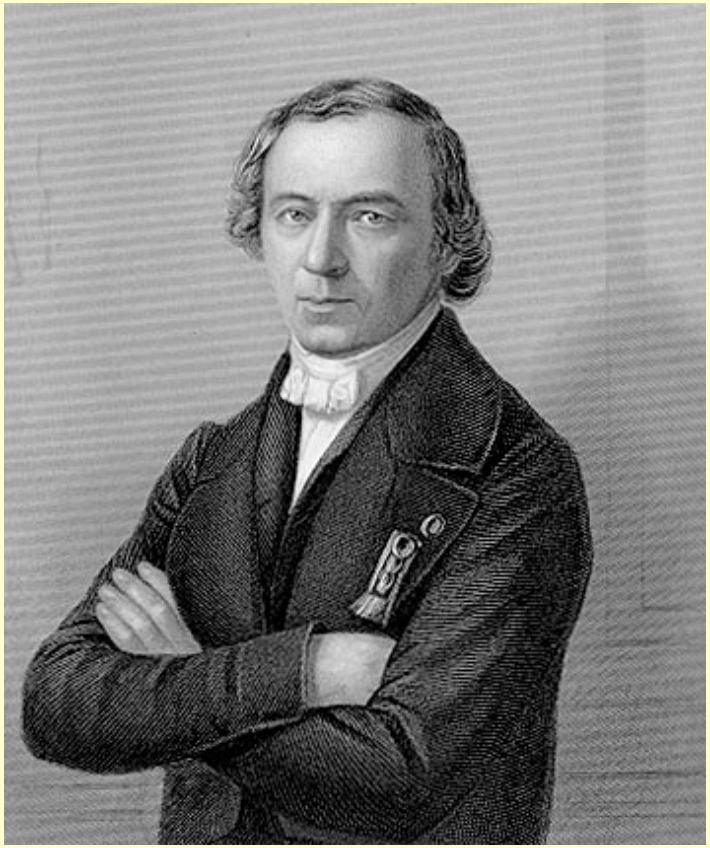
Radical Chain Reactions

Substitution Theory



J. B. Dumas
(1800 -1884)

1838 - chlorination of acetic acid

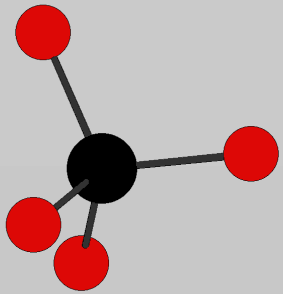
$$\underline{C}_4H_4O_2 + Cl_6 = \underline{C}_4HCl_3O_2 + H_3Cl_3$$

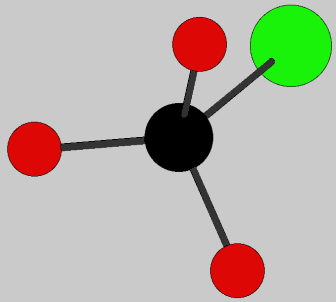
$\underline{C}$ = 6, O = 16

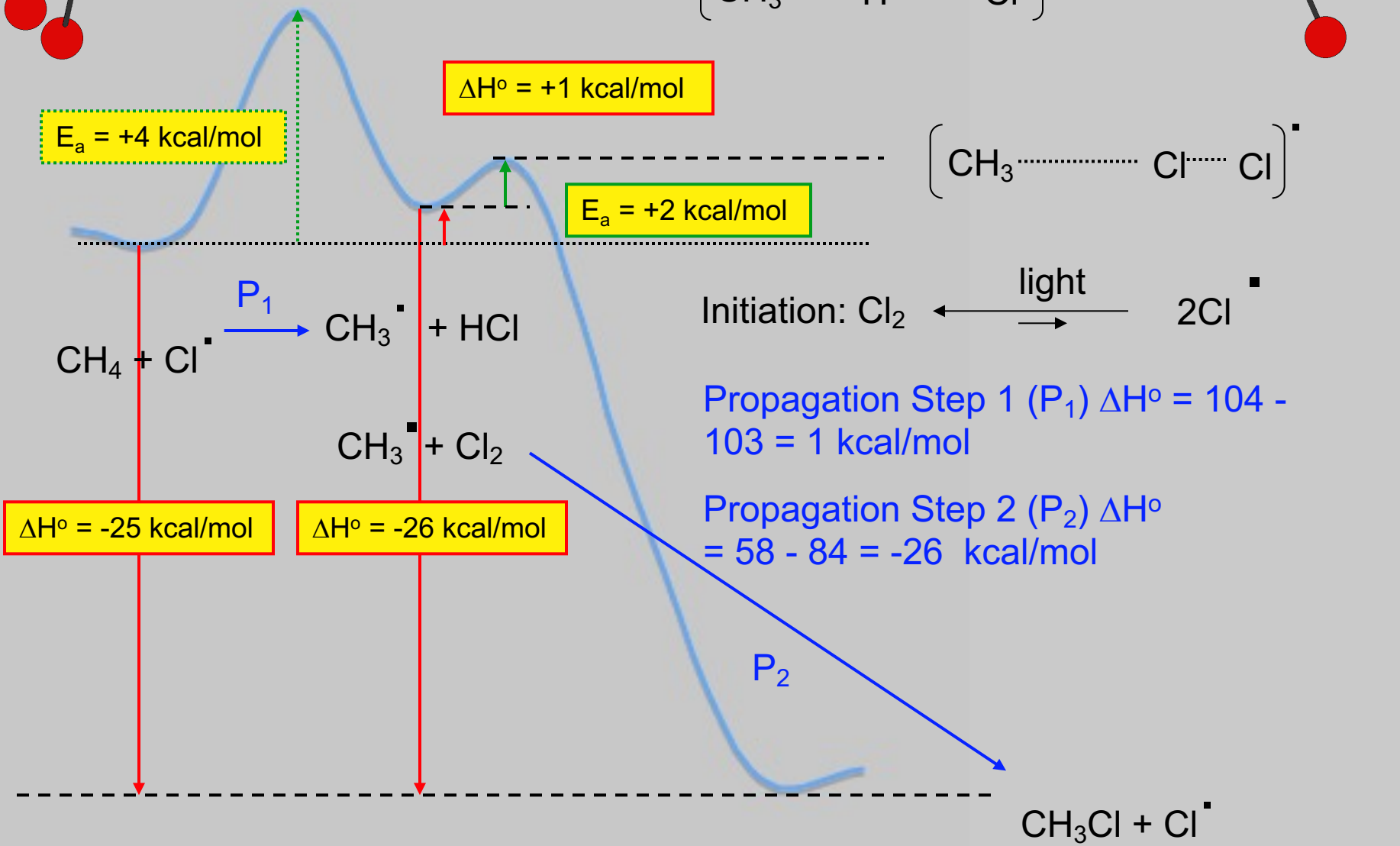
$$C_2H_4O_2 + 3Cl_2 = C_2HCl_3O_2 + 3HCl$$

Free Radical Chain Reaction of Methane with Chlorine

$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$







Initiation: $Cl_2 \xleftrightarrow{\text{light}} 2Cl^{\cdot}$

Propagation Step 1 (P_1) ΔH^o = 104 - 103 = 1 kcal/mol

Propagation Step 2 (P_2) ΔH^o = 58 - 84 = -26 kcal/mol

Free Radical Chain Reaction of Methane with Chlorine: An Alternative Mechanism?

$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$

+104 kcal/mol -103 kcal/mol

$CH_4 + Cl^{\cdot} \rightarrow CH_3^{\cdot} + HCl$

+58 kcal/mol -84 kcal/mol

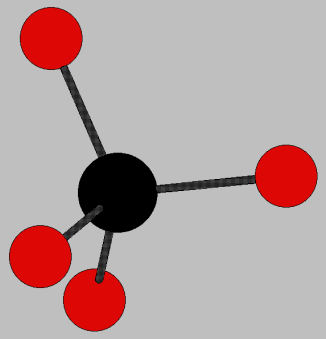
$CH_3^{\cdot} + Cl_2 \rightarrow CH_3Cl + Cl^{\cdot}$

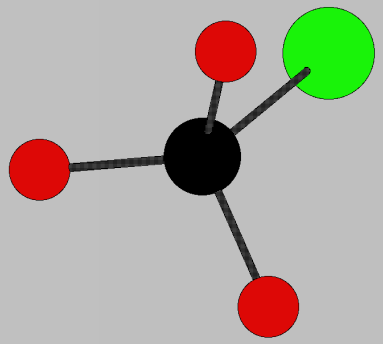
+104 kcal/mol -84 kcal/mol

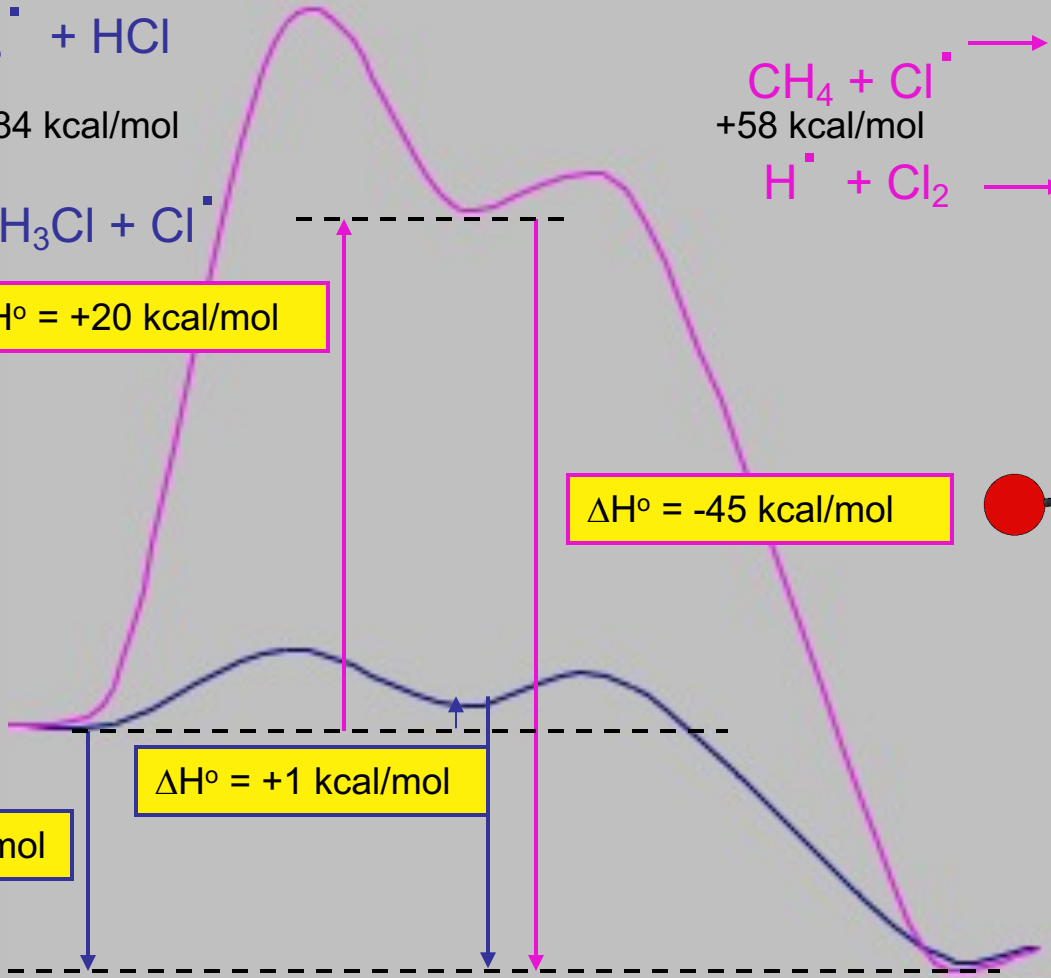
$CH_4 + Cl^{\cdot} \rightarrow H^{\cdot} + CH_3Cl$

+58 kcal/mol -103 kcal/mol

$H^{\cdot} + Cl_2 \rightarrow HCl + H^{\cdot}$

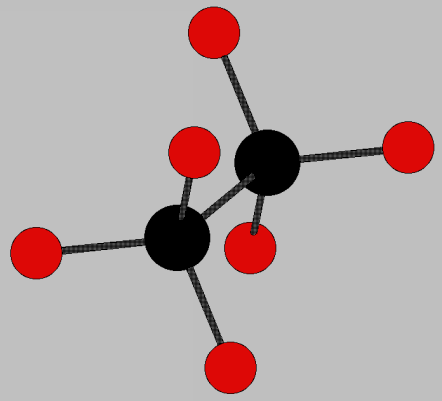


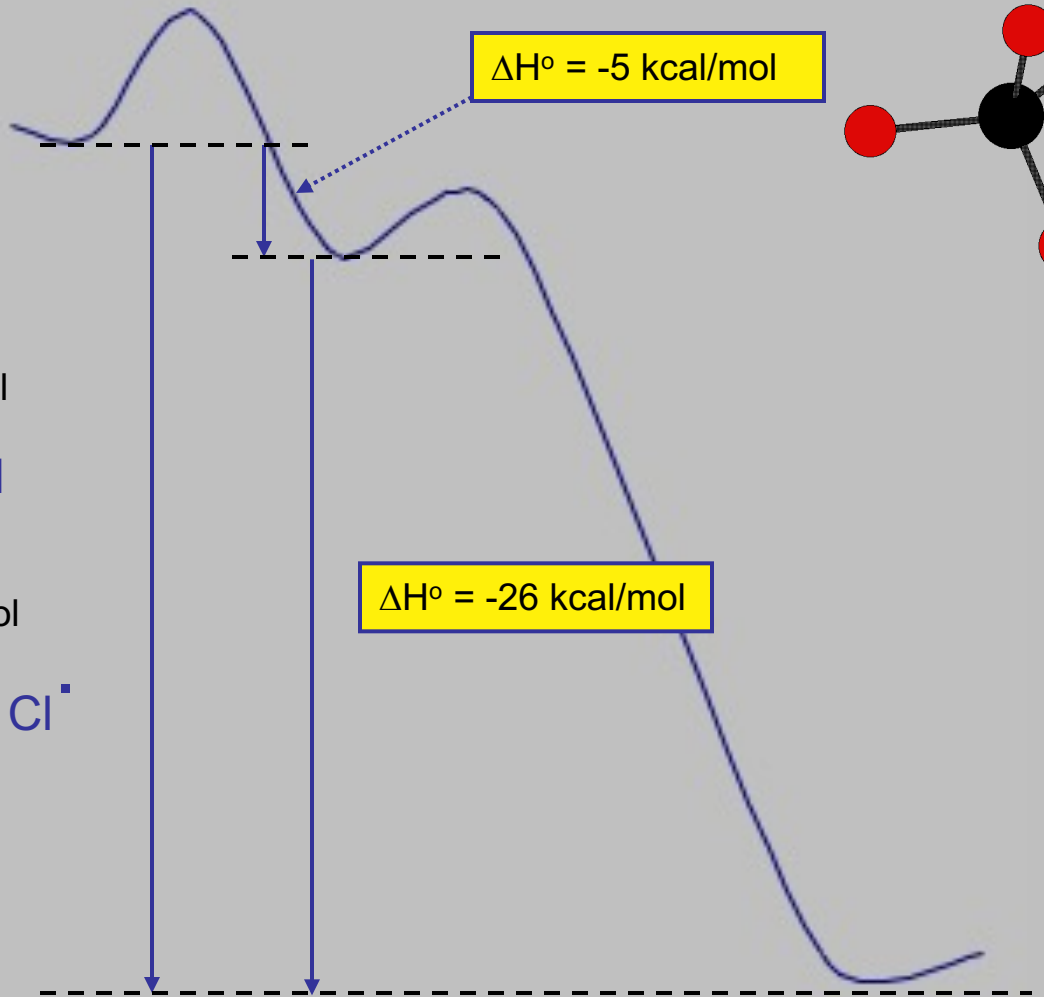




Free Radical Chain Reaction of Ethane with Chlorine

$$C_2H_6 + Cl_2 \longrightarrow C_2H_5Cl + HCl$$





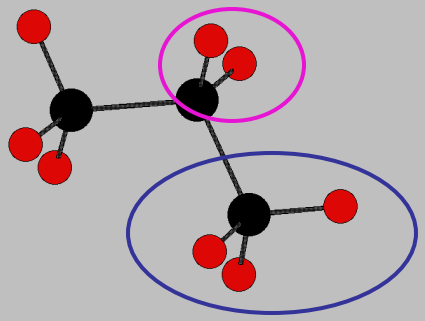
+98 kcal/mol -103 kcal/mol

$$C_2H_6 + Cl^{\cdot} \longrightarrow C_2H_5^{\cdot} + HCl$$

+58 kcal/mol -81 kcal/mol

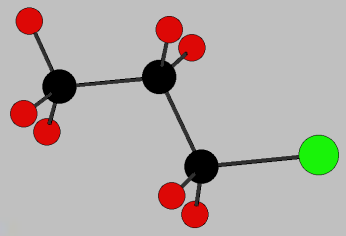
$$C_2H_5^{\cdot} + Cl_2 \longrightarrow C_2H_5Cl + Cl^{\cdot}$$

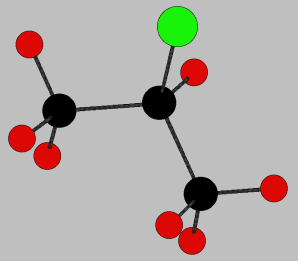
Free Radical Chain Reaction of Propane with Chlorine
Reactivity of 1° vs. 2° C-H Bonds



$C_3H_8 + Cl_2 \longrightarrow C_3H_7Cl + HCl$

ΔH^o = -5 kcal/mol





ΔE_{act} = ~ 1 kcal/mol

1-Chloropropane 40%

2-Chloropropane 60%

ΔH^o = -8 kcal/mol

Propagation Step 2

+58 kcal/mol

$1\text{-}C_3H_7^{\bullet} + Cl_2 \longrightarrow 1\text{-}C_3H_7Cl + Cl^{\bullet}$ -81 kcal/mol

+58 kcal/mol

$2\text{-}C_3H_7^{\bullet} + Cl_2 \longrightarrow 2\text{-}C_3H_7Cl + Cl^{\bullet}$ -80 kcal/mol

ΔH^o = -22 kcal/mol

Propagation Step 1

+98 kcal/mol

$C_3H_8 + Cl^{\bullet} \longrightarrow 1\text{-}C_3H_7^{\bullet} + HCl$ -103 kcal/mol

ΔH^o = -23 kcal/mol

+95 kcal/mol

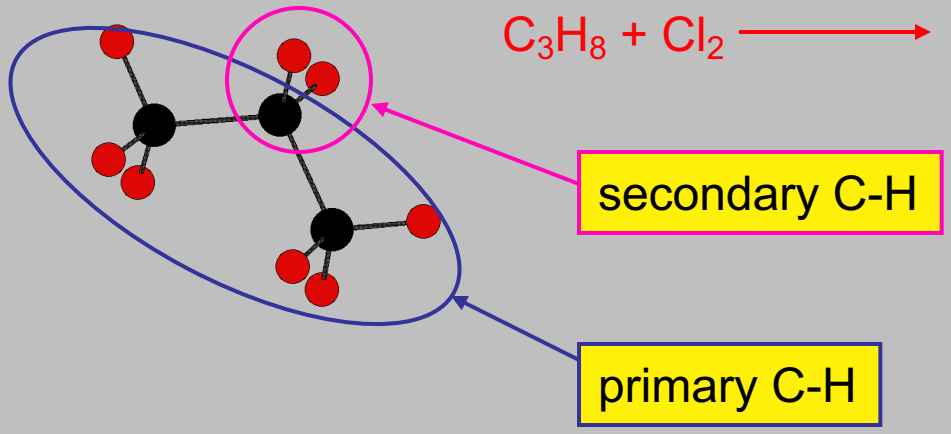
$C_3H_8 + Cl^{\bullet} \longrightarrow 2\text{-}C_3H_7^{\bullet} + HCl$ -103 kcal/mol

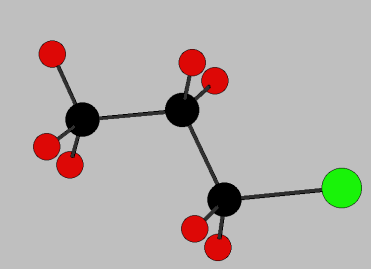
ΔH^o = -28 kcal/mol

ΔH^o = -30 kcal/mol

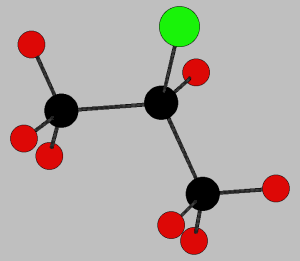
Free Radical Chain Reaction of Propane with Chlorine
Reactivity of 1° vs. 2° C-H Bonds

$C_3H_8 + Cl_2 \longrightarrow C_3H_7Cl + HCl$





1-Chloropropane 40%



2-Chloropropane 60%

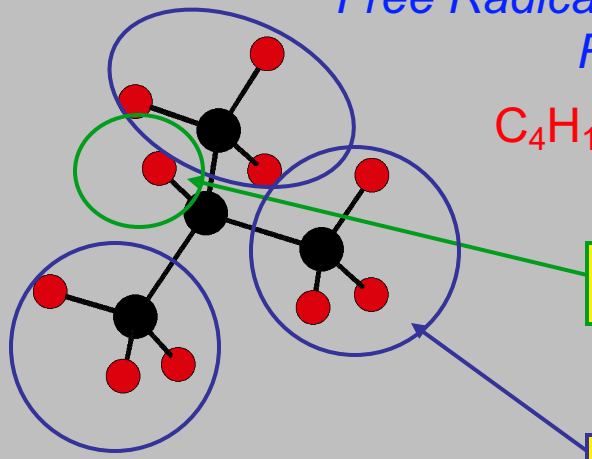
Primary C-H bonds are less reactive (BDE = 98 kcal/mol) than secondary C-H bonds (BDE = 95 kcal/mol), but

there are more primary C-H bonds than secondary C-H bonds.

Type C-H	#	Yield (%)	%/#	Relative Reactivity
1°	6	40	6.67	**1**
2°	2	60	30	**4.5**

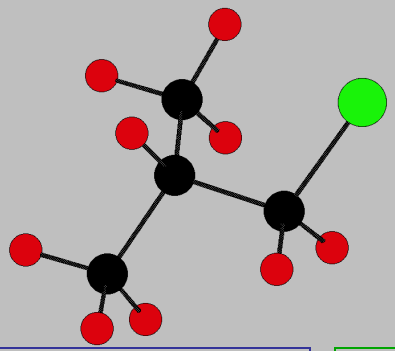
Free Radical Chain Reaction of Isobutane with Chlorine
Reactivity of 1° vs. 3° C-H Bonds

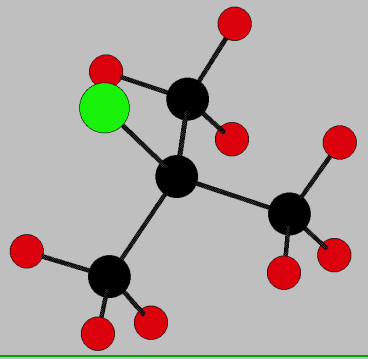
$C_4H_{10} + Cl_2 \longrightarrow C_4H_9Cl + HCl$



tertiary C-H

primary C-H





1-Chloro-2-methylpropane 62%

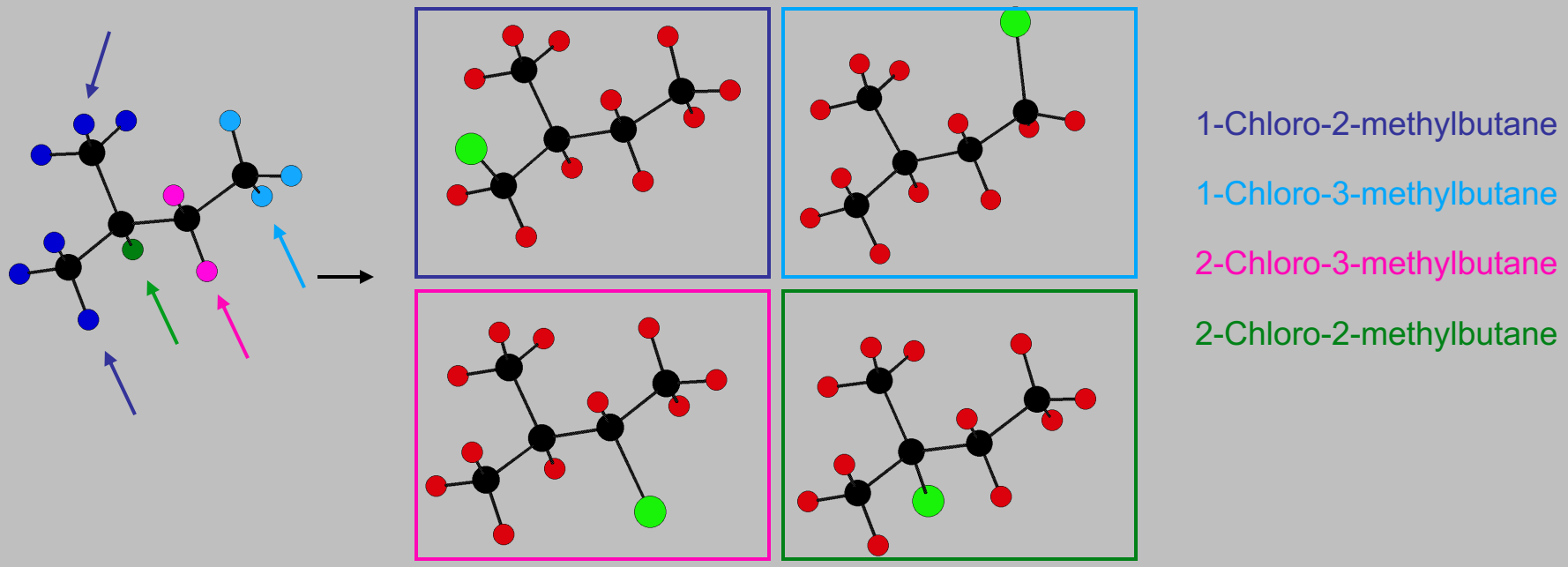
2-Chloro-2-methylpropane 38%

Primary C-H bonds have the numbers but not the reactivity!
(Tertiary C-H bond: 91 kcal/mol)

Type C-H	#	Yield (%)	%/#	Relative Reactivity
1°	9	62	6.88	**1**
3°	1	38	38	**5.5**

Free Radical Chain Reaction of 2-Methylbutane with Chlorine
Predicting Product Ratios

$C_5H_{12} + Cl_2 \longrightarrow C_5H_{11}Cl + HCl$



1-Chloro-2-methylbutane

1-Chloro-3-methylbutane

2-Chloro-3-methylbutane

2-Chloro-2-methylbutane

Type	#	Relative Reactivity	# x R.R.	fraction	%
Primary 1	6	1	6	6/23.5	25.5
Primary 2	3	1	3	3/23.5	12.8
Secondary	2	4.5	9	9/23.5	38.3
Tertiary	1	5.5	5.5	5.5/23.5	23.4

Why do radical halogenations stop at the monochloro compound?

They don't!

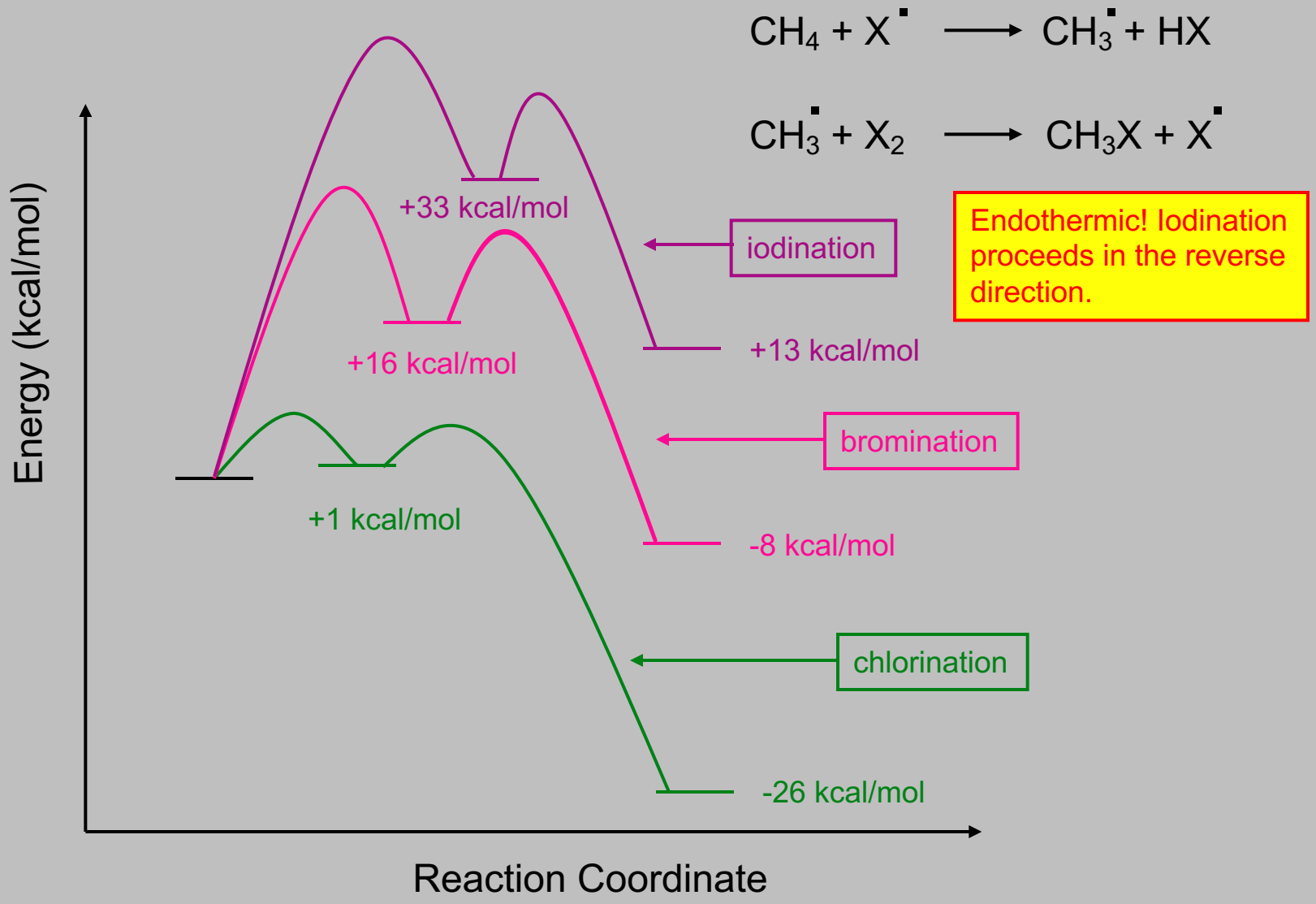
The reaction of molar quantities of methane and chlorine yields a distribution of chlorinated methanes.

Chloromethane (Methyl chloride)	CH_3Cl	b.p. -24°C
Dichloromethane (Methylene chloride)	CH_2Cl_2	b.p. 40°C
Trichloromethane (Chloroform)	$CHCl_3$	b.p. 61°C
Tetrachloromethane (Carbon tetrachloride)	CCl_4	b.p. 77°C

Readily separated by distillation.

What about bromination and iodination?

At 27°C, the chlorination of methane is ~10^{11} times faster than the bromination and, bromination is ~10^{10} times faster than iodination under the same conditions!



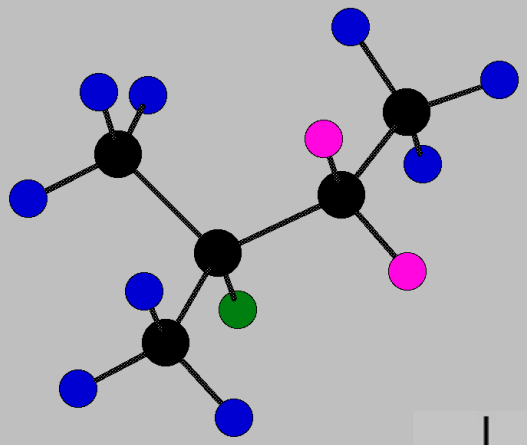
Activation Energy of Fluorine, Chlorine and Bromine Atoms with Methane And the Relative Reactivity of the Halogen Atoms with C-H Bonds

$$CH_4 + X_2 \longrightarrow CH_3X + HX$$

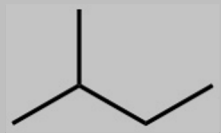
X	E_a (kcal/mol)	BDE HX [CH_3X]	°C	1°	2°	3°
F	1.2	136 [115]	27	1	1.2	1.4
Cl	4	103 [84]	27	1 1	3.9 4.5	5.1 5.5
Br	18	88 [70]	127	1 1	82 97	1600 -

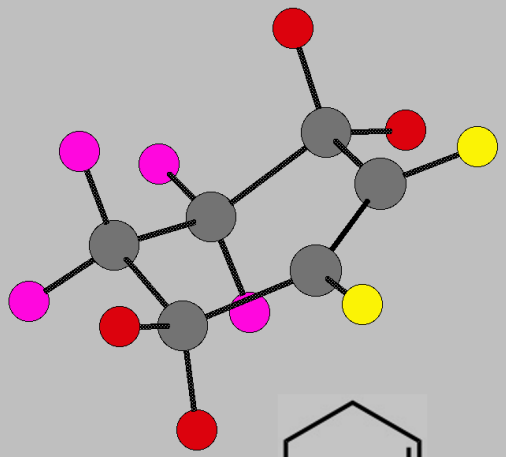
Reaction Selectivities: Anson, Fredricks, Tedder (1958); Wade's Text

Typical C-H Bond Dissociation Energies

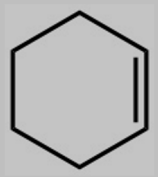


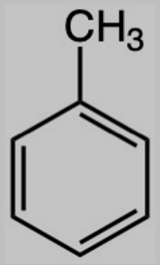
2-Methylbutane

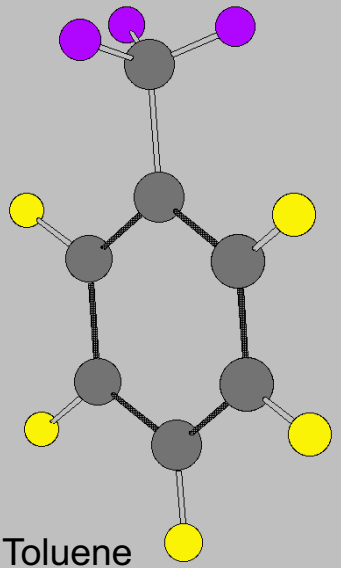




Cyclohexene







Toluene

BDEs (kcal/mol)	1°	2°	3°	allylic	vinylic & aromatic	benzylic
2-Methylbutane	98	95	91	-	-	-
Cyclohexene	-	95	-	87	108	-
Toluene	-	-	-	-	108	85

The End