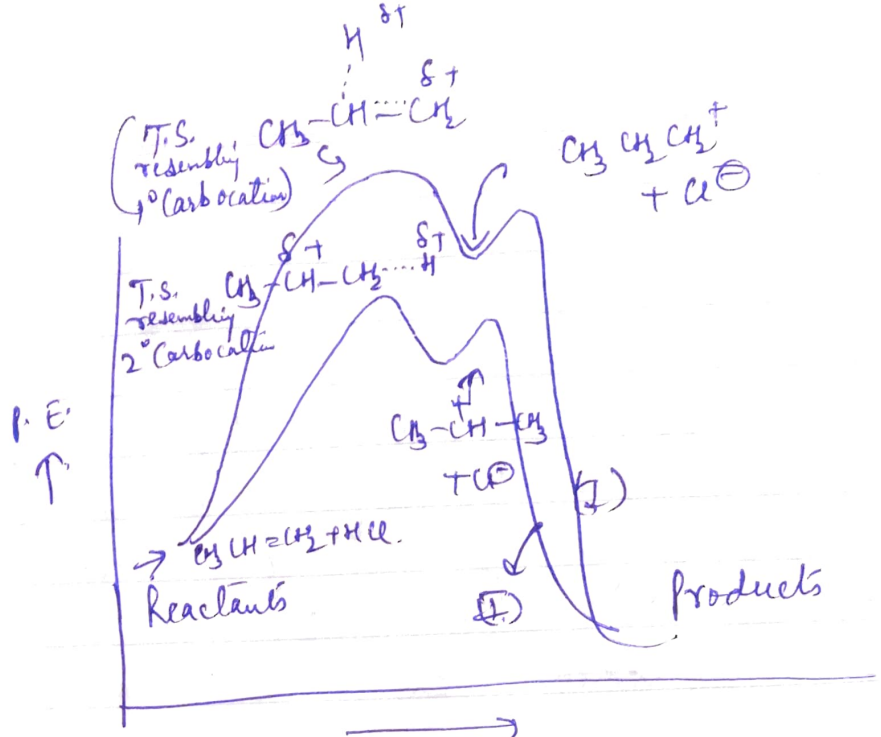
Applications of Kinetic Principles:-

HAMMOND'S POSTULATES:-

→ It states that in any individual step in a rx, geometry & structure of T.S. resembles either reactants or products or intermediate state, provided one is present.

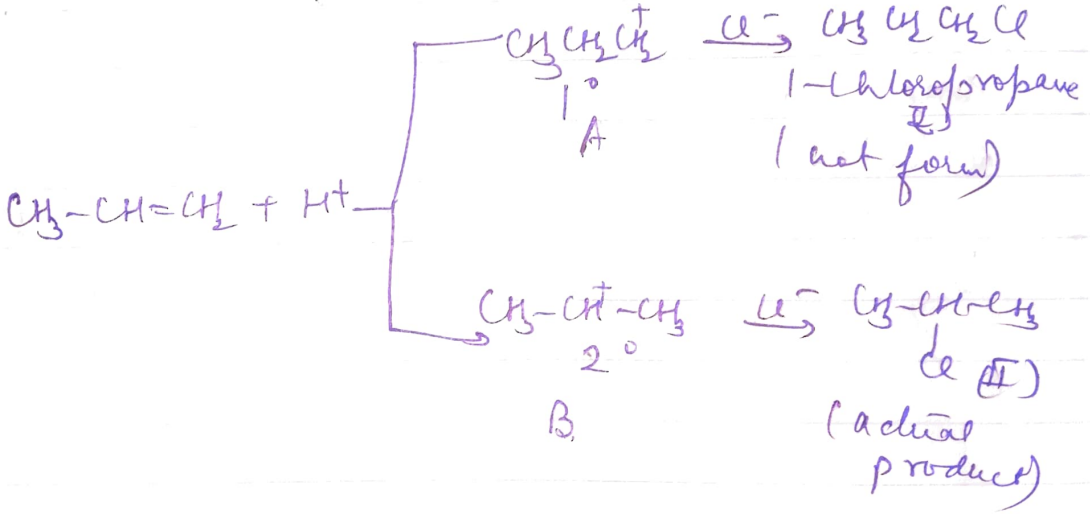
→ It depends on, ~~how~~ which one is closer in energy to TS.
For eg. In an exothermic rx., T.S. resembles the Reactants more as compared to products.

→ Considering Rx, I T.S. (rate determining) lies much closer in energy to intermediate rather than to reactants, ~~thus~~, here T.S. geometry resembles intermediate more than the reactants.
Similarly II T.S. has also free energy, closer to intermediate rather than products. Thus both T.S. resembles int. more as compared to products or reactants.



C

D



Considering Eg. → add^{n} of HCl to propylene for explaining Hammond's postulate.

→ Rate of formation of these two ions is not immediately dependent on their stabilities, but rather on relative free energies of T.S. which precede the ions.

→ T.S. of are not known, here C-H bond is partly formed..

∴ Carbocations are of relatively high free energies as compared with reactants & only a small change in energy when T.S. are tranformed into intermediate carbocations than to products.

→ Thus, only Smaller reorganization of mol. geometry from T.S. to intermediate than from T.S. to reactant;

Thus two T.S. may be represented as C & D.

→ Therefore, the factors which determine the relative stabilities of carbocations are also effective in determining relative stabilities of T.S. so that more stable of two ions is formed faster & corresponds to a lower max in energy profile.

★ Conseq

Curtin–Hammett Principle

→ proposed by David Yarrow Curtin & Louis Plack Hammett.

→ It states, that, for a rx., that has a pair of reactive intermediates or reactants that interconvert rapidly, each going irreversibly to a diff. product, the product ratio will depend, both 1) on diff in ergy b'n two conformers
2) free energy of T.S. going to each product.

→ As a result, product distribution will not necessarily reflect Eq. ~~constant~~ distribution of two intermediates.

→ This principle applies to system in a diff. products were formed from 2 substrates in eq. with one another.
Rapidly interconverting reactants can be enantiomers/diastereomers or constitutional isomers.

* Suppose A & B are conformational isomers & both are in rapid Eq. $A \rightleftharpoons B$

$$C \xleftarrow[\text{slow}]{k_1} A \underset{k_B}{\overset{k_A}{\rightleftharpoons}} B \xrightarrow[\text{slow}]{k_2} D$$
(fast)

C.–H principle tells us that C:D product ratio is not equal to A:B reactant ratio but instead, determined by relative energy of T.S.

$K_A \ll K_B$??? $k_1 \ll k_2$

$K = \frac{[B]}{[A]}$ or $[B] = K \cdot [A]$

rate of formation of Product C $\frac{d[C]}{dt} = k_1[A]$

rate of formation of Product D $\frac{d[D]}{dt} = k_2[B] = k_2 K[A]$

$$\text{Product ratio} = \frac{\frac{d[D]}{dt}}{\frac{d[C]}{dt}} \cdot \frac{\frac{k_2[B]}{k_1[A]}}{} \text{ (2)} = \frac{k_2 K[A]}{k_1[A]} = \frac{k_2 K}{k_1}$$

$$\frac{[D]}{[C]} = \frac{k_2 K}{k_1} = \frac{e^{-\Delta G_2^{\ddagger}/RT} \cdot e^{-\Delta G/RT}}{e^{-\Delta G_1^{\ddagger}/RT}}$$

$[\Delta G_1^{\ddagger} \& \Delta G_2^{\ddagger} \gg \Delta G]$

$\therefore \Delta G^{\ddagger} = \Delta G_2^{\ddagger} - \Delta G_1^{\ddagger}$

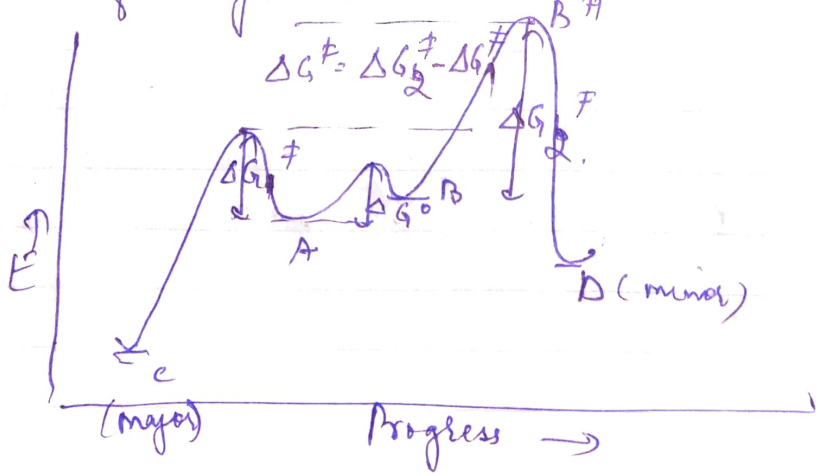
where $\Delta G^{\ddagger}$ is diff in activation energy for formation of two products

If A & B at same energy level than $\Delta G \approx 0$

$$\therefore \frac{[D]}{[C]} = e^{-\Delta G^{\#}/RT}$$

$\therefore$ Product ratio

★ → Acc to C & H → Relative amount of products formed from two pertinent conformers are completely independent of relative population of the conformers & depend only on the diff. in free energy of T.S., provided rate of Rx is slower than rate of conformational interconversion.



Thus, Product ratio is ∴ determined not by ΔG° but by relative energy of two T.S. A^* & B^*

Thus In a Rx that yields one product from one conformer & a diff. product from another conformer (& provided both are rapidly interconvertible relative to rate of product formation) while products do not interconvert, (product composition) not solely depend on relative prop. of conformers in substrate but by diff in standard Gibb's free energy of representative T.S.) Imp.

** If both conformers react at same rate, product dist. will be same as ratio of conformers at Eq.

* If major conformer is also faster reacting conformer, product from major conformer should prevail & will not reflect Eq. distribution

If minor conformer is faster reacting conformer product ratio will depend on three variables & observed product dist. will not reflect Eq. distribution.