

Fundamentals of Chemistry, Module III: Organic Chemistry

Semester-1, CCF-2022 (NEP)

Course: CHEM-H-CC-2-2-TH

Course taught by: Kaushik Basu, Department of Chemistry, SPCMC, Kolkata

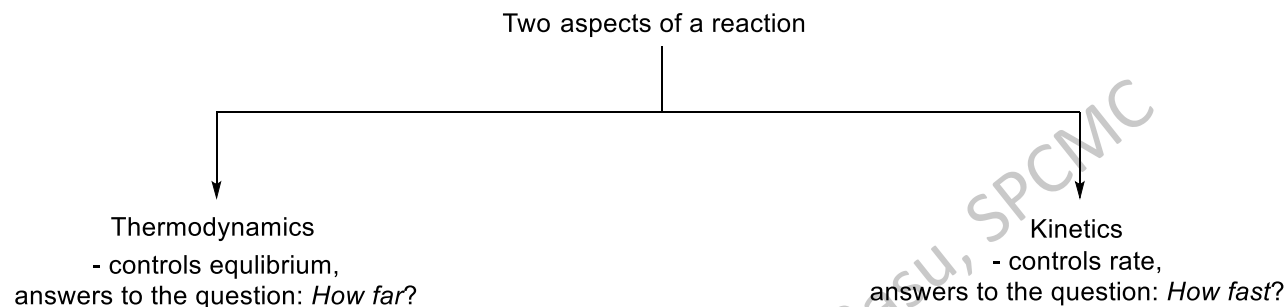
email: chiralkaushik@gmail.com

Recommended texts:

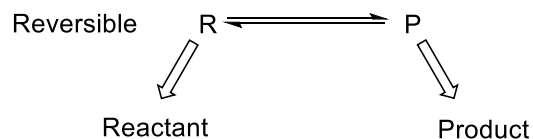
1. Study Guide to Organic Chemistry, Volume 1, Second Ed., by Saha, Chakraborty, Saha & Basu, Techno World, ISBN 978-8192669564,
2. The Organic Chemistry Lifesaver 2, Mandal & Basu, Techno World, ISBN 978-8119777884.
2. Organic Chemistry, Second Ed. by Clayden, Greeves & Warren, OUP, ISBN 978-0198728719

Energetics of organic reactions:

Energetically favourable reactions generally involve breaking of weaker bonds and formation of stronger bonds. In this case, your knowledge on qualitative aspects of bond energy will help you.



Hypothetical reaction:



When equilibrium is reached, how much R and P is present?
This question will be answered by the thermodynamics of the reaction.

To know this, we must look at the equilibrium constant K_{eq} .

$$K_{\text{eq.}} = \frac{[\text{P}]_e}{[\text{R}]_e}$$

$[\text{P}]_e$ = Product concentration at eqm.
 $[\text{R}]_e$ = Reactant concentration at eqm.

However, thermodynamic analysis does not tell you how long will it take to reach the eqm. stage. That depends on how fast is R converted to P and vice versa. So, that question can be answered from a kinetic analysis of the reaction under consideration.

To clearly understand the distinction between the domains of thermodynamics and kinetics of a reaction, we need to first understand the concept of *reaction energy diagram*. It is also known as energy profile, reaction profile or reaction coordinate diagram.

An energy diagram is a plot of energy versus the *reaction coordinate*. The reaction coordinate is a measure of the degree of a molecule's progress toward complete reaction.

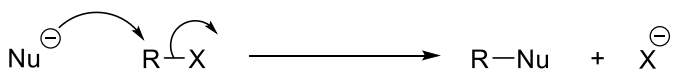
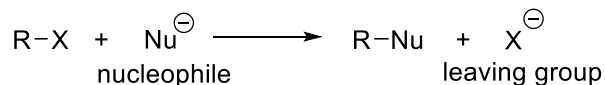
IUPAC defines reaction coordinate as: A geometric parameter that changes during the conversion of one (or more) reactant molecular entities into one (or more) product molecular entities and whose value can be taken for a measure of the progress of an elementary reaction (for example, a bond length or bond angle or a combination of bond lengths and/or bond angles; it is sometimes approximated by a non-geometric parameter, such as the bond order of some specified bond).

Energetics of organic reactions:

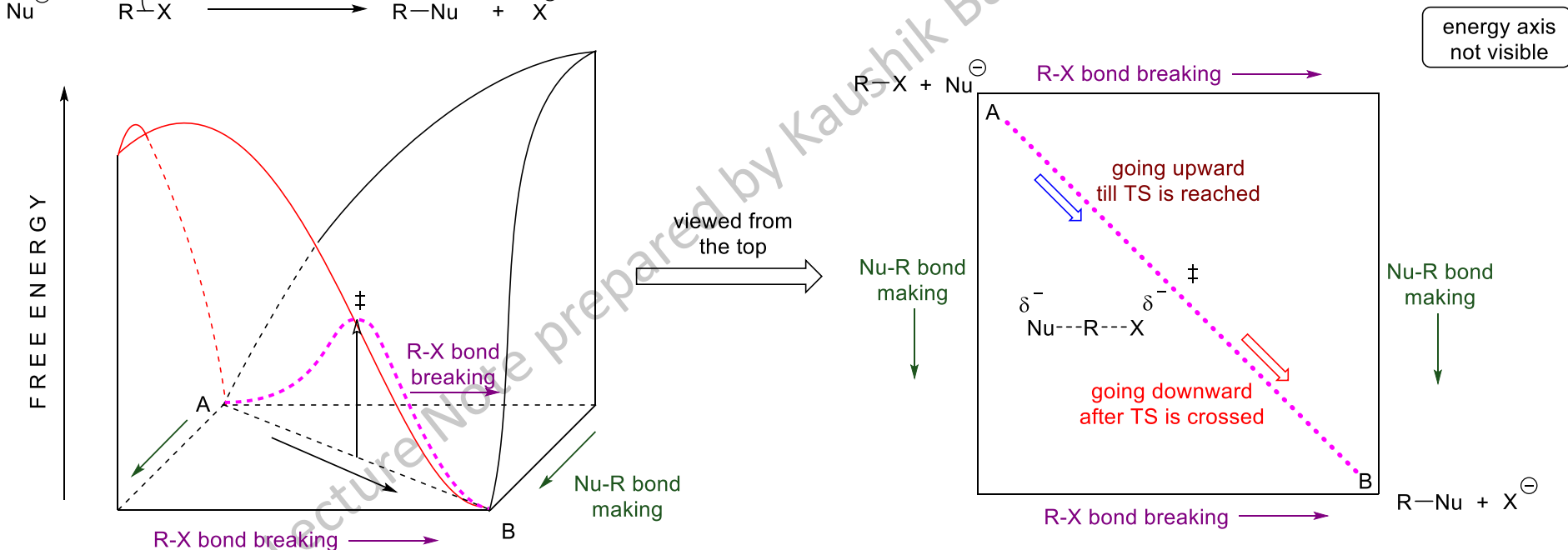
To clearly understand the distinction between the domains of thermodynamics and kinetics of a reaction, we need to first understand the concept of *reaction energy diagram*. It is also known as energy profile, reaction profile or reaction coordinate diagram.

A chemical reaction is associated with a *change in energy* on going from reactant(s) to product(s). The question is, how does such an energy change take place?

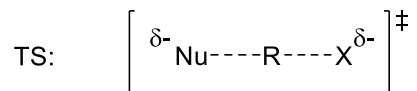
Let us take a simple organic reaction as an example. The nucleophilic substitution of R-X with the nucleophile Nu^- :



As the bond between R and Nu starts to form, the bond between R and X starts to break. So when Nu^- approaches the R-X molecule, the distance between R and Nu progressively decreases and the distance between R and X increases.

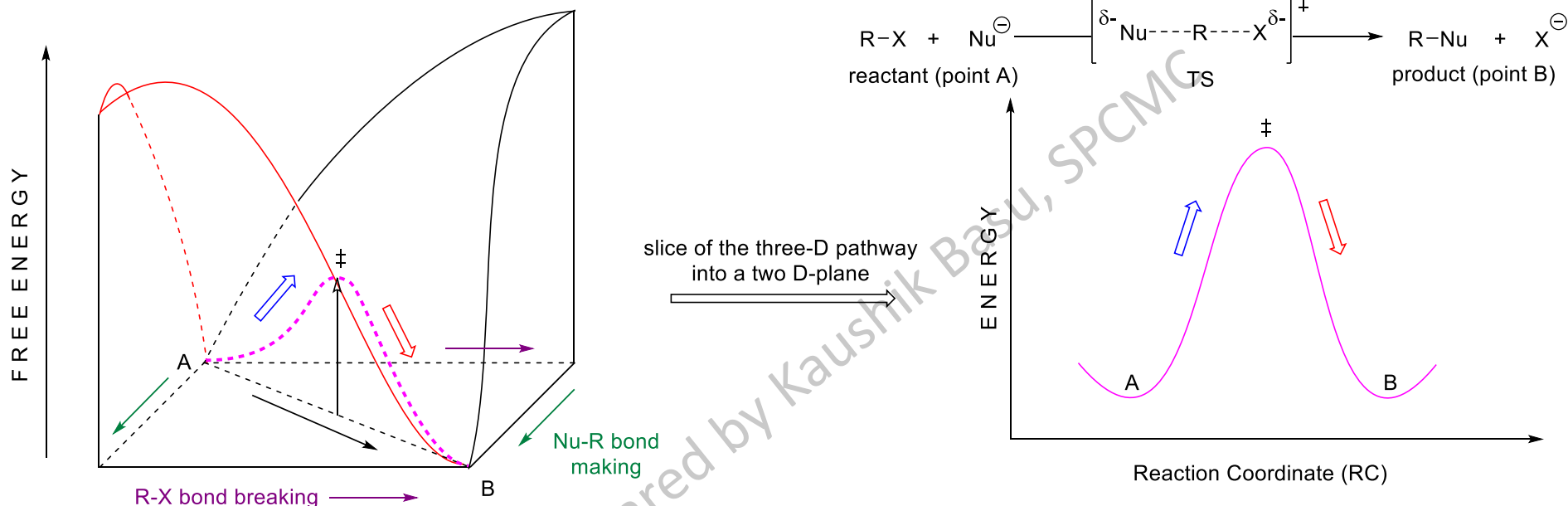


In between the two ends of the diagonal, there exists a point of highest energy. This point is called the **transition state (TS)** which is represented by the symbol " \ddagger " (double dagger). When our reacting species are at the TS, the R-X bond is partially broken and the R-Nu bond is only partially formed.



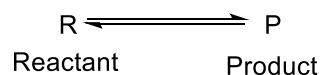
Energetics of organic reactions:

Drawing of the three-dimensional energy diagram is cumbersome task. Thus we have a two-dimensional energy profile diagram which is the slice of the energy landscape along the diagonal bold line from A to B as shown below. The vertical axis is energy, and the horizontal axis becomes the reaction coordinate which is a combined function of the changes in both bond lengths, R-X and Nu-R:



Evidently, this diagram indicates that as the reaction proceeds, the overall energy of the system *will increase* and reach a maximum point where R is partially bonded to both Nu and X. This maximum point is the TS. After reaching the TS the energy *decreases continually* and the reaction is over when X has left with the bonding pair of electron as X^{-} .

All reactions are, in principle, reversible. In that case we have,



The equilibrium constant K_{eq} is expressed as,

$$K_{\text{eq.}} = \frac{[\text{P}]_e}{[\text{R}]_e}$$

$[\text{P}]_e$ = Product concentration at eqm.
 $[\text{R}]_e$ = Reactant concentration at eqm.

If the potential energy is expressed as Gibbs free energy (G° , the superscript zero signifying the standard state) then the difference of standard free energy between the reactant and the product is given by ΔG° , the free energy of reaction. It is related to the equilibrium constant, K_{eq} , of the reaction by the following equation:

$$\Delta G^{\circ} = -2.303RT \log K_{\text{eq.}}$$

R = universal gas constant,
T = temp. in K

$$\Delta G^{\circ} = G^{\circ}_{\text{P}} - G^{\circ}_{\text{R}}$$

G°_{P} = Free energy of product P
 G°_{R} = Free energy of product R

Energetics of organic reactions:

All reactions are, in principle, reversible.
In that case we have,

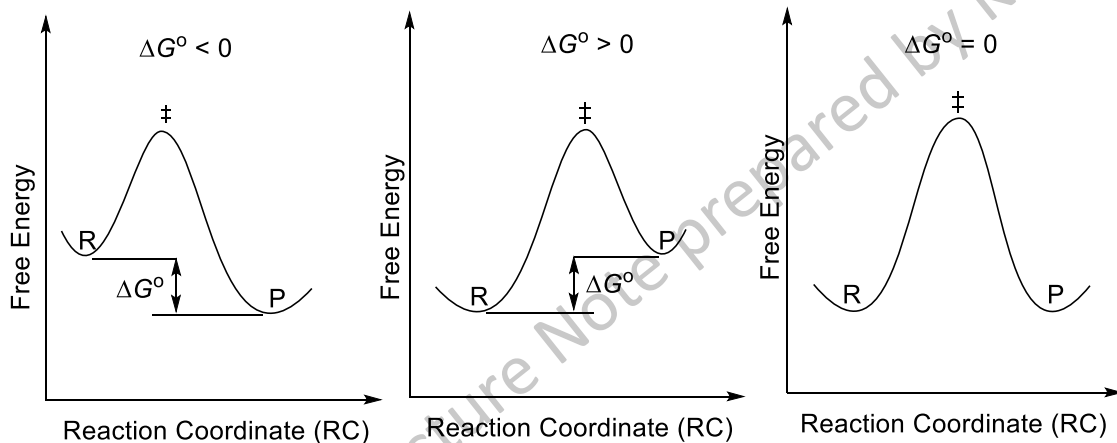


The equilibrium constant $K_{eq.}$ is expressed as,

$$K_{eq.} = \frac{[P]_e}{[R]_e}$$

$[P]_e$ = Product concentration at eqm.

$[R]_e$ = Reactant concentration at eqm.



$$\Delta G^\circ < 0$$

$$G^\circ_P < G^\circ_R$$

$$K_{eq.} > 1$$

$$[P]_e > [R]_e$$

exergonic

$$\Delta G^\circ > 0$$

$$G^\circ_P > G^\circ_R$$

$$K_{eq.} < 1$$

$$[P]_e < [R]_e$$

endergonic

$$\Delta G^\circ = 0$$

$$G^\circ_P = G^\circ_R$$

$$K_{eq.} = 1$$

$$[P]_e = [R]_e$$

thermoneutral

$$\Delta G^\circ = -2.303RT \log K_{eq.}$$

\Rightarrow

$$\log K_{eq.} = - \frac{\Delta G^\circ}{2.303RT}$$

\Rightarrow

$$K_{eq.} = 10^{(-\Delta G^\circ / 2.303RT)}$$

R = universal gas constant,
T = temp. in K

R = 1.99×10^{-3} kcal/mol and T is the temp. in K
At 25°C, T = 298 K, so 2.303 RT = 1.36 kcal/mol

$$\Delta G^\circ = G^\circ_P - G^\circ_R$$

G°_P = Free energy of product P

G°_R = Free energy of product R

$$K_{eq.} = 10^{(-\Delta G^\circ / 1.36)}$$

For every 1.36 kcal/mol change in the ΔG° ,
the equilibrium constant changes by a factor of 10.

ΔG° (kcal/mol)	$K_{eq.}$	$[Reactant]_e$	$[Product]_e$
+ 5.44	0.0001	99.99	0.01
+ 4.08	0.001	99.9	0.1
+ 2.72	0.01	99	1
+ 1.36	0.1	91	9
+ 0.5	0.43	70	30
0	1	50	50
- 0.5	2.33	30	70
- 1.36	10	9	91
- 2.72	100	1	99
- 4.08	1000	0.1	99.9
- 5.44	10000	0.01	99.99

Energetics of organic reactions:

All reactions are, in principle, reversible.
In that case we have,



$$\Delta G^\circ = -2.303RT \log K_{\text{eq.}}$$

R = universal gas constant,
T = temp. in K



$$\log K_{\text{eq.}} = - \frac{\Delta G^\circ}{2.303RT}$$

$$\Delta G^\circ = G^\circ_{\text{P}} - G^\circ_{\text{R}}$$

G°_{P} = Free energy of product P
 G°_{R} = Free energy of product R

$$K_{\text{eq.}} = \frac{[\text{P}]_e}{[\text{R}]_e}$$

$[\text{P}]_e$ = Product concentration at eqm.

$[\text{R}]_e$ = Reactant concentration at eqm.

Shifting an unfavourable eqm. towards the desired side:

Le Chatelier's principle: Every change of one factor of an equilibrium occasions a rearrangement of the system in such a direction that the factor in question experiences a change in a sensed opposite to the original change.

In other words, if a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium shifts to counteract the change to reestablish an equilibrium.

For reactions with $\Delta G^\circ > 0$: $\text{R} \rightleftharpoons \text{P}$ $K_{\text{eq.}} < 1$ $[\text{P}]_e < [\text{R}]_e$

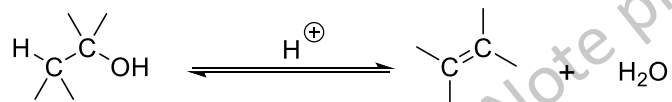
and for reactions with $\Delta G^\circ \approx 0$ $\text{R} \rightleftharpoons \text{P}$ $K_{\text{eq.}} \approx 1$ $[\text{P}]_e \approx [\text{R}]_e$

To shift the eqm. towards the right side, one may do two things:

- either use excess R, or
- remove P from the reaction mixture

Manipulating the reaction conditions to drive the eqm. in one particular direction:

Example-1. Acid-catalyzed dehydration of an alcohol to an alkene and acid-catalyzed hydration of the alkene to the alcohol:



nature of the reaction:

can be achieved by...

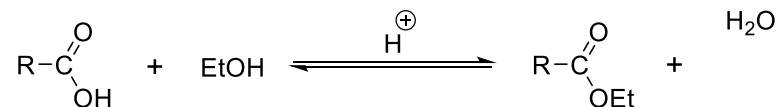
In the forward direction:
dehydration of alcohol

removing water (one of the product)
from reaction medium

In the backward direction:
hydration of alkene

using excess water (one of the reactant)
in reaction medium

Example-2. Acid-catalyzed esterification of an alcohol and a carboxylic acid, and acid-catalyzed hydrolysis of an ester:



nature of the reaction:

can be achieved by...

In the forward direction:
esterification

using excess EtOH (one of the reactant)
in reaction medium

In the backward direction:
ester hydrolysis

using excess water (one of the reactant)
in reaction medium

Energetics of organic reactions:

Enthalpy and entropy: The components of Gibbs free energy:

To understand the nature of ΔG° completely, we must look into its two components, namely, enthalpy and entropy: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

ΔH° is the standard enthalpy change of the reaction (the *heat of reaction*) on going over to product from reactant, and is defined as:

$$\Delta H^\circ = H^\circ_P - H^\circ_R$$

when, $\Delta H^\circ < 0$,

$$H^\circ_P < H^\circ_R$$

exothermic

when, $\Delta H^\circ > 0$,

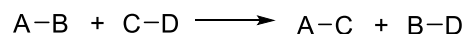
$$H^\circ_P > H^\circ_R$$

endothermic

For an exothermic reaction weak bonds are broken and strong ones are formed while the opposite is true for all endothermic reactions.

When a bond breaks, energy must be supplied from outside, so it is an *endothermic process* and $\Delta H^\circ > 0$.

On the other hand, formation of new bonds between unbonded atoms or groups releases energy, i.e. it is an *exothermic process* and $\Delta H^\circ < 0$



bonds broken in this reaction : A-B and C-D

bonds formed in this reaction: A-C and B-D

Enthalpy of molecule A-B

= Energy released when the A-B bond is formed = $-BDE_{A-B}$

Enthalpy of reactant: $-(BDE_{A-B} + BDE_{C-D})$

Enthalpy of product: $-(BDE_{A-C} + BDE_{B-D})$

$$\Delta H^\circ = H^\circ_P - H^\circ_R = -(BDE_{A-C} + BDE_{B-D}) - \{-(BDE_{A-B} + BDE_{C-D})\}$$

$$\Delta H^\circ = H^\circ_P - H^\circ_R = (BDE_{A-B} + BDE_{C-D}) - (BDE_{A-C} + BDE_{B-D})$$

$$\Delta H^\circ = H^\circ_P - H^\circ_R = \sum BDE_{\text{bonds broken}} - \sum BDE_{\text{bonds formed}}$$

Change in entropy on going over to the product from reactant, ΔS° is defined by:

$$\Delta S^\circ = S^\circ_P - S^\circ_R$$

when, $\Delta S^\circ < 0$,

$$S^\circ_P < S^\circ_R$$

when, $\Delta S^\circ > 0$,

$$S^\circ_P > S^\circ_R$$

For our purpose we shall consider entropy as a *measure of microscopic disorder* which increases as the disorder increases. In short, if the number of degrees of freedom (be it translational, rotational, or vibrational) increases, so will the entropy. The following guide is useful:

- For a given number of total atoms, a process that converts few large molecules into many smaller molecules proceed with a significant increase in entropy.
- If the total number of molecules remains unchanged, a process that converts a single molecular species into a mixture of different molecules proceed with a significant increase in entropy. In this respect entropy of mixing may be recalled.
- In general, a change from the condensed phase (solid or liquid) to the gaseous state will proceed with a significant increase in entropy

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

ΔH°	ΔS°	$-T\Delta S^\circ$	ΔG°
negative	positive	negative	negative
positive	negative	positive	positive
negative	negative	positive	?
positive	positive	negative	?

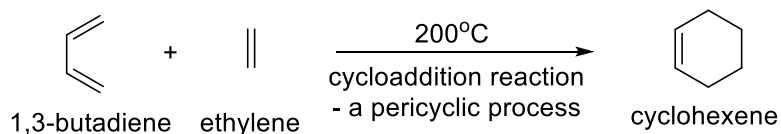
} sign of ΔG° will depend on the magnitude of T
Recall T (in K) is always > 0

Energetics of organic reactions:

Enthalpy and entropy: The components of Gibbs free energy:

To understand the nature of ΔG° completely, we must look into its two components, namely, enthalpy and entropy:

Let us take the following example:



$$\Delta H^\circ = H^\circ_{\text{P}} - H^\circ_{\text{R}} = \sum \text{BDE}_{\text{bonds broken}} - \sum \text{BDE}_{\text{bonds formed}}$$

Given that BDE for C=C is 146 kcal/mol and that for C-C is 83 kcal/mol, we can calculate:

$$\Delta H^\circ = \{(3 \times 146) + 83\} - \{(5 \times 83) + 146\} = -40 \text{ kcal/mol}$$

The reaction is exothermic by 40 kcal/mol, so enthalpically very favorable.

Thus at 200°C , $T = 473 \text{ K}$, $T\Delta S^\circ = -20.6 \text{ kcal/mol}$. Therefore, $\Delta G^\circ_{473\text{K}} = -40 + 20.6 = -19.4 \text{ kcal/mol}$, i.e. exergonic and $K_{\text{eq.}} = 10^{12}$ at 200°C

If the reaction is done at 900°C , $T = 1173 \text{ K}$, $T\Delta S^\circ = -51.1 \text{ kcal/mol}$. Therefore, $\Delta G^\circ_{1173\text{K}} = -40 + 51.1 = 11.4 \text{ kcal/mol}$, i.e. endergonic and $K_{\text{eq.}} = 10^{-8}$ at 900°C

At this temperature then, the cycloaddition reaction is very much unfavourable despite having a favorable enthalpy term. In fact, the reverse reaction (cycloreversion) is more favoured.

Do not commit on the nature of ΔG° of a reaction without knowing T .

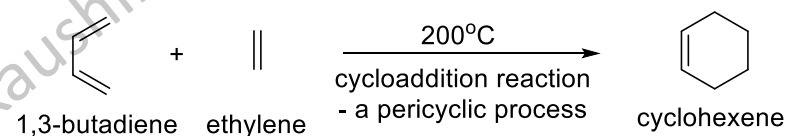
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

ΔH°	ΔS°	$-T\Delta S^\circ$	ΔG°
negative	positive	negative	negative
positive	negative	positive	positive
negative	negative	positive	?
positive	positive	negative	?

sign of ΔG° will depend on the magnitude of T
Recall T (in K) is always > 0

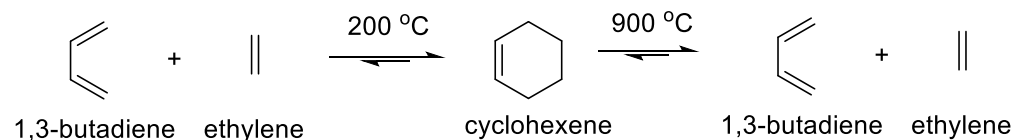
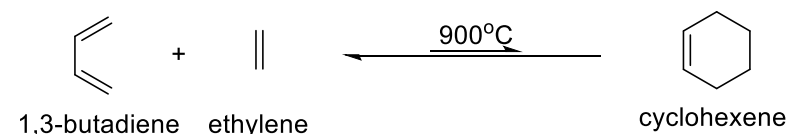
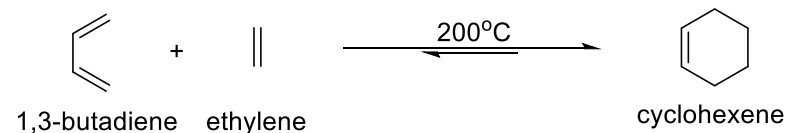
Best case scenario: ΔH° is negative and ΔS° is positive

Worst case scenario: ΔH° is positive and ΔS° is negative



The reaction is entropically *unfavourable* as two molecules of reactants combine to give one molecule of product, so entropy change is negative.

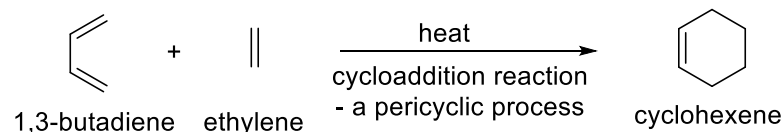
It is calculated to be $\Delta S^\circ = -43.6 \text{ cal}/(\text{mol.K})$



Energetics of organic reactions:

Kinetics: Energy of activation:

Our example:



$$\text{At } 200^{\circ}\text{C}, K_{\text{eq.}} = 10^{12} \text{ M}^{-1} \quad \text{At } 900^{\circ}\text{C}, K_{\text{eq.}} = 10^{-8} \text{ M}^{-1}$$

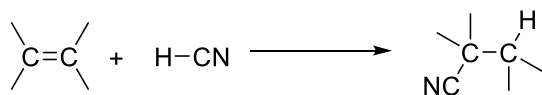
As we lower the temp., the unfavourable $T\Delta S^{\circ}$ will be smaller further and ΔG° should become more and more favourable.

Does this mean that if we were to carry out the reaction at even lower temp. say, at room temp. the eqm. constant would be even bigger than it is at 200°C ?

Answer is yes, it would be. But the reaction, although now thermodynamically even more favourable, will not take place at all!

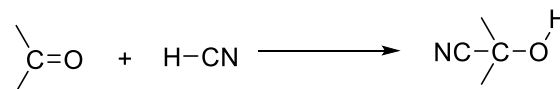
Why is that? The answer is that such cycloaddition is *kinetically unfavourable* at room temperature.

Consider the following two addition reactions:



BDE (kcal/mol)

C=C bond energy = 145	} ΔH° for HCN addition across C=C = (145 + 99 - 83 - 99 - 83) kcal mol ⁻¹ = - 21 kcal mol ⁻¹
H-C bond energy = 99	
C-C bond energy = 83	
C-H bond energy = 99	
C-C bond energy = 83	



BDE (kcal/mol)

C=O bond energy = 166	} ΔH° for HCN addition across C=O = (166 + 99 - 80 - 111 - 83) kcal mol ⁻¹ = - 9 kcal mol ⁻¹
H-C bond energy = 99	
C-O bond energy = 80	
O-H bond energy = 111	
C-C bond energy = 83	

Both reactions are *entropically unfavourable*, as in both cases *two reactants combine to give one product molecule*, i.e. $\Delta S^{\circ} < 0$.

Considering enthalpy calculations, the addition of HCN across the C=C should be more favourable than HCN addition across C=O. Yet, the former does not proceed at all while the latter is commonly observed. The addition of HCN across C=C is *kinetically unfavourable*.

What does this "kinetically unfavourable" phrase mean? What is stopping these reactions from occurring?

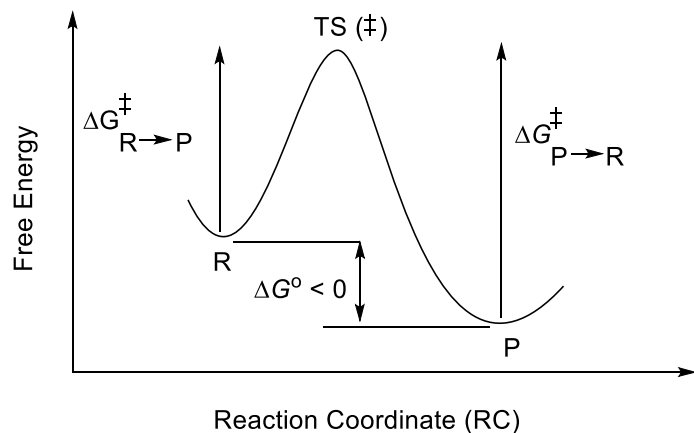
Clearly, there is an aspect to all reactions, other than thermodynamics, which play a critical role in deciding whether the reaction will be successful or not. Let us discuss what it is and how it operates.

Energetics of organic reactions:

Kinetics: Energy of activation:

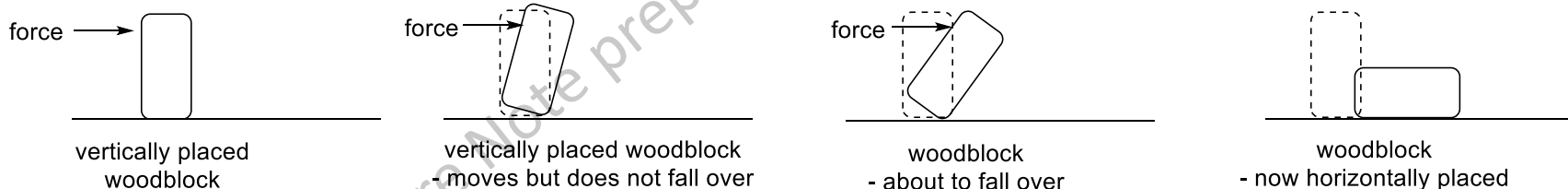
What does the phrase "*kinetically unfavourable*" mean exactly?

To get a clear picture, we shall have to reconsider the reaction coordinate diagram that we constructed at the beginning of this chapter



for R to convert to P, the energy of the system gradually increases till a highest energy point (the transition state, TS) is reached, and then continually decreases till it reaches P. Thus there is an energy barrier which separates R and P. The height of the energy barrier for R to P conversion is the vertical distance between R and TS. This is called the *activation energy* (E_a), or, if energy is expressed as Gibbs' function, the free energy of activation ($\Delta G^\ddagger_{R \rightarrow P}$) for converting R to P. So E_a is the minimum energy that has to be supplied to reactants so that any conversion to products becomes possible.

This situation is analogous to moving a block of wood placed vertically on the table. To place it horizontally you have to push, i.e. apply a little force. Without the push the wood block will not move, and only after application of a certain force it will tilt over, although the system's potential energy is lower when it is placed horizontally on the table. There exists an energy barrier that must be crossed to fall over. It cannot fall over on its own.



Similarly, reactions won't go, i.e., reactants will not be converted to products if a certain amount of energy is not supplied. This energy is the Gibbs energy difference between the transition state of a reaction (either an elementary reaction or a stepwise reaction) and the ground state of the reactants and is known as the free energy of activation. When potential energy is used instead of Gibbs energy, the difference between reactant and TS is known as the activation energy.

Kinetics: Energy of activation:

From where do the reactant molecules get the energy to cross the activation energy barrier?

This energy is necessarily derived from the kinetic energy of molecules. Due to thermal motions molecules are in constant state of agitation and running around to and fro. For a reaction to take place molecules must collide first. If that collision has sufficient energy to overcome the barrier for that reaction, the reactant molecules cross that barrier and changes to products.

The rate at which the transformation from R to P takes place is the reaction rate. It is thus obvious that greater the number of collisions with sufficient energy to pass the TS per unit time, greater is the rate.

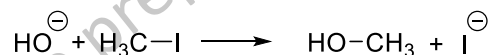
Qualitatively, we may express the reaction rate as a product of three factors:

$$\text{Reaction Rate} = \left(\text{Number of collisions between reactant molecules per unit time} \right) \times \left(\text{Fraction of collisions with enough energy to cross the activation energy barrier} \right) \times \left(\text{An orientational / probability factor} \right)$$

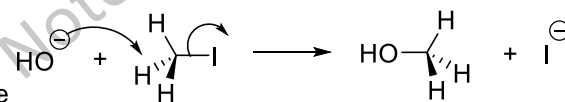
- (a) concentration of the reactant molecules (higher concentration means higher number of collisions),
 (b) molecular speed (higher it is, higher the energy of collisions), and
 (c) size of the reactant molecules (larger molecules have a greater probability of colliding with each other, but their speeds will be slower, so there is a trade-off there)

Orientation factor:

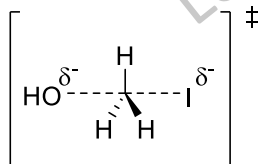
Consider the following bimolecular substitution reaction:



For a successful reaction, the attack of the nucleophile HO^- has to take place on the carbon atom of $\text{H}_3\text{C-I}$ from the side opposite to that from where the leaving group I departs, i.e. the famous back side attack:



via the TS:

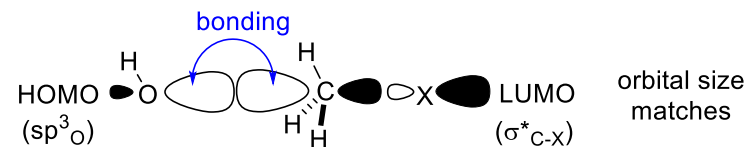


Note - a) how in the TS the C-O bond is partly formed, and the C-I bond is partly broken,
 b) how the O atom carries a diminishing -ve charge, and c) how the iodine atom carries a developing -ve charge.

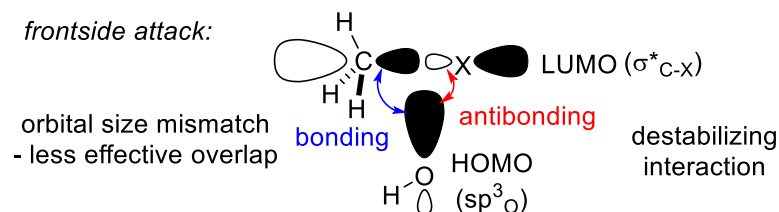
This is an *approximate* representation of the TS

In this reaction the electrons are transferred from the HOMO of hydroxide to the LUMO of methyl iodide -

backside attack:



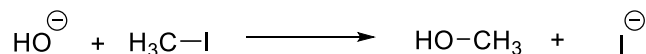
frontside attack:



Kinetics: Energy of activation:

Not all collisions will be effective for conversion of R to P, only those collisions occurring in the *right orientation* and *with enough energy* to surmount the energy barrier will count. An important consequence arises out of this condition. As rate of collisions between reactant molecules is expected to be directly proportional to the concentrations of those species in reaction medium, rate is also directly proportional to concentrations of reactant(s). This relationship of reaction rate with concentration term(s) is called the *rate law* (or rate equation) of that reaction.

Consider the following bimolecular substitution reaction:



Rate $\propto [\text{CH}_3\text{I}][\text{HO}^{\ominus}]$ i.e. Rate = $k [\text{CH}_3\text{I}] [\text{HO}^{\ominus}]$ the proportionality constant k is the *rate constant*

The order of reaction (or order of the rate law) is the sum of the exponents of the concentration terms in the rate law. This reaction is first order w.r.t. both MeI and hydroxide, overall order is two, i.e. a second order reaction.

Svante Arrhenius empirically found the following relationship between rate constant (k) and activation energy (E_a), now known as the Arrhenius equation:

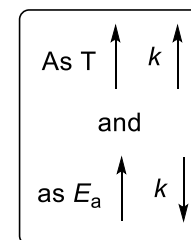
$$k = A.e^{\left(-\frac{E_a}{RT}\right)}$$

A is the pre-exponential factor and R is the universal gas constant

The pre-exponential factor A is comprised of the following factors : the fraction of collision which have correct geometry, the size of molecules and the speeds of molecules.

Arrhenius equation tells us that:

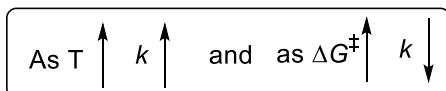
- k has strong dependence upon T and increasing the temperature by even a small amount will increase k to a great extent due to the exponential dependence.
- if E_a is increased there will be a sharp drop in k . This means that as the height of the energy barrier increases, the rate constant for that step decreases.



Just as the Arrhenius equation relates activation energy with rate constant, Eyring equation shows the relationship between the free energy of activation and rate constant:

$$k = \frac{k_B T}{h} e^{\left(-\frac{\Delta G^\ddagger}{RT}\right)}$$

k_B = Boltzmann's constant
 h = Planck's constant
 $e = 2.71828$
 R = universal gas constant



For a first order reaction, we have the following data:

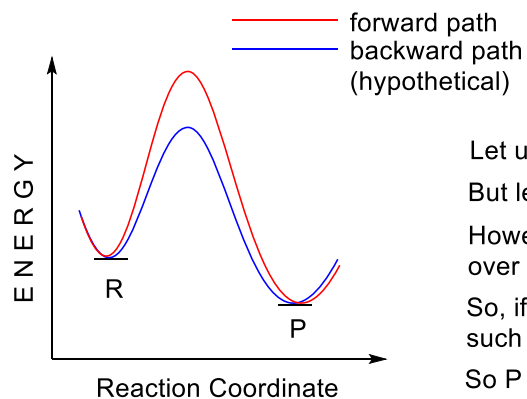
ΔG^\ddagger (kcal/mol)	k_{298} (s^{-1})	$t_{1/2}$	97% complete in...
15	64.1	0.01 s	0.05 s
19	7.5×10^{-2}	9.2 s	45.9 s
22	4.8×10^{-4}	24 min	2 hours
24	1.6×10^{-5}	11.7 min	2.4 days

At room temp., lowering ΔG^\ddagger by 1.36 kcal/mol increases the rate by 10 fold. For a reaction with free energy of activation about 20 kcal/mol, the rate is reasonable at room temp. Similarly, for every 10 deg C rise in temp., the rate of reaction becomes double.

Energetics of organic reactions:

Kinetics: PMR and the concept of catalysis

Principle of Microscopic Reversibility (PMR): The pathway drawn for conversion of R to P is the lowest-energy path available for that particular change. Now, if P gets converted to R, it is logical to expect that the reverse reaction should follow the exact same path, but in the reverse direction. This is precisely what PMR says, *the reverse of a chemical transformation involves the microscopic reverse of the reactions of that transformation, and of none other, under the same conditions.*



Let us assume the R converts to P via the red path.

But let us also assume that PMR does not work and P converts back to R via a lower energy blue path.

However, if the blue path is available at the first place, R should have taken the blue path instead of the red path in going over to P.

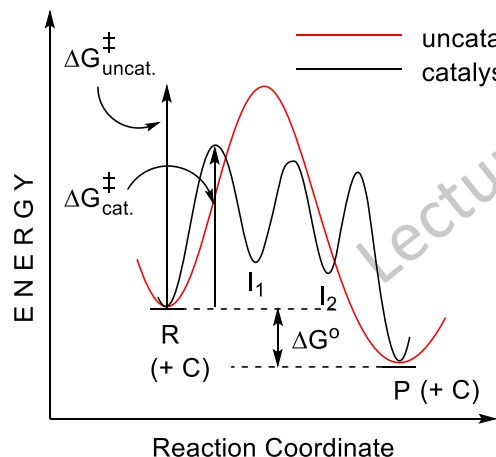
So, if the R to P conversion is taking place through the red path, it must be the lowest energy pathway that is available for such conversion.

So P should come to R via the red path only, validating the PMR.

Catalysis: A substance that increases the rate of a reaction *without modifying* the overall standard Gibbs energy change in the reaction; the process is called catalysis. The catalyst improves the rate by lowering the free energy of activation of the reaction. This implies that the mechanism of the catalysed reaction is essentially different from the uncatalysed version. The catalysts actively takes part in the reaction but returns chemically unchanged when the reaction is over. In that sense, the catalyst is both a reactant and a product of the catalysed reaction. Let us consider a hypothetical reaction's catalysed and uncatalysed version graphically:

uncatalysed reaction: proceeds in one step $R \longrightarrow P$

catalysed reaction: proceeds in more one step $R + C \longrightarrow I_1 \longrightarrow I_2 \longrightarrow P + C$ (C : catalyst)



Points to note: $\Delta G_{\text{cat}}^{\ddagger} < \Delta G_{\text{uncat}}^{\ddagger}$.

but, ΔG° is the same for both uncat. and catalysed version is the same

So, the equilibrium constant (K_{eq}) does not change on catalysis, only the time it takes to establish eqm. changes. Eqm. is established at a much faster rate under catalysis.

Following the PMR, the pathway of R to P for the catalysed version is exactly the same for P to R under the same catalysis condition. This implies that the catalyst that is responsible for lowering the free energy of activation for the forward direction (R to P) is also responsible for lowering the free energy of activation for the backward direction (from P to R).

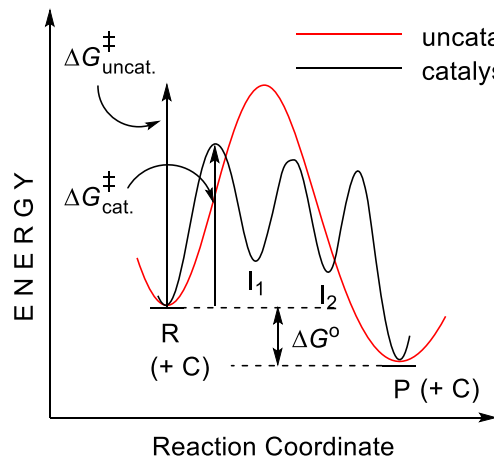
This means that the catalyst that speeds up conversion of R to P also speeds up conversion of P to R. That is why the eqm. is established much faster than it happens in the uncatalysed version.

Energetics of organic reactions:

Kinetics: PMR and the concept of catalysis

uncatalysed reaction: proceeds in one step $R \longrightarrow P$

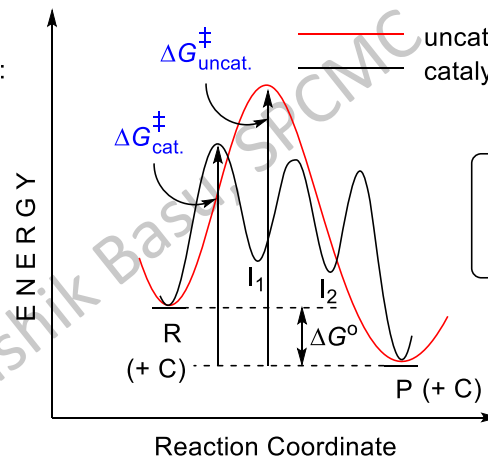
catalysed reaction: proceeds in more one step $R + C \longrightarrow I_1 \longrightarrow I_2 \longrightarrow P + C$ (C : catalyst)



Considering the
backward reaction:

$$\Delta G_{\text{cat}}^{\ddagger} < \Delta G_{\text{uncat}}^{\ddagger}$$

$$\Delta G^{\circ} \text{ is unchanged}$$



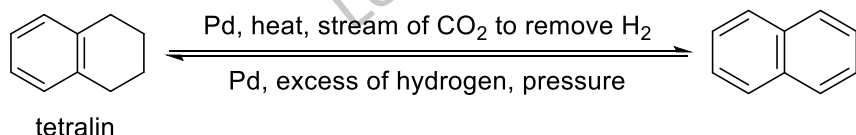
$$\Delta G_{\text{cat}}^{\ddagger} < \Delta G_{\text{uncat}}^{\ddagger}$$

$$\Delta G^{\circ} \text{ is unchanged}$$

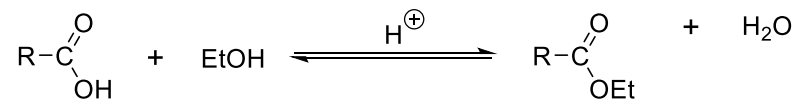
Following the PMR, the pathway of R to P for the catalysed version is exactly the same for P to R under the same catalysis condition. This implies that the catalyst that is responsible for lowering the free energy of activation for the forward direction (R to P) is also responsible for lowering the free energy of activation for the backward direction (from P to R).

This means that the catalyst that speeds up conversion of R to P also speeds up conversion of P to R. That is why we can use the same catalyst to achieve either conversion at an enhanced rate.

Example: Naphthalene is reduced to tetralin via a hydrogenation reaction using Pd-catalysis. So it is not surprising that the dehydrogenation of tetralin to naphthalene can also be done with the same catalyst. Thus we have the following observation:



Esterification of carboxylic acid with alcohol and hydrolysis of ester to carboxylic acid and alcohol both are catalysed by mineral acid. thus we have the following observation:



use excess ethanol and/or remove water to drive the eqm. towards the RHS (esterification)

use excess water to drive the eqm. towards the LHS (ester hydrolysis)