Overheads: - Outline
- Feedback & Questions

Go over feedback/questions (overhead)

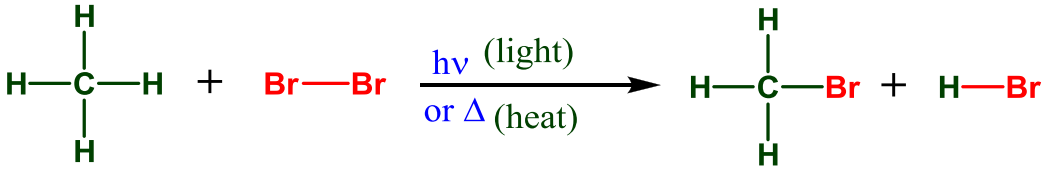
Recap Monday

Radical: atom with unpaired electron *e.g.* CH_3•

break a bond:

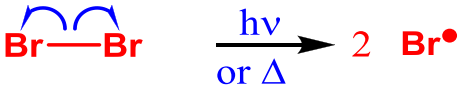
or make a bond:

Radical Halogenation:

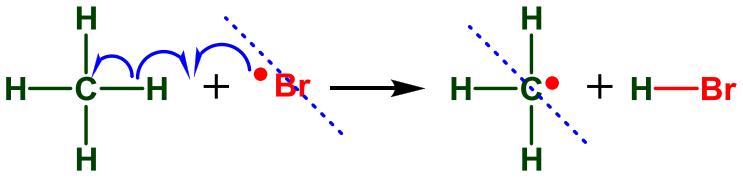


Mechanism: three "parts"

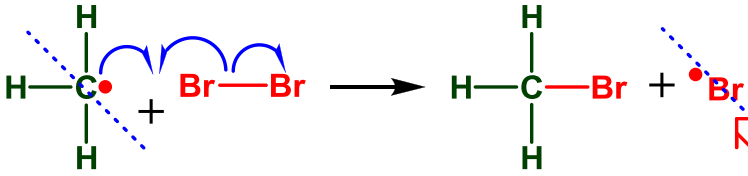
1 Initiation - make small amount of radicals



Then… radical reacts with alkane:

2a 

- Br wants to make bond (wants 8 e-) so takes H from C
- all 4 H's same, so any can react

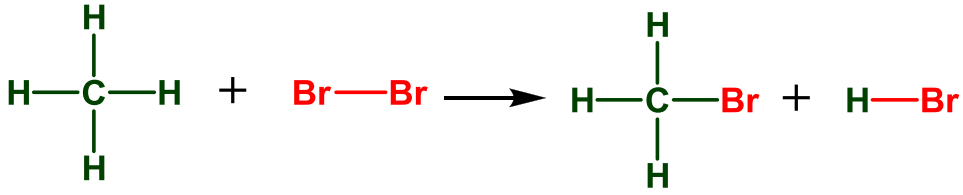
2b 

- now C radical wants to make bond, so takes Br

Propagation
- happens 1000's of times for each Br* from initiation

get Br* back, so can react again

② sum of propagation steps ≡ overall reaction:



Where do radicals go in the end?

③ Termination: any 2 radicals combine

a)  (reverse of initiation - no net effect)

b)  (same as propagation product - no net effect)

** this is NOT the way >99% of product is formed!

c)  *small amount* of side-product formed

⇨ Called a Radical Chain Reaction: Br• kicks off chain reaction = propogation

Always has 3 parts:

- Initiation: make small amount of radicals
- Propagation: form products 1000's of times
- Termination: radicals eventually get used up

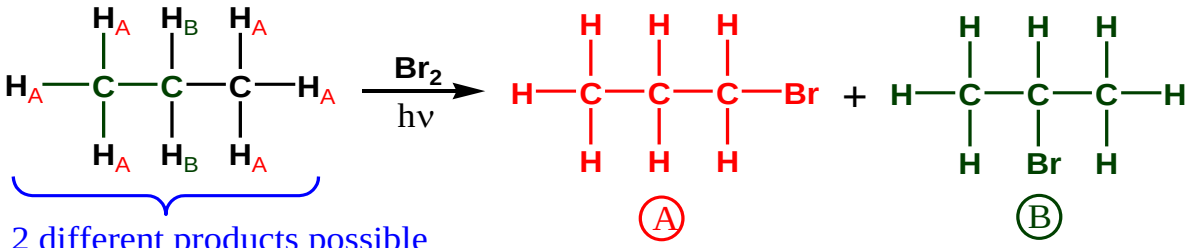
⇨ Reaction works for Br_2 and Cl_2 *only*

					$\Delta H°_{(propagation)}$	
R—H	+ Br_2	→	R—Br	+ H—Br	$\Delta H°$ = -36 kJ/mol	exo :-)
"	Cl_2	→	R—Cl	"	$\Delta H°$ = -100 kJ/mol	
"	I_2	✗	R—I	"	$\Delta H°$ = +40 kJ/mol	endo ∴ N.R.
"	F_2	→	R—F	"	$\Delta H°$ = -450 kJ/mol	

BOOM! too exothermic

NOTE: if have excess Cl_2 or Br_2, can replace more H's, get CCl_4 for example

What if Molecule has different H's?



2 different products possible

A — replace one of 6 H_A's

B — replace one of 2 H_B's

Ratio? If equally likely (random), expect: 6 : 2

75% A : 25% B

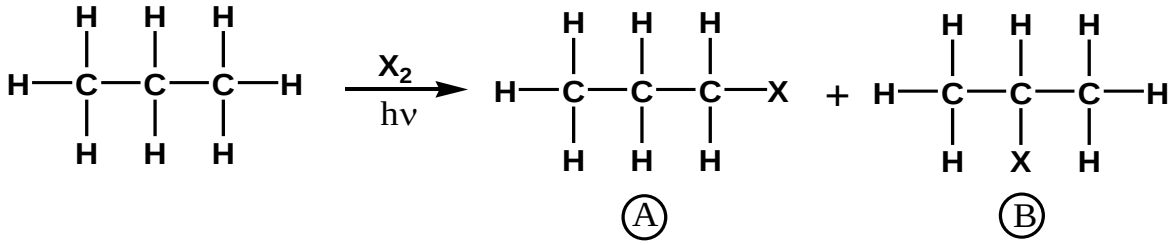
Actual Ratio: 4% A : 96% B

Why? 2° radical > 1° radical

⇨ like C+, R_3C• is electron deficient ∴ more sub = more stable

⇨ ratio of products results from combination of probability (# of H's) and radical stability

Throw in a Wrench:



A B

statistically: 75% A : 25% B

$X_2 = Br_2$: 4% A : 96% B

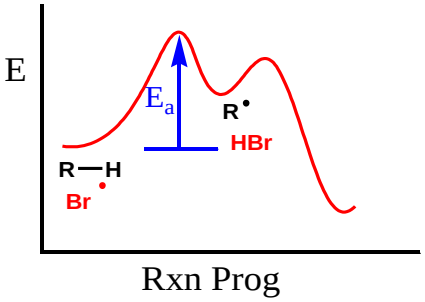
$X_2 = Cl_2$: 44% A : 56% B

still 2° > 1° but MUCH less selective

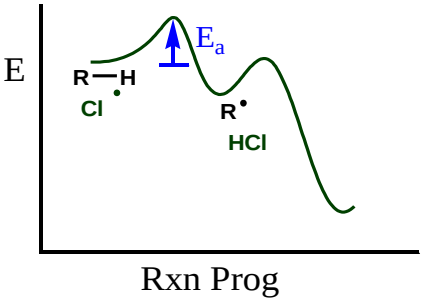
Why? Compare thermodynamics of propagation steps

	Br_2		Cl_2	
Step 2a	+55 kJ/mol	endo	-10 kJ/mol	exo
Step 2b	-90 kJ/mol	exo	-90 kJ/mol	exo
	-35 kJ/mol		-100 kJ/mol	

Br_2:

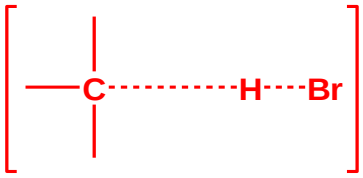


Cl_2:

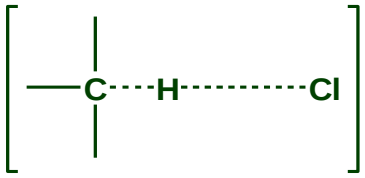


Hammond Postulate: T.S. is more like the species to which it is closer in energy

Br_2: endothermic RDS
∴TS more like intermediate (radical)
aka "late TS"



Cl_2: exothermic RDS
∴TS more like reactants
aka "early TS"



∴ stability of radical makes more difference to Br_2 reaction (TS more like radical)
∴ Br_2 more selective