Radical Halogenation

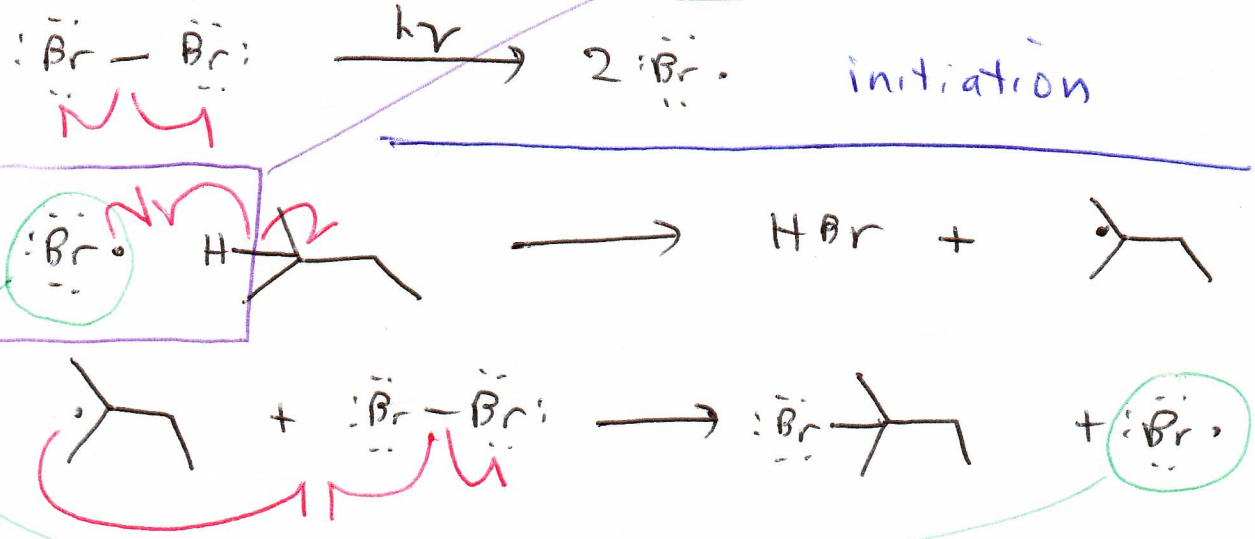
1) synthetic utility
2) Cl_2 or Br_2
3) conditions
4) mechanism
5) stereochemistry
6) regiochemistry

alkane → alkyl halide

→ reagents

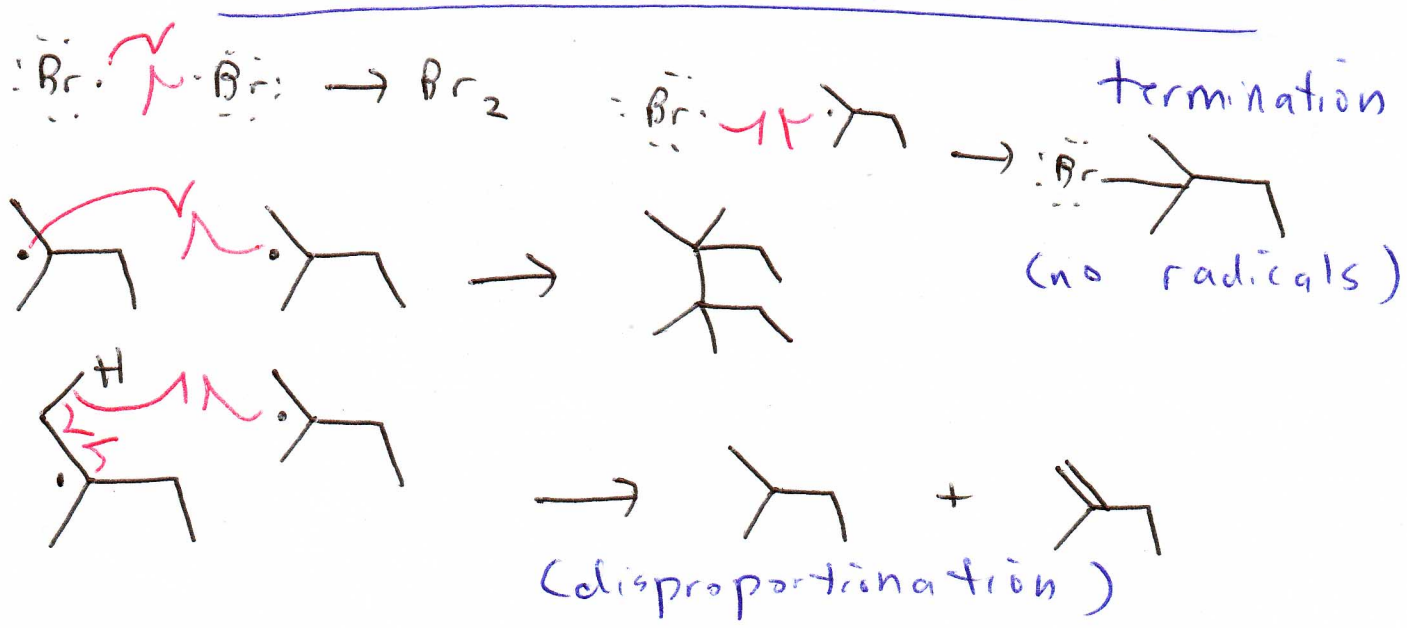
hν (light, usually UV)

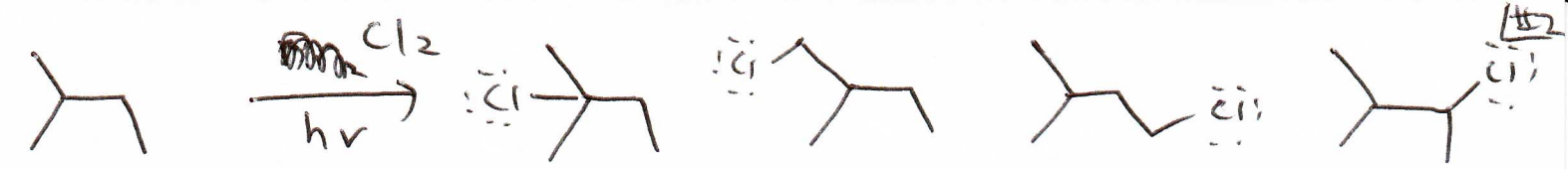
abstraction – removal of a hydrogen

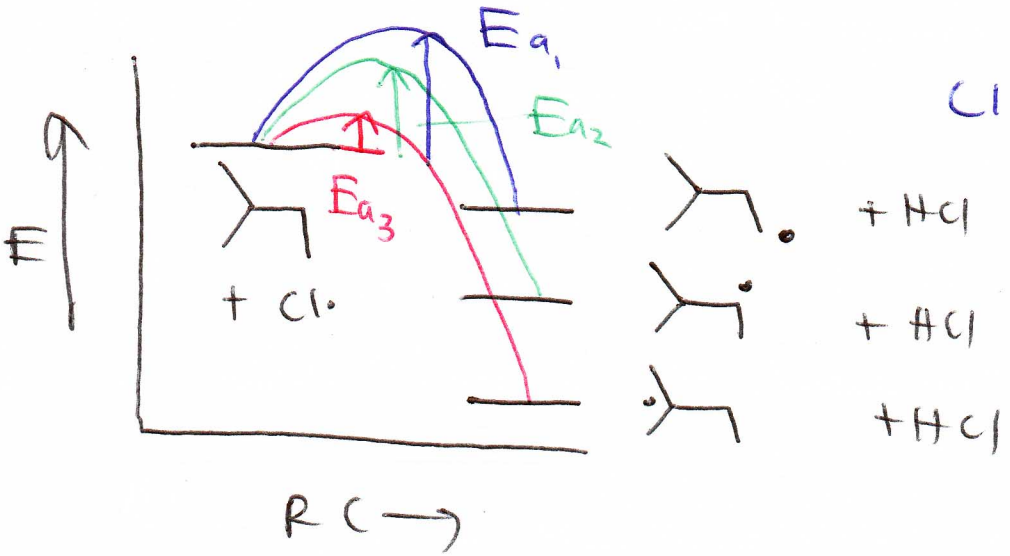


chain reaction – a mechanism that repeats continuously (until reagents run out) since one of the products produced is itself a reactant.

propagation







$Cl\cdot + R \longrightarrow HCl + R\cdot$

$\Delta H < 0$

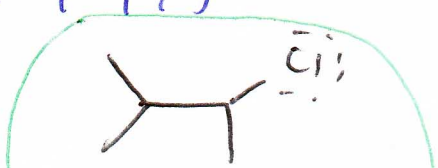
Hammond Postulate — The structure of the transition state (‡) more closely matches the structure of the product/reactant/intermediate that is closer to the transition state in energy,

— In this case, the ‡ more closely resembles the reactant, so there is not a huge difference in the Ea for forming a 1° vs 2° vs 3° radical,

relative reactivity of Cl· to 1°:2°:3°

1 : 4 : 5

1H × 5 = 5 6H × 1 = 6 3H × 1 = 3



2H × 4 = 8

Product formed in greatest quantity

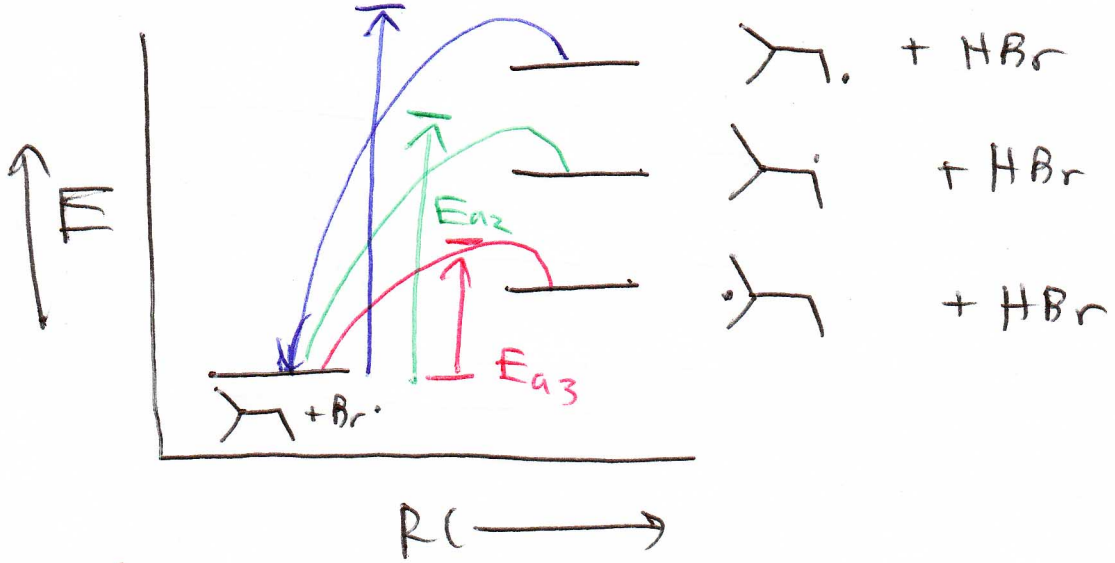
regiochemistry — Every possible monohalogenated product would form, and the most likely product depends on both the reactivity of the hydrogen involved along with the number of hydrogens.

Relative reactivity of Br• 1° : 2° : 3°

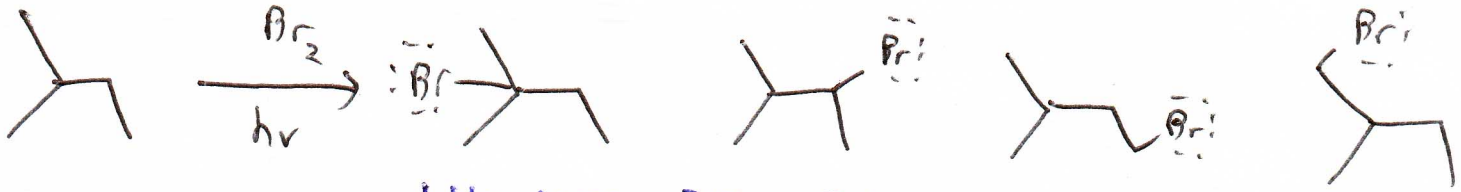
1 : 80 : 1600

$Br\cdot + R\text{-}H \rightarrow Br\text{-}H + R\cdot$

$\Delta H > 0$ (endothermic)



Since the transition state in this step more closely resembles the product, there is a greater difference in the activation energies for the formation of a 1° vs 2° vs 3° radical,



1H × 1600 = 1600

2H × 80 = 160

3H × 1 = 3

6H × 1 = 6

- when possible, bromine is used instead of chlorine due to bromine's greater selectivity,
- Chlorination is more frequently used when only one major product forms,

Ex:

$|\Delta H_F| \gg |\Delta H_{Cl}| > |\Delta H_{Br}|$ ← all are $\Delta H < 0$

The reaction with F_2 is so exothermic that there is almost no difference in the E_a for forming different radicals. $1^\circ : 2^\circ : 3^\circ \longrightarrow 1 : 1.2 : 1.4$

$\Delta H_I > 0$

Halogenation using I_2 is not possible since the reaction is endothermic (alkyl iodides would decompose under light).