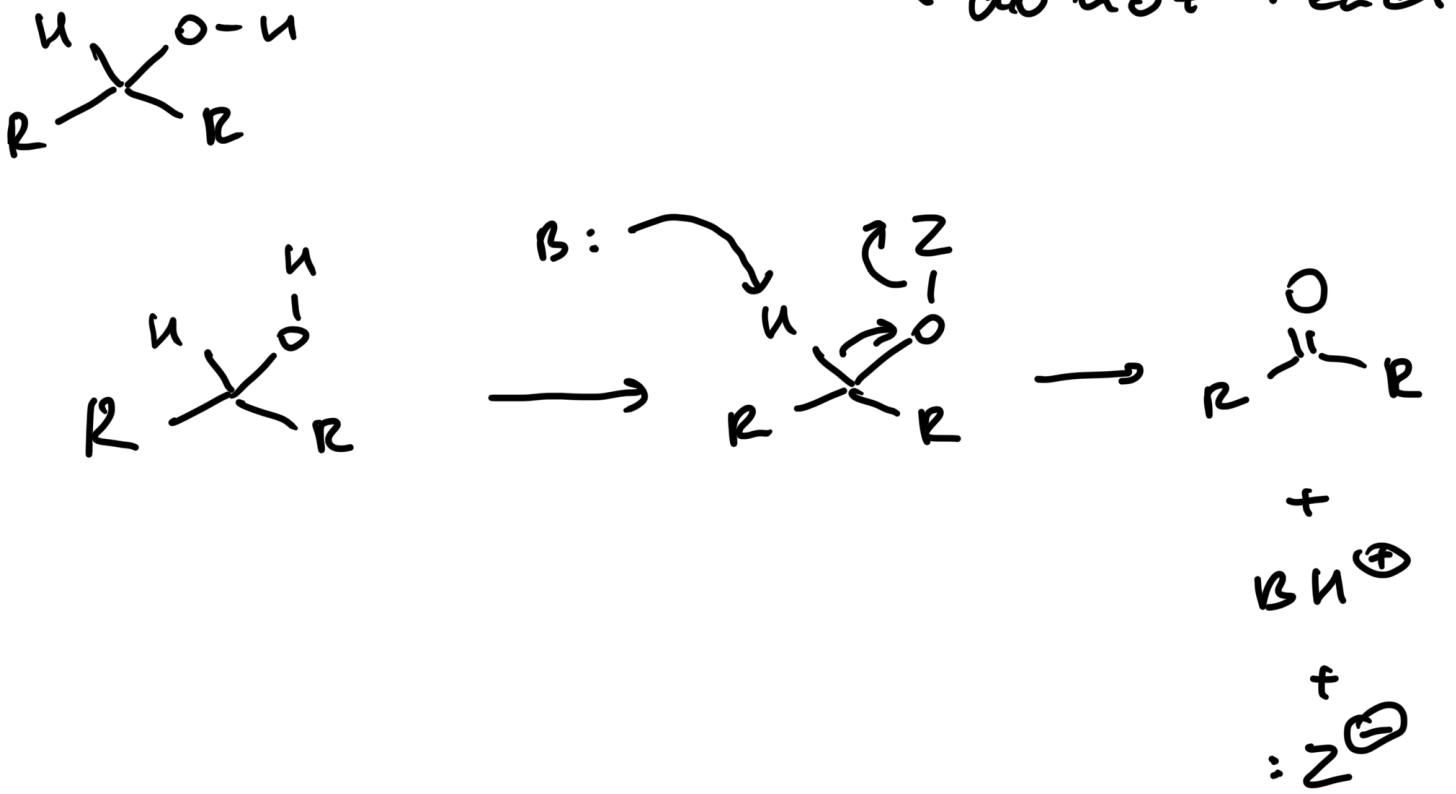
Oxidation of alcohols

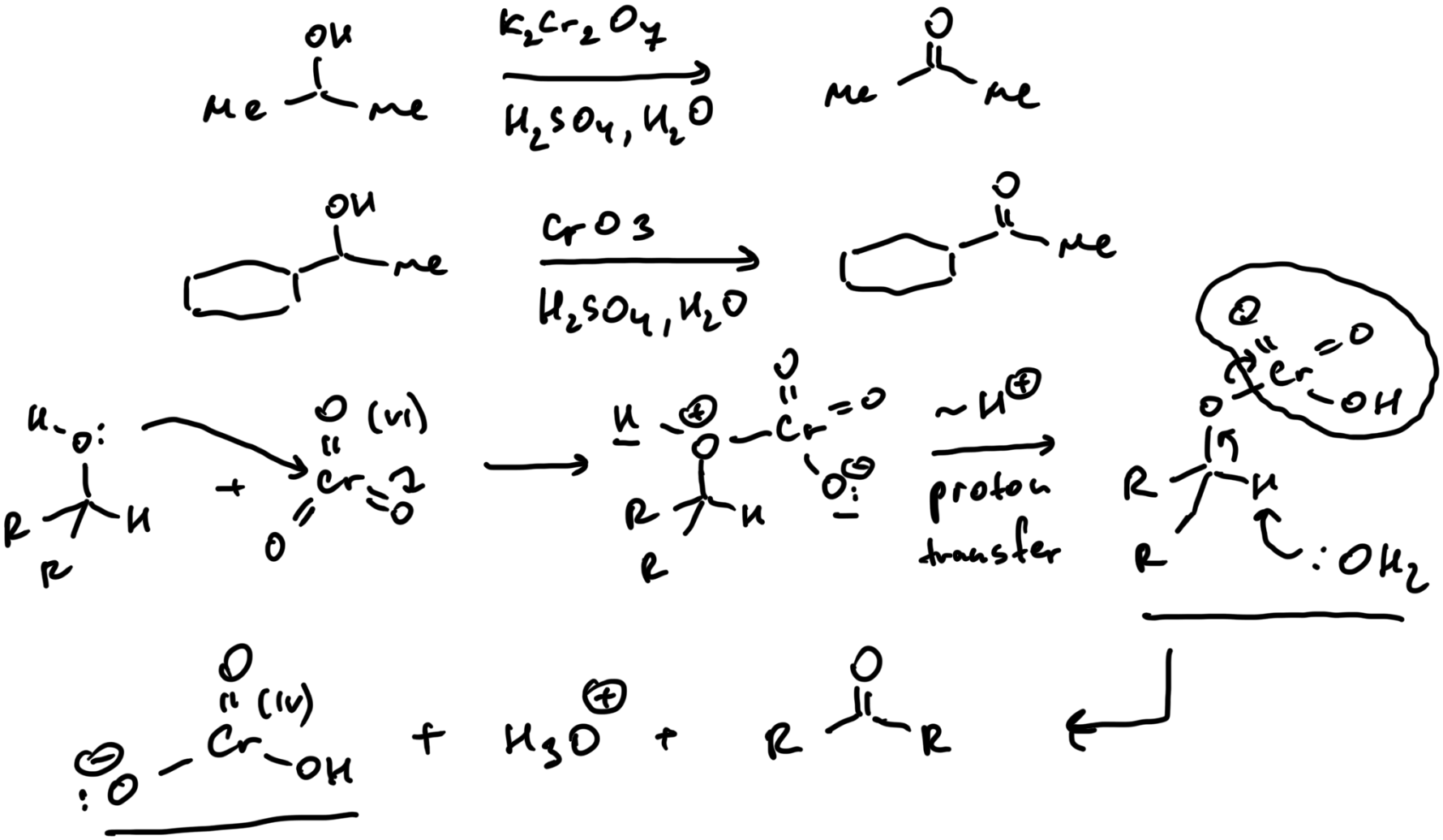
General considerations. 1°, 2°, and 3° alcohols

do not react



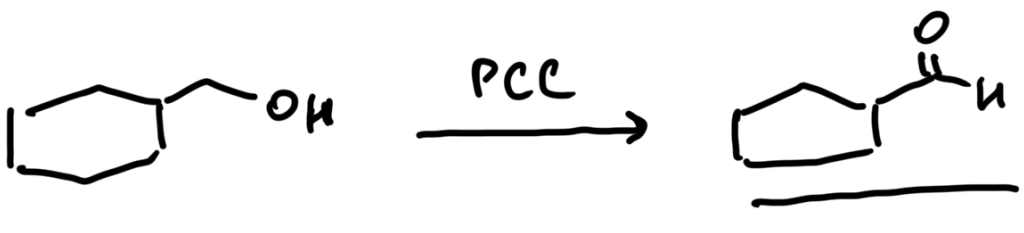
Oxidation of alcohols: secondary alcohols

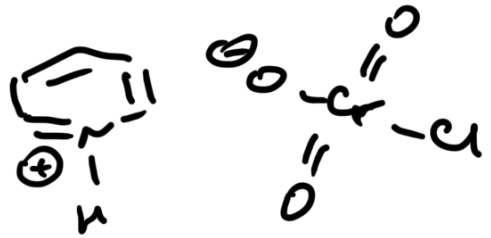
Mechanism of oxidation with CrO_3



Oxidation of alcohols: primary alcohols

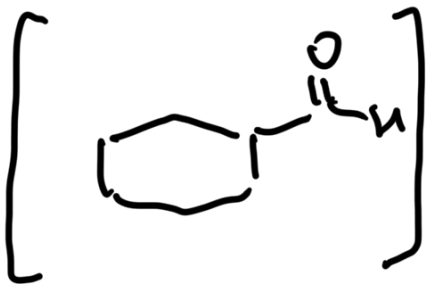
Oxidation with PCC to aldehydes. Oxidation to carboxylic acids



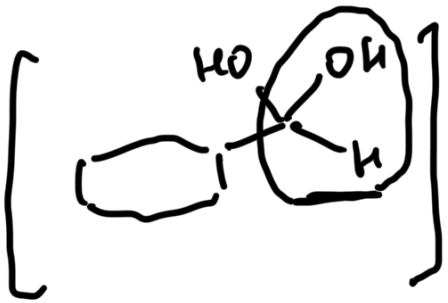


pyridinium chlorochromate

✓ CrO_3, H_2SO_4, H_2O

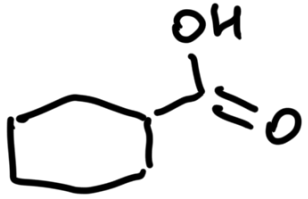


H_2O, H_2SO_4



CrO_3, H_2SO_4, H_2O

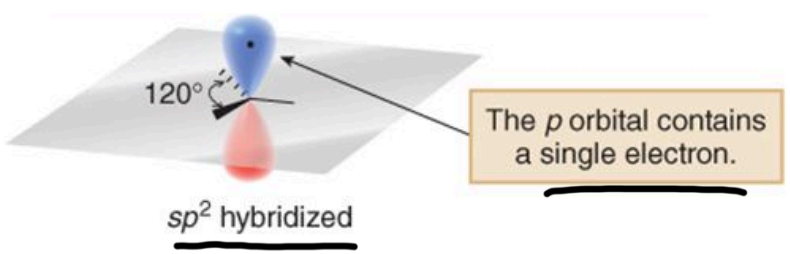
✓



read 12.13

Radicals

Structure of alkyl radicals. Stability of alkyl radicals. BDEs



ΔH^0 = 410 kJ/mol = BDE

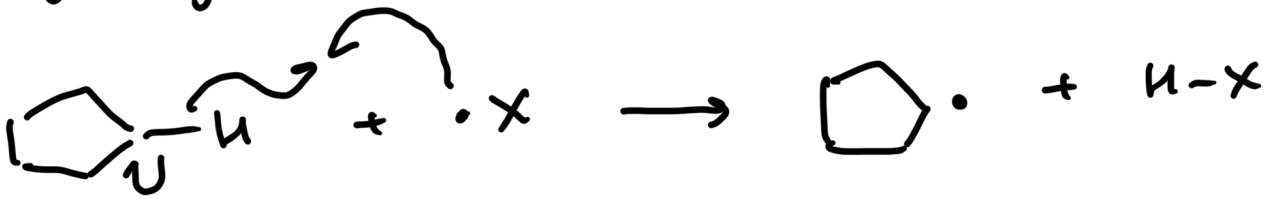
ΔH^0 = 397 kJ/mol = BDE

increasing stability

Radical reactions

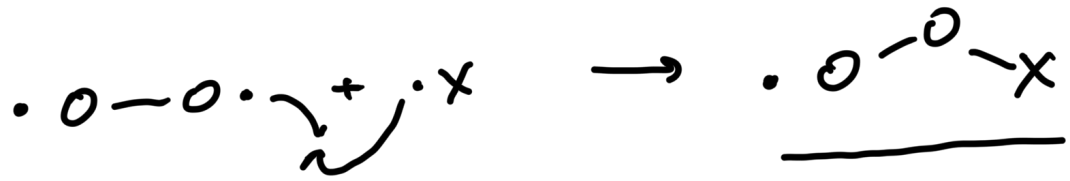
Common radical reactions

- hydrogen atom abstraction



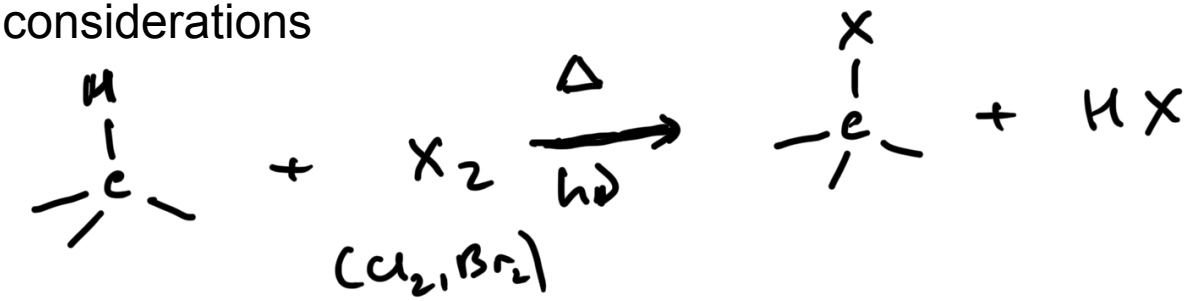
- addition (to alkenes)

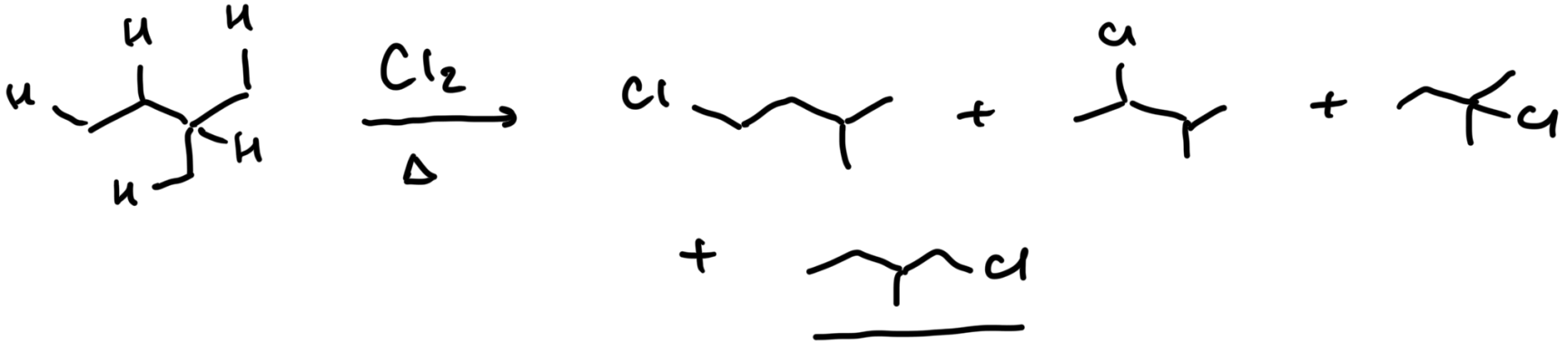
- recombination

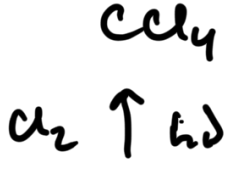


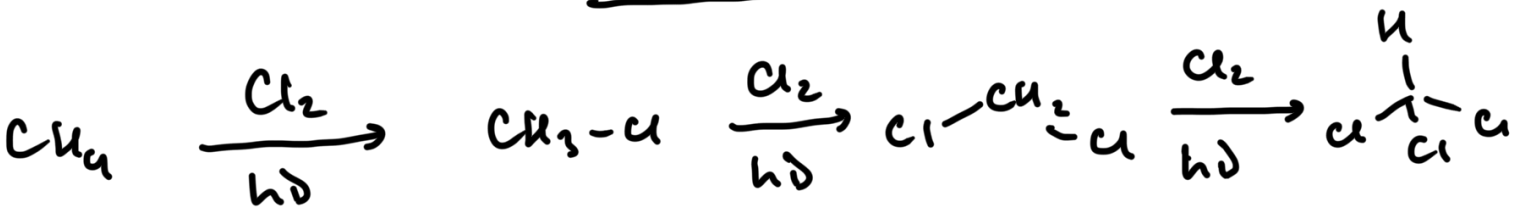
Radical reactions: halogenation

General considerations



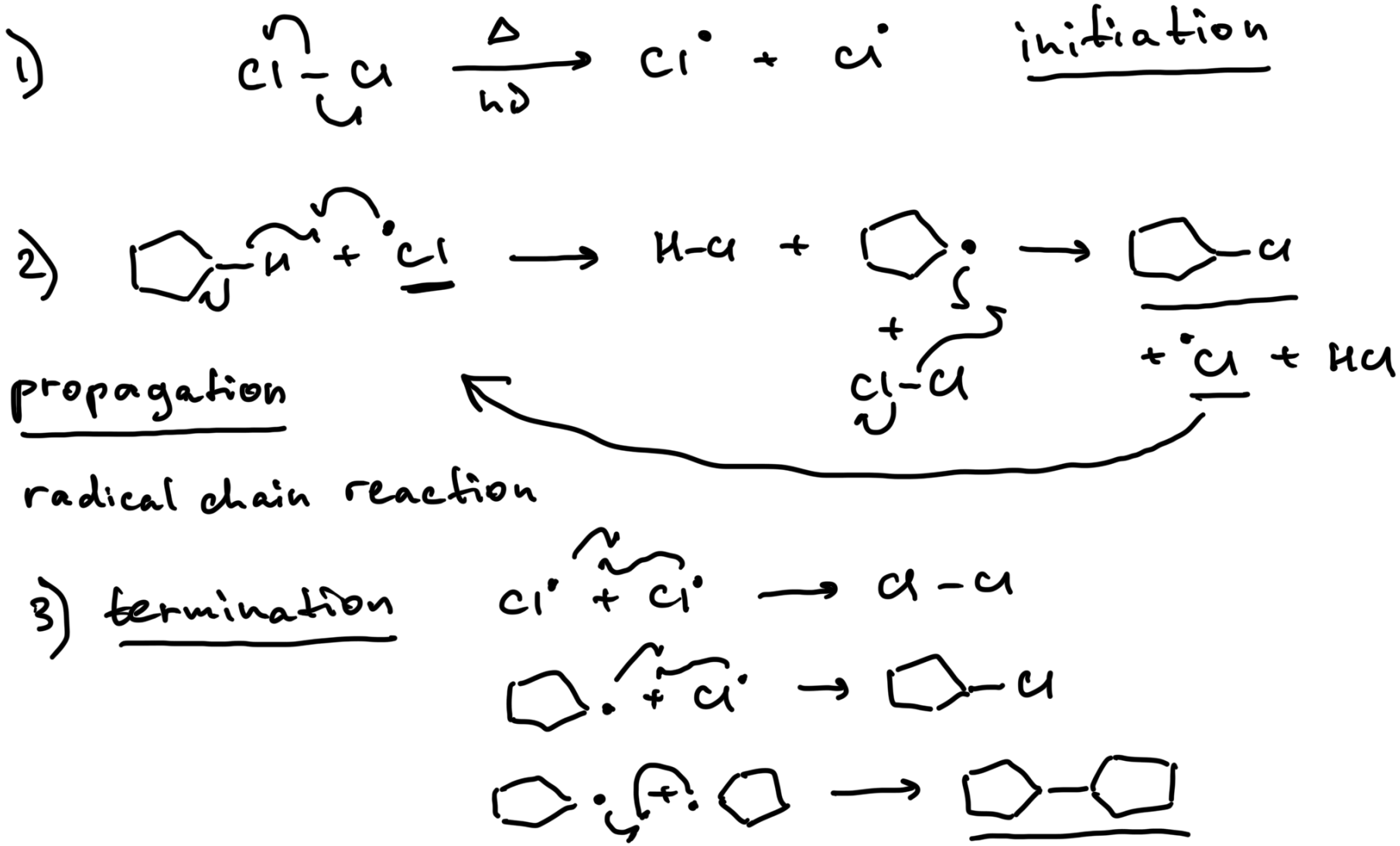






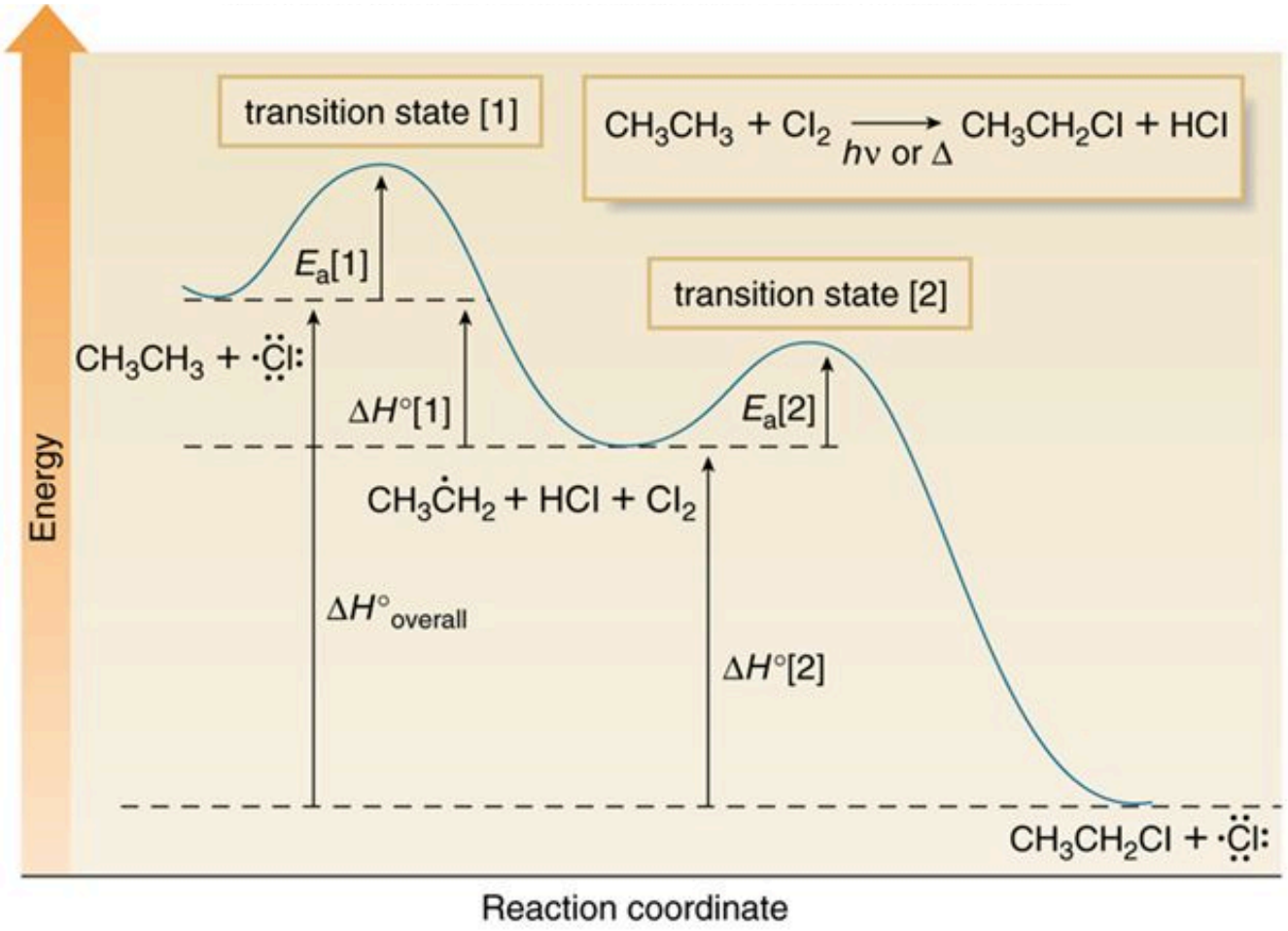
Radical reactions: halogenation

Mechanism



Radical reactions: halogenation

The propagation steps in the chlorination of ethane



Radical reactions: halogenation

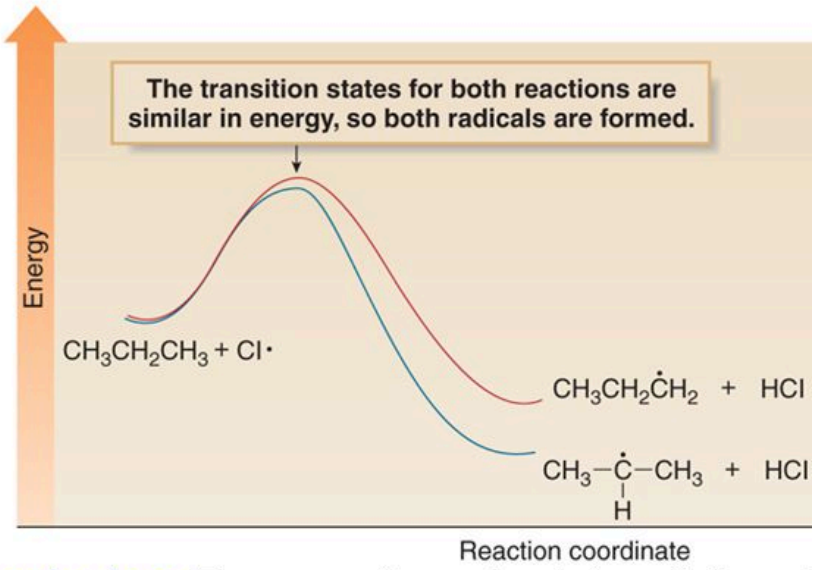
Selectivity in the radical chlorination. Relative reactivity of C–H bonds

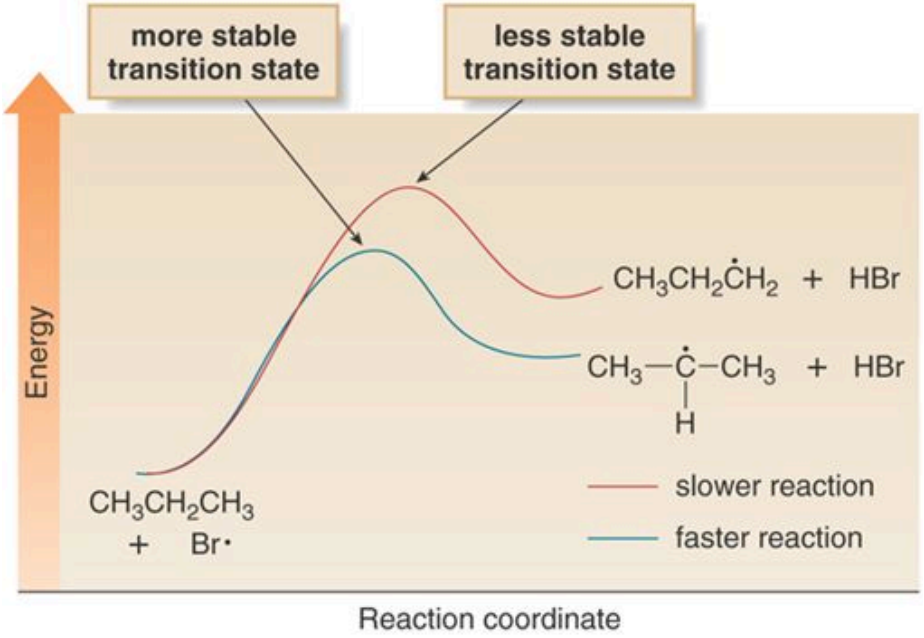
Radical reactions: halogenation

Selectivity in the radical bromination

Radical reactions: halogenation

Chlorination vs. bromination: applying Hammond postulate





Radical reactions: halogenation

Stereochemistry of the radical halogenation

Radical reactions: halogenation

Allylic halogenation of alkenes. Resonance stabilization of radicals

Radical reactions: halogenation

Regioselectivity of allylic halogenation