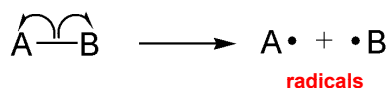


## Reactions of Alkanes: Radical Halogenations

Sections 5.3, 5.8, 5.9, 10.3 in McMurry; Chapter 3 in Vollhardt

homolytic cleavage or bond homolysis:

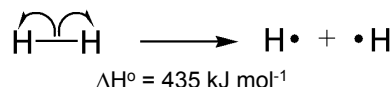


heterolytic cleavage:



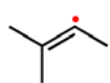
Fish-hook (or single-headed) arrows indicate single-electron transfer; double-headed arrows are for electron-pair transfer.

bond-dissociation energy or bond strength:

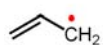


**Relative stability radicals :**

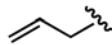
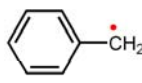
vinyl < methyl < primary < secondary < tertiary < allylic < benzylic



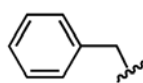
vinyl radical



Allylic and benzylic radicals

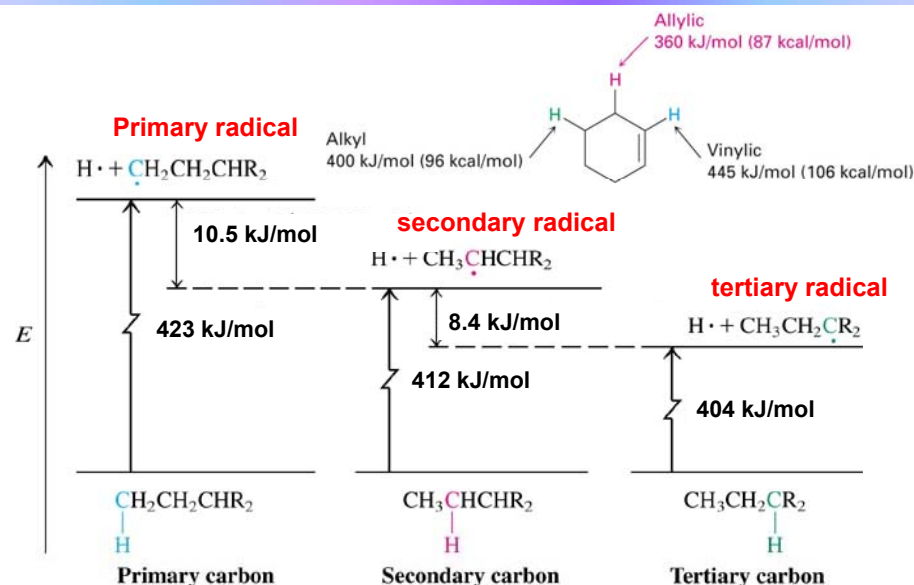


Allyl and benzyl groups



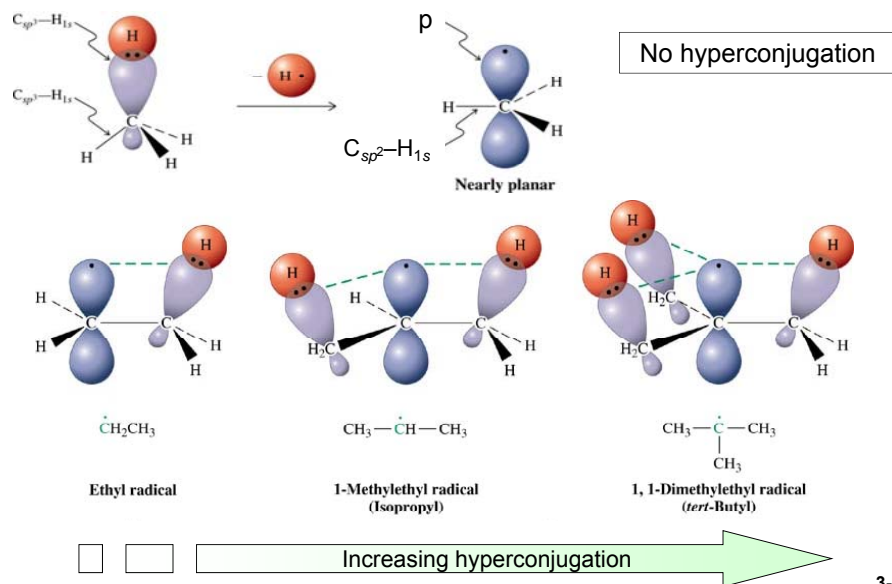
3-1

## Classification and Stability of Radicals



3-2

## Structures of Alkyl Radicals and Hyperconjugation



3-3

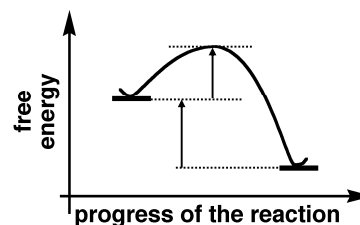
## Energy Diagram of a Reaction

By tracking the energy changes along each step of a reaction pathway, it is possible to determine:

- how much
- how fast

product is formed. A reaction coordinate diagram describes the energy changes that take place in each step of the mechanism.

This diagram represents one step in a reaction mechanism

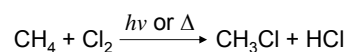


Indicate:

- Reactants
- Transition state
- Products
- $\Delta G^\circ$  free energy change
- $\Delta G^\ddagger$  free energy of activation

3-4

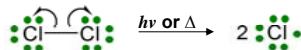
## Chlorination of Methane: the Radical Chain Mechanism



During the reaction, the first product formed is  $\text{CH}_3\text{Cl}$  (and  $\text{HCl}$ ). If sufficient chlorine is present, further substitution may occur, forming  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and finally  $\text{CCl}_4$ .

A mechanism is a detailed, step-by-step description of all of the changes in bonding that occur in a reaction.

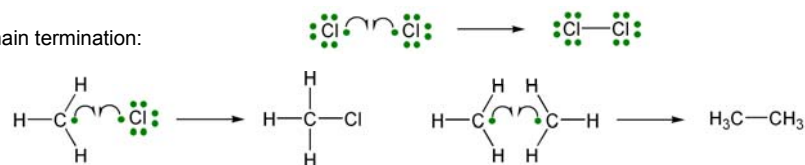
Initiation:



Propagation:

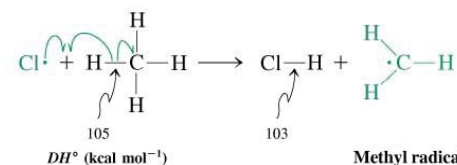
These two reactions happen repeatedly:  
chain reaction

Chain termination:

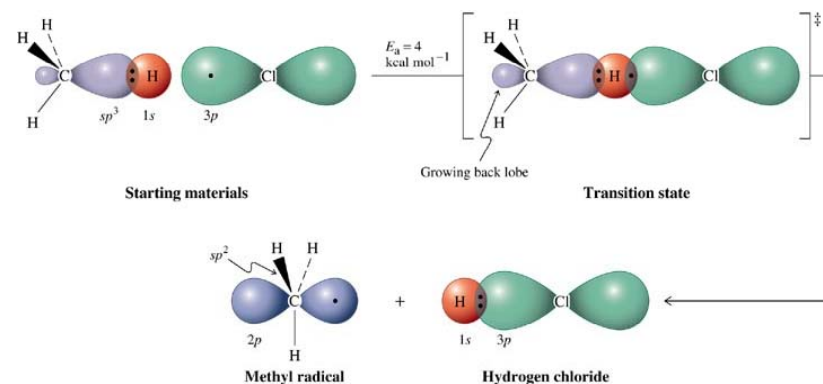


3-5

## Propagation Step 1: Potential Energy Diagram

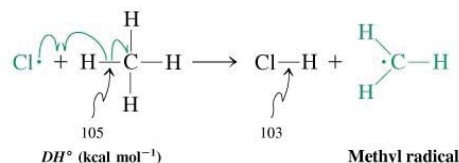


$$\begin{aligned} \Delta H^\circ &= DH^\circ(\text{CH}_3-\text{H}) \\ &\quad - DH^\circ(\text{H}-\text{Cl}) \\ &= + 8 \text{ kJ mol}^{-1} \end{aligned}$$

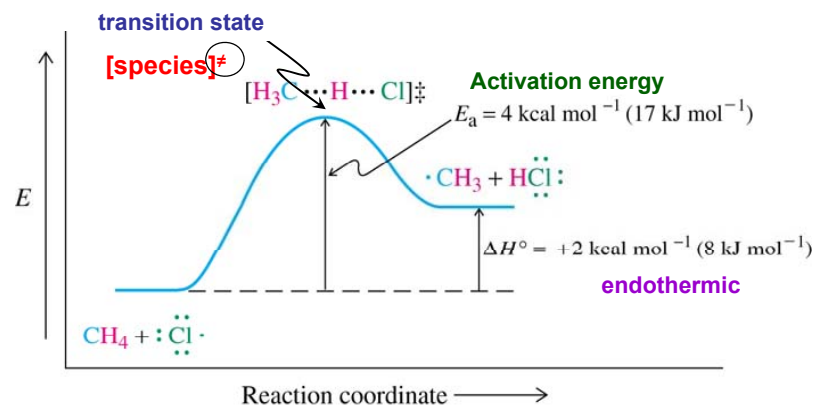


3-6

## Propagation Step 1: Potential Energy Diagram

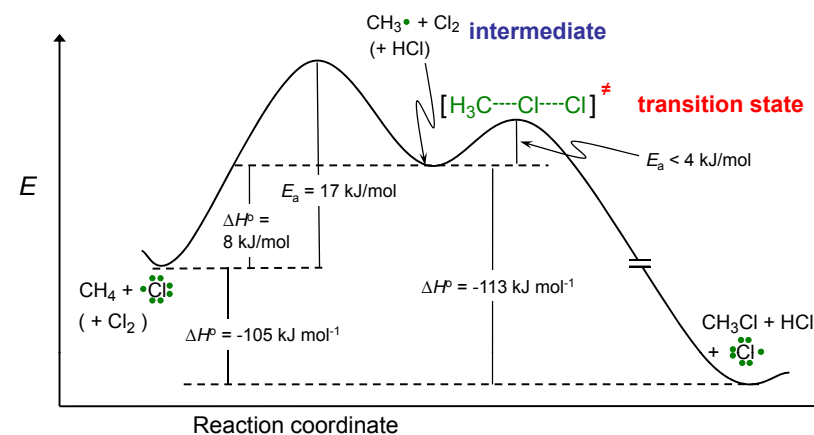
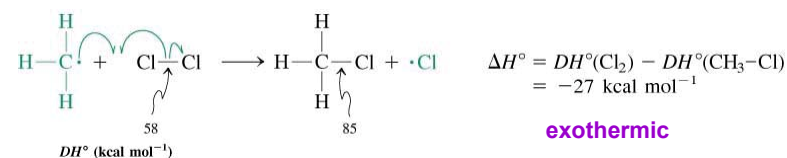


$$\begin{aligned} \Delta H^\circ &= DH^\circ(\text{CH}_3-\text{H}) \\ &\quad - DH^\circ(\text{H}-\text{Cl}) \\ &= + 8 \text{ kJ mol}^{-1} \end{aligned}$$



3-7

## Propagation Step 2



3-8

## Energetics of Methane Halogenations

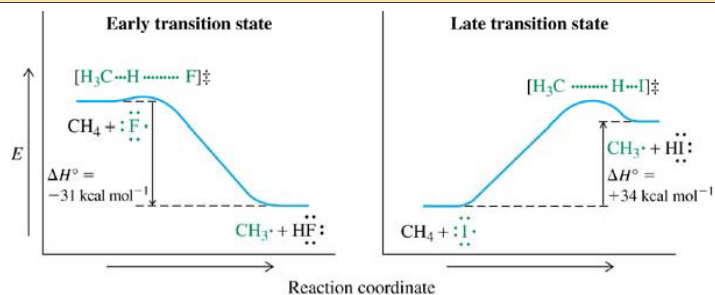


slightly  
unfavorable

very favorable;  
"drives" the overall equilibrium

**TABLE 3-5** Enthalpies of the Propagation Steps in the Halogenation of Methane [kcal mol<sup>-1</sup> (kJ mol<sup>-1</sup>)]

Reaction	F	Cl	Br	I
$\text{X}\cdot + \text{CH}_4 \longrightarrow \cdot\text{CH}_3 + \text{HX}$	-31 (-130)	+2 (+8)	+18 (+75)	+34 (+142)
$\cdot\text{CH}_3 + \text{X}_2 \longrightarrow \text{CH}_3\text{X} + \text{X}\cdot$	-72 (-301)	-27 (-113)	-24 (-100)	-21 (-88)
$\text{CH}_4 + \text{X}_2 \longrightarrow \text{CH}_3\text{X} + \text{HX}$	-103 (-431)	-25 (-105)	-6 (-25)	+13 (+54)

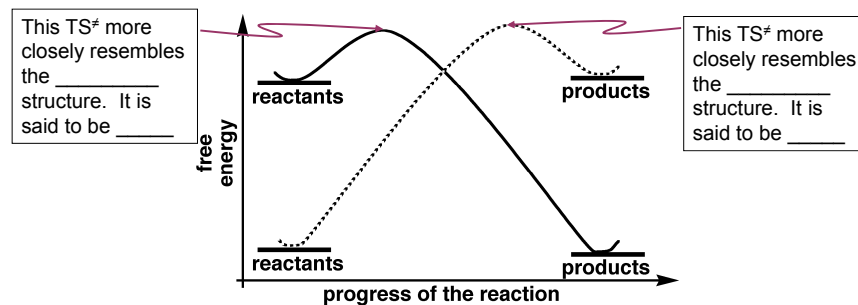


3-9

## On the Energy of the TS<sup>‡</sup>

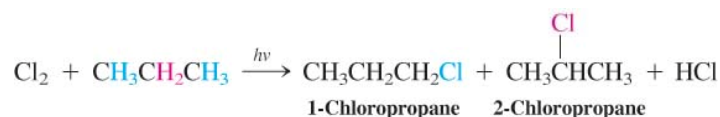
In the TS<sup>‡</sup>, bonds are being made and bonds are being broken. How far along is bond forming and bond breaking at the time the TS<sup>‡</sup> is crossed?

**The Hammond Postulate** - The structure of the TS<sup>‡</sup> will more closely resemble the species it is more similar to in energy.



3-10

## Chlorination of Propane: Relative Reactivity



Statistical ratio:

3 : 1

Experimental ratio (25 °C):

43 : 57

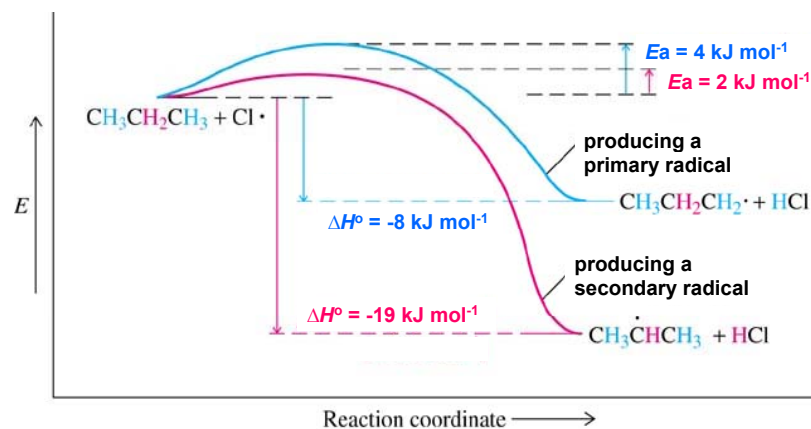
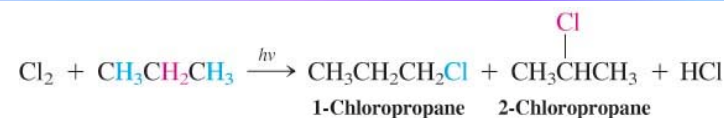
Relative reactivity:

$$\frac{2^\circ \text{H}}{1^\circ \text{H}} = \frac{\text{product \% from } 2^\circ \text{H abstraction} / \text{number of } 2^\circ \text{Hs}}{\text{product \% from } 1^\circ \text{H abstraction} / \text{number of } 1^\circ \text{Hs}}$$

= \_\_\_\_\_ ≈ ?

3-11

## Chlorination of Propane: Relative Reactivity



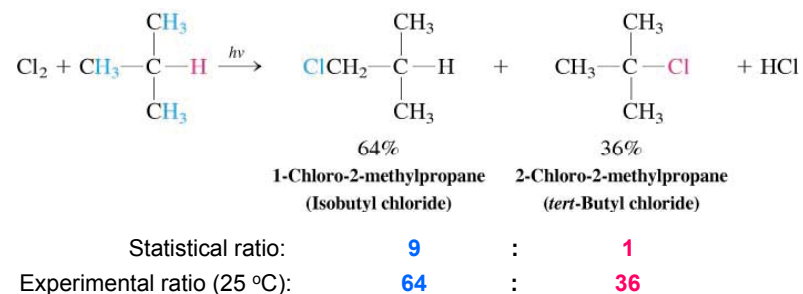
The more stable the product, the lower the activation energy.

3-12

## Relative Reactivity Calculation

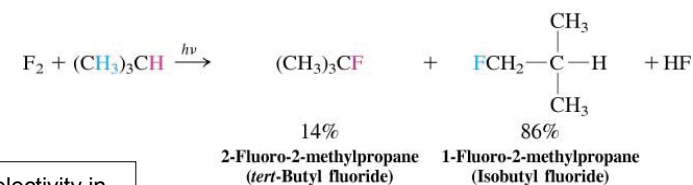
Relative reactivity:  $\frac{3^\circ \text{H}}{1^\circ \text{H}} = \frac{\text{product \% from } 3^\circ \text{H abstraction} / \text{number of } 3^\circ \text{Hs}}{\text{product \% from } 1^\circ \text{H abstraction} / \text{number of } 1^\circ \text{Hs}}$

= ——— ≈ ?



3-13

## Selectivity in Radical Halogenation

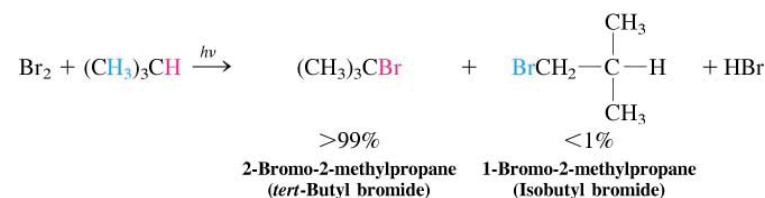


Very **low** selectivity in the fluorination reaction

Calculate the relative selectivity by yourself.

Very **high** selectivity in the bromination reaction

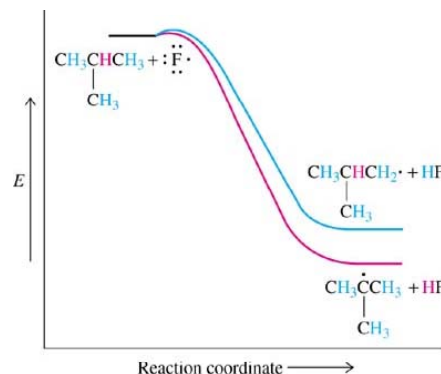
### Bromination of 2-Methylpropane



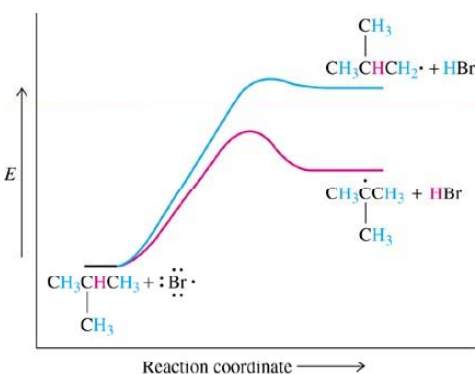
3-14

## Selectivity in Radical Halogenation

Very **low** selectivity in the fluoronation reaction



Very **high** selectivity in the bromination reaction

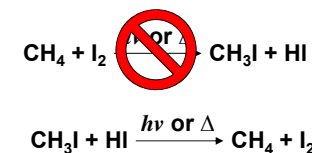


3-15

## Relative Reactivity of Various Carbon Centers in Halogenations

TABLE 3-6 Relative Reactivities of the Four Types of Alkane C-H Bonds in Halogenations			
C-H bond	F• (25 °C, gas)	Cl• (25 °C, gas)	Br• (150 °C, gas)
CH <sub>3</sub> -H	0.5	0.004	0.002
RCH <sub>2</sub> -H <sup>a</sup>	1	1	1
R <sub>2</sub> CH-H	1.2	4	80
R <sub>3</sub> C-H	1.4	5	1700

<sup>a</sup>For each halogen, reactivities with four types of alkane C-H bonds are normalized to the reactivity of the primary C-H bond.



3-16