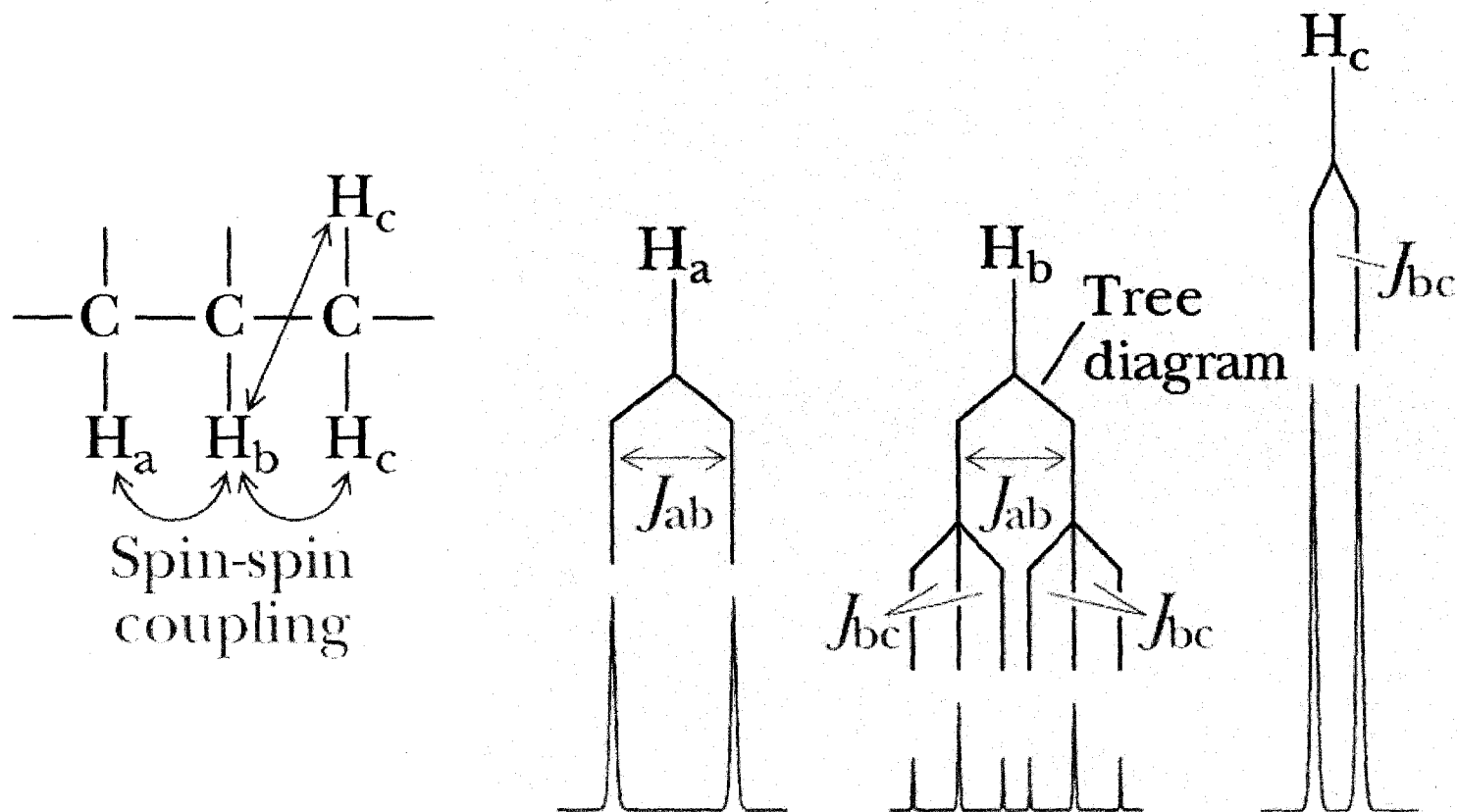


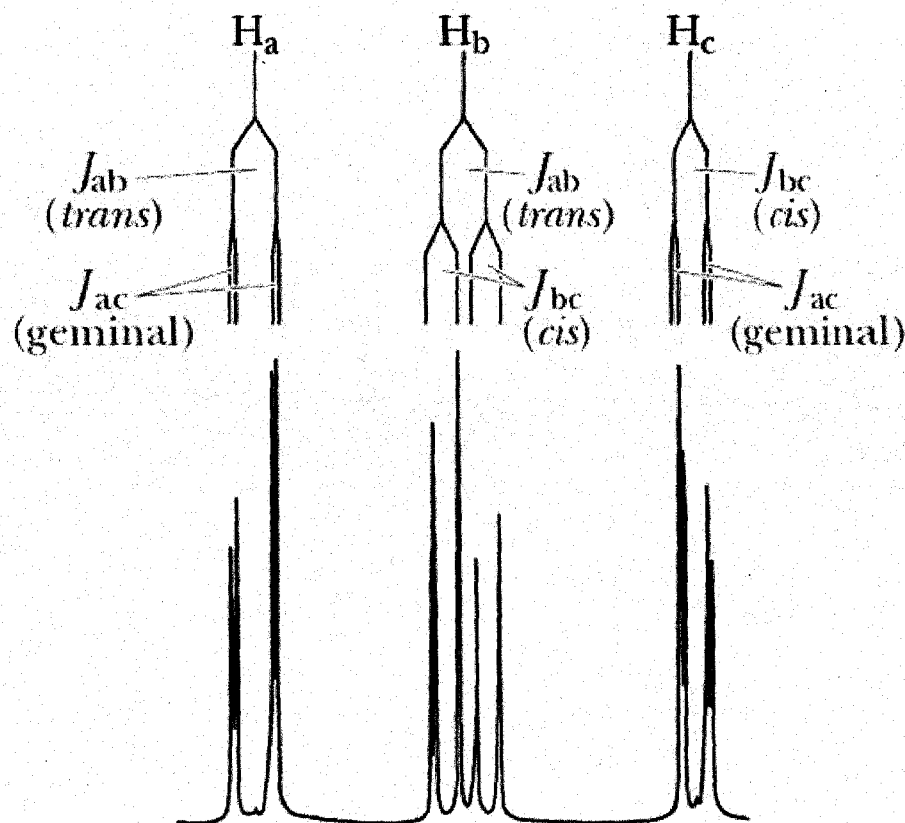
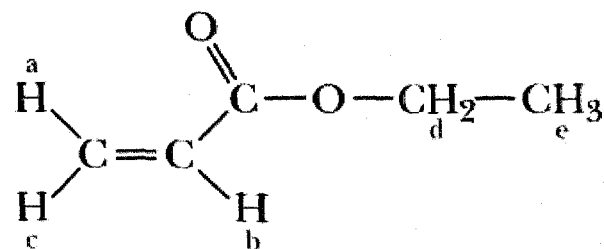
# More Complex Splitting Patterns

- if  $H_c$  is a set of two equivalent H, then the observed splitting is a doublet of triplets



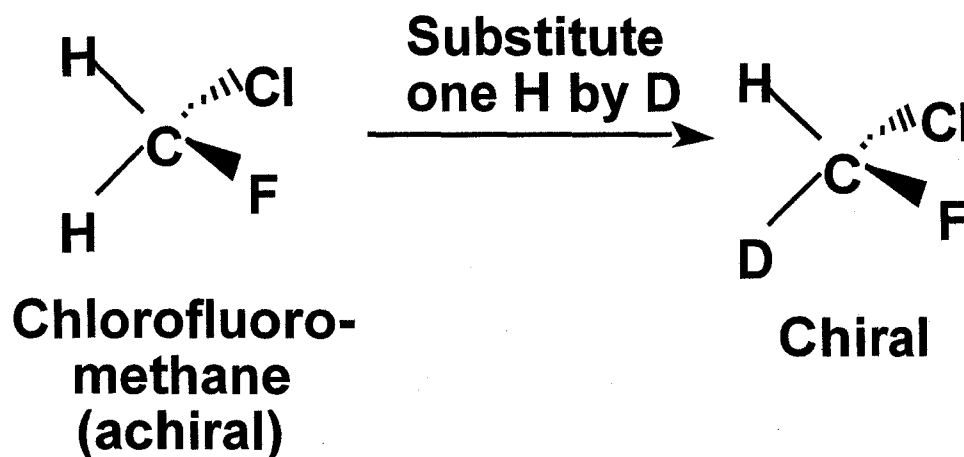
# More Complex Splitting Patterns

- a tree diagram for the complex coupling of the three vinylic hydrogens in ethyl propenoate



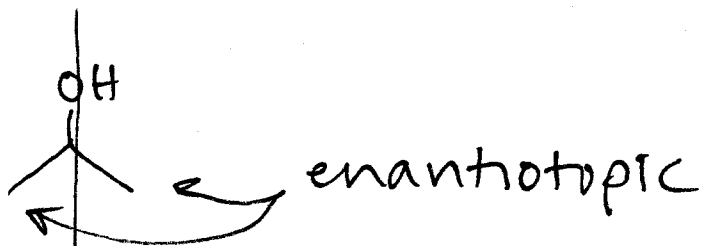
# Stereochemistry & Topicity

## ◆ Enantiotopic groups



Substitution produces a stereocenter; therefore, hydrogens are enantiotopic. Both hydrogens are prochiral; one is pro-R-chiral, the other is pro-S-chiral.

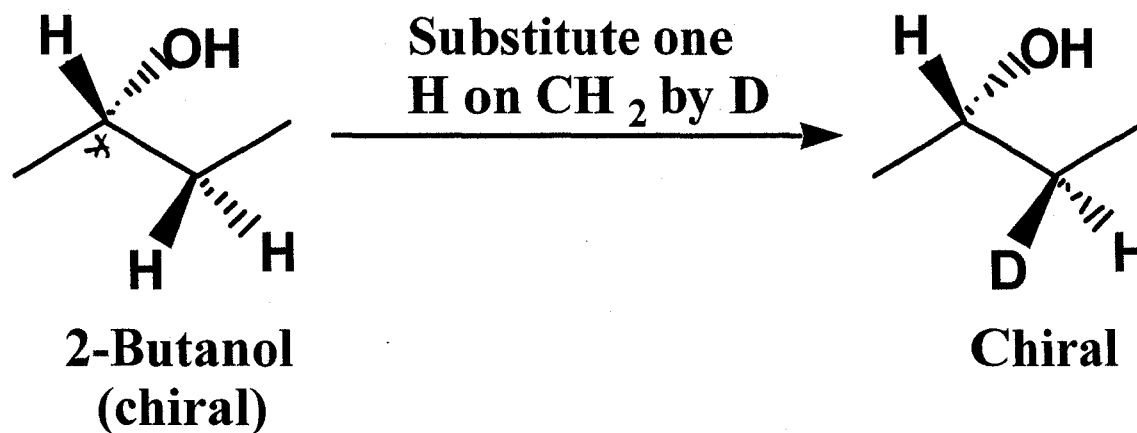
- enantiotopic atoms or groups have identical chemical shifts in achiral environments
- they have different chemical shifts in chiral environments



# Stereochemistry & Topicity

## ◆ Diastereotopic groups

- H atoms on C-3 of 2-butanol are diastereotopic
- substitution by deuterium creates a chiral center
- because there is already a chiral center in the molecule, diastereomers are now possible

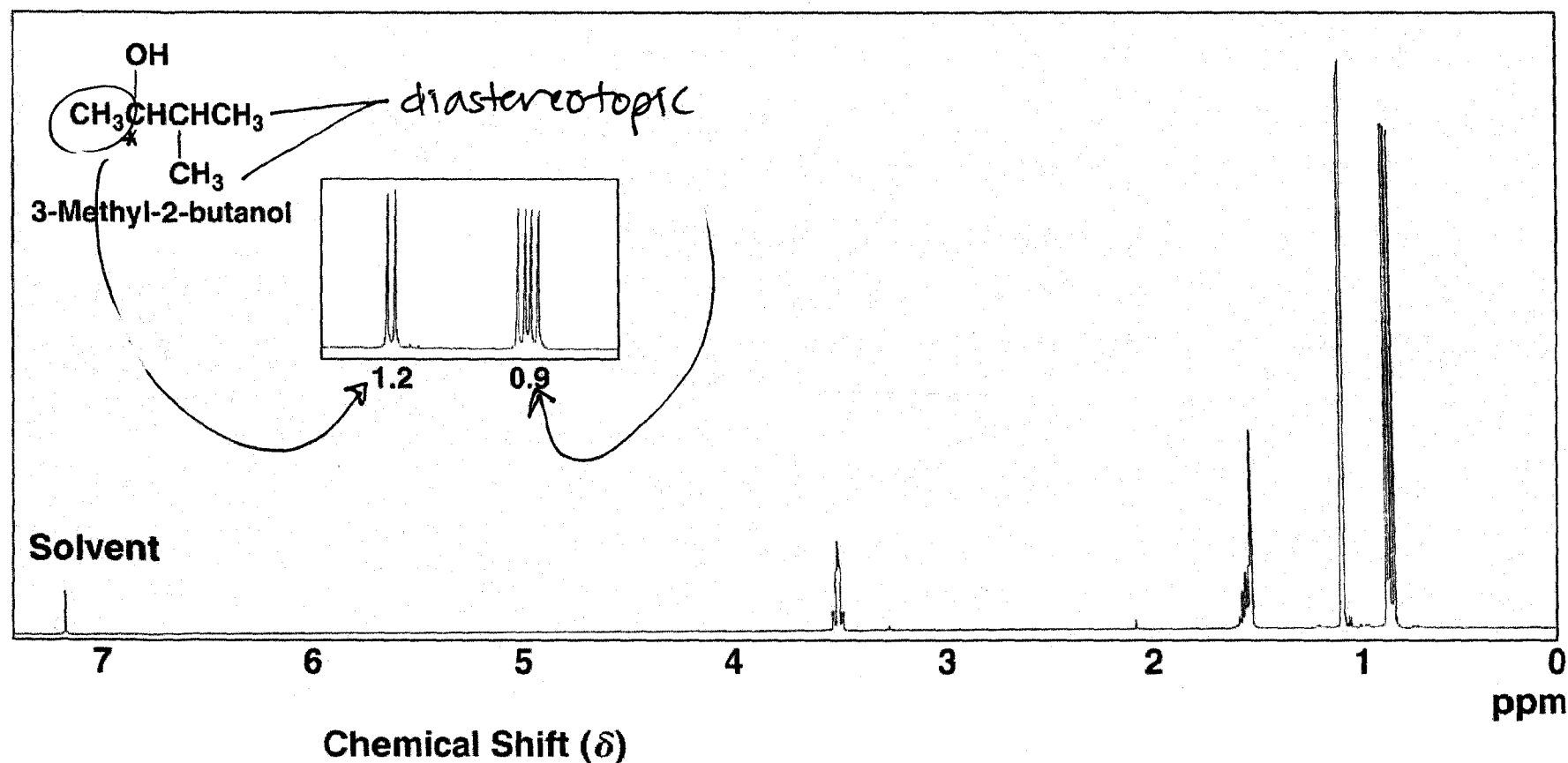


- diastereotopic hydrogens have different chemical shifts under all conditions

# Stereochemistry and Topicity

## ◆ $^1\text{H}$ -NMR spectrum of 3-methyl-2-butanol

- the methyl groups on carbon 3 are diastereotopic and appear as two doublets



## Ch. 10- Free Radicals

- a reactive intermediate w/ an unpaired  $e^-$
- formed by homolytic bond cleavage - (not heterolytic)

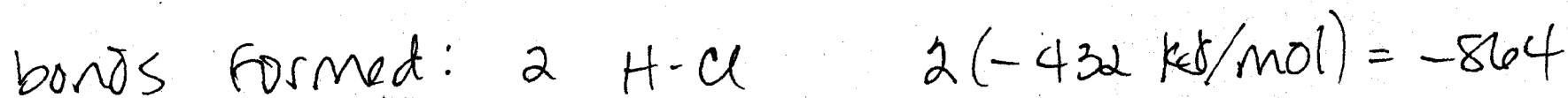
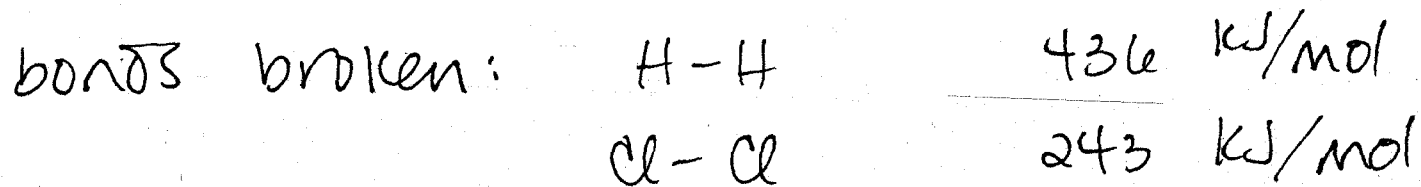
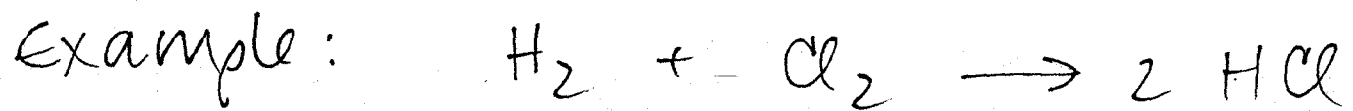
$DH^\circ$  - amt of energy required to break a bond  
homolytically - table 10.1 p. 430

numbers are all  $\oplus$  - require energy  
(endothermic)

if you are going to make a bond - it's  
the same number, just change the sign.

generally  $\ominus$  - energy is ~~required~~  
(exothermic) produced

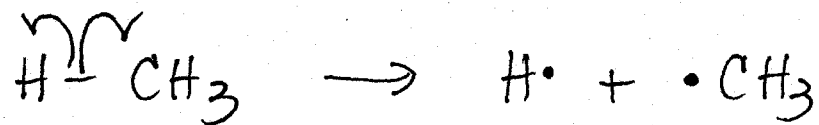
can use these  $DH^\circ$  values to calculate  $\Delta H^\circ$   
for the rxn.



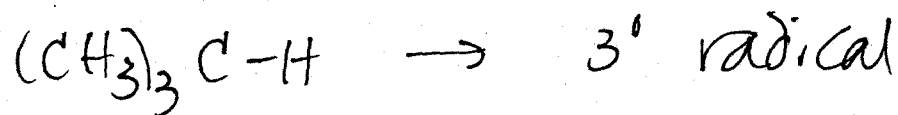
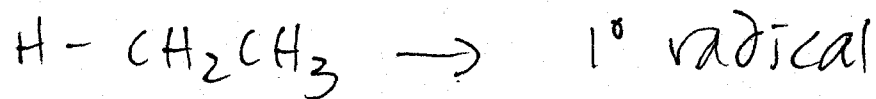
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$$\Delta H^\circ = -185 \text{ kJ/mol}$$

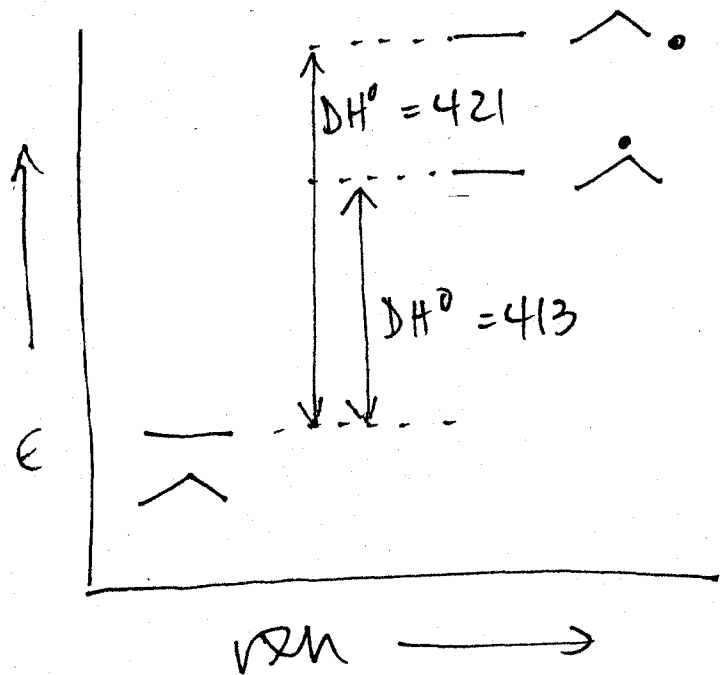
These #s can help us predict relative stabilities of carbon-based free radicals.



$$\Delta H^\circ = 440 \text{ kJ/mol}$$



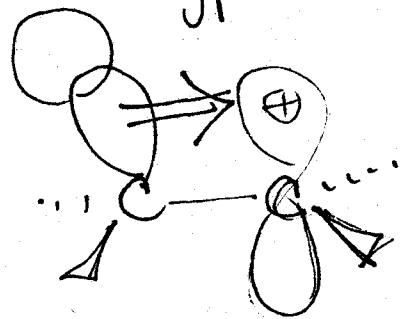
most stable



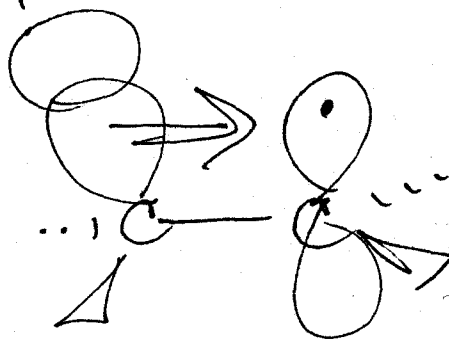
the lower the amount of energy required to break the bond, the more stable the radical (relatively speaking)

The order of stability for radicals is the same as for cations — rationale is the same

- stabilized by alkyl substitution
- hyperconjugation!



cation

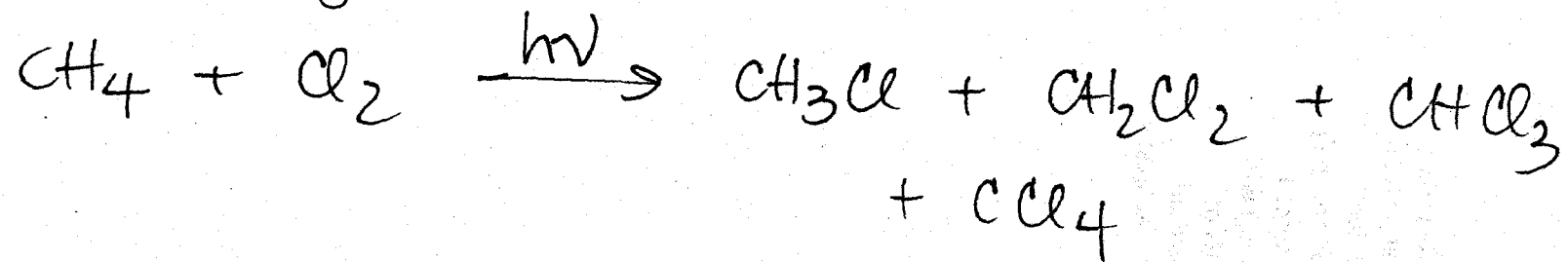


radical

radicals are planar  
 $sp^2$   
 (get racemic products)



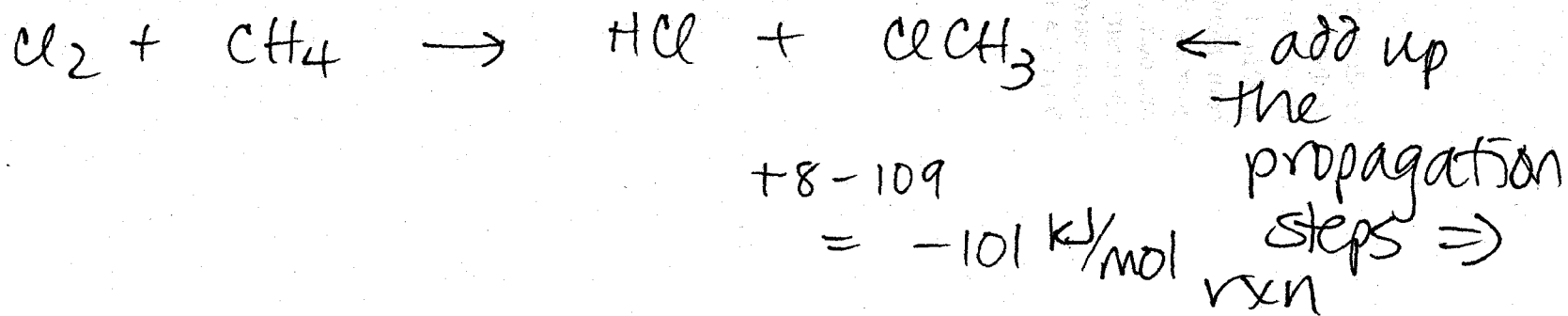
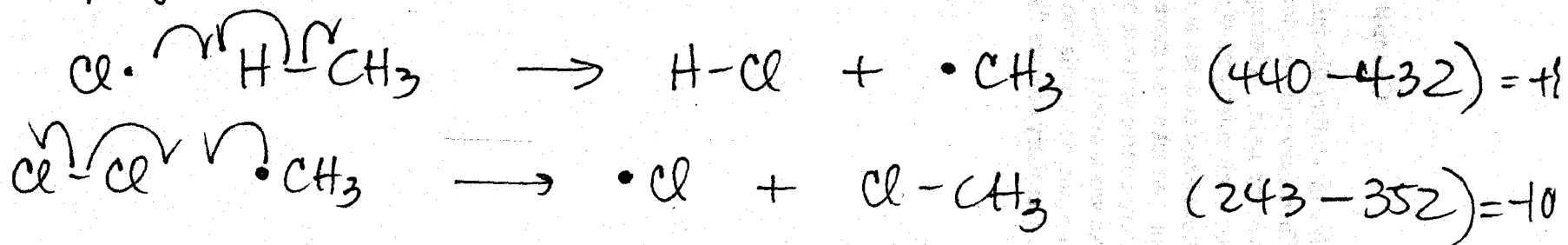
# Radical Halogenation of Alkanes



1. Initiation - radicals are formed as products from non-radical reactants.



2. Propagation - radicals on both sides.



3. Termination - radicals as reactants but not products - lots of possibilities

