Lec (14) CHEM 30A May 6th

1. MECHANISMS
2. ENERGY DIAGRAMS
3. KINETICS vs THERMODYNAMICS
4. ADDITION ALKENES

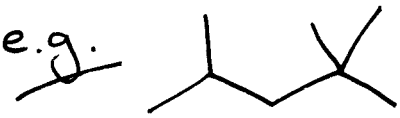
READ 6.1–6.3 PROBLEMS 6.1, 6.2 (3rd)

(1)+(2) Pages 6–8 from LEC 13

(3) KINETICS vs THERMODYNAMICS

how fast will it happen

will it happen

e.g.  + $O_2 \rightleftharpoons 8CO_2 + 9H_2O$

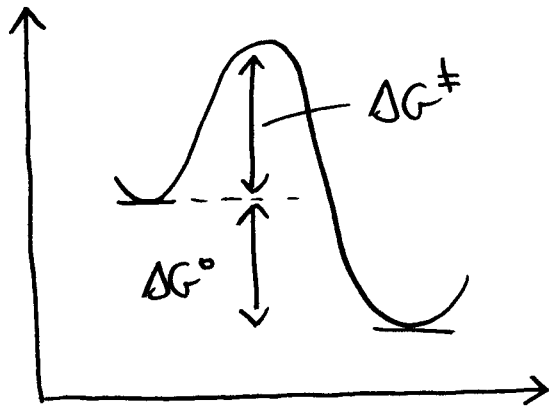
isooctane

$\Delta G^\circ = -1000\ kJ\,mol^{-1}$

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

<u>BUT</u> isooctane is stable
(you put it in your car)

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



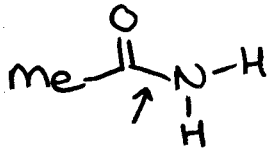
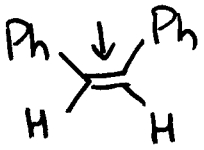
Isooctane + O_2

THERMODYNAMICALLY UNSTABLE, BUT KINETICALLY STABLE

However, apply a burst of energy to a mixture of H_2O & CO_2 will NOT reconvert to octane and oxygen

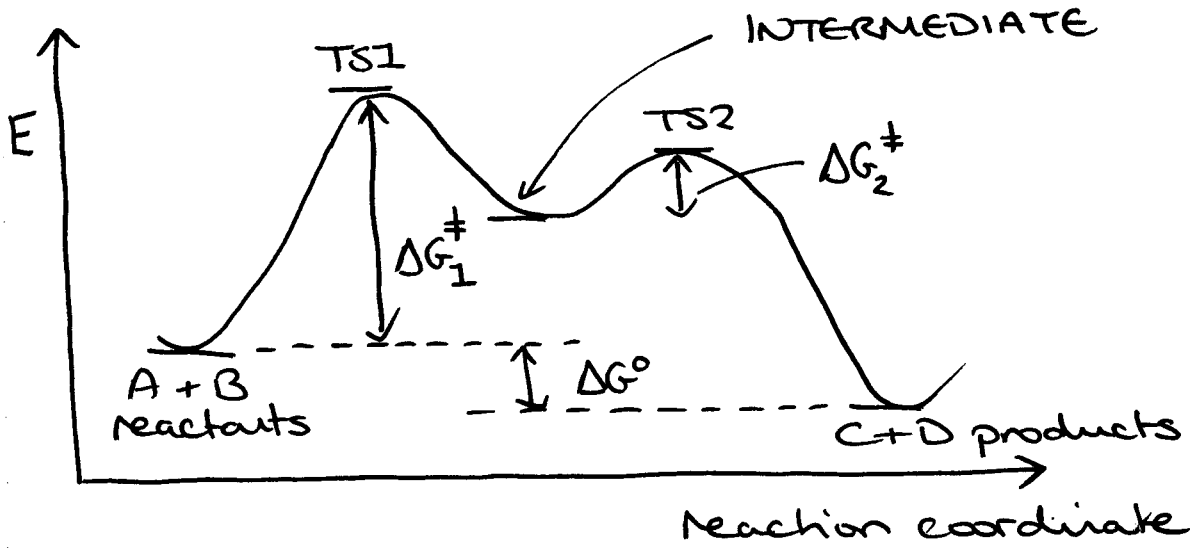
(MENTION GRAPHITE/DIAMOND)

Energy barries and rate (consider BOND ROTATIONS → some principles as reactions)

	E_A (kcal/mol)	k (s^{-1}) (298 k)	$t_{1/2}$
H_3C-CH_3	3	5×10^{10}	0.02 ns
Cl_3C-CCl_3	11	8×10^{4}	10 ps
	17	3	0.2 s
	45	2×10^{-19}	~10^{11} years

(Age of the earth ~ 4.6×10^9 YEARS)

- energy profiles ⇒ 2 STEP RXN

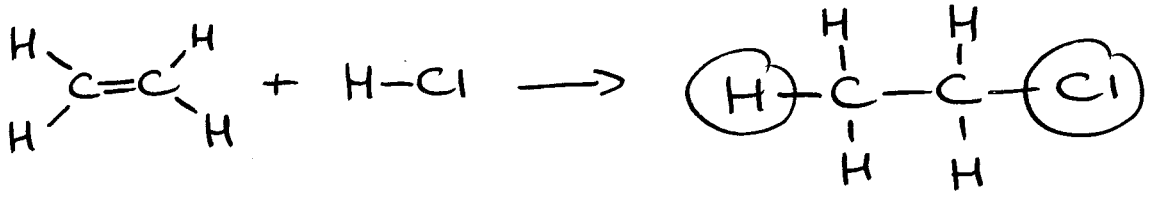


REACTION INTERMEDIATE ⇒ localized energy minimum between two TRANSITION STATES (sometimes possible to isolate)

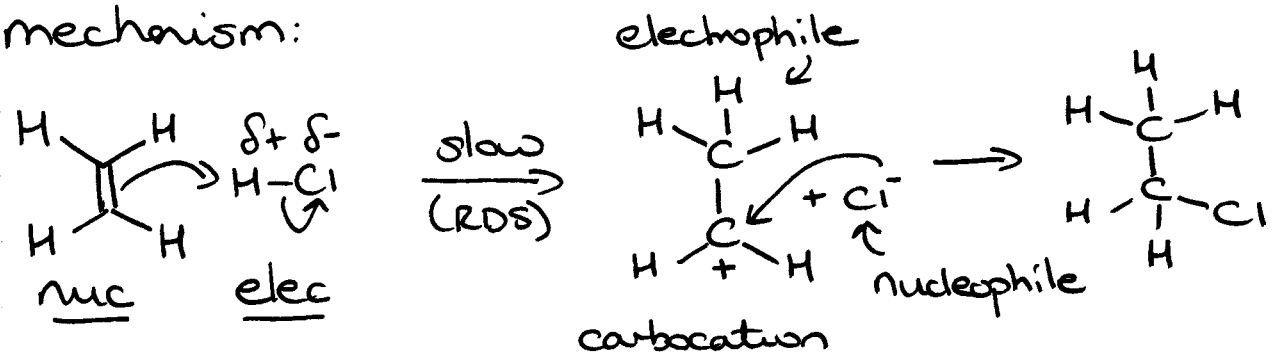
SLOWEST STEP in a multistep process (one w/ highest barrier) is called the RATE DETERMINING STEP (RDS)

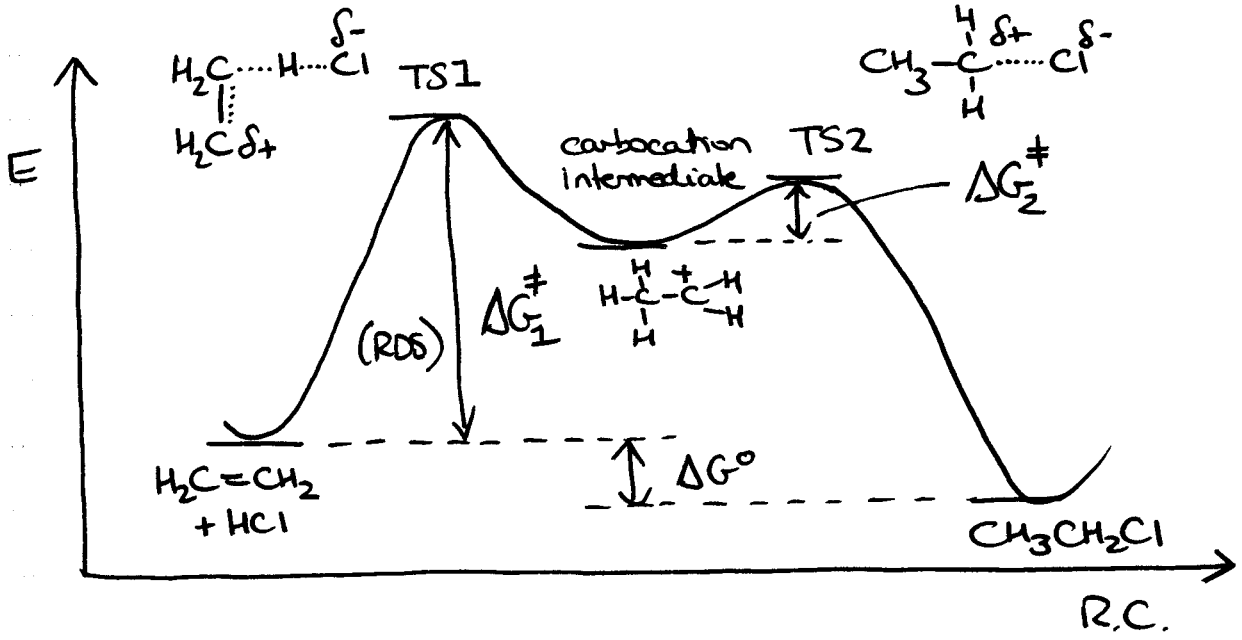
- fill RDS in on graph above

④ ELECTROPHILIC ADDITION TO ALLENES



mechanism:


δ+ δ-
H–Cl
slow
(RDS)
nuc
elec
electrophile
+ Cl⁻
nucleophile
carbocation


E
TS1
carbocation intermediate
TS2
(RDS)
ΔG₁‡
ΔG₂‡
ΔG°
H₂C=CH₂ + HCl
CH₃CH₂Cl
R.C.