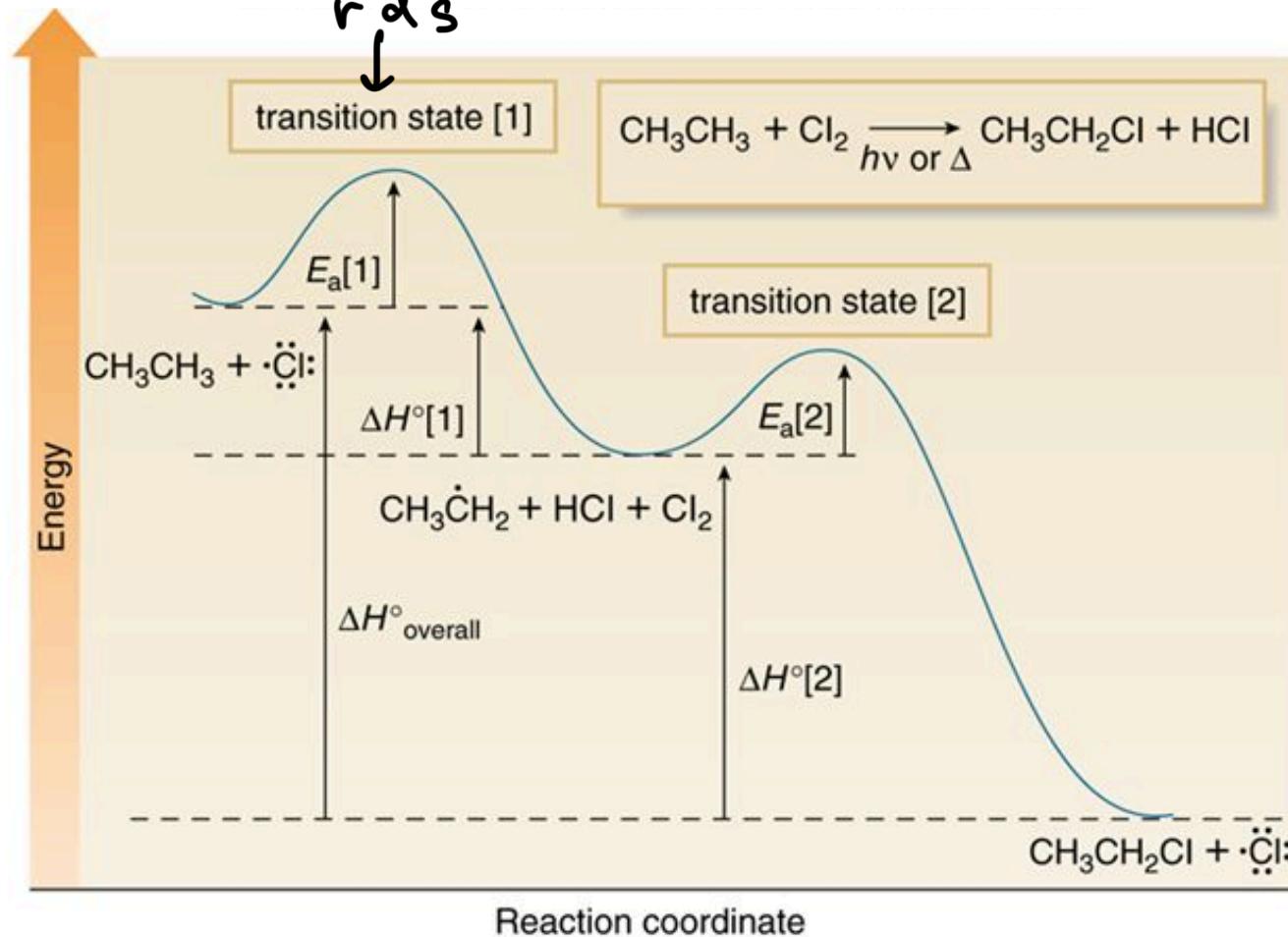
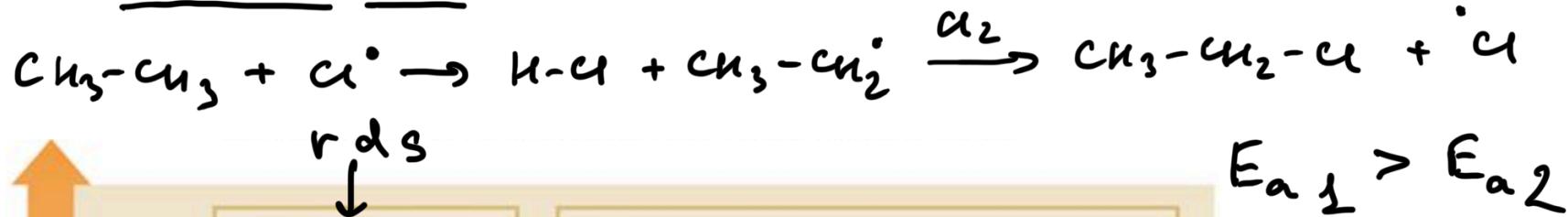


Radical reactions: halogenation

The propagation steps in the chlorination of ethane

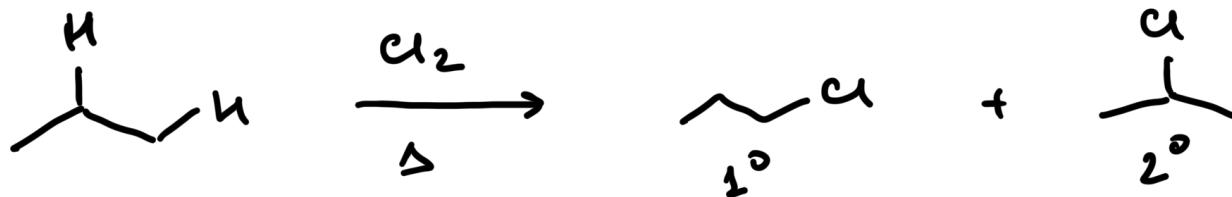


$$\Delta H_1^\circ = -21 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta H_2^\circ = -97 \frac{\text{kJ}}{\text{mol}}$$

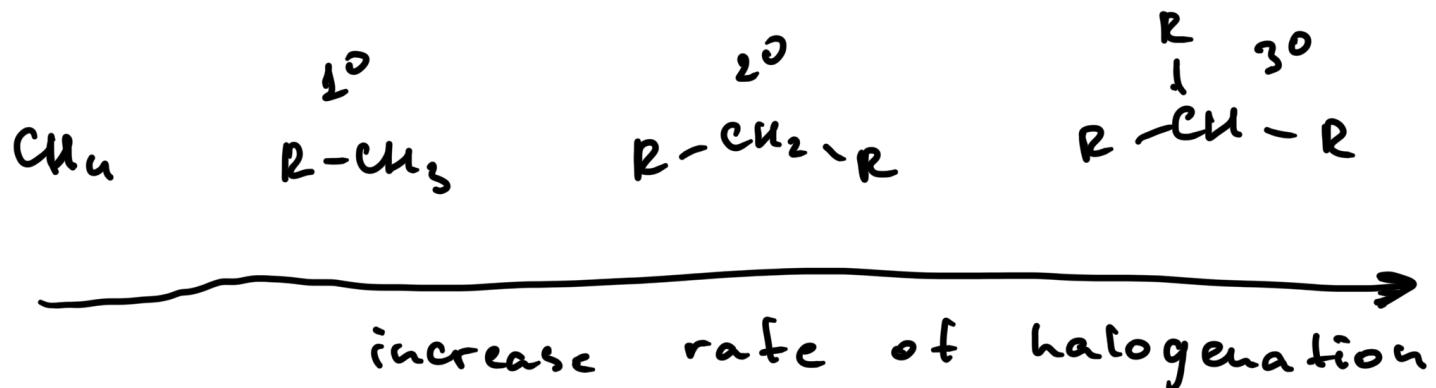
Radical reactions: halogenation

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



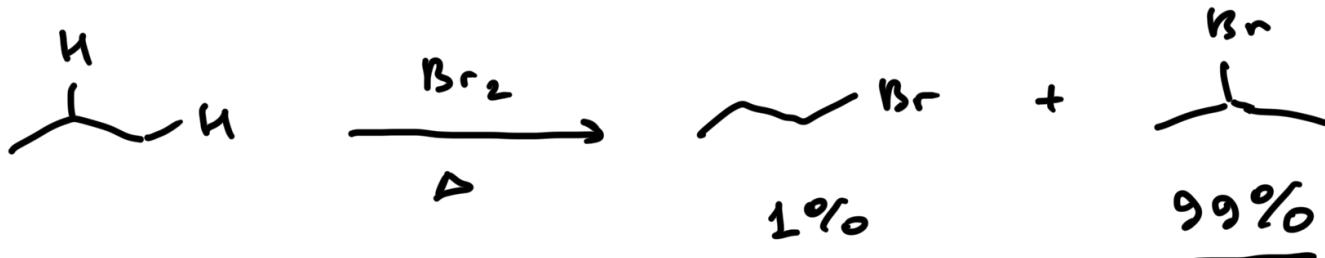
observed ratio 1 : 1

expected (statistics) 3 : 1



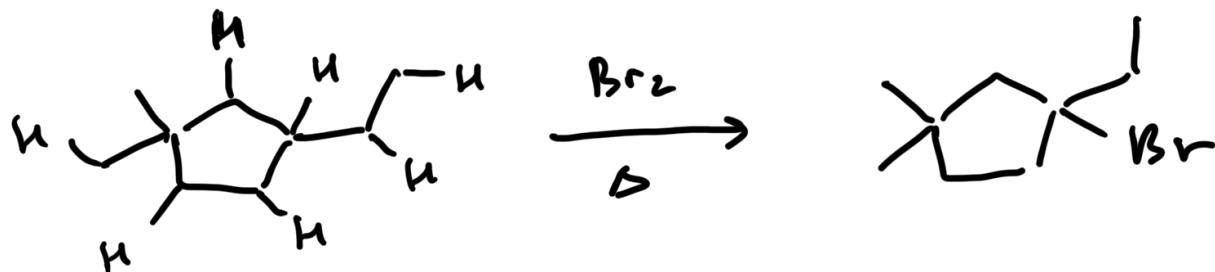
Radical reactions: halogenation

Selectivity in the radical bromination



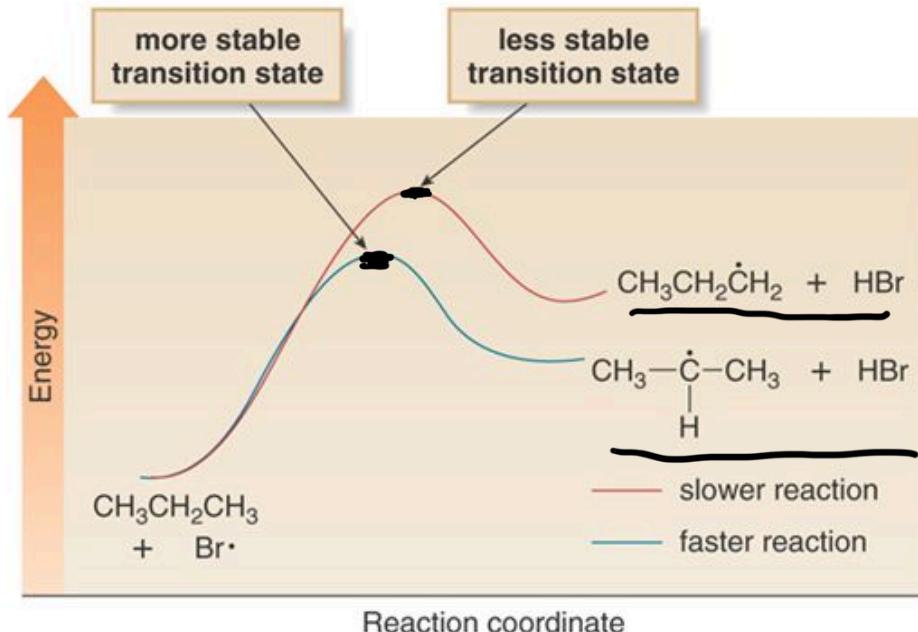
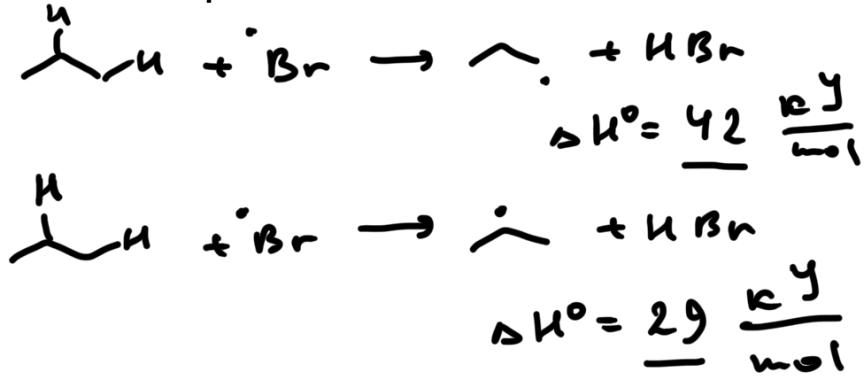
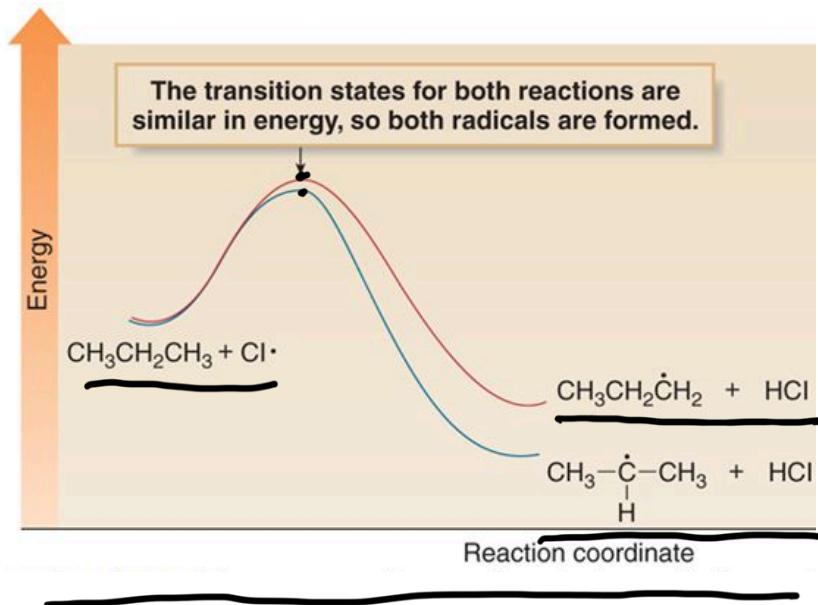
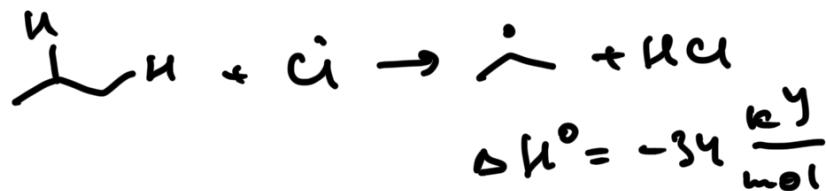
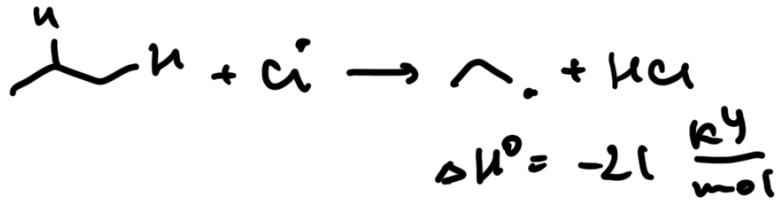
bromination is selective and slow

(cf. chlorination is fast and unselective)



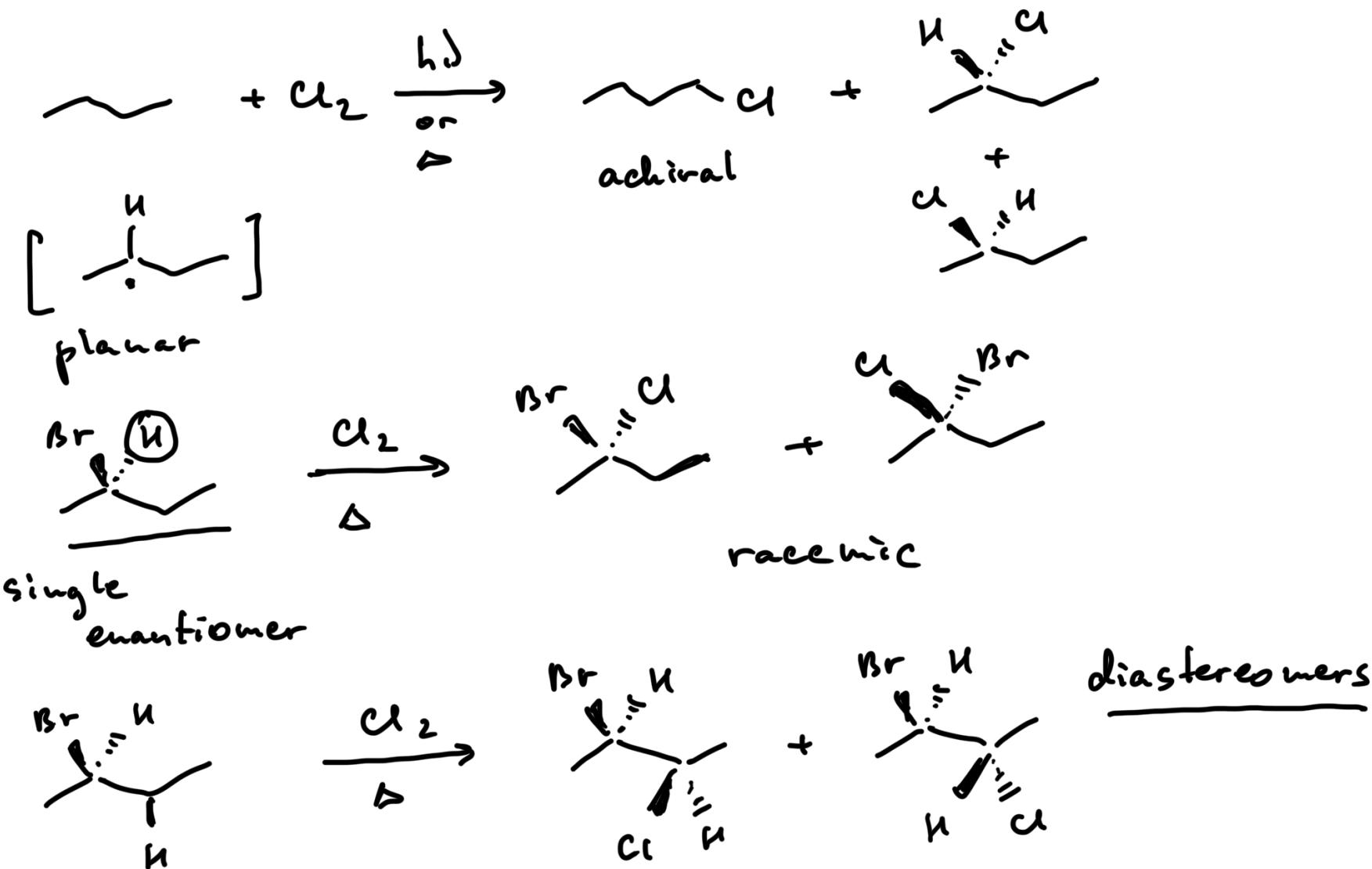
Radical reactions: halogenation

Chlorination vs. bromination: applying Hammond postulate



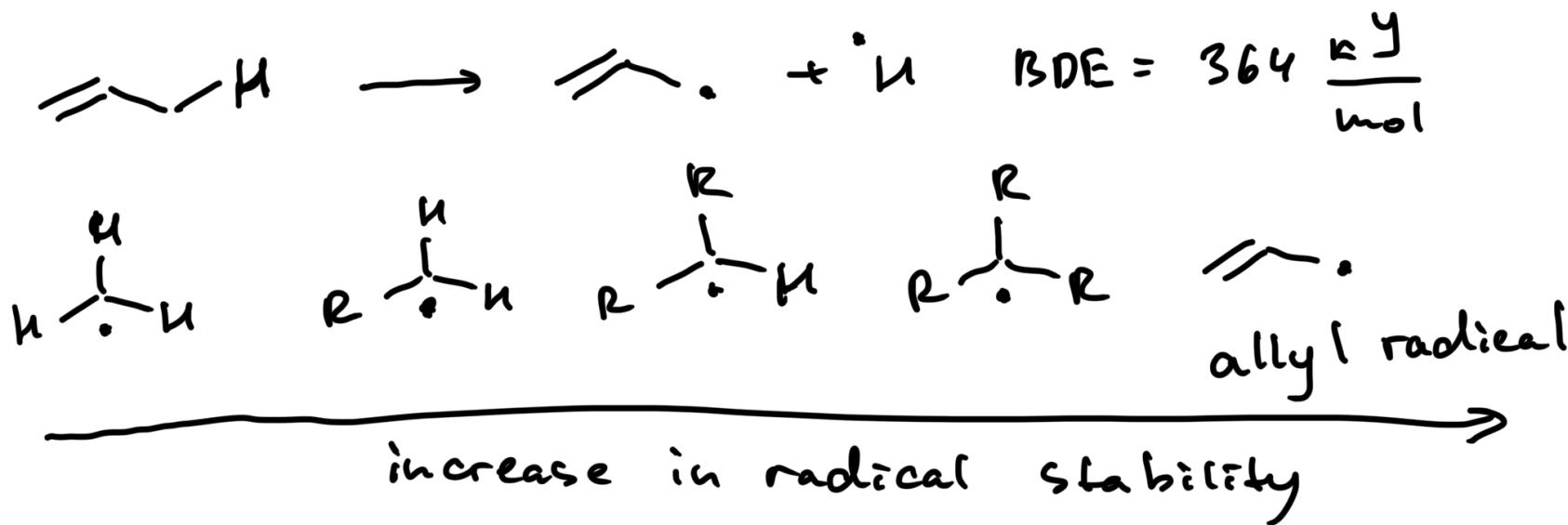
Radical reactions: halogenation

Stereochemistry of the radical halogenation



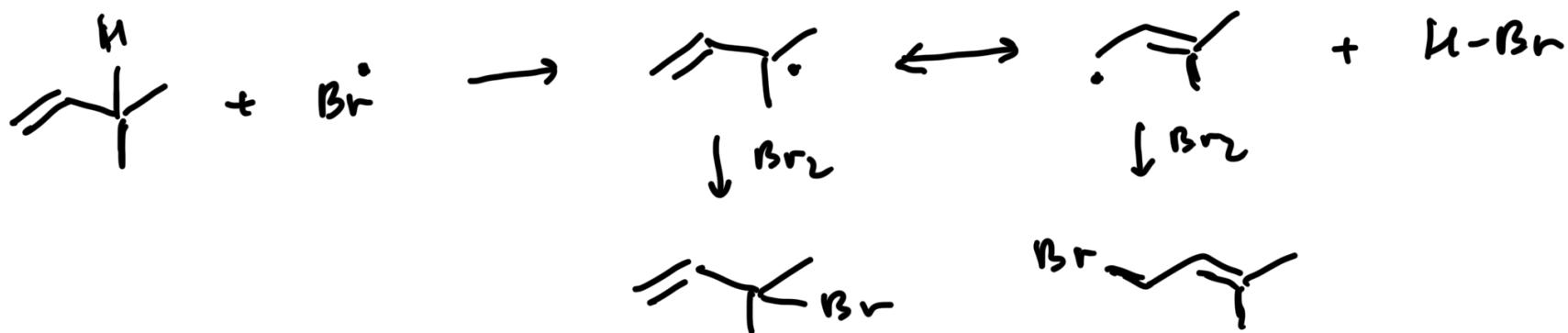
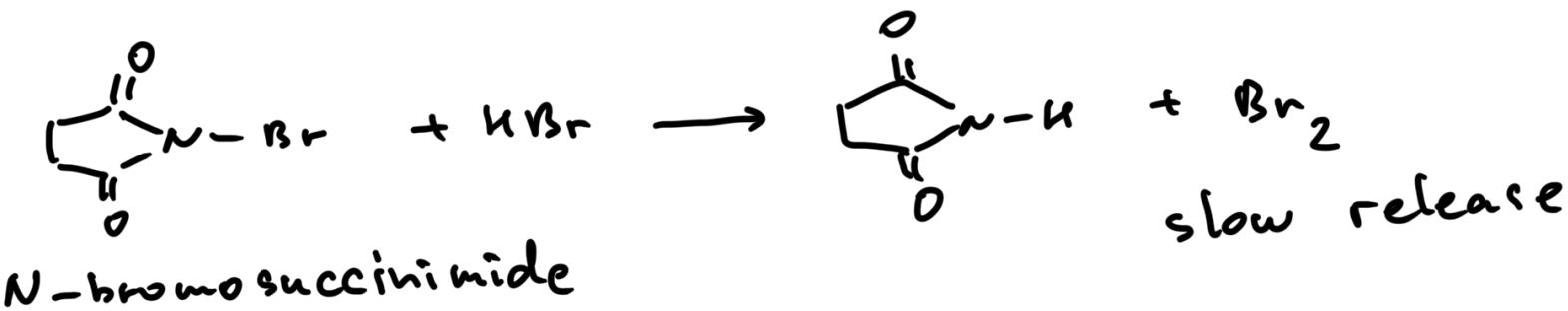
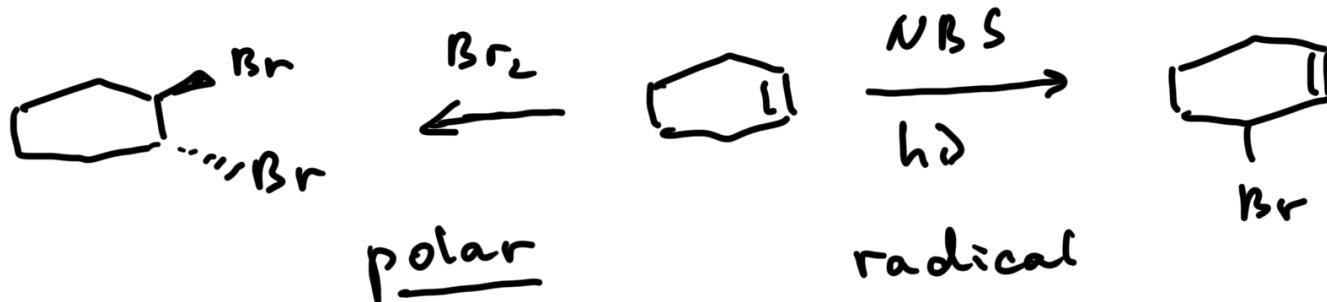
Radical reactions: halogenation

Allylic halogenation of alkenes. Resonance stabilization of radicals



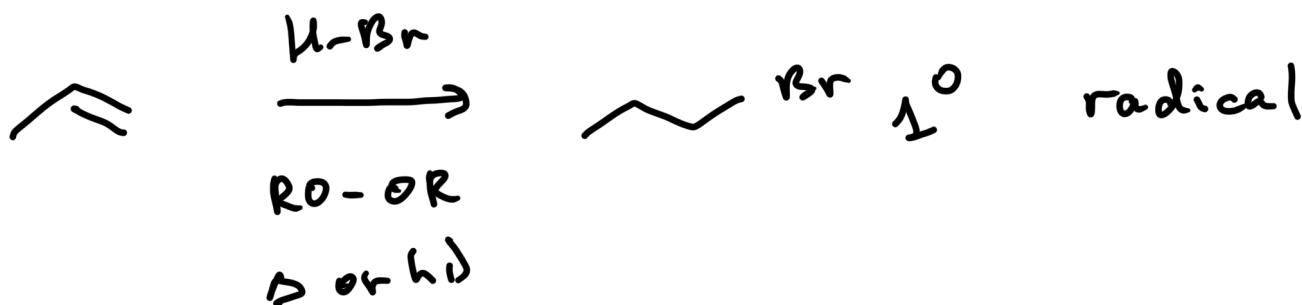
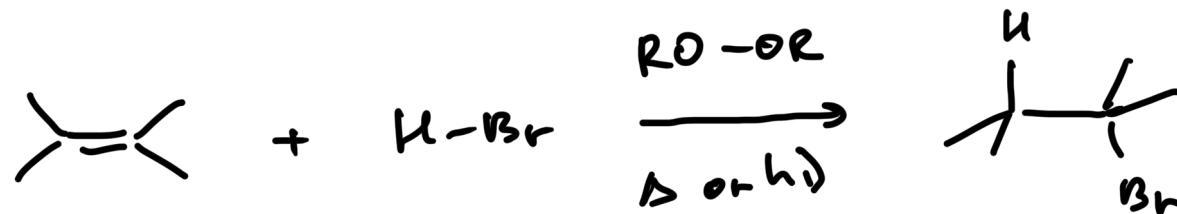
Radical reactions: halogenation

Regioselectivity of allylic halogenation



Radical reactions: addition of HBr to alkenes

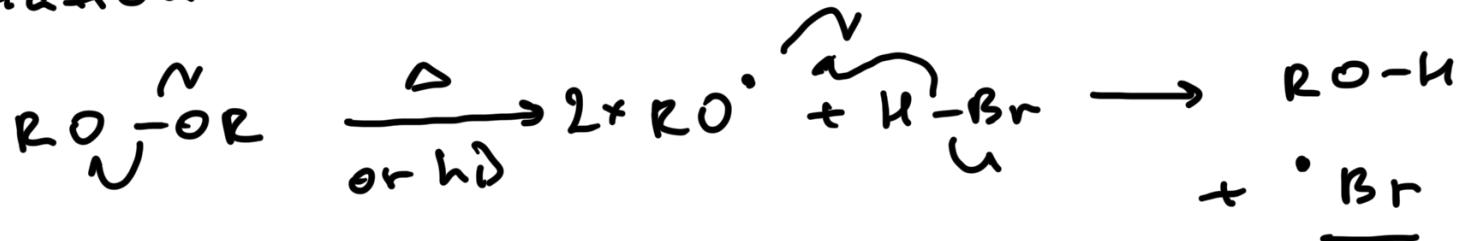
General considerations. Regioselectivity



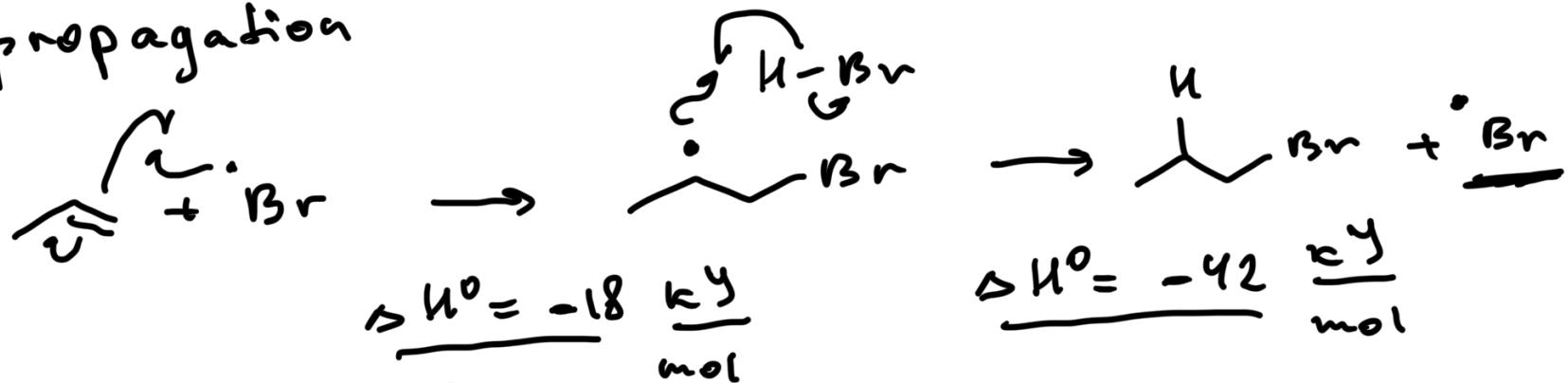
Radical reactions: addition of HBr to alkenes

Mechanism. Thermodynamics of the propagation step

- initiation



- propagation



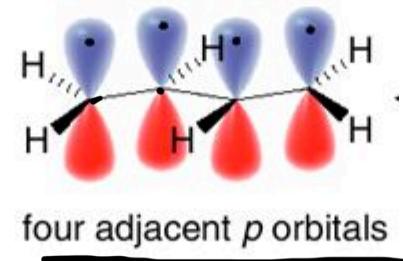
does not work w/ $H-Cl$ strong bond

Conjugation and resonance

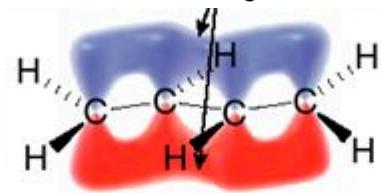
General considerations



1,3-diene



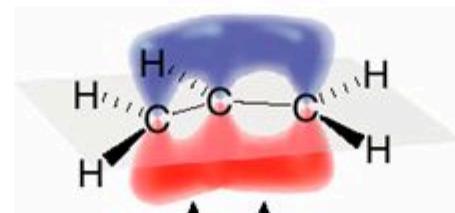
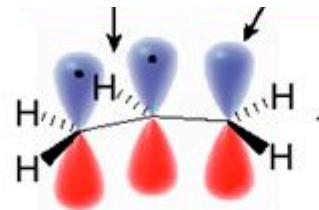
C_2 C_3



bonding
in 1,3-diene

Conjugation and resonance

Allylic carbocations. Resonance. Stability of carbocations



Resonance: examples

Resonance: examples

Choosing the most contributing resonance structure

Resonance: examples

Choosing the most contributing resonance structure