

Reaction Kinetics

Dr. Satyajit Dey

Tamralipta Mahavidyalaya

A favourable thermodynamics (i.e., a negative ΔG°) is a necessary but not a sufficient condition for a reaction to occur successfully. Thermodynamics says that a reaction will be spontaneous if ΔG° for reaction is negative. However, it says nothing about the speed of a chemical reaction. For example, the conversion of H_2 and O_2 into water is thermodynamically a favourable process since ΔG° of this conversion is large negative. Though the reaction is thermodynamically allowed, a mixture of H_2 and O_2 at room temperature never produces water molecules because the rate of reaction is very, very slow. Therefore, some spontaneous reactions are fast, while some others are slow. Kinetic is the study of how concentrations of reactants or products vary with time. In other words, kinetics describes the speed at which a reaction goes to completion. Both thermodynamics and kinetics must be favourable for a reaction to be successful.

Rate of organic reactions:

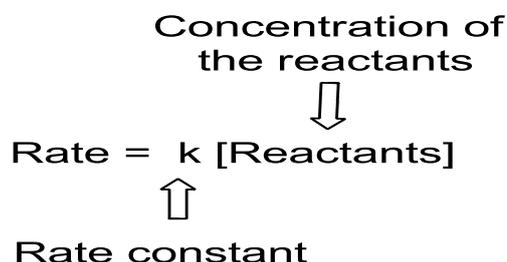
The rate of an organic reaction describes how fast a particular reactant will be converted to a particular product and this is proportional to the product of the concentrations of all reactants. The rate of a chemical reaction is described by a rate equation which has the general form:

$$\text{Rate} = - \frac{d[R]}{dt} = \frac{d[P]}{dt}$$

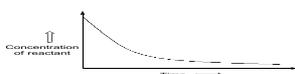
Where the rate constant (k) is the proportionality factor and this is specific for each reaction. The rate is dependent only on concentration of the reactants and the temperature. But the rate constant varies with temperature, pressure, and solvent; but does not depend on concentrations.

Rate-Concentration relationship:

We have seen that the rate of any chemical reaction is directly proportional to the product of the concentration of all the reactant molecules. If there is no reactant, then no reaction will occur and the rate of reaction will be zero. Conversely, if there is a large concentration of reactant, the rate will be very large. The rate of reaction depends on concentration. This also means that the rate of reaction is time dependent because as the time passes the reactant's concentration decreases and, accordingly the reaction rate decreases. Generally, the rate is highest at the beginning of the reaction and gradually slows down to zero when equilibrium is reached or at the end of the reaction. Plotting the concentration of the reactant against time yields a typical curve shown in the figure below.



From this plot the rate at a particular concentration is obtained from the tangent to the curve at that point. This tangent (i.e., the rate) can mathematically be expressed as a derivative reflecting the rate of disappearance of the reactant or the rate of appearance of the product with time. Thus;



Order of reaction and rate laws:

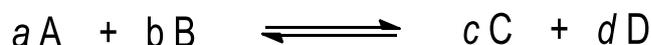
We know that the speed of a chemical reaction depends on the concentrations of reacting molecules or species involved in a reaction. According to the Law mass action "The rate of a reaction is proportional to the

concentrations of the reacting species, each raised to a power which is equal to the corresponding stoichiometric number of the substance appearing in the reaction”.

Consider the following reaction:

$$\text{Rate} = - \frac{d[A]}{dt} = - \frac{d[C]}{dt} = k [A]^a [B]^b \quad \text{--- Equation 1}$$

For this reaction, rate law is given by



Where k is called rate constant, and $[A]$ and $[B]$ are the concentrations of reactant species. In this case, the exponent a is the order of reaction with respect to the reactant A , and b is the order of the reaction with respect to reactant B . These orders are known as partial orders. The overall reaction order is $(a+b)$. The reaction order is purely experimental quantities and therefore, can be determined only by experiment. The reaction order does not depend on the concentration of the reactants. The knowledge about order of reaction allows us to draw and understand organic reaction mechanisms, and also helps us to identify the rate-determining step of a multistep organic reaction. The order of a single-step organic reaction is equal to the stoichiometric coefficients for each reactant, but for complex multistep reaction, the order may or may not be equal to their stoichiometric coefficients.

The exponents a and b in the rate equation-1 can be determined experimentally by examining how the rate is affected by changing the concentration of A and B each separately. If, doubling the concentration of A doubles the rate of reaction, but doubling the concentration of B has no effect on the rate, the reaction is called first order reaction. The rate equation is given by:

$$\text{Rate} = - \frac{d[A]}{dt} = k [A]$$

If, on the other hand, doubling the concentration of A doubles the rate of reaction, and doubling the concentration of B also doubles the rate, the reaction is said to be a second-order reaction, whose rate equation is:

$$\text{Rate} = - \frac{d[A]}{dt} = k [A] [B]$$

If, doubling the concentration of A quadruples the rate of reaction, and doubling the concentration of B has the effect of doubling the rate, the reaction is second order in $[A]$ and first order in $[B]$. In such cases, the reaction is overall third-order reaction. The rate equation is:

$$\text{Rate} = - \frac{d[A]}{dt} = k [A]^2 [B]$$

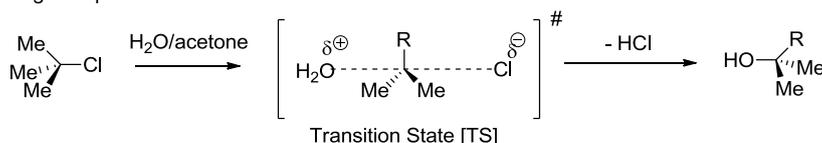
There are examples of higher-order reactions, but they are relatively rare.

Determination of the rate equation gives us an inside into the mechanism of the organic reactions. Any proposed reaction mechanism must fit the experimentally derived rate expression. We can illustrate this by taking the following examples.

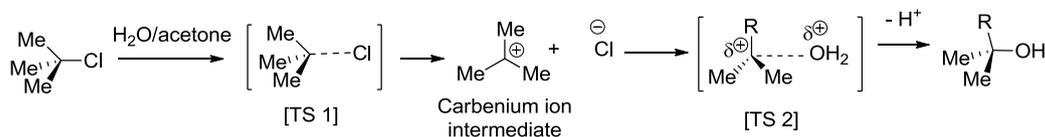
Example:

The solvolysis reaction of tert-butylchloride in aqueous acetone may be a two-step process (S_N1 mechanism) in which two transition states and one carbocation intermediate are formed or a single-step process (S_N2 mechanism) which proceeds through the formation of only one transition state as depicted in the following schemes.

Single-step mechanism:



Two-step mechanism:



However, if we measure how the rate of reaction varies with the concentration of tert-butyl chloride and of the water, we can find that the rate equation

$$\text{Rate} = k [\text{Me}_3\text{C-Cl}]$$

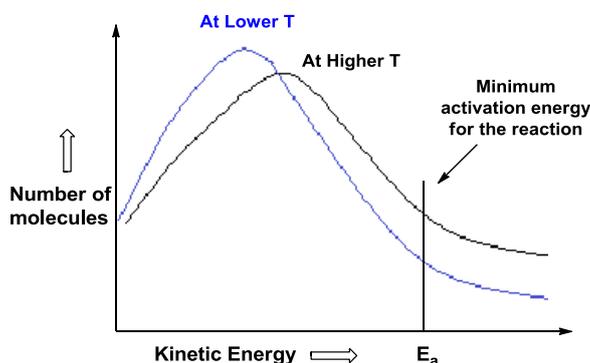
The reaction is thus first order overall. Therefore, only tert-butyl chloride must be involved in the rate-limiting step. On the basis of this rate law we must say that the solvolysis of tert-butyl chloride in aqueous acetone follows a two-step mechanism and the rate-limiting step is the breaking of the C-Cl bond to form the carbocation intermediate.

Molecularity of the reaction:

The molecularity of an elementary reaction can be defined as the number of reacting species that take part in the formation of transition state. While the order of a reaction is determined experimentally, the molecularity is purely a theoretical concept. If only one molecule is involved in the formation of transition state, the molecularity of the reaction is 1 (*unimolecular*), and if two molecules are involved in the formation of transition state, the molecularity of the reaction is 2 (*bimolecular*) and so on.

Rate-Temperature relationship:

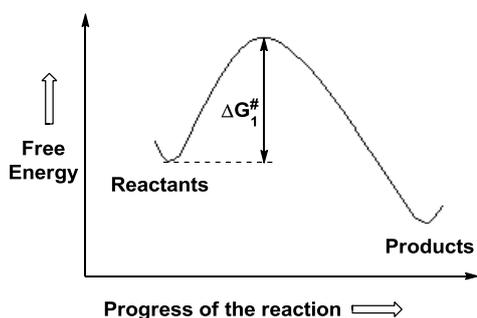
The rate of chemical reaction is also sensitive to change in temperature of the reaction. We know that a chemical reaction occurs when there is a collision between the reactant molecules. However, every collision between reactant molecules does not lead to product formation. The fraction of collisions that occur with sufficient energy to overcome the energy barrier of the reaction will give the product. These collisions may be called successful collisions. The greater the number of successful collisions, the faster is the rate of reaction. The rates of chemical reactions increase by raising the temperature. This is because raising the temperature of the reaction causes an increase in the average kinetic energy of the reacting molecules. Consequently, at higher temperature, a greater number of reacting molecules will have the sufficient kinetic energy for successful collisions leading to the formation of product. This can be shown by plotting the distribution of molecular kinetic energies at two different temperatures. If the activation energy of the reaction, E_a , is as shown in the diagram, it is clear that the reaction proceeds faster at higher temperature because there is a larger area under the curve after the activation energy (E_a). A reaction rate approximately doubles for every increase in temperature of 10 °C.



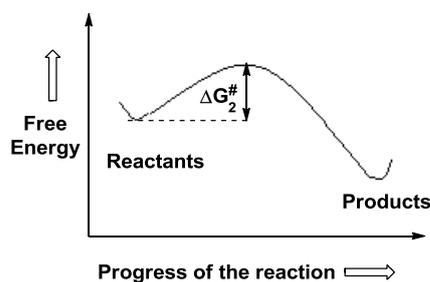
Rates of Chemical Reactions and activation energies:

Rates of chemical reactions are determined not by the free energy difference (ΔG°) between starting material and product, but by the height of the energy barrier separating starting material from product. The difference in free energy between the starting material and the transition state represents the energy barrier for the conversion of reactants to products. This barrier that has to be overcome when reactant molecules are converted into products is called **activation energy barrier**. The activation energy (ΔG^\ddagger) is the energy difference between the reactants and the transition state. Large activation energy results in a slow reaction and small activation energy results in a fast reaction.

a) Exergonic reaction of slower rate



b) Exergonic reaction of faster rate



The free energy of activation (ΔG^\ddagger) is related to enthalpy of activation and entropy of activation by the following equation:

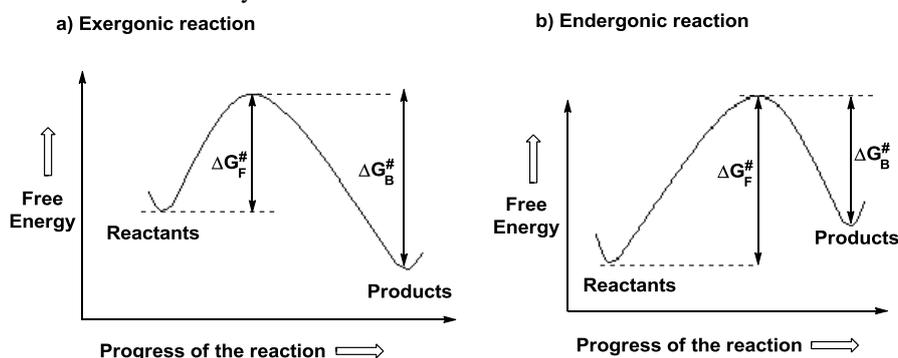
$$\Delta G^\ddagger = \Delta H^\ddagger + (-T\Delta S^\ddagger)$$

where ΔH^\ddagger is the enthalpy of activation, which depends on the bond stretching in the transition state and ΔS^\ddagger is the entropy of activation, which measures the degree of disorder in the transition state. T is the temperature in Kelvin. The contribution of entropy to the free energy of activation depends on the temperature and it will have greater contribution when the temperature is high. Under this condition, the reaction is called entropy controlled. However, at lower temperature the contribution of entropy to the free energy of activation is diminished. Under this condition, the enthalpy of activation will control the reaction and the reaction is called enthalpy controlled.

The free energy of activation is also related to the rate constant (k) for the reaction by the relation:

$$\Delta G^\ddagger = -RT \ln k \quad \text{where R is the gas constant and T is the temperature in Kelvin.}$$

If ΔG^\ddagger is large, i.e., the free energy difference between the starting material and the transition state is large; it will be very difficult for the starting materials to overcome this barrier. Such reactions are called kinetically stable because these reactions will not proceed rapidly. If, on the other hand, the ΔG^\ddagger is small; it will be quite easy for the starting materials to overcome the barrier. Such reactions are called kinetically stable because these reactions will proceed quickly. For elementary reversible reaction (exergonic and endergonic reactions), this can be represented by the energy profile diagram such as in fig. below. In these figures, the ΔG_F^\ddagger represents the activation energy for the forward reaction and the ΔG_B^\ddagger represents the activation energy for the backward reaction. In case of exergonic reaction (Fig. a), the activation energy for forward reaction is smaller than the activation energy for backward reaction i.e., $\Delta G_F^\ddagger < \Delta G_B^\ddagger$. As a result, the rate of forward reaction is faster than the backward reaction and these reactions are called kinetically unstable. Conversely, in case of endergonic reaction (Fig. b), the activation energy for forward reaction is greater than the activation energy for backward reaction, i.e., $\Delta G_F^\ddagger > \Delta G_B^\ddagger$. As a result, the rate of forward reaction is slower than the backward reaction and these reactions are called kinetically stable.



Multistep reactions and rate-determining step:

For multistep reaction, the rate is determined by the activation energy of the rate determining step of the reaction. When an organic reaction proceeds through more than one elementary step, one or more intermediates are formed during the reaction. These intermediates are generally less stable than the reactants and the products, but more stable than the transition states. Moreover, in multistep reactions, there will be more than one energy barrier (or more than one transition state) that must be traversed during the reaction. In such cases, it is commonly the step that involves the highest energy transition state determines the rate of product formation. This step is called **rate-determining step or rate-limiting step**. However, the observed rate of a multistep reaction is related to the overall energy barrier between the reactants and the highest energy transition state. The concept of the rate-determining step is very important in understanding organic reaction mechanisms. The experimental rate equation can help us to identify which step is rate-determining. In other words, in multistep reactions, the rate-determining step can be determined from the kinetic study of the reaction.

Figure a and **b** are the reaction coordinate diagram for the two-step exergonic reactions which proceeds via the formation of two transition states (TS1 and TS2) and one intermediate (I). The figures show the relationship among the energies of the reactant, the product, the intermediate, and the two transition states. According to this diagram in **Fig. a**, the transition state 1 is higher in energy than the transition state 2 and therefore, the 1st step i.e., the formation of intermediate via the TS1 is rate-limiting. According to **Fig. b**, the transition state 2 is higher in energy than the transition state 1 and therefore, the 2nd step i.e., the conversion of intermediate into product via TS2 is rate-limiting in this case. However, the overall activation energy of this reaction will be

ΔG_0^\ddagger , which is the free energy difference between the reactant and the highest energy transition state, i.e., the TS2. Another information that can be obtained from **Fig. a** is that the activation energy barrier for conversion of the intermediate into the product is much lower than that for conversion of the intermediate back to the reactant and consequently, as soon as the intermediate is formed in rate-limiting step, it is immediately transformed into the product. There is no equilibrium between the reactant and the intermediate. However, as in **Fig. b**, the activation energy barrier for conversion of the intermediate into the product is much higher than that for conversion of the intermediate back to the reactant. Consequently, as soon as the intermediate is formed, it immediately reverts to the reactant before it is going to produce the product. The result is that there will be equilibrium between the reactant and the intermediate. In such cases the steady state approximation can be used to derive a rate equation.

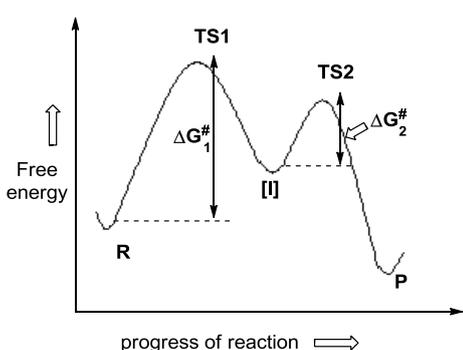


Fig.a: Energy diagram of a two step reaction for which 1st step is rate-limiting.

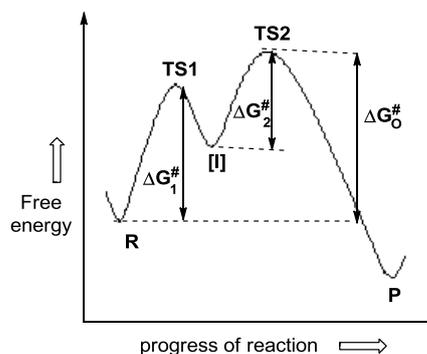


Fig b: Energy diagram of a two step reaction for which 2nd step is rate-limiting.

Figure c represents energy profile of a three step exergonic reaction for which the 1st step is rate-limiting, and the third transition state is higher in energy than the second transition state and the second unstable intermediate is more stable than the second. Figure d represents energy profile of a three step exergonic reaction for which second step is rate-limiting and the first transition state is higher in energy than the third transition state.

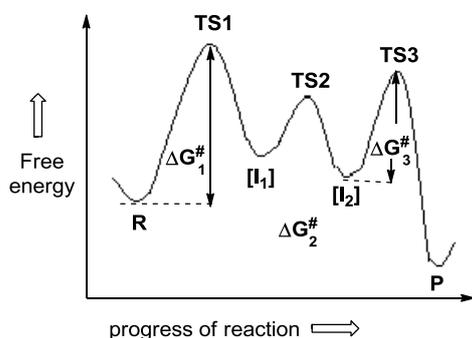


Fig. c: Energy diagram of a three step exergonic reaction for which 1st step is rate-limiting.

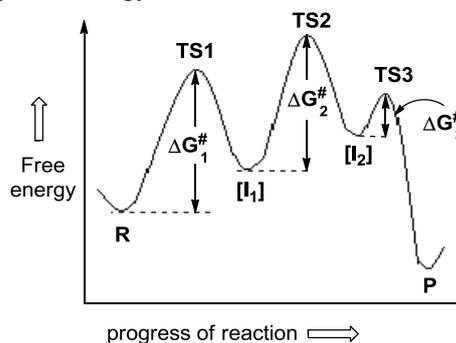


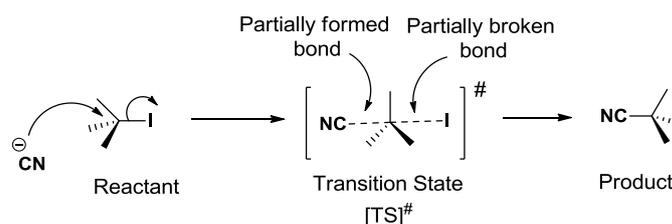
Fig d: Energy diagram of a three step exergonic reaction for which 2nd step is rate-limiting.

Thus, the overall activation energy (ΔG^\ddagger) of this reaction is the energy difference between the reactants and the highest energy transition state.

Activated Complex or Transition State:

The activated complex or transition state is a strained and unstable molecular entity which has the bonds and electrons distribution distorted relative to those in both the reactant and product. In energy diagram, the point of maximum free energy in the conversion of reactants into products represents the transition state. The structure of the transition state is determined not by a discrete, molecular species, but by a unique arrangement of reacting species in which existing bonds are partially broken and new bonds is partially formed i.e., it shows some structural characteristics of both reactant and product. It is represented by the bracketed structure, [TS], with a superscripted double dagger, #. Because the transition states have a lifetime of approximately one molecular vibration ($\approx 10^{-12}$ sec) they cannot be isolated. By convention, the partially formed and broken bonds in the transition state structure are represented by dotted lines, and the whole structure is shown in brackets with a superscripted double dagger in the reaction mechanism. For example, the displacement of iodide ion in alkyl iodide by cyanide ion involves back-side attack of the cyanide ion. In the transition state of this reaction, the

NC-C sigma bond is partly formed and the C-I bond is partly broken, which is represented in the following scheme.



A transition state has probability of forming the reactant or product. That is, the reactant and products are in equilibrium with the transition state. Therefore, product formation cannot be assured even if the transition state is attained, because the transition state may revert back into the reactant.

Rate Constant & Activation energy:

Though the rate constant is independent on the concentration of the reactant molecules or the product molecules, it is dependent on the temperature of the reaction. Arrhenius observed that the rate of reaction increased exponentially as the temperature of the reaction is raised. He correlates the rate constants to the experimental activation barriers and to the reaction temperatures by his famous equation known as **Arrhenius Equation**.

The Arrhenius equation is:

$$k = A e^{-E_a/RT} \quad \text{Or} \quad \ln k = \ln A - E_a/RT$$

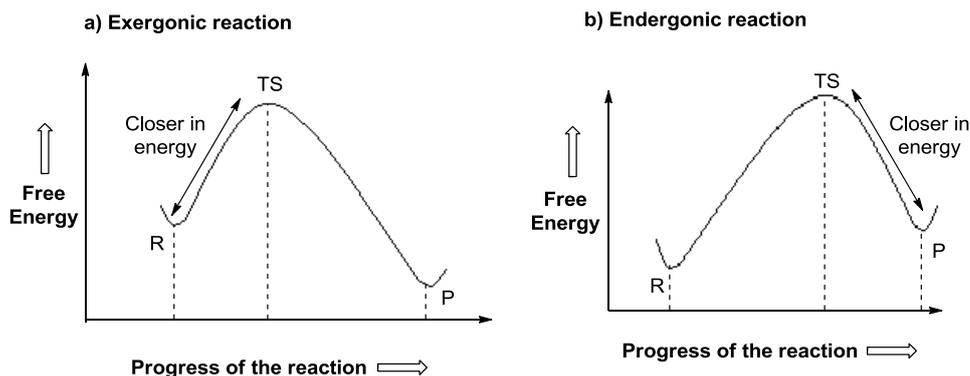
In this equation for rate constant, k , R is the gas constant and T is the absolute temperature. A is a constant, which represents the fraction of the total number of collisions that result in the formation of products successfully, and it is independent of temperature. E_a is the experimental activation energy barriers.

Since the temperature term is appeared in the denominator of the second equation, raising the temperature will increase the rate constant of the reaction and, therefore, faster will be the rate of the reaction. Furthermore, Since the exponential term has negative sign, increasing the experimental activation energy (E_a) will decrease rate constant of the reaction and therefore, causes the reaction to be slower. The rate constant of the reaction can be increased by decreasing stability of the reactants or by increasing stability of the transition state because these changes decrease the activation energy barrier of the reaction.

Note: If we consider free energy, the activation energy of the reaction is designated as ΔG^\ddagger ; if we consider enthalpy, the activation energy is designated by ΔH^\ddagger . The basic difference between the free energy of activation (ΔG^\ddagger) and experimental activation energy (ΔH^\ddagger) is that free energy of activation is composed of both enthalpy and entropy terms, whereas the experimental activation energy contains only the enthalpy term ($E_a = \Delta H^\ddagger + RT$) because the entropy term can be understood through the A term in the Arrhenius equation. The experimental activation energy, ΔH^\ddagger , in the Arrhenius equation comprises the energy necessary to increase the vibrations in bonds that are going to break in the overall reaction. Consequently, the ΔH^\ddagger is the approximate activation energy barrier of the reaction, whereas the ΔG^\ddagger is the true energy barrier of the reaction because most of the reactions depend on the changes of both the enthalpy and entropy.

The Hammond Postulate:

The transition states (or the activated complexes), as discussed before, are very high energy and transient species, which contain partially broken and formed bonds. But this extent of bond breaking and bond formation cannot be directly predicted by any experimental techniques. The Hammond postulate is likely the most useful guiding principle that allows us to quickly predict the structure of these transition states and the shape of a reaction coordinate diagram. It states that "for any step of the reaction the structure of the transition state resembles the adjacent reactant, intermediate or product that is closer in energy to, as long as the energy difference between the transition state and the adjacent structure is not too large". Using this principle, we can make a generalization about the structure of a transition state in any exothermic or endothermic reaction (Figure X). For an exothermic process, in which the reactants are higher in energy than the products, the energy of the transition state is closer to the reactants than to the products. Consequently, the structure of the transition state more closely resembles the structure of the reactants. For an endothermic reaction, in which the products are higher in energy than the reactants, the energy of the transition state is closer to the products than the reactants. Consequently, the structure of the transition state more closely resembles the structure of the products. Transition states close to reactants have rather little bond breaking or making. Transition states close to products have almost completed bond breaking and making. The former transition state is called early transition state and the latter is called late transition state.



In multistep reactions, each individual step can be considered as a separate elementary chemical reaction and each step has a transition state, reactant and product, the structure of transition state of each step can be predicted readily using Hammond postulate. Since intermediates are higher in energy than the reactants and the products, the transitions states lie much closer in energy to the intermediates than to the reactants or the products. In a two-step reaction, the first step is endothermic, and therefore, TS1 resembles the product of that step, which is the intermediate (I) for the overall reaction, more than it resembles the reactant. The second step is exothermic, and therefore, TS2 resembles the reactant (Intermediate for the overall reaction) of that step more than it resembles the reaction product. Therefore, for two step reactions (as depicted in fig. below), irrespective of whether the first step or the second step is rate-limiting, the structures of both transition states closely resembles to the structure of the intermediate rather than to the structure of reactant or product.

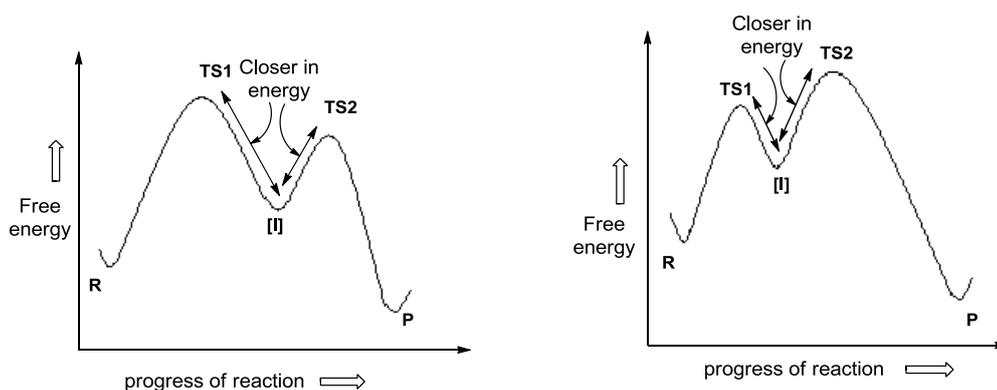
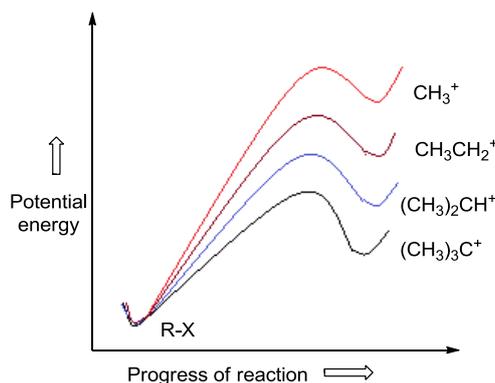


Fig.a: Energy diagram of a two step reaction in which 1st step is rate-limiting.

Fig b: Energy diagram of a two step reaction in which 2nd step is rate-limiting.

Hammond postulate can be applied to predict reactivity and to draw the reaction coordinate diagrams of the reactions that involve rate-limiting formation of carbocation intermediate. Since the transition state leading to carbocation intermediate resembles the structure of carbocation itself, the stability of the carbocation intermediates directly affect the barrier height. Therefore, anything that tends to stabilize a carbocation intermediate lowers the energy of the transition state leading up to it. And as the transition state decreases in energy, the energy barrier of ionization to produce carbocation must also decrease.

We know that the stability of the alkyl carbocation decreases in the order: $(\text{CH}_3)_3\text{C}^+ > (\text{CH}_3)_2\text{CH}^+ > \text{CH}_3\text{CH}_2^+ > \text{CH}_3^+$. Therefore, the transition state leading to 3° carbocation is more stable and lower in energy than one leading to a 2° carbocation, which, in turn, is lower in energy than 1° and methyl carbocations. Therefore, rate of heterolytic cleavage of the bond between the carbon and the leaving group in an $\text{S}_{\text{N}}1$ mechanism increases with increasing carbocation stability.



Application of Hammond postulate to other specific reactions will be illustrated in the problem solving approach of this chapter and also in the upcoming chapters of this book.

Limitation of Hammond postulate: Though the Hammond postulate predicts the position of transition state along the reaction coordinate, it cannot give any idea about the height of the barrier compared to the reactant or the product.

Principle of microscopic reversibility:

This principle states that “every reaction is reversible to some extent and the pathway (or the mechanism) for transformation of product back to the reactant is the exact microscopic reverse of the forward pathway”. It follows from this principle that the same sequence of transition states and reactive intermediates in the mechanism of any reversible reaction must be achieved in reverse order for the backward reaction as for the forward reaction. Suppose conversion of R into P is a two-step process in which the first step is rate-limiting. Also suppose that two transition states (TS1 and TS2) and one intermediate (I) are involved in the reaction. Principle of microscopic reversibility says that conversion of P into R (the reverse reaction) must proceed through the same transition states and same intermediate, and through same rate-limiting step.

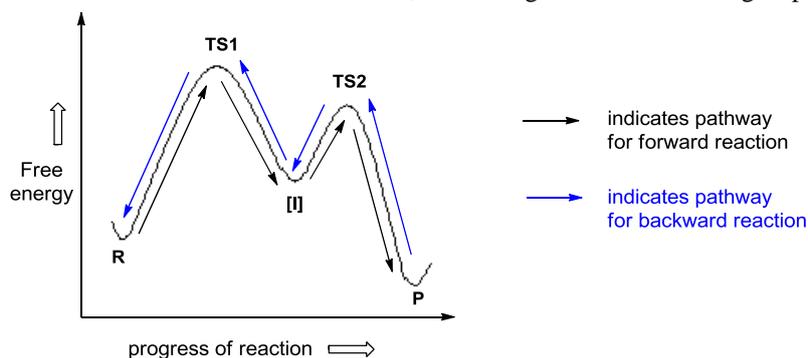
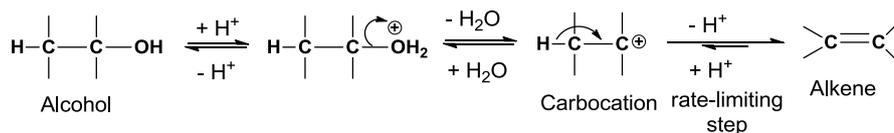


Fig.a: Energy diagram describing the principle of microscopic reversibility

For example, in the hydration of an alkene, because the step involving protonation of the alkene to give a carbocation is rate-limiting, the reverse of this step, i.e., the removal of the proton from carbocation will be the rate-limiting in the dehydration of alcohol. This principle also demonstrates that if a catalyst accelerates a reaction in one direction, the reaction in reverse direction will also be accelerated by catalyst. Therefore, both hydration of alkene and dehydration of alcohol are accelerated by acid catalyst.

Mechanism of dehydration of alcohol:



Mechanism of hydration of alkene:

