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FRONTIER MOLECULAR ORBITAL THEORY

FMO Theory proposed by Kenichi Fukui in 1952, explains whether a pericyclic reaction is allowed or not under given set of reactions condition based on interactions between Frontier molecular orbitols (FMO) like HOMO, LUMO and SUMO.

HOMO = Highly Occupied Molecular Orbital
LUMO = Lowest Unoccupied Molecular Orbital
SOMO = Singly Occupied Molecular Orbital

The interaction b/w one FMO of one molecule with one FMO of another molecule result in two types of new molecular orbitals (MOs) i.e, bonding and antibonding. The bonding orbitals possess low energy, whereas the antibonding orbitals possess higher energy.

If both of these resulting MOs are filled with electrons, the bonding interaction is concelled by the antibonding interaction. Hence the net result is no bonding between molecules.

However, if only bonding orbital are filled with electrons, the two molecules attract with each other.

* Interaction b/w HOMO & LUMO causes repulsion ie, no bonding interaction since both bonding & antibonding MOs are filled with electrons.

* Interaction b/w HOMO & LUMO cause attraction i.e, bonding interaction, since only the bonding MO is filled with electrons.

* Interaction b/w LUMO & LUMO cause neither attracti nor repulsion since all the MOs are empty.

* Interaction of SOMO with either HOMO or LUMO or another SUMO also cause attraction between interacting species.

The effects of interactions b/w frontier molecular orbital is summarized in the following table.

Interacting Frontier Molecular Orbital	Types of Interaction
HOMO + HOMO	No bonding
HOMO + LUMO	Attraction – Bonding
LUMO + LUMO	No electrons, – No bonding
SOMO + HOMO	
SOMO + LUMO	Attraction – Bonding
SOMO + SOMO	

WOODWARD – HOFFMANN RULES:

To predict whether a pericyclic reaction is allowed or not under given condition, Woodward and Hoffmann proposed following set of rules based on conservation or symmetry Orbital symmetry concept.

A Thermal pericyclic reaction is allowed in the ground state, when the total number of $(4q+2)_s$ & $(4r)_a$ components is odd.

otherwise, If the total of $(4q+2)_s$ and $(4r)_a$ components is even, the pericyclic reaction is allowed in the excited state. i.e, under photochemical reaction.

Number of $(4q+2)_s$ and $(4r)_a$ components	The condition under which the reaction is allowed.
odd	Thermal
Even	Photochemical

Component:- A bond(s) or an orbital(s) taking part in the pericyclic reaction as a single unit can be considered as a component. It can have any number of electrons but may not have mixture of π and σ electrons.

Eg:- A double bond is considered a π^2 component, since there are two π electrons.

A conjugated diene can be considered π^4 component since there are four π electrons.

'S' → Suprafacial. A suprafacial component forms new bonds on the same face at its both ends. In some cases suprafacial is equivalent to "dis-rotation."

'a' → Antrafacial. An antrafacial component forms new bonds on the opposite faces of its both ends. In some cases antrafacial is equivalent to "con-rotation."

$\pi^2{}_s$ represents a component containing two π electrons and forming new bonds in suprafacial manner.

$\pi^4{}_a$ represents a components containing four π electrons and is going to form new bonds in antrafacial manner.

---

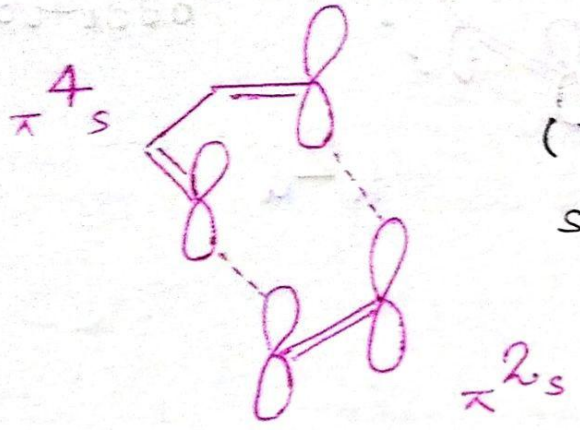
q & r:

$(4q+2)_s$ component:- The suprafacial component which may have either 2 or 6 or 10 or -- electrons of same type. These no are obtained by substituting 'q' by 0 or 1 or 2 or ----

$(4r)_a$ component :- The antrafacial component, which may have either 4 or 8 or 12 or electrons of same type. These no. are obtained by substituting 'r' by 1 or 2 or 3 -----.

Application:-

Let us assume the diene and dienophile in Diels-Alder reaction are approaching suprafacially as shown below:-



(Thermally allowed suprafacial addition)

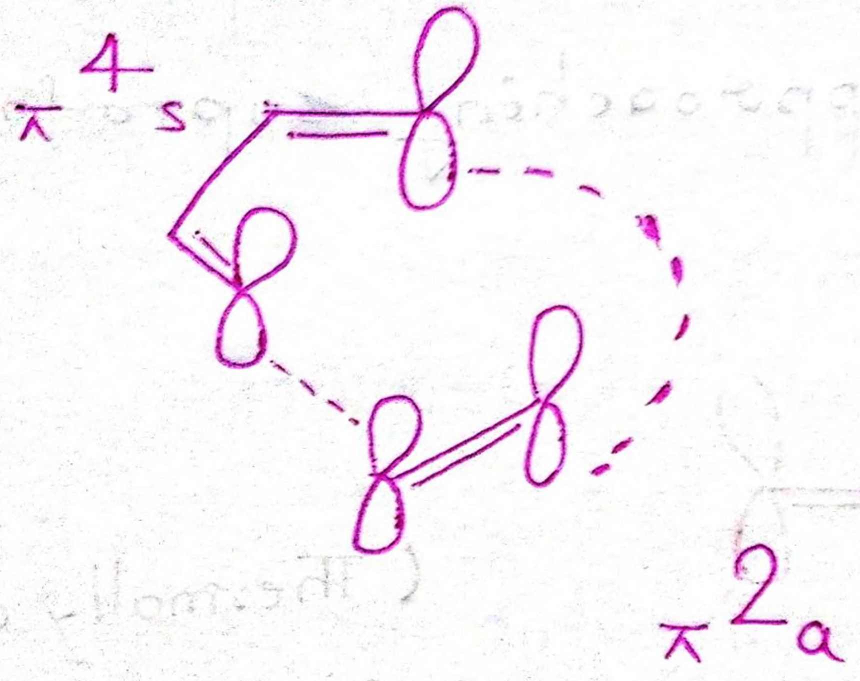
#Since there are 4π electrons in diene, which is making bonds in suprafacial manner it is a $(4q+2)_s$ component i.e, there is one $(4q+2)_s$ component.

#And the alkene is a $(4r)_s$ component, since it has 2π electrons and is approaching the diene suprafacially ie, there are no $(4r)_a$ components.

Hence, the total no. of $(4q+2)_s$ and $(4r)_a$ components $= 1 + 0 = 1$, an odd number.

Therefore, Diels-Alder reaction is thermally allowed in ground state when both the components are approaching suprafacially. Hence it is termed as ${}_{\pi}4_s + {}_{\pi}2_s$ cycloaddition.

Antrafacial addition, for this reaction, is not allowed under photochemical conditions in the excited state. However the strain in the transition state while doing so forbids to do so.



(Photochemically &
Allowed antrafacial
addition)

LINEAR FREE ENERGY RELATIONSHIPS

HAMMETT EQUATION

The Hammett equation is a Linear Free Energy Relationship (LFER) which attempts to explain the structural effects on reactivity quantitatively.

It can be written as–

$$\log \frac{K}{K_o} = \rho\sigma \qquad ①$$

where,

K = Equilibrium constant for reactions involving substituted benzoic acid.

K_o = Equilibrium constant for reactions involving un-substituted benzoic acid.

ρ = Hammett reaction constant

σ = Hammett substituent constant.

Hammett proposed this equation for reactions involving meta and para substituted benzoic acids - (XC_6H_4COOH, where X = either electron withdrawing or electron donating substituent) and their derivates (XC_6H_4Y, where Y = group like ester).

It is also valid for related reactions of phenols, aryl amines. However, modifications may be needed to account for reactions involving other substrates or substituents at ortho position.

In case of ortho substituents, steric factors may complicate the relation.

The Hammett equation can be written as:

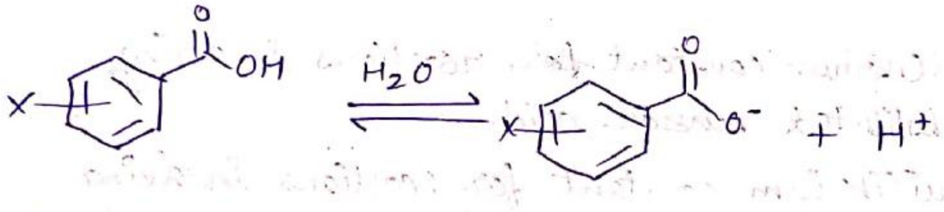
$$\log \frac{k}{k_o} = \rho\sigma \qquad ②$$

where, k = rate constant for the reaction involving substituted benzoic acid.

k_0 = rate constant for the reaction involving unsubstituted benzoic acid.

Hammett substituent constant, σ

The value of ρ was set at 1 for ionization of benzoic acids in water at 25°C.



$\therefore$ Equation 1 can be written as –

$$\log \frac{K}{K_0} = \sigma \quad \text{③}$$

i.e. σ is the ratio of ionization constants of substituted to un-substituted benzoic acids.

Thus, it is possible to get σ values from the acid dissociation constants of benzoic acids.

Case 1. $\sigma = 0$.

It is when $\log K = \log K_0$

i.e. the substituent has no effect on the acidic strength of benzoic acid. It is electronically same as H.

Case 2. $\sigma = +ve$

It is when $\log K > \log K_0$

i.e. the substituent is of EWG type and increases the acidic strength of benzoic acid.

e.g. substituent like $-NO_2$, $-CN$, – halo, COR, CO_2R, etc.

Case 3. $\sigma = -ve$.

It is when $\log K < \log K_0$
i.e. the substituent is of EDG type and decreases the acidic strength of benzoic acid.

e.g. substituents like $-CH_3$, $-C_2H_5$, etc.

Note: The ionization constants or acid dissociation constants measure the acidic strength of acids.
Electron withdrawing groups (EWG) increase the acidic strength of benzoic acids, whereas electron donating groups (EDG) decrease the strength.

Thus, the parameter σ actually represents how electron donating or electron withdrawing a group is relative to H (i.e. unsubstituted).

σ_p and σ_m

The σ value also depends on the position of substituent relative to $-COOH$ group. Hence, for para and meta substituents the values are different and are denoted by σ_p and σ_m respectively.

σ_I and σ_R

σ values are actually the numbers which sum up the total electronic effects (polarization and resonance) of a substituent attached to a benzene ring. It can be expressed as a sum of two position - independent parameters, σ_I and σ_R, which measure the polar and resonance effects of the substituent, respectively.

According to Taft,
the σ_p and σ_m are related to σ_I and σ_R as follows:

$$\sigma_p = \sigma_I + \sigma_R$$

$$\sigma_m = \sigma_I + 0.33\sigma_R$$

Note: The resonance effect at meta position is not zero, because the substituent can donate or withdraw electrons to or from the positions ortho to the reacting group, from which the effect can be passed on by inductive and/or field mechanisms.

From the above equations, we can also approximate to

$$\sigma_R = 1.5(\sigma_p - \sigma_m)$$

$$\sigma_I = \sigma_p - \sigma_R = 1.5\sigma_m - 0.5\sigma_p$$

Substituents operating through polarization of sigma bond (inductive effect) are more effective when they are at meta position due to proximity, whereas, those operating through conjugation are more effective in para position.

It is also observed that above mentioned electronic effects i.e. polarization and conjugation may operate in same direction or in opposite directions.

1> σ_p and σ_m values for $-NO_2$ group are 0.77 and 0.73 respectively, which ~~suf~~ suggests electron withdrawal occurs mainly through conjugation.

2> σ_p and σ_m values for $-Cl$ group are 0.22 and 0.37 respectively, which suggests inductive withdrawal of electrons.

3> σ_p and σ_m values for $-NH_2$ group are -0.62 and 0 respectively. The negative σ_p value is because of electron donation by $-NH_2$ group through conjugation, which is only possible when it is at para position. However, at meta position, no conjugation is possible.
Hence, $\sigma_p < \sigma_m$.

4> σ_p and σ_m values for $-OMe$ group are -0.29 and 0.11 respectively. The negative value for σ_p is because of electron donation through conjugation. However, when it is at meta position electron withdrawal effect is more important and hence σ_m is positive.

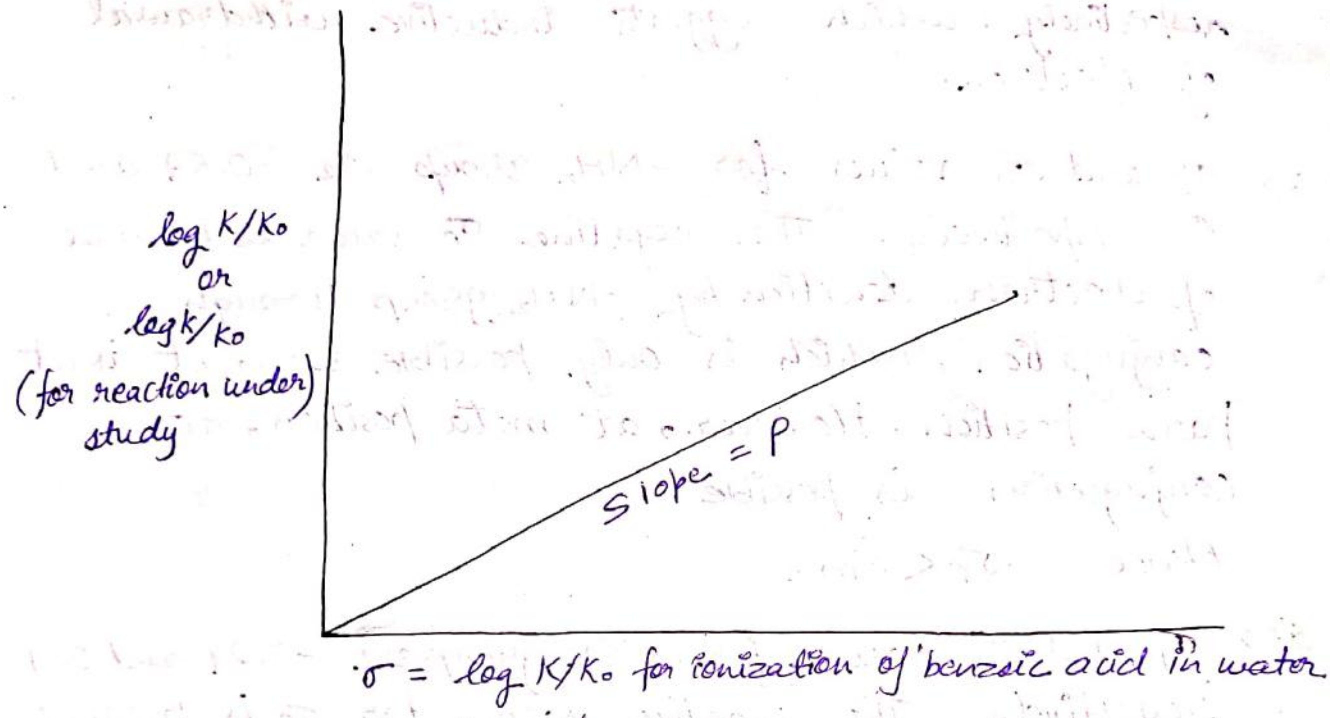
Applications:

→ It is possible to get ρ values for other reactions, once a set of σ values was obtained by measuring acid dissociation constants for benzoic acids with different substituents.

→ From the ρ value thus calculated and the knows σ values for other groups, it also possible to predict the rates of reactions that have not yet been run.

Importance of Hammett Reaction Constant, ρ

→ The graphical representation of Hammett equation is shown below :



* The gradient of the curve, ρ is specific for a given reaction. It is determined by plotting log (K/K₀) or log (k/k₀) values for a given reaction carried out with different substituents against σ values of those substituents.

* ρ is known as Hammett reaction constant that measures the sensitivity of the reaction to electronic effects. It may have positive or negative values.

* A positive ρ value indicates more negative charge density nearer to the ring (or on the ring) in the transition state than in the reactant.

- A negative value indicates less negative charge (more positive charge) density in the transition state.

- Reactions with positive ρ values are helped by electron withdrawing groups i.e., rates are increased with the introduction of EWG on the ring.
  → It is because of development of negative charge on the ring or nearer to the ring in the transition state.
  → Recall that the negative charge is stabilized by electron withdrawing groups.

- Rates of reactions with negative ρ values increase with the introduction of EDG on the ring.
  → It is because of development of positive charge on the ring or nearer to the ring in the ring in transition state.
  → Recall that electron donating groups stabilize positive charge.

Note: It is very important to compare the relative charge density on the transition state with that on the reactant rather than the absolute charge.

- The magnitude of ρ is ~~almost~~ an indicator of extent of charge development in the transition state.
  → For example, the reactions involving the formation of carbocations have strongly negative ρ values.

- Thus, it is possible to predict the mechanisms of reactions from ρ values.

KINETIC ISOTOPE EFFECT

In physical organic chemistry, a kinetic isotope effect (KIE) is the change in the reaction rate of a chemical reaction when one atom in the reaction is replaced by one of its isotope.

Formerly, it is the ratio of rate constants for the reactions involving the light (k_L) and the heavy (k_H) isotopically substituted reactants (isotopologous).

$$\boxed{KIE = \frac{k_L}{k_H} \quad \text{or} \quad KIE = \frac{k_H}{k_D}} \text{———} ①$$

where, k_H is the rate with substrate containing H (^1H) and k_D with deuterium (^2H).

This change in reaction rate is a quantum mechanical effect that primarily results from heavier isotopologues having lower vibrational frequencies compared to their lighter counterparts.

The study of kinetic isotope effect can help the elucidation of the reaction mechanism of certain chemical reaction and is occasionally exploited in during development to improve unfavourable pharmacokinetics

The kinetic isotope effect is considered to be one of the most essential and sensitive tools for the study of reaction mechanism, the knowledge of which allows the improvement of the ~~dri~~ desireable qualities of the corresponding reactions.

For example:- Kinetic isotope effects can be used to reveal whether a nucleophilic substitution reaction follows a Unimolecular (SN^1) or Bimolecular (SN^2) Pathway.

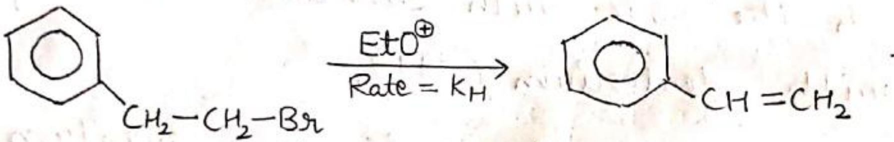
Primary Kinetic Isotope Effects

$\because$ KIE = $\frac{k_H}{k_D}$

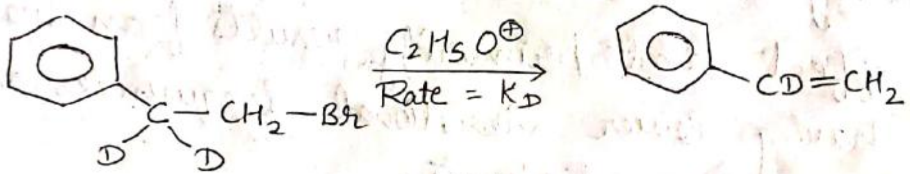
Changing H for D can effect the rate of the reaction only if that H (or D) is involved in the rate-determining step. In this case, the ratio k_H/k_D is known as

Primary Kinetic Isotope Effect

e.g:- The rates of these two reaction (eqⁿ ② & ③) can be compared and k_M/k_D turns out to be 7.1 at 25°C.



②



③

- The kinetic effect tells us that the C-H or C-D bond is broken during the rate determining step.

Vibrational frequency of a bond (C-H) is given by -

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{K(m_1+m_2)}{m_1 m_2}} \quad \text{———} \quad ④$$

where, k = the force constant for the bond C-H (or C-D)
m_1 = mass of carbon atom
m_2 = mass of hydrogen (or deuterium atom)
and ν = vibrational frequency of the bond

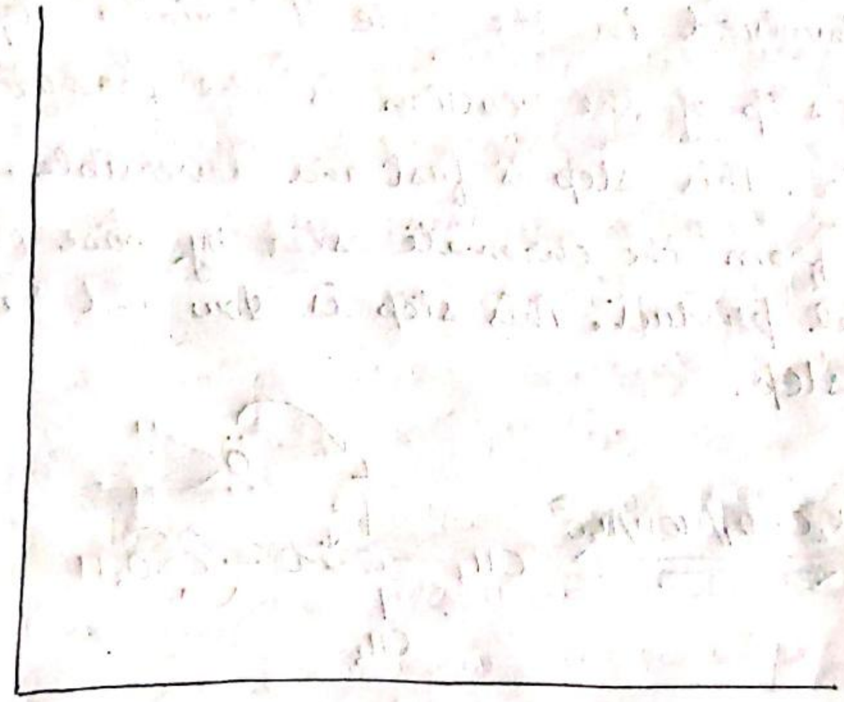
- The bond energy, therefore, depends upon the frequency of the vibration, which depends on reduced mass of the two atoms which form the bond.

Consequently, the energies of protium and deuterium analogous in the same vibrational state are different.

- Due to greater mass of deuterium, the vibrational energy of a C-H bond is greater than that of a C—D bond.

Hence less energy is required to break a C-H bond than a C-D bond.

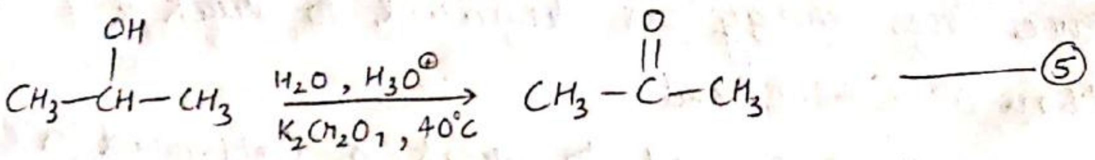
- The energy required to break a C-H bond is less than that of required to break a C-D bond. So, reaction involving breaking of C-H bonds go faster than those breaking C-D bonds, provided that bond breaking is occuring in the rate determining step.



- Since, differences in vibrational energy b/w C-H and C-D bonds decreases with increasing temperature, k_H/k_D ratio falls as the temperature of reaction rises.
- The ratio is much smaller (but always greater than 1) for weakening or partial cleavage of a C-D bond Very small values indicates no primary kinetic isotope effect.
- The primary kinetic isotope effect has proved extremely useful in deciding the finer details of many mechanism.

For example.

i) Oxidation of 2-propanol with acidified potassium dichromate.


$$CH_3-\overset{OH}{\overset{|}{C}H}-CH_3 \xrightarrow[K_2Cr_2O_7,\ 40^\circ C]{H_2O,\ H_3O^\oplus} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \quad ⑤$$

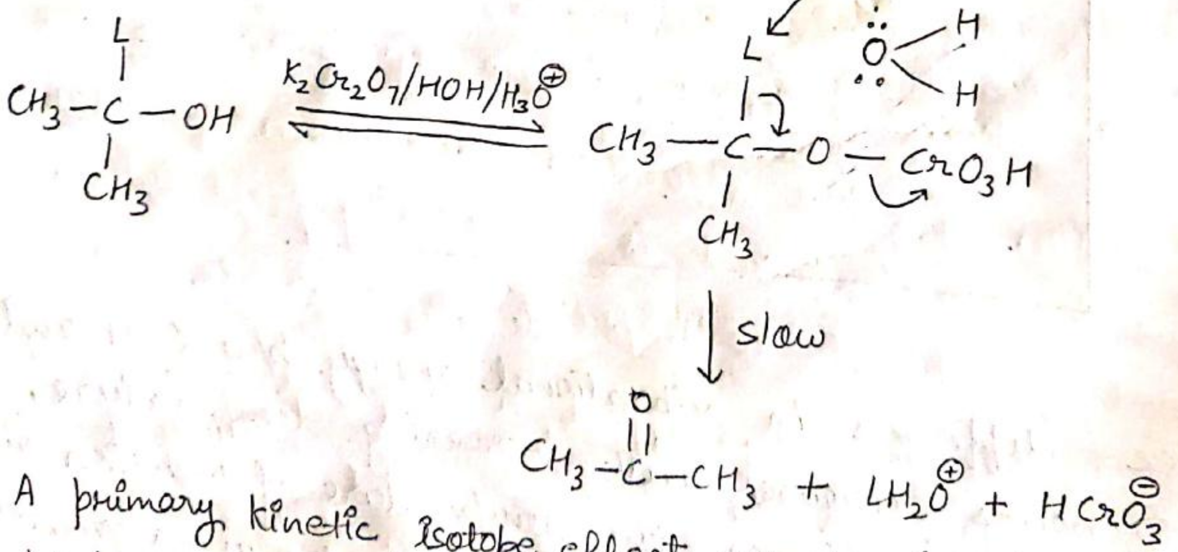
$$k_H/k_D = 5.9$$

The rate of reaction will be given by -

$$Rate = k[HCrO_4^\ominus][H^\oplus]$$

- Primary kinetic isotope effect confirmed that C-H bond breaking is involved in the rate determining step.

The first step of the reaction is the formation of Chromate ester. This step is fast and reversible. Proton is removed from the chromate ester by base (H_2O) to give the final product. This step is slow and rate determining step.



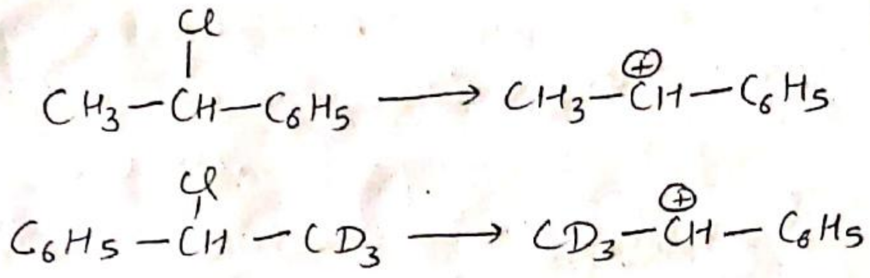
- A primary kinetic isotope effect may be found when a bond to the isotopically labeled atom is being formed or broken.

Secondary Kinetic Isotope Effect

- A second kinetic isotope effect is observed when no bond to the isotopically labelled atom in the reactant is broken or formed.
- Secondary kinetic isotope effects tend to be much smaller than primary kinetic isotope effect and are still very useful for elucidating reaction mechanism.
- Isotope effect may also be observed when the substituted hydrogen atom is not directly involved in the reaction. Such effects are called secondary kinetic isotope effects. and are usually in the range of $k_H/k_D = 0.7$-
- Secondary isotope effects may be normal ($k_H/k_D > 1$) or inverse ($k_H/k_D < 1$). They are also classified as α or β, depending on the location of the isotopic substitution with respect to the reacting carbon. Secondary isotope effect result from a tightening or loosening of a C–H bond at the transition state. The strength may change because of hybridisation change or a change in the extent of hyperconjugation.
- Secondary isotope effects at the β-position have been specially studied in nucleophilic substitution reactions.
- When carbocations are involved as intermediates, substantial β-isotope effects are observed. This is because the hyperconjugation stabilisation by the β-hydrogens weakens the C–H bond.

For example- $k_M/k_D = 1.15$ for solvolysis of 1-chloro-1-phenyl ethane in 50% aqueous ethanal at 25°C.

Here, the C-Cl bond breaks to form the carbocation which is stabilised by hyperconjugation, by H or D.



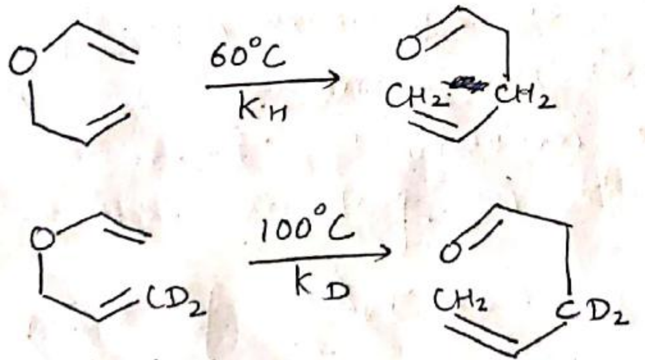
$$CH_3-\overset{Cl}{\overset{|}{C}}H-C_6H_5 \longrightarrow CH_3-\overset{\oplus}{C}H-C_6H_5$$

$$C_6H_5-\overset{Cl}{\overset{|}{C}}H-CD_3 \longrightarrow CD_3-\overset{\oplus}{C}H-C_6H_5$$

Heavier D stabilises the carbocation less effectively than H. Hence the fall in reaction rate.

- The range of α-deuterium isotope effect for SN^2 rxn. is 0.87 to 1.08, which is significantly lower than that for SN^1 reaction.

- In Cope Rearrangement, Secondary Deuterium isotope effect is observed due to conversion of sp^2 hybrid carbon into sp^3 hybrid carbon in the transition state.



$$\boxed{\frac{k_H}{k_D} = 0.976}$$

- Secondary deuterium isotope effect is also observed in nucleophilic addition reaction of carbonyl compounds. In these species, this effect is due to the conversion of sp^2 hybrid carbon into sp^3 hybrid carbon.

Heavy Atom Isotope Effect

An isotope effect due to isotopes other than those of hydrogen is known as Heavy Atom Isotope Effect.

For ex- Isotope effects with elements heavier than carbon

Interpretation of carbon isotope effect are usually complicated by simultaneously forming and breaking bonds to carbon.

Even reaction that involve only bond cleavage from the carbon, such as SN' reaction, involve strengthening of the remaining bonds to carbon. In many such reactions, leaving group isotope effects tend to be easier to interpret.

For ex:- Substitution and elimination reaction in which chlorine acts as a leaving group are convenient to interpret, especially since chlorine acts as a monoatomic species with no internal bonding to complicate the reaction coordinate and it has two state isotopes, ^{35}Cl and ^{37}Cl, both with high abundance.

The major challenge to the interpretation of such isotope effects is the solvation of the leaving group. Isotope effects are determined through complementary studies on a series of isotopers.

Accordingly, it is quite useful to combine hydrogen isotope effects with heavy-atom isotope effects.

For instance, determining nitrogen isotope effect along with hydrogen isotope effect ~~along with~~ was used to show that the reaction of 2-phenylethyltrimethylammonium ion with ethoxide in ethanol at 40°C follows an E^2 mechanism, as opposed to alternative non-concerted mechanism. This conclusion was reached upon showing that this reaction yields a nitrogen isotope effect, k_{14}/k_{15}, of 1.0133 to 0.0002 along with a hydrogen kinetic isotope effect of 3.2 at the leaving hydrogen.

Similarly, combining nitrogen and hydrogen isotope effect was used to show that syn elimination of simple ammonium salts also follow a concerted mechanism.

- A thumb rule for heavy atom isotope effect is that the maximum isotopic rate ratio is proportional to the square root of the inverse ratio of isotopic masses.

$$\boxed{\frac{k_{32}}{k_{34}} = \sqrt{\frac{34}{32}}}$$

SOLVENT EFFECTS IN REACTIONS

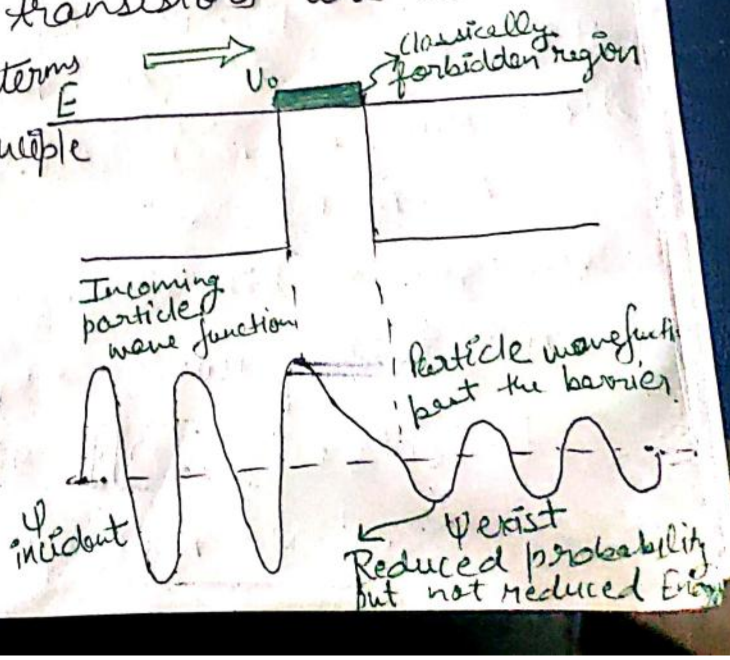
Reaction may be affected by the type of solvent used. (for example - H_2O to D_2O or ROH to ROD).

There are three main solvent effects in reactions -

- The solvent can act as a reactant resulting in a primary isotope effect.
- Rapid hydrogen exchange can occur b/w substrate molecules labeled with deuterium and hydrogen atoms in the solvent. Deuterium may change positions in the molecule resulting in the RDS of the reaction.
- The nature of solvent and solute interactions may also change with differing solvents. This could change the energy of the transition state and result in a secondary isotope effects.

TUNNELING EFFECT

- Tunneling is the Quantum mechanical phenomenon where a subatomic particle passes through a potential barrier that is it cannot surmount under the provision of classical mechanics.
- Quantum tunneling plays an essential role in several physical phenomena, such as the nuclear fusion that occurs in main sequence stars like the Sun.
- It has important applications in the tunnel diode, quantum computing and in scanning tunneling microscope. The effect is predicted in the early 20th century, and its acceptance as a general physical phenomenon came mid-century.
- Fundamental quantum mechanical concepts ~~art~~ are central to this phenomenon, which makes quantum tunneling one of the novel implications of quantum mechanics. Quantum tunneling is projected to create physical limits to the size of the transistors used in microprocessors, due to electrons being able to tunnel past them if the transistors are too small.
- Tunneling is often explained in terms of the Heisenberg uncertainty principle that the quantum object can be known as a wave or as a particle in general.



ENTHALPY

The enthalpy of a thermodynamic system is defined as

$$\boxed{H = U + PV}$$

where, H is enthalpy
U is the internal energy of the system
P is pressure and
V is Volume of the system.

- Enthalpy is an extensive property.
- This means that, for homogenous systems, the enthalpy is proportional to the size of the system.
- It is convenient to introduce the specific enthalpy.

$h = \frac{H}{m}$, where m is the mass of the system or

the Molar Enthalpy $H_m = \frac{H}{n}$, where, n is the no. of moles. (h and H_m are intensive properties).

- For inhomogenous system, the enthalpy is the sum of the enthalpies of the composing subsystems:

$$H = \sum_K H_K ,$$

where, H is the total enthalpy of all the subsystems.
K refers to the various subsystems.
H_K refers to the enthalpy of each subsystem.
$\sum_K H_K$ refers to the sum of the enthalpies of all subsystems.

Enthalpy Of Vapourisation

When a liquid evaporates it absorbs some heat from the surroundings. Thus, evaporation of a liquid is accompained by increase in enthalpy. The increase for the evaporation of 1 mole of water at 25°C is 40.70kJ.

We may express this result in the form of a thermochemical equation:

$H_2O(l) \longrightarrow H_2O(g)$ $\Delta H_{vap} = +40.70$ kJmol⁻¹

When vapours condense to liquid state, they give out (evolve) heat. Thus, condensation of vapours is accompained by decrease in enthalpy.

Therefore, we may write -

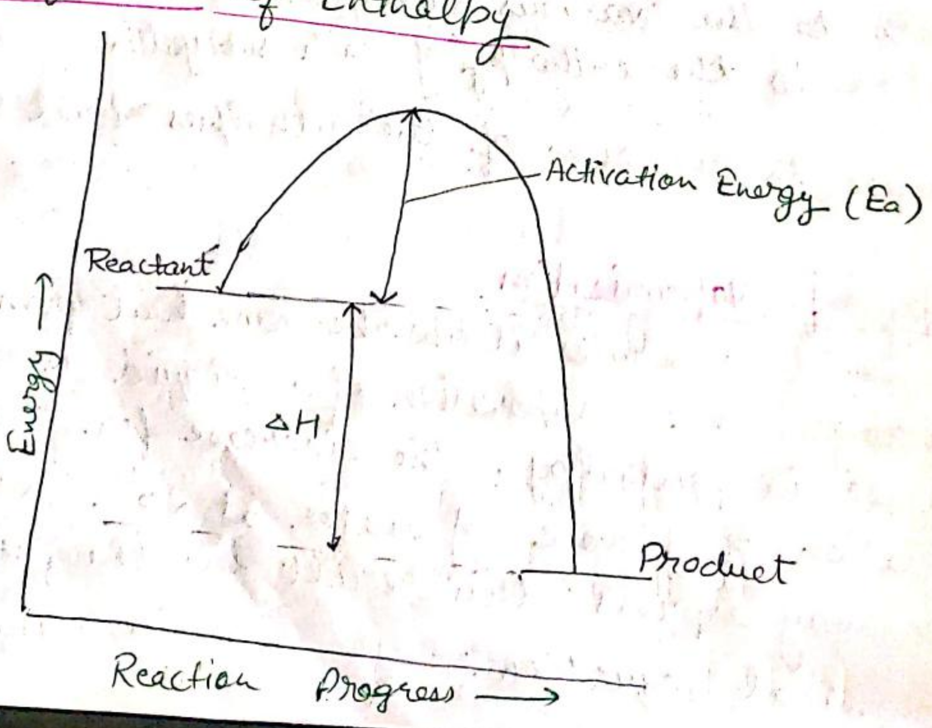
$H_2O(g) \longrightarrow H_2O(l)$ $\Delta H = -40.70$ kJmol⁻¹

The change in Enthalpy (ΔH), when a liquid changes into vapour state or when vapour change into liquid state, is known as Enthalpy Of Vapourisation.

Enthaalpy Of Fusion

When a solid melts and change into liquid state, it abstracts heat. On the contrary, when a liquid freezes and changes into solid state, & it gives out heat. In the first case, enthalpy of the system increases. In the later case, the enthalpy of the system decreases. The change in enthalpy for this type of phase-transformation is known as Enthalpy of Fusion.

Significance Of Enthalpy



Enthalpy is important because it tells us how much heat (energy) is in a system. Heat is important because we can extract useful work from it.

In terms of a chemical reaction, an enthalpy change tells us how much enthalpy was lost or gained, enthalpy means the heat energy of the system.

GIBB'S FREE ENERGY

The energy associated with a chemical reaction that can be used to do work.

The free energy of a system is the sum of its enthalpy (H) and product of temperature (in Kelvin) and the entropy (S).

$$G = H - TS$$

The Gibb's free energy of a system at any moment in time is defined as the enthalpy of the system

The Gibb's free energy is a state function.

ARRHENIUS EQUATION

Van't Hoff showed that the value of equilibrium constant changes with temperature. On this basis, he suggested that the logarithm of the specific reaction rate must be a linear function of the reciprocal of absolute temperature.

Arrhenius extended this suggestion and gave his own hypothesis.

According to this, ~~all~~

1) All molecules of a system cannot take part in a chemical rxn.
2) It is only a certain number of molecules which react. These reacting molecules are known as active molecules.
3) The molecules which do not take part in the chemical reaction are known as passive molecules.
4) An equilibrium exist b/w active and passive molecules i.e.,

$$M\ (\text{active}) \rightleftharpoons M\ (\text{passive})$$

When temperature is raised, the above equilibrium shifts to the left. This increased the no. of active molecules which are ready to take part in a reaction.

Thus, the increase in reaction rate with increase in temperature is due to an increase in the number of active molecules not due to the number of collisions.

So, the basic concept of Arrhenius theory is that the passive or non-active molecules become active due to the absorption of heat energy.

Derivation :- Consider the following reversible rxn.

$$A + B \rightleftharpoons C + D.$$

Rate of forward rxn, $r_f = k_1 [A][B]$

Rate of backward rxn, $r_b = k_2 [C][D]$

At equilibrium, $r_f = r_b \Rightarrow k_1 [A][B] = k_2 [C][D]$

$$k_c = \frac{k_1}{k_2} = \frac{[C][D]}{[A][B]} \quad \text{———} ①$$

From thermodynamics, Van't Hoff Equation is

$$\boxed{\frac{d \ln k_c}{dT} = \frac{\Delta E}{RT^2}}$$

, where ΔE is the heat of reaction, k_c is the equilibrium constant.

As $k_c = k_1/k_2$, where k_1 and k_2 are the rate constants of the forward and the backward reaction, respectively. Eqⁿ ① becomes,

$$\frac{d \ln k_1 - d \ln k_2}{dT} = \frac{\Delta E}{RT^2} \quad \text{or} \quad \frac{d \ln k_1}{dT} - \frac{d \ln k_2}{dT} = \frac{\Delta E}{RT^2}$$

The heat of reaction ΔE may be written as $E_1 - E_2$.

and then $$\frac{d \ln k_1}{dT} - \frac{d \ln k_2}{dT} = \frac{E_1}{RT^2} - \frac{E_2}{RT^2}$$

If E_1 and E_2 are assumed to be characteristics of the forward and backward reactions only, then,

$$\left.\begin{aligned} \frac{d \ln k_1}{dT} &= \frac{E_1}{RT^2} + I \\ \frac{d \ln k_2}{dT} &= \frac{E_2}{RT^2} + I \end{aligned}\right\}$$

It has been found that I is independent of temperature and is equal to zero.

So, we can write, $$\boxed{\frac{d \ln k_1}{dT} = \frac{E_1}{RT^2}} \quad \text{———} ②$$

and $$\boxed{\frac{d \ln k_2}{dT} = \frac{E_2}{RT^2}} \quad \text{———} ③$$

Equation ② and ③ were proposed by Arrhenius and are known as Arrhenius Equations.

The term E is called the energy of activation, defined as the energy in excess to the average energy of the molecules at at given temperature which a molecule must have to enter ~~a~~ into a chemical reaction.

Integrating ② and ③, we get,

$$\ln k_1 = \frac{-E_1}{RT} + \text{constant } A$$

$$\ln k_2 = \frac{-E_2}{RT} + \text{constant } A$$

$$k_1 = Ae^{-E_1/RT} \quad \text{and} \quad k_2 = Ae^{-E_2/RT}$$

These equations are alternative forms of Arrhenius eqn.

In general,
$$\boxed{k = Ae^{-E/RT}} \quad \text{—— ④}$$

In eqn ④, A is constant.

The factor $e^{-E/RT}$ is responsible for the marked influence of temperature on the reaction rate.

The factor A is known as frequency factor of the reaction or collision number.

It is also called pre-exponential factor.

Integrating eqn ④, between limits, we get,

$$\int_{k_1}^{k_2} d\ln k = \int_{T_1}^{T_2} \frac{E}{RT^2} \cdot dT$$

$$\boxed{\ln \frac{k_2}{k_1} = \frac{-E}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]}$$

Main characteristics of Arrhenius Equation:-

i) Larger the activation energy, smaller the value of rate constant. This follows from the equation.

$$k = A\exp(-E/RT)$$

ii) Larger the activation energy, smaller the effect of a given temperature rise on k.

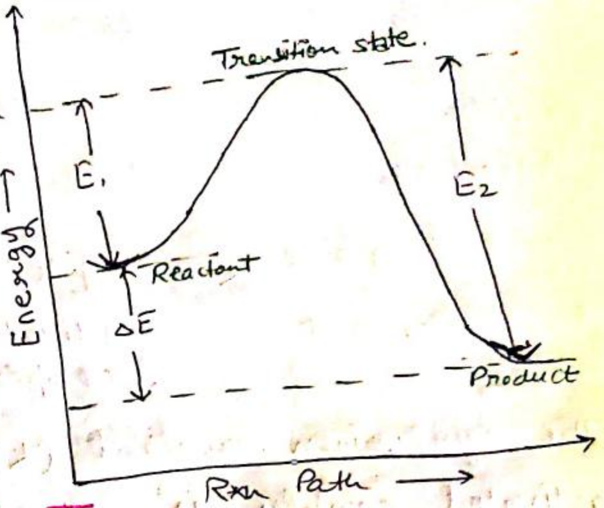
iii) At low temperatures, increase in temperature causes more change in the value of k than that of at higher temperature.

TRANSITION STATE THEORY

According to transition state theory, the rate of a reaction is the number of activated complex passing per second over the top of potential energy barrier.

The rate of is equal to the conc^n of activated complex times the average velocity with which a complex moves acrossto the product side.

The activated complex is not in a state of stable equilibrium, since it lies at a maximum potential energy.



Postulates Of Transition State Theory

These are as follows:-

1) As the reacting molecules approach each other, there is a continuous series of changes in bond distance. These changes are accompanied by energy changes.

2) The reactant molecules are changed into an energy rich intermediate called activated complex or transition state.

3) The activated complex may be formed by some loose association or bonding of reactant molecules with necessary rearrangement of valence bonds and energy.

If it is a unimolecular rxn, the reactant molecule may produce the activated complex by ~~re~~ rearrangement of atoms and redistribution of energy.

4) The activated compeex, though unstable has a transient existence. It is treated formally as a definite molecule with an independent entity.

The activated complex remains in equilibrium with the reactants and its potential energy is maximum. Finally, the activated complex decomposes into products.

5) The activation energy of a reaction in the light of this theory, is the additional energy which the reacting molecules must acquire to form the activated complex.

Thermodynamic or Mathematical treatment of Transition State Theory.

Consider a bimolecular reaction b/w reactant A and B. According to T.S. theory -

$$\underset{\text{Reactant}}{A + B} \rightleftharpoons \underset{\substack{\text{Activated}\\ \text{complex}}}{[X^*]} \longrightarrow \text{Product}$$

The equilibrium constant (K^*) for the formation of activated complex is

$$K^* = \frac{[X^*]}{[A][B]} \quad \text{or} \quad [X^*] = K^*[A][B] \longrightarrow ①$$

According to T.S. theory, the rate of reaction is the number of activated complexes which pass over the potential barrier unit time. This, in turn, is equal to the concⁿ of the complex would multiplied by the frequency at which the complex would decompose into products.

Mathematically,

$$\frac{dx}{dt} = [X^*] \times \text{Rate (or frequency) of dissociation of activated complex} \longrightarrow ②$$

From eqⁿ ① and ②, we get,

$$\frac{dx}{dt} = K^*[A][B] \times \text{Rate of dissociation of activated complex}$$

Frequency of dissociation of activated complex $= E_{vib}/h \longrightarrow ③$

where, E_{vib} = average vibrational energy at temp T and
h = Planck's constant

But, $E_{vib} = kT = \frac{RT}{N} \quad (\because k = R/N)$ —— ④

From eqⁿ ③ and ④, frequency of dissociation of activated complex = RT/Nh

$\frac{dx}{dt} = k^*[A][B] = \frac{RT}{Nh}$ —— ⑤

For conversion of reactions into product

$\frac{dx}{dt} = k[A][B]$ —— ⑥

From eqⁿ ⑤ & ⑥,

$$k = (A)[B] = k^*(A)[B] \,.\, RT/Nh$$

$\boxed{k = k^* . RT/Nh}$ —— ⑦

Eqⁿ ⑦ is the mathematical statement of transition state theory.

Acc. to thermodynamics, k^* can be correlated with ΔG^* through the following reaction.

$$\Delta G^* = -RT \ln k^*$$

where, ΔG^* = (Free energy of activated complex) — (Free energy of reactant) ~~and~~

and is known as standard free energy change.

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

$$\therefore -RT \ln k^* = \Delta H^* - T\Delta S^*$$

$$\ln k^* = \frac{-(\Delta H^* - T\Delta S^*)}{RT}$$

$k^* = e^{-(\Delta H^* - T\Delta S^*)/RT}$ —— ⑧

From eqⁿ ⑦ and ⑧, we get,

$$k = \frac{RT}{Nh} \cdot e^{-(\Delta H^* - T\Delta S^*)/RT}$$

$$\boxed{k = \frac{RT}{Nh}\, e^{-\Delta H^*/RT}\, e^{-\Delta S^*/R}}$$

where, ΔH^* = standard enthalpy change, i.e. standard heat of activation.

ΔS^* = Standard entropy change, i.e., standard entropy of activation.

HAMMOND'S POSTULATE

(George Hammond developed the postulate)

Hammond's postulate is a hypothesis in physical organic chemistry which describes the geometric structure of the transition state in an organic chemical reaction.

First proposed by George Hammond in 1955, the postulate states that:

If two states, as for example, a transition state and an unstable intermediate, occur consecutively during a reaction process and have nearly the same energy content, their interconversion will involve only a small recognization of the molecular structure. Therefore, the geometric structure of a state can be predicted by comparing its energy to the species neighbouring it along the reaction coordinate.

For example, in an exothermic reaction the to the products.

Therefore, the T.S. will be more geometrically similar to the reactants than to the products. However, in an endothermic reaction the T.S. is closer in energy to the products than to the reactants.

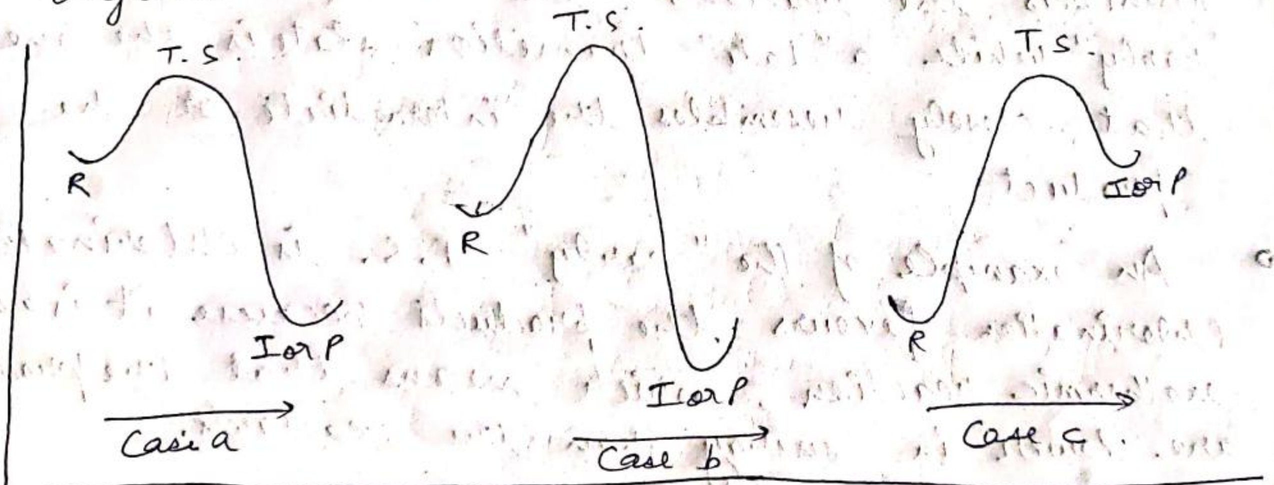
So, according to Hammond's postulate the structure of the transition state would resemble the products more than the reactants. This type of comparison is especially useful because most transition states cannot be characterized experimentally.

- Hammond's Postulate also helps to explain and rationalize the Bell - Evans - Polanyi Principle.
- The Postulate has also been used to predict the shape of reaction coordinate diagrams.

For example, electrophilic aromatic substitution involves a distinct intermediate and two less well defined states. By measuring the effects of aromatic substituents and applying Hammond's postulate it was concluded that the rate - determining step involves formation of a T. S. that should resemble the intermediate complex.

- Effectively, the postulate states that the structure of a transition state resembles that of the species nearest to it in free energy.

This can be explained with reference to potential energy diagrams.



In case a - which is an exothermic reaction, the energy of the T.S. is closer in energy to that of the reactant than that of the intermediate or the product.
Therefore, from the postulate, the structure of the T. S. also more closely resembles that of the reactant.

In case b. - The energy of the transition state is close to neither the reactant nor the product, making none of them a good structural model for the T.S.

Further information would be needed in order to predict the structure or characteristics of the transition state.

In case c. Depicts the potential diagram for an endothermic reaction, in which according to the postulates, the transition state should more closely resemble that of the intermediate or the product.

- Another significance of Hammond's postulate is that ~~the~~ it permits us to discuss the structure of the T.S. in terms of the reactants, intermediates or products.
- In this case, where the transition state closely resembles the reactants, the T.S. is called "Early" while a "Late" transition state is the one that closely resembles the intermediate or the product.
- An example of the "early" T.S. is chlorination. Chlorination favours the products because it is an exothermic reaction, which means that the products are lower in energy than the reactants.

An example of the "late" T.S. is Bromination. Bromination favours the reactants because it is an endothermic reaction which means that the reactants are lower in energy than the product.