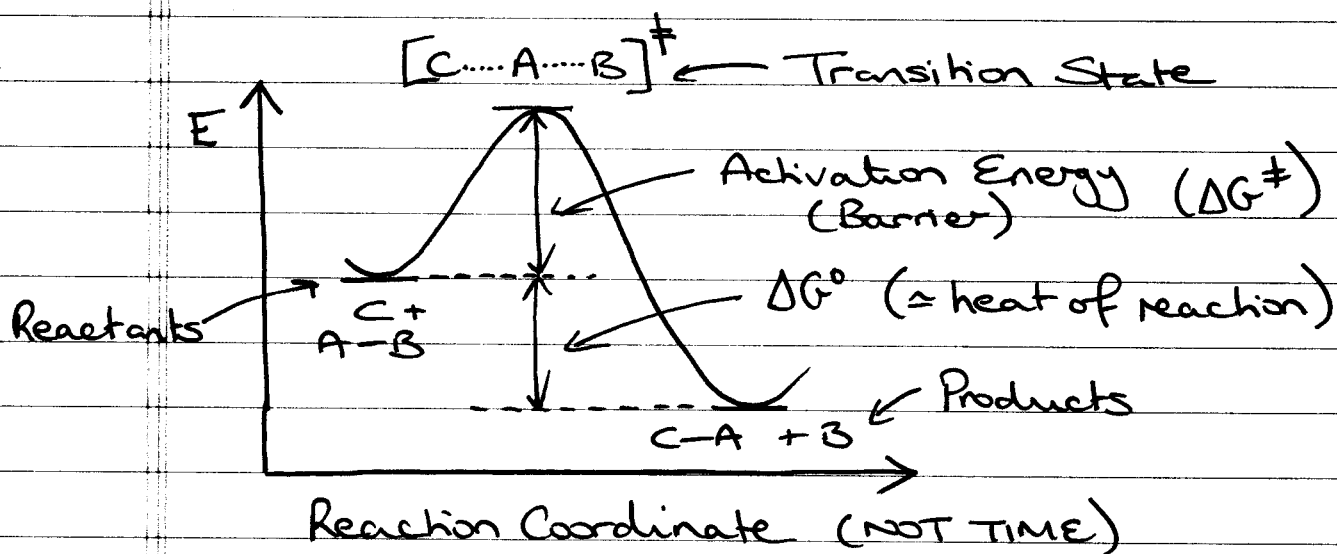
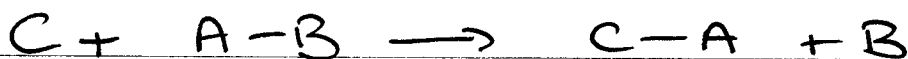


- ① ENERGY DIAGRAMS
- ② KINETICS vs THERMODYNAMICS
- ③ ADDITION TO ALKENES
- ④ CARBOCATIONS

READ 6.3-6.6 Q 6.1-6.3, 6.13-6.15

① ENERGY DIAGRAMS

- one step reaction



For a reaction to occur as written
 $\Delta G^\circ < 0$ (proceeds spontaneously)

if $\Delta G^\circ > 0$ reaction does not proceed.

- HEAT OF REACTION

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

↑ change in enthalpy (can be measured directly)

← change in entropy (more significant at higher T)

ΔH° -ve EXOTHERMIC rxn
 ΔH° +ve ENDOTHERMIC rxn

- TRANSITION STATE

energy maximum along reaction coordinate

⇒ definite geometry of atoms, but CANNOT be isolated, structure cannot be determined experimentally (COMPUTATION)

- ACTIVATION ENERGY

difference in energy between starting materials and the transition state

ΔG^\ddagger or E_A

Arrhenius equation

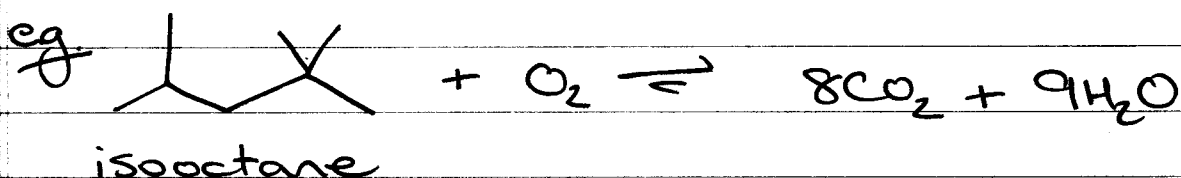
$$k = A e^{(-E_A/RT)}$$

↑ rate constant for reaction

↖ pre-exponential factor

② KINETICS vs THERMODYNAMICS

↓ how fast
 ↓ will it happen?

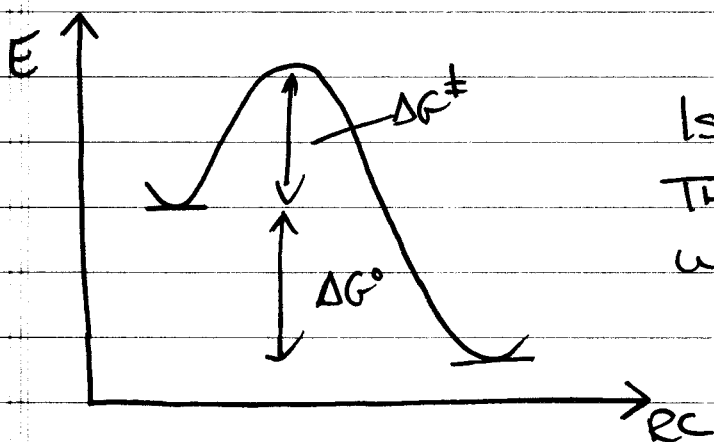


$$\Delta G^\circ = -1000 \text{ kJ/mol}$$

$k_{eq} = 10^{175}$ at 298K
 (only 10^{86} atoms in observable universe)

But isooctane is stable
 (you put it in your car)

- Energy required to start the reaction
 ⇒ ACTIVATION ENERGY (spark plug)



Isooctane + O₂
 THERMODYNAMICALLY
 UNSTABLE, BUT
 KINETICALLY STABLE

However, apply a burst of energy to H₂O/CO₂ mixture
 you will not reconvert to octane + oxygen

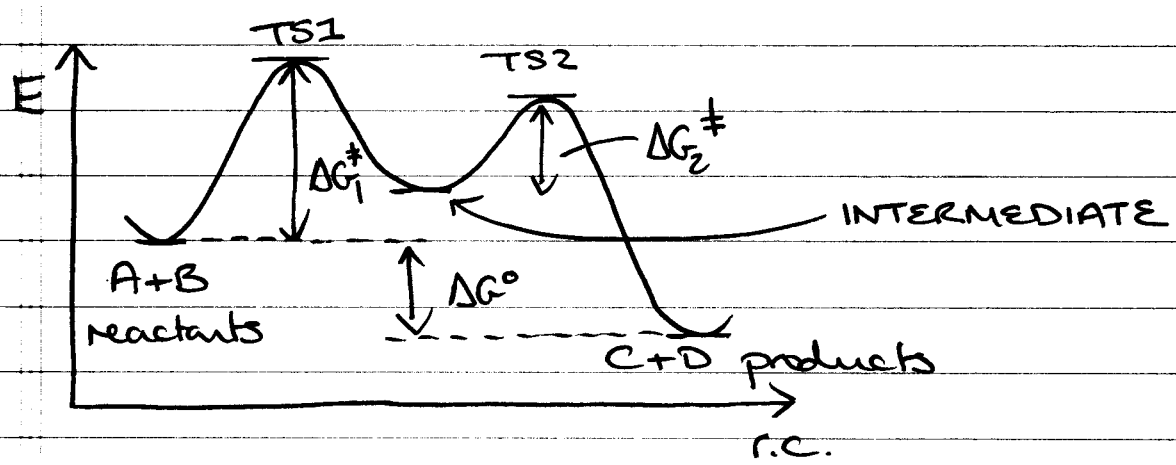
(MENTION GRAPHITE / DIAMOND)

Energy barriers and rate (consider BOND rotations → same principle as reactions)

	E_A (Kcal/mol)	k (s ⁻¹) (298K)	$t_{1/2}$
<chem>H3C-CH3</chem>	3	5×10^{10}	0.02 ns
<chem>Cl3C-CCl3</chem>	11	8×10^4	10 ps
<chem>Me-C(=O)-NH2</chem>	17	3	0.2 s
<chem>Ph-CH=CH-Ph</chem>	45	2×10^{-19}	$\sim 10^{11}$ yrs

(age of the earth $\sim 4.6 \times 10^9$ yrs)

— ENERGY PROFILE (2 step rxn)

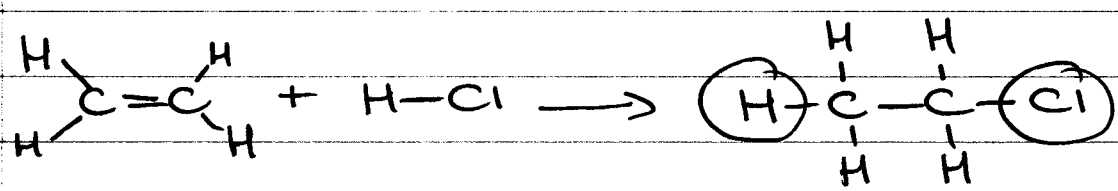


REACTION INTERMEDIATE \Rightarrow localized energy minimum between two TRANSITION STATES (sometimes possible to isolate)

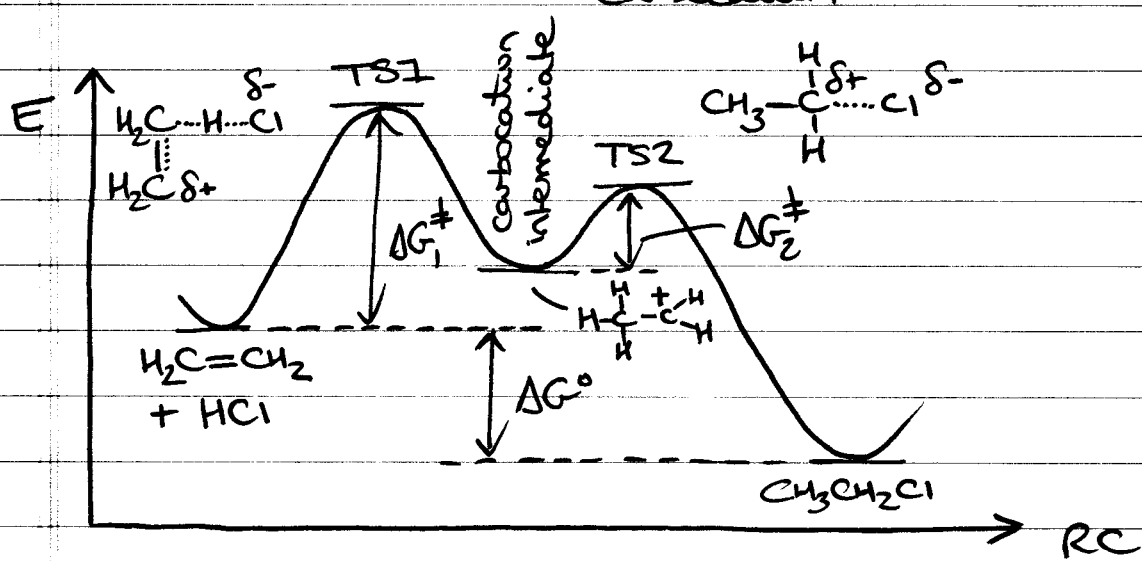
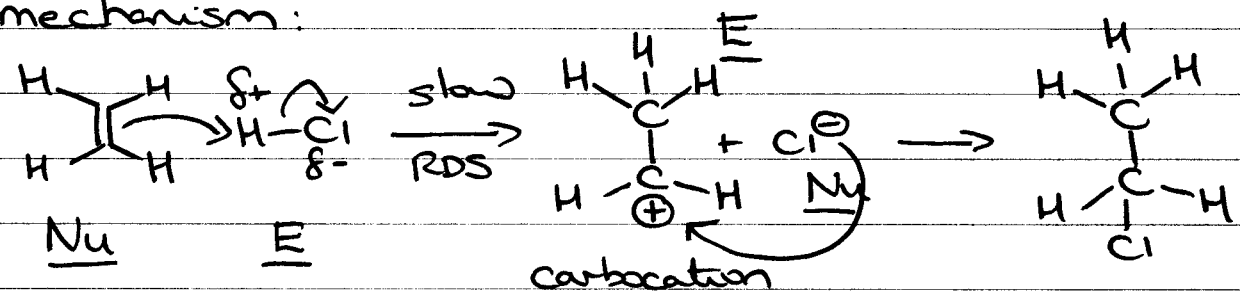
Slowest step in a multistep process (one w/ highest barrier) is called the RATE DETERMINING STEP (RDS)

- fill in RDS on graph above.

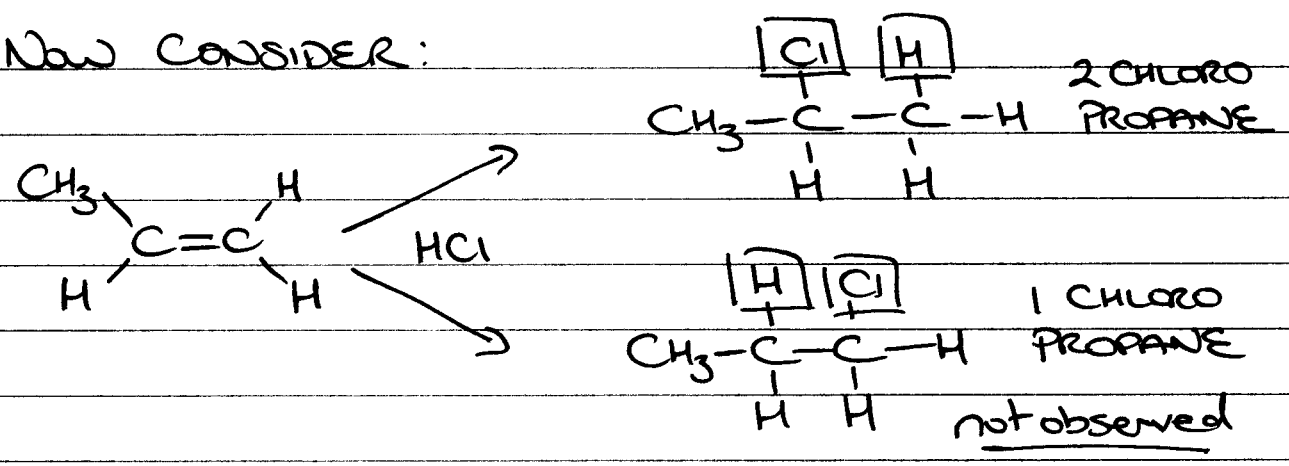
③ ELECTROPHILIC ADDITION TO ALKENES



mechanism:



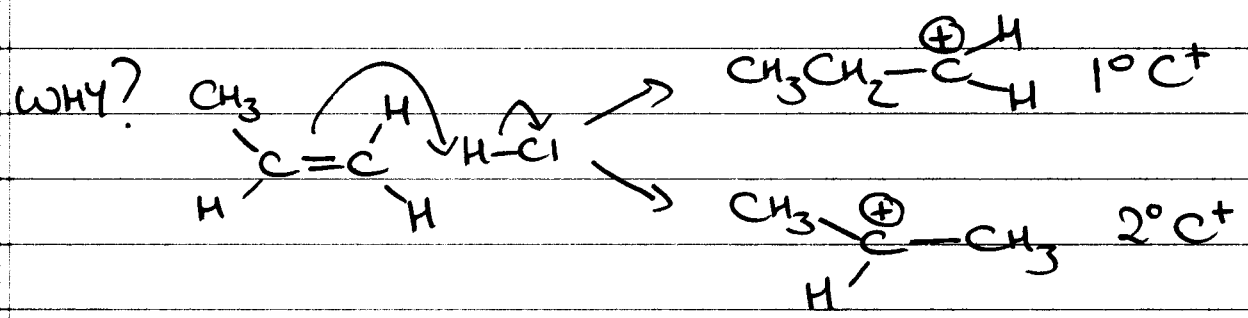
Now CONSIDER:



REGIOSELECTIVE REACTION

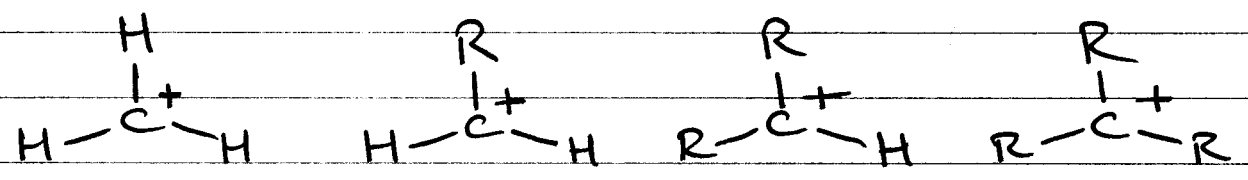
⇒ MARKOVNIKOV'S RULE

H ADDS TO DOUBLE BONDED C WITH MOST HS ALREADY ATTACHED



④ CARBOCATIONS

(stability)
R = alkyl



methyl

1°

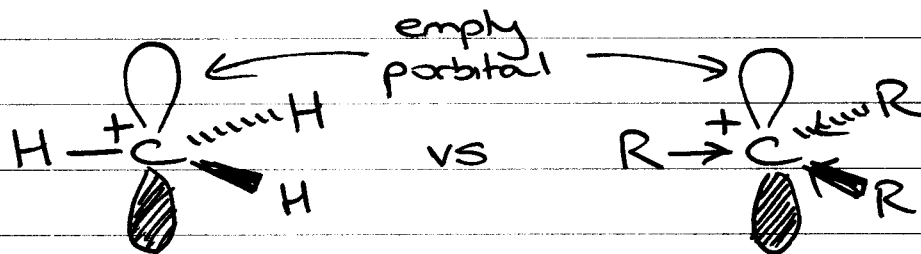
2°

3°

————— INCREASING STABILITY —————>

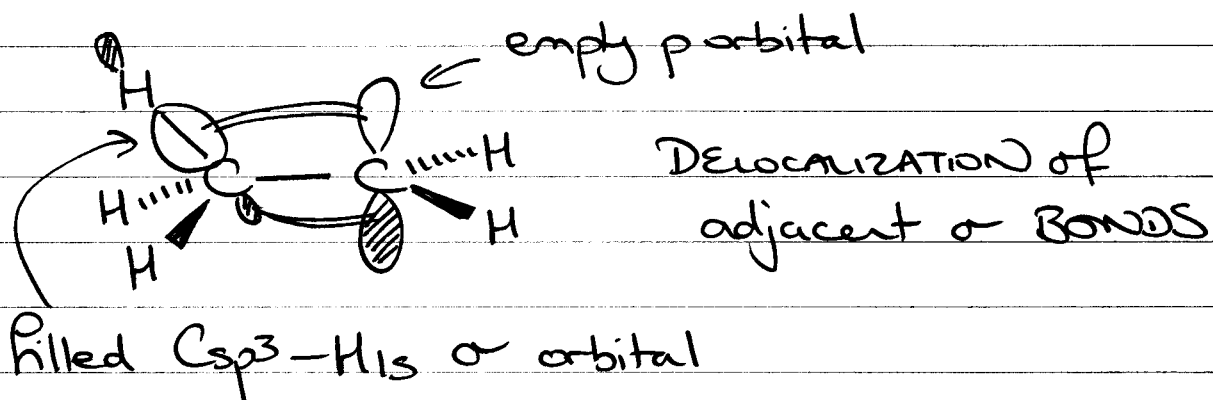
Two factors

(i) Inductive Effect



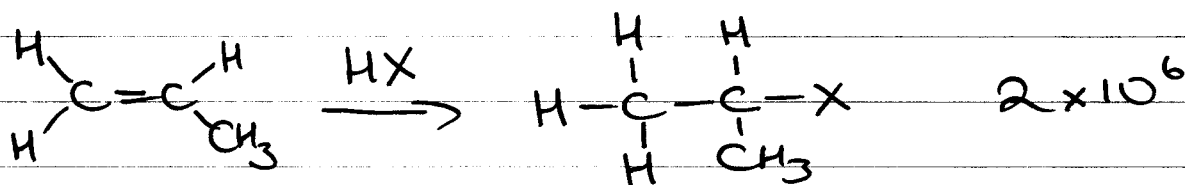
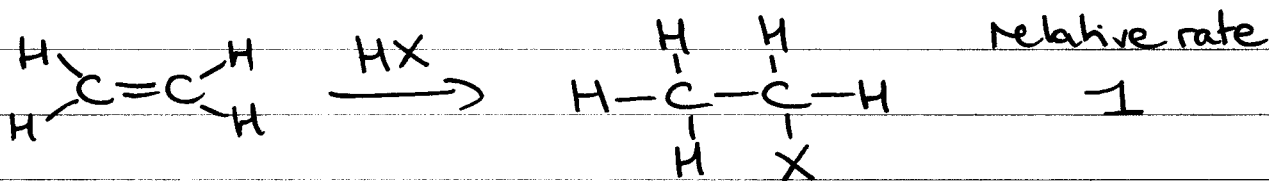
ALKYL GROUPS ARE INDUCTIVELY DONATING.

(ii) Hyperconjugation



The more C-H or C-C bonds, the more significant the stabilization, so $\text{Me}^+ < 1^\circ < 2^\circ < 3^\circ$

..... and other factors (RESONANCE)



(8)

