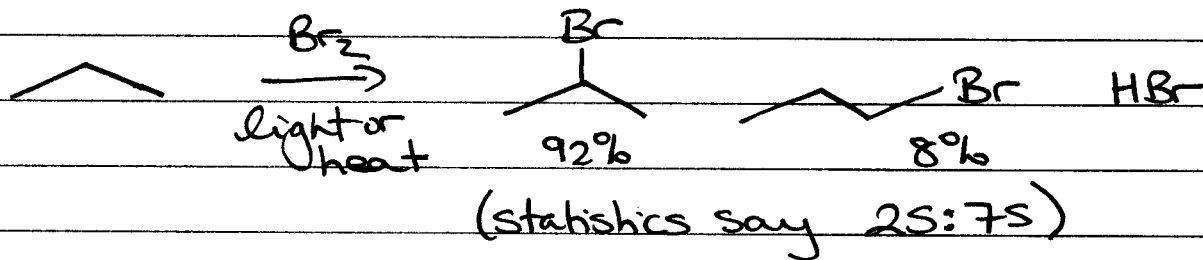
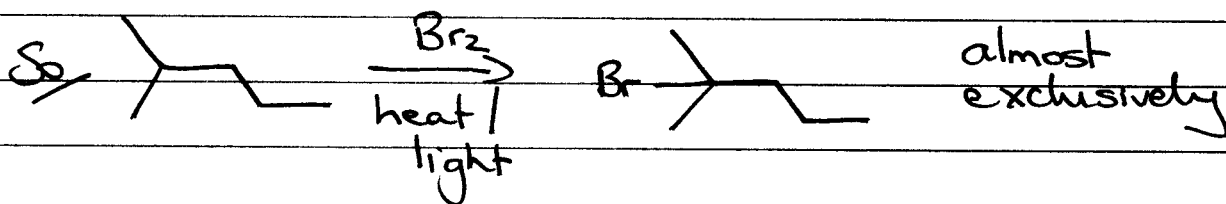


- ① REGIOSELECTIVITY OH Mon
- ② BOND ENERGETICS Reviews Tues/Wed
- ③ MECHANISMS FINAL THREE
- ④ HAMMOND POSTULATE ROOM
- ⑤ RADICAL STRUCTURE / STABILITY
- ⑥ ALLYLIC HALOGENATION

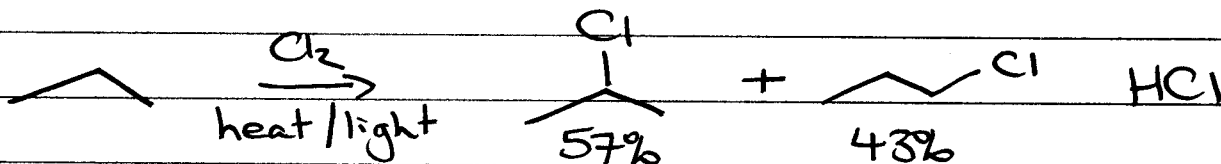
① REGIOSELECTIVITY



2° favored over 1° (also 3° favored over 2°)

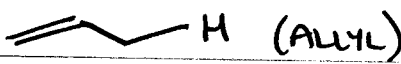
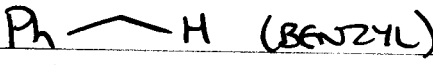
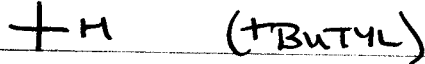





REGIOSELECTIVITY LESS FOR Cl₂

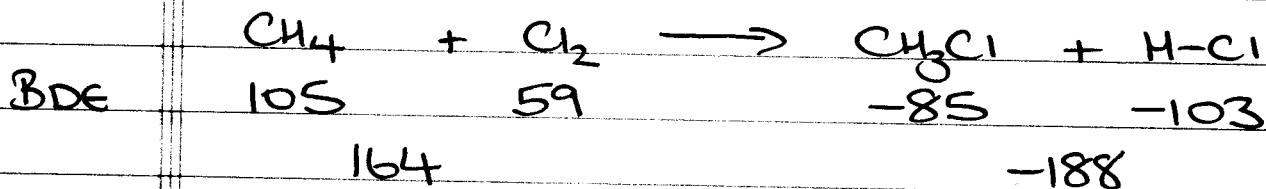


Br ₂	3°/2°/1°	1600/80/1
Cl ₂		5/4/1

2) BOND ENERGETICS

C-H BOND	BDE (kcal/mol)
 H (ALLYL)	86
 H (BENZYL)	88
 H (TERT-BUTYL)	93
 H (ISOPROPYL)	96
 H (ETHYL)	100
CH ₃ -H (METHYL)	105
 H (VINYL)	106

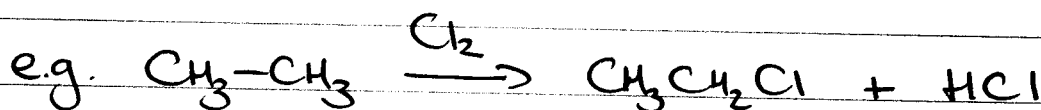
So, consider:



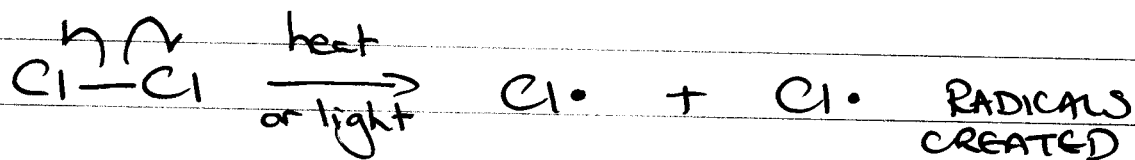
$\Delta H = -24 \text{ kcal/mol}$ (EXOTHERMIC RXN)

3) MECHANISMS

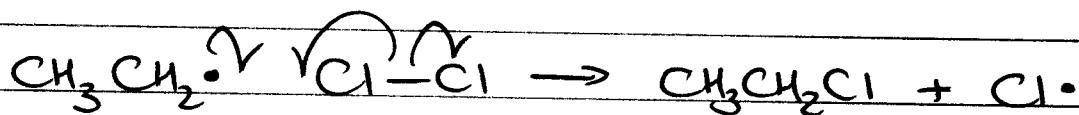
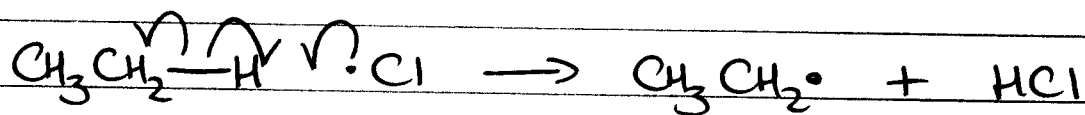
3 steps: INITIATION / PROPAGATION / TERMINATION



(i) CHAIN INITIATION

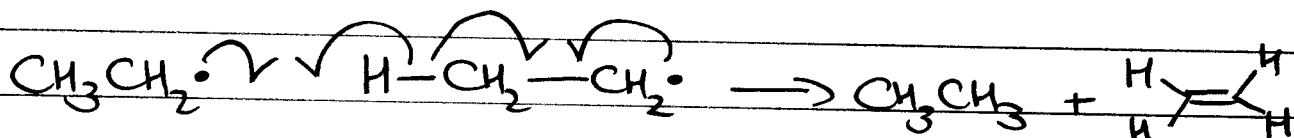
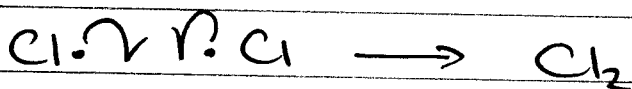
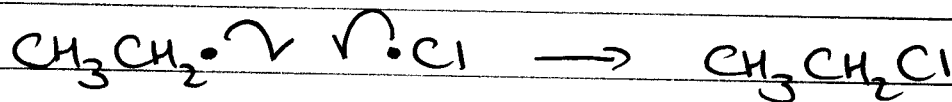
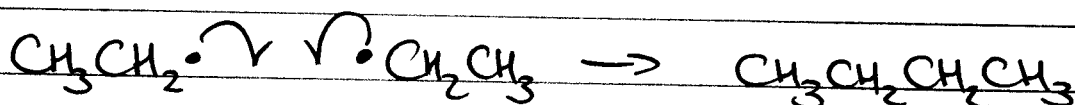


(ii) CHAIN PROPAGATION



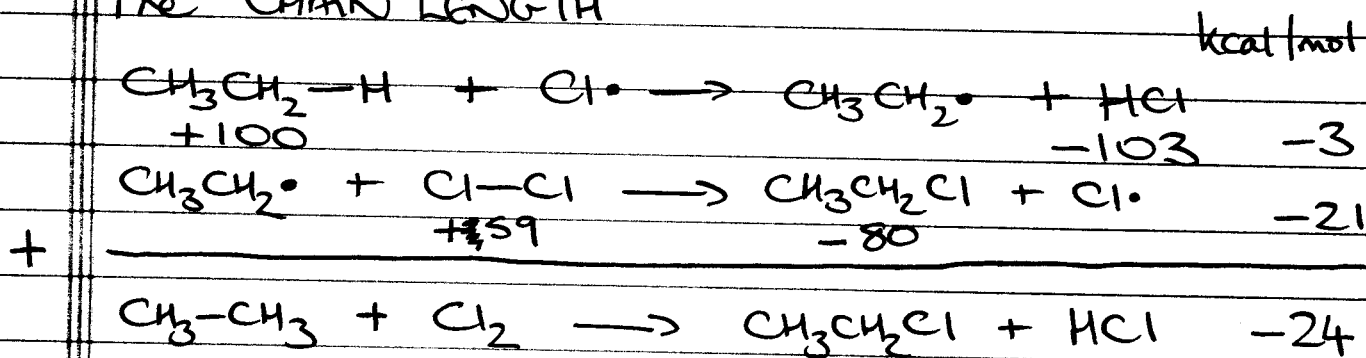
PROPAGATES RADICALS

(iii) CHAIN TERMINATION



CONSUMES RADICALS

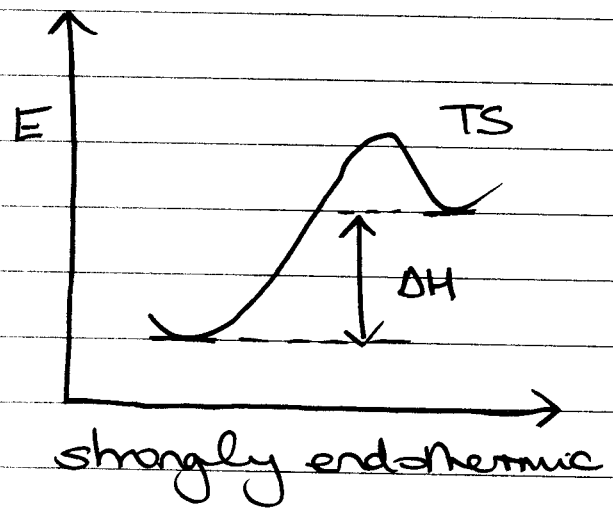
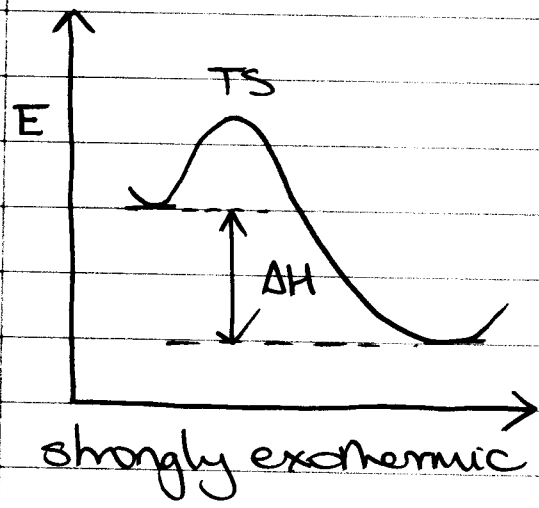
CHAIN PROPAGATION happens many times before termination → number of cycles is called the CHAIN LENGTH



gives: REACTION STOICHIOMETRY
and ΔH for REACTION

④ HAMMOND POSTULATE

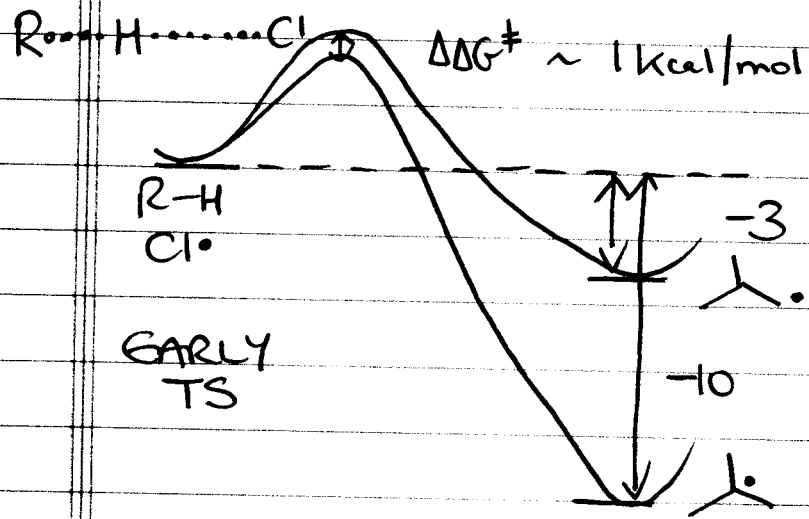
- a transition state will be most like the reactant, the intermediate, or the product, if it is close in energy to one of these structures.



TS looks like reactant

TS looks like product

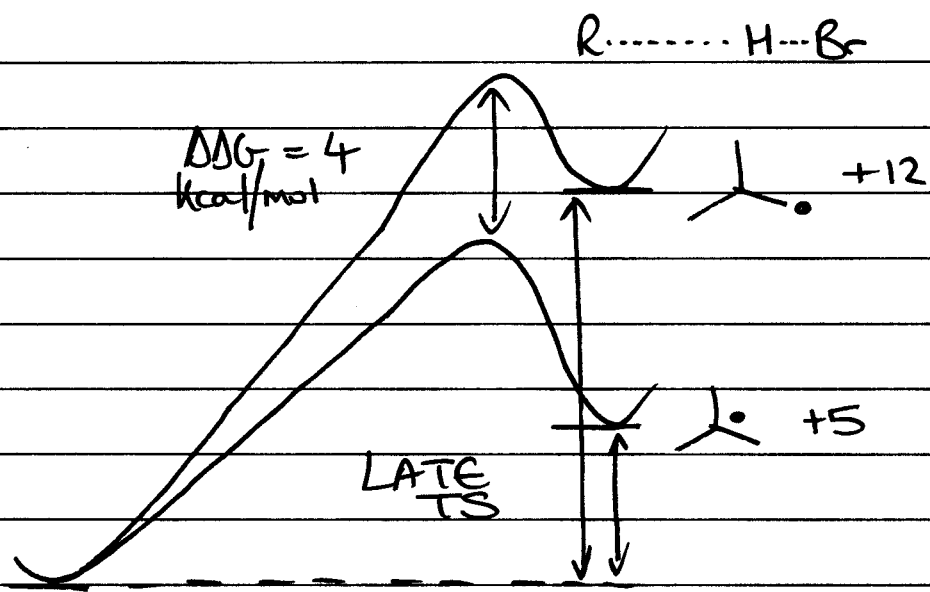
- Abstraction of H is RDS, consider CHLORINATION (exothermic RDS)



VERY LITTLE
RADICAL
CHARACTER
IN THE TS

-BROMINATION (endothermic RDS)

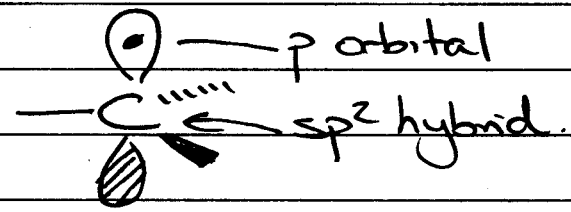
(5)



A LOT of ATL RADICAL CHARACTER IN TS

In Bromination, stability of radical is MUCH MORE reflected in TS than in CHLORINATION, so REGIOSELECTIVITY greater for bromination.

(5) RADICAL STRUCTURE



actually a SHALLOW PYRAMID

