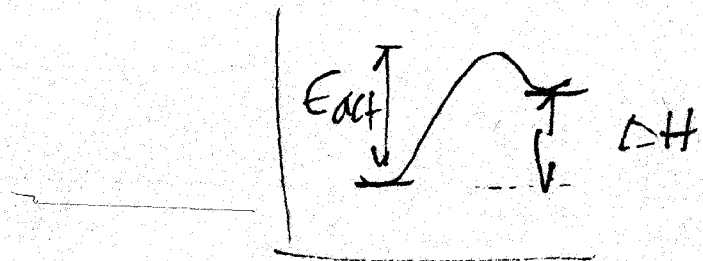


Discussing E_{act} - can't be predicted
can be measured

A few useful generalities.

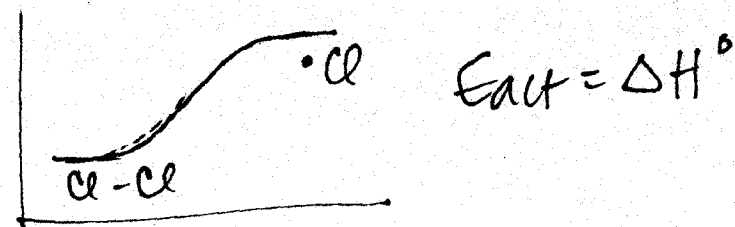
1. If bonds are broken, $E_{act} \geq 0$

2. endothermic rxn - both breaking + formation -
 $E_{act} > \Delta H^\circ$



3. Gas-phase - bonds are broken but no bonds are formed. $E_{act} = \Delta H^\circ$

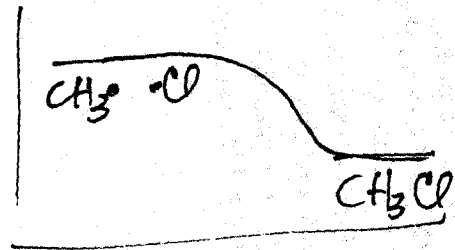
ex: chain initiation



4. Gas-phase - small radicals combine to form molecules (bonds formed but not broken)

$$E_{act} \approx 0$$

ex. chain termination

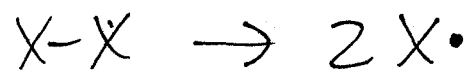


Alkanes + Halogens (F, Cl, Br, I)

methane + X_2 - wide variety of reactivities



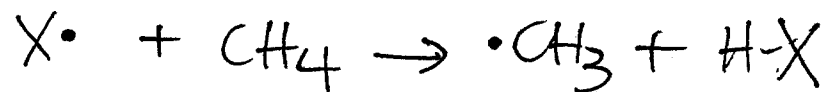
1. Look @ Initiation Steps



<u>Halogen</u>	<u>E_{act}</u>	<u>ΔH°</u>	<u>kJ/mol</u>
F_2	159	159	
Cl_2	243	243	
Br_2	193	193	
I_2	151	151	

These #s do not match the observed relative reactivities.

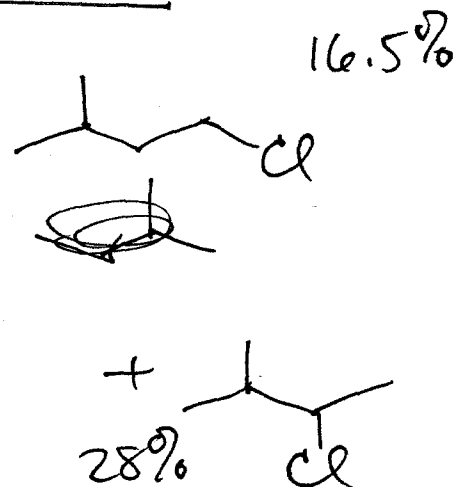
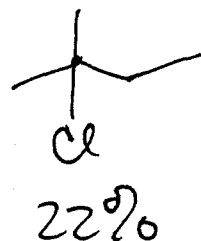
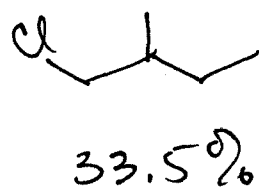
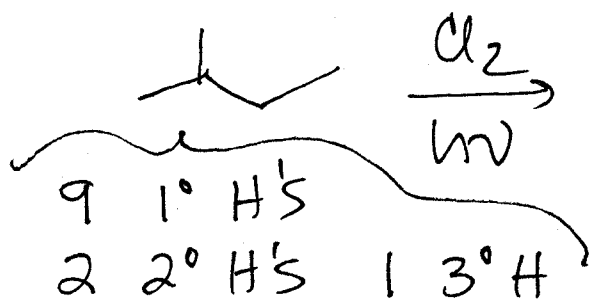
2. Look @ Propagation



<u>Halogen</u>	<u>Eact</u>	<u>ΔH°</u>	<u>Overall ΔH°</u>	<u>Reactivity</u>
F_2	+5	-130	-432	Explosive
Cl_2	+16	+8	-101	Controllable
Br_2	+78	+74	-26	slow
I_2	+140	+142	+53	nonreactive

This does predict the relative reactivities - seems to be the H abstraction that matters.

Halogenation of Higher Alkanes



The product distribution is not a statistical ratio of products - there is a bias towards forming 2° + 3° halides.

Calculate the bias:

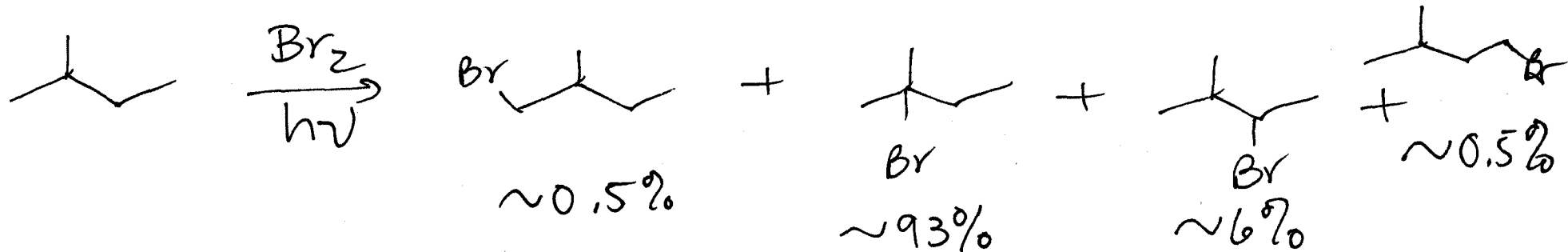
$$3^\circ/1^\circ : \frac{(22/1)}{(50/9)} = \frac{4}{1}$$

A 3° H is 4x as reactive as a 1° H.

$$2^\circ/1^\circ : \frac{(28/2)}{(50/9)} = \frac{2.5}{1}$$

A 2° H is 2.5x as reactive as a 1° H.

Not selective enough, unfortunately, to reliably get just one product.



This looks much more selective - calculate the bias.

$$\frac{3^\circ}{2^\circ} = \frac{[93/1]}{[6/2]} = \frac{93}{3} = \frac{31}{1}$$

$3^\circ H$ is 31x as reactive as $2^\circ H$.

$$\frac{3^\circ}{1^\circ} = \frac{[93/1]}{[1/9]} = \frac{837}{1}$$

$3^\circ H$ is at least 837x as reactive as $1^\circ H$

$$\frac{2^\circ}{1^\circ} = \frac{[6/2]}{[1/9]} = \frac{27}{1}$$

$2^\circ H$ is 27x as reactive as $1^\circ H$.

This is very selective.

Why the difference? Again, the Hammond-Leffler Postulate is the explanation.
exothermic: TS resembles reactants
endothermic: TS resembles products.

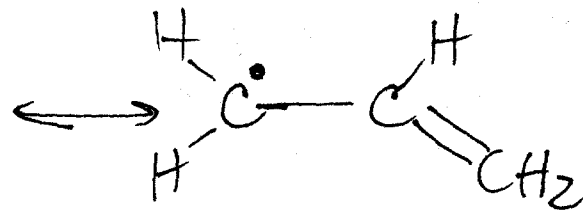
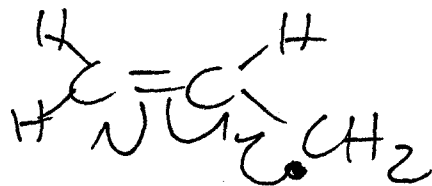
Chlorination is exothermic. \Rightarrow Type of radical doesn't matter.
Bromination is endothermic.

\Rightarrow radical that is being formed is important (think stabilities here)

other radicals:

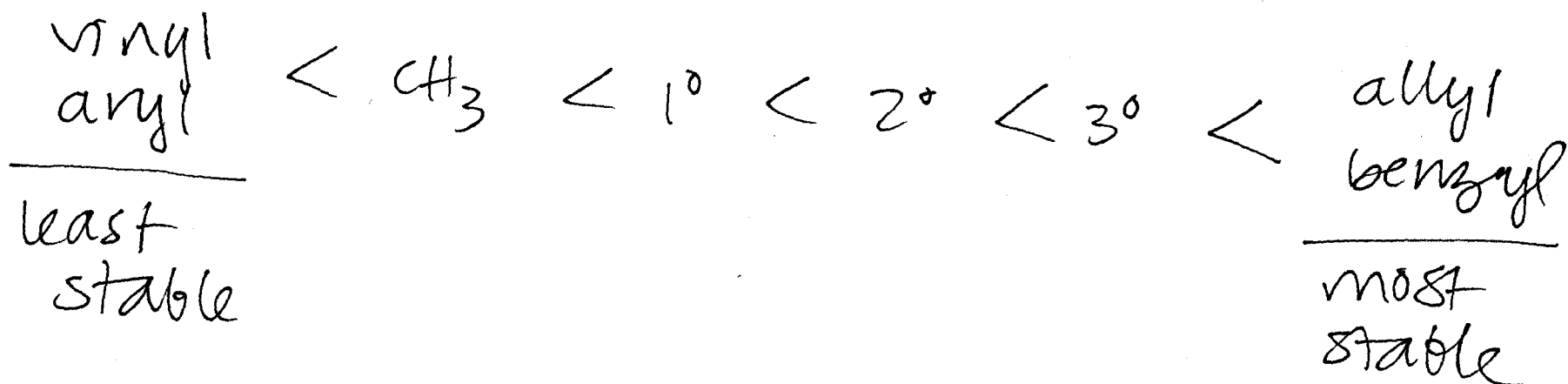
allylic

benzylic

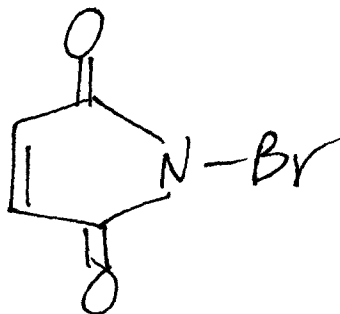
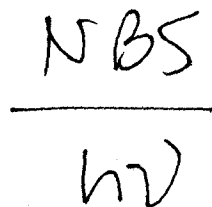
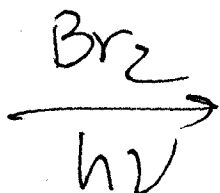


both are resonance-stabilized.

overall radical stabilities



Rxn conditions:



N-bromosuccinimide

source of
 $\cdot\text{Br}$