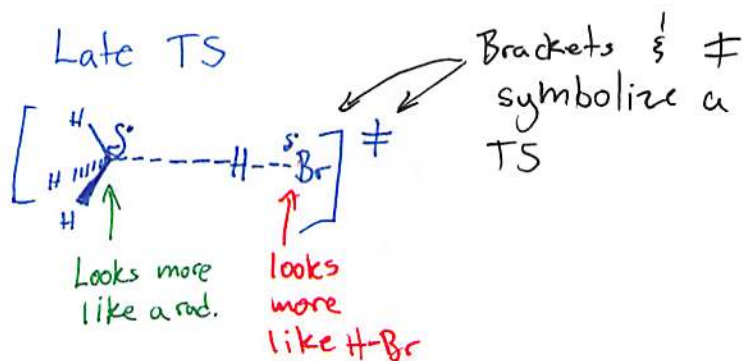
The Transition State represents the highest Energy structure involved in this step of the reaction.

Hammond*
Postulate = The higher the E_a , the "later" the TS is reached.
Early TS "looks like reactants"
Late TS "looks like products"

ex. Early TS

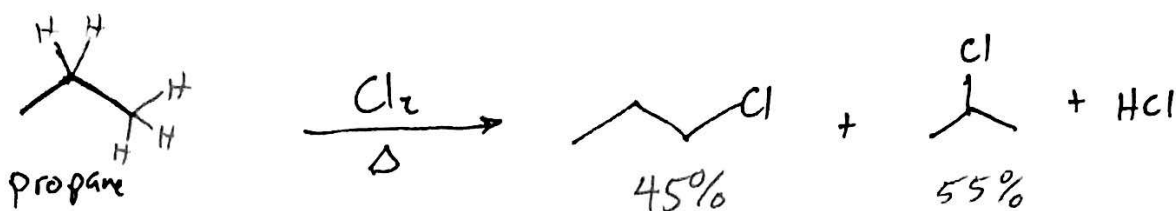


Late TS

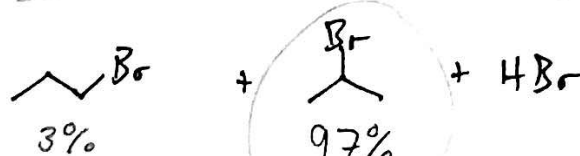


(6)

Larger Alkanes



Mixture



considered only product

Regioselective rxn. (prefers one site out of various possibilities)

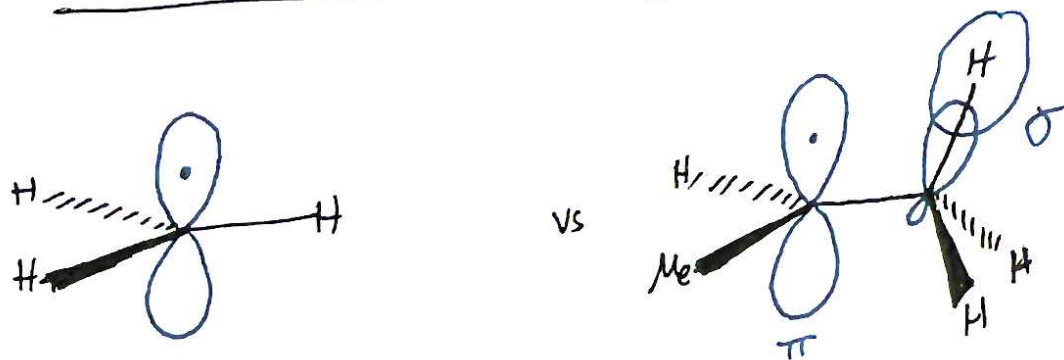
Why? Consider RLS

* Radical stability:

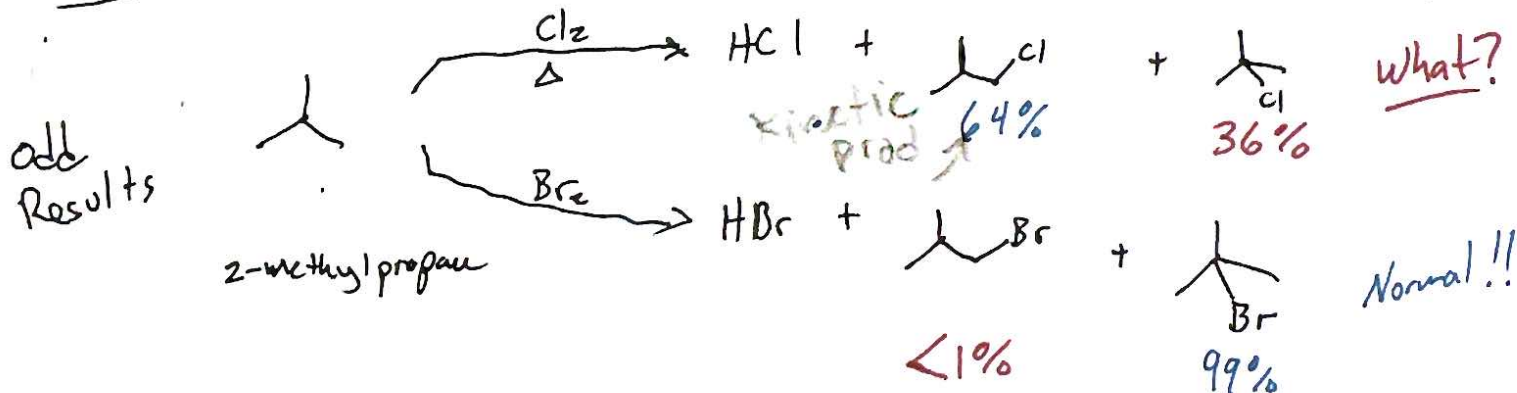
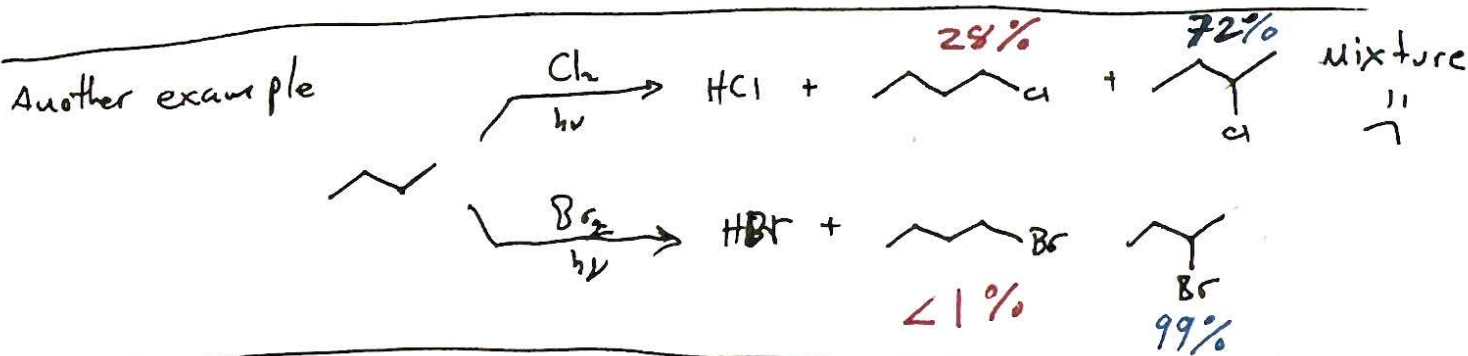
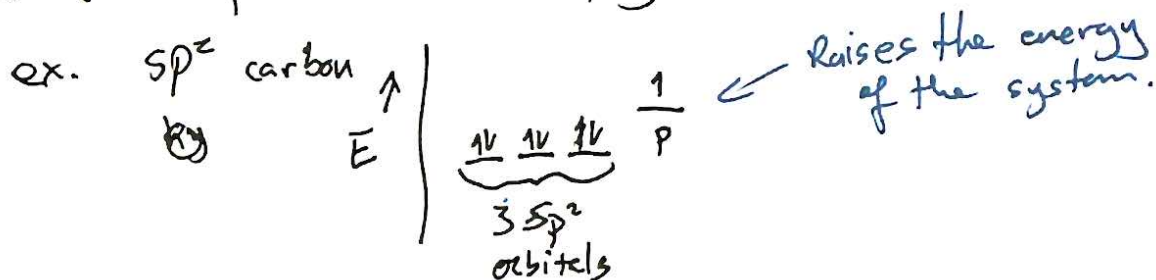


• Cl is very reactive, leading to both radicals Kinetic control
 • Br is less " , & prefers to form the most stable radical } thermodynamic control

Radical Stabilization : Hyperconjugation



Better if the p orbital was empty



Remember: Chlorination is very fast!! ← Kinetic control
Bromination is slow! ← Thermodynamic control