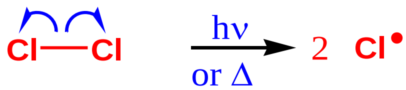
Overheads: - Outline

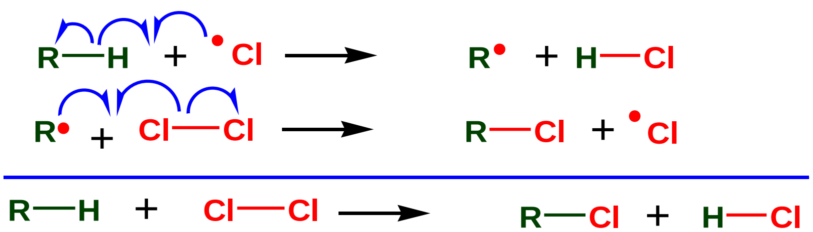
Test dates: Midterm moved to Feb 10

<u>Recap Chain Reactions:</u> 3 parts to mechanism?

(1) <u>Initiation</u> - make <u>small amount</u> of radicals



(2) <u>Propagation</u> - make <u>lots</u> of product



(3) <u>Termination</u> - any 2 radicals combine, stops reaction

e.g. 

<u>Selectivity:</u> more substituted radicals formed more easily

BUT, Cl_2 less selective than Br_2

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

Cl_2: exothermic RDS
∴TS more like reactants

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

<u>Why</u> is Br* RDS endothermic, but Cl* exo?

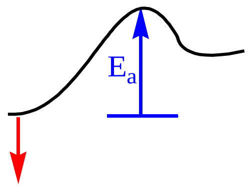
- only difference is energy of reactants!
⇨ Cl* must be higher E (less stable) than Br*

$\Delta H°_f = +122$ kJ.mol $\Delta H°_f = +96$ kJ.mol

Cl* higher E ∴ wants to react more

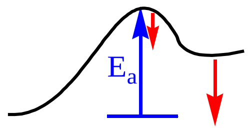
Clarify: talking about stability of Cl• vs Br• (= reactant, not product)

more stable reactant,
does not want to react



lower E reactant, Ea↑

more stable product,
formed faster



lower E product, Ea↓

SO, Cl• higher E, more reactive, ⇨ reacts faster, grabs whatever it can

Br• reacts slower, more choosy (selective) ⇨ waits for 3° > 2° > 1°

I• even more stable ⇨ too choosy! Doesn't react at all
F• too reactive ⇨ reacts with anything it can find!

How much less selective is Cl• ?

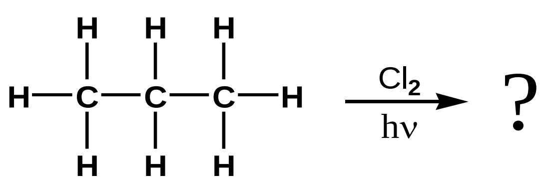
	3° >	2° >	1°
Br•	1600	82	1
Cl•	5	3.8	1

} Can use to predict ratios

Amount 3° = (#3°H)(3° preference) = x
2° = (#2°H)(2° preference) = y
1° = (#1°H)(1° preference) = z
Total = x+y+z

% 3° = x / (x+y+z) x 100%
% 2° = y / (total) x 100%
% 1° = z / (total) x 100%

e.g.



3° = (0)(5) = 0
2° = (2)(3.8) = 7.6
1° = (6)(1) = 6
Total = 13.6

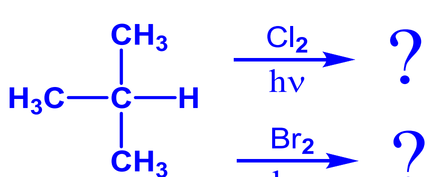
% 2° = 7.6 / (13.6) x 100% = 56%
% 1° = 6 / (13.6) x 100% = 44%

Same as experimental!

NOTE: Unlike carbocations, radicals do not rearrange, so ratio "stays" as predicted

"Homework"
1) Predict Br_2 ratios (should be 4:96!)

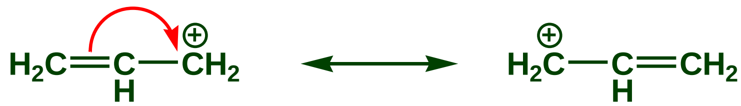
2) Predict ratios for:



} answers will be posted on moodle

Resonance-Stabilized Radicals:

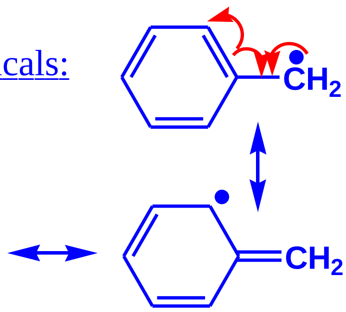
Recall: C^+:



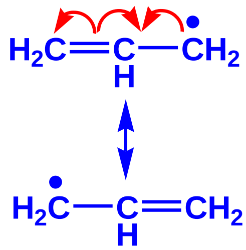
+ charge shared between 2 C's (delocalized) more stable

$\boxed{\text{Resonance = stability}}$

Radicals:



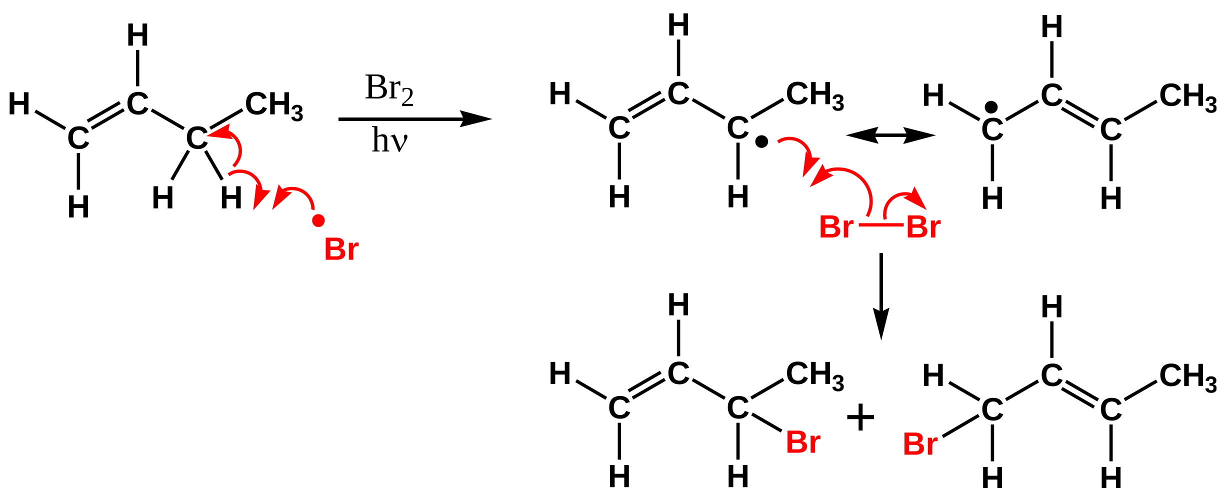
or



>3°>2°>1°

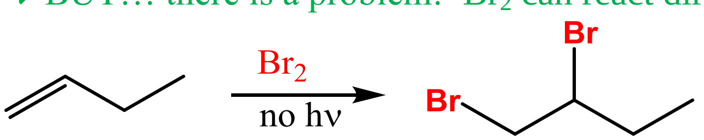
etc.

e.g.



➩ get 2 products (ratio depends on conditions)

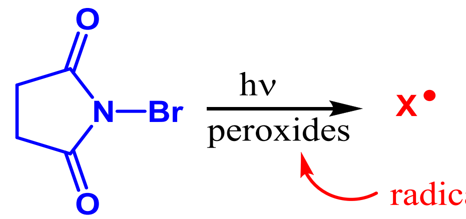
➩ BUT… there is a problem! Br_2 can react directly with C=C! (CHEM 241)



- electrophilic addition competes with radical halogenation
- since $[Br_2] >> [Br^\bullet]$, get more addition

Solution: use another source of Br•

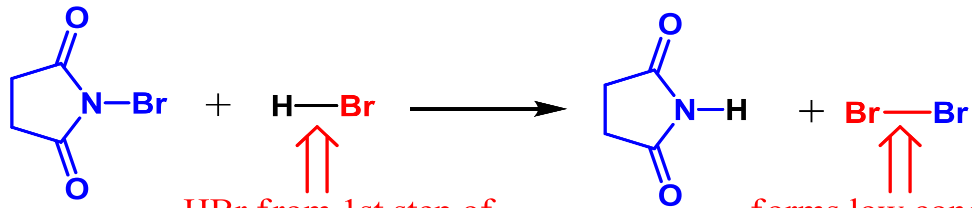
NBS = N-bromosuccinimide



$\Longrightarrow$ Initiation ($X^{\bullet}$ can be $Br^{\bullet}$ or $R_2N^{\bullet}$)

radical initiator... will see more later

- NBS can be used to make small amount of radicals, then acts as source of <u>small</u> <u>amount</u> of Br_2 during the reaction



HBr from 1st step of propagation

forms <u>low</u> <u>conc</u> of Br_2

→ just enough to react with radicals in second propagation step, but not enough to add to C=C

⇨ NBS does same reaction as Br_2, but avoids competing Electrophilic Addition