Module 7 : Theories of Reaction Rates

Lecture 33 : Transition State Theory

Objectives

After studying this Lecture you will be able to do the following.

- Distinguish between collision theory and transition state theory.

- Obtain the rate constant in terms of an equilibrium constant of the transition state.

- Express the transition state equilibrium constant in terms of the partition functions of the transition state and the

- reactants.

- Associate the rate constant for the reaction {transition state $\rightarrow$ products} with the vibrational frequency of the

- transition state.

- Express the partition function of the transition state $q_c^{\neq}$ as a product of the partition functions for translational and

- other modes.

- Define free energy, entropy and enthalpy of activation.

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- Rationalise the isotope effect on reaction rates.

33.1 Introduction

In collision theory, the detailed nature of the interactions between reactants was not considered. The detailed interactions are best represented through the potential energy surface which will be considered in the next lecture. From the Arrhenius equation, only those collisions with the minimum required energy can lead to the products. Consider one such path which is represented in Fig 33.1.

Figure 33.1 Potential energy of reaction as a function of the reaction coordinate.

The ordinate is the potential energy (PE) and the absissa is the reaction coordinate. At a specific state (configuration of the reactants), the potential energy is maximum, the slope is zero and the PE falls to lower values in both the forward and the reverse direction. All the structures in the vicinity of this transition state may be considered as the "activated complex", which is very reactive. A motion along the "forward" direction will lead to the products. The activated complex theory or the transition state theory provides a way to calculate the rate constant for the reaction. The assumptions involved in the transition state theory are:

1) The electronic motion (which can only be described only quantum mechanically) may be separated from the motion of the nucleii and a classical description of the nuclear motion is used to evaluate the rate constant.

2) The energy distribution of the reactants is described by the equilibrium Boltzmann distribution throughout the reaction.

3) The activated complex which has crossed the transition state can not return to the reactant configuration.

4) In the transition state, motion along the reaction coordinate may be separated from all other motions.

5) The activated complex is also distributed according to the Boltzmann distribution even when the reactants and products are not in equilibrium. This is often called the quasi equilibrium postulate.

Although the terms transition state and activated complex are often used synonymously, the transition state does not have a chemically significant life time. Consider the reaction

$$A + B \rightarrow C_{\neq} \rightarrow P \tag{33.1}$$

In the equation (32.1), C is the activated complex which forms the products P with a unimolecular rate constant $k_{\neq}$

$$d[C_{\neq}] / dt = k_{\neq}[C_{\neq}] \tag{32.2}$$

The concentration of C is expressed in terms of the concentrations of A and B through the proportionality,

$$[C_{\neq}] = K_{\neq}[A][B] \tag{33.3}$$

substituting eq. (33.3) into (33.2), we have

$$d[C_{\neq}] dt = k_2[A][B] \text{ where } k_2 = k_{\neq} K_{\neq} \tag{33.4}$$

We now will determine the values of the constants $k_{\neq}$ and $K_{\neq}$. It should be obvious that the process represented in Eq. (33.3) is not a regular equilibrium process because, as the products are formed, [A] and [B] are decreasing with time and $[C_{\neq}]$ is not increasing with time since the collisions responsible for the formation of $C_{\neq}$ are themselves decreasing in frequency as the reaction evolves. Although transition state theory has contributed enormously to the growth of chemical kinetics, this is one of its weak links.

The activated complex can exhibit several motions such as translations, rotations and vibrations, since it has a finite life time. The motion leading to the product is assumed to be a specific vibration with a frequency ν. This vibrational motion is along the reaction coordinate is equated to the constant $k_{\neq}$.

$$k_{\neq} \approx \nu \tag{33.5}$$

Our next task is the determination of the concentration of C . Let us express the equilibrium constant for the reaction $A + B \rightarrow C$ in terms of the partial pressures of A, B and C (p_A , p_B and p_C)

$$K = [C_{\neq}]/[A][B] = [p_{C_{\neq}}/\bar{p}]/[(p_A/\bar{p})(p_B/\bar{p})] \tag{33.6}$$

Where $\bar{p}$ is the standard pressure of 1 bar. These partial pressure can be expressed in terms of molar concentrations of A, B and C as follows.

$$[A] = n_A / V \; ; V = n \, RT / p; \; p_A = x_A \, p = n_A \, p / n$$

$$[A] = n_A \, p / nRT = x_A p / RT = p_A / RT \text{ or } p_A = RT[A] \tag{33.7}$$

In eq. 33.7, V = total volume, p = total pressure, n = total number of moles, n_A = number of moles of A, x_A = n_A / n, the mole fraction, RT = gas constant x absolute temperature.

Substituting each partial pressure in terms of the mole fractions we have

$$K = RT[C_{\neq}]/\bar{p}/[(RT[A]/\bar{p})(RT[B]/\bar{p})] \tag{33.8}$$

$$= [C_{\neq}]\bar{p}/[A][B]RT \tag{33.9}$$

$$\text{or } C_{\neq} = [A][B]RT/\bar{p}K \tag{33.10}$$

Comparing this equation with eq. (33.3), we have

$$\text{or } K_{\neq} = RT/\bar{p}K \tag{33.11}$$

In eq (33.3), $K_{\neq}$ was merely a proportionality constant and now it has been related to the equilibrium constant for the formation of the activated complex.

Specific vibration of the activated complex along the reaction coordinate leads to product formation. We need to express K of eq. (33.11) in terms of molecular characteristics. In the present case, they are the molecular partition functions. In Lecture 29, we have already learnt that the population of electronic, vibrational, rotational and translational levels is governed by their energies and the temperature through molecular partition functions.

Consider the energy levels for the following equilibrium,

$$A \rightleftharpoons B \tag{33.12}$$

The energy levels of systems containing only A, only B and both A and B are schematically shown in fig (33.2)

Figure 33.2 (a) Energy levels of individual molecules A, B and the individual populations of these levels, (b) Energy levels of the combined system A and B and the relative populations of the combined levels at equilibrium (schematic).

If the molecules of A and B are kept in separate containers, each container will be in a state of equilibrium with the populations of A and B given by their separate Boltzmann distributions. This is shown in Fig 33.2(a). The partition functions of the systems A and B are given by q_A and q_B. Fig 33.2(b) shows the combined system and the population of the levels of the combined system. The population of the ith level of the combined system is given by

$$\eta_i = (N/q)\, e^{-\beta E_i} \tag{33.13}$$

$$\eta_i = NP_i = N\, e^{-\beta E_i/q} \tag{33.14}$$

Where q is the partition function of the combined system and E_i is the energy of the ith level of the combined system. In the combined system, the total population of A molecules at equilibrium is given by summing n_i for A molecules. Similarly for B. We thus have,

$$N_A = \sum_{\text{All levels of A}} \eta_i = N/q \sum_{\text{levels of A}} e^{-\beta (E_i)_A} = (N/q)\, q_A \tag{33.15}$$

$$N_B = \sum_{\text{All levels of B}} \eta_i = N/q \sum_{\text{levels of B}} e^{-\beta (E_i)'_B} \tag{33.16}$$

The prime in eq (33.16) indicates that the levels $(E_i)'_B$ are now measured from the lowest level of the combined states of A and B, which is $(E_0)_A$. Expressing E'_i in terms of E_i, we have,

$$(E_i')_B = (E_i)_B + \Delta E_0 = (E_i)_B + (E_0)_B - (E_0)_A \tag{33.17}$$

we have for N_B,

$$N_B = N/q \sum e^{-\beta E_i - \beta \Delta E_0} = N (q_B/q)\, e^{-\beta \Delta E_0} \tag{33.18}$$

The equilibrium constant is now given by

$$K = N_B/N_A = (q_B/q_A)\, e^{-\beta \Delta E_0} \tag{33.19}$$

For a more general reaction $A + B \rightleftharpoons C + D$, the equilibrium constant is given by

$$K = q_C q_D / q_A q_B\, e^{-\beta \Delta E_0} \tag{33.20}$$

where $\Delta E_0 = (E_0)_C + (E_0)_D - (E_0)_A - (E_0)_B$ (33.21)

When we have a reaction such as $A + B \rightleftharpoons C^{\neq}$, the equilibrium constant given by

$$K = (N_A \, q_C^{\neq} / q_A \, q_B) \, e^{-\beta \Delta E_0}$$ (33.22)

Where $\Delta E_0 = (E_0)_C^{\neq} - (E_0)_A - (E_0)_B$. Here N_A is the Avogadro number.

Returning to eq (33.4), $k_2 = k^{\neq} K^{\neq}$, the unimolecular rate constant $k^{\neq}$ is taken as proportional to the vibrational frequency along the reaction coordinate

$k^{\neq} = \nu$

The partition functions for this vibrational motion of the transition state is

$$(q_V)_C^{\neq} = 1/(1 - e^{-h\nu/k_BT})$$ (33.24)

Usually this frequency is quite small because the transition state falls apart into products with this frequency- Very high frequencies of the transition state are improbable and they would lead, not to the usual products but to rather highly disintegrated products.

Expanding the denominator, $e^{-h\nu/k_BT} \approx 1^{-h\nu/k_BT}$,

$$(q_V)_C^{\neq} = k_BT / h\nu$$ (33.25)

Writing $q_C^{\neq}$ in terms of the vibrational modes $(q_v)_C$ [which is approximated as $k_BT / h\nu$] and all the other remaining modes [$\bar{q}_C^{\neq}$], we have for $q_C^{\neq}$,

$$q_C^{\neq} = (k_BT / h\nu) \, \bar{q}_C^{\neq}$$ (33.26)

Combining (33.26), (33.23) and (33.4), we have,

$$k_2 = k^{\neq} K^{\neq} = \nu (RT / p^0) K = (\nu \, k_BT / h\nu)[(N_A \, \bar{q}_C^{\neq} / q_A \, q_B) \, e^{-\beta \Delta E_0} RT / p^0)$$ (33.27)

$$= k_B T / h \, \overline{K}$$ (33.28)

Where $\overline{K}$ is the second, square bracketed expression in eq (33.27) which is akin to an equilibrium constant. There are often factors not included in (33.27) and they are included through a transmission coefficient κ and the rate constant in the transition state theory becomes,

$$k_2 = \kappa (k_BT / h) \, \overline{K}$$ (33.29)

We want to express $\overline{K}$ in terms of molecular partition functions. Let us obtain a formula for simple species of A and B where A and B are atoms. The partition function of atoms is simply the translational partition function (as rotations and vibrations are absent). The translational partition function was given earlier in Lecture 29 as

$$q_T = (2\pi m k_BT / h^2)^{3/2} V$$ (33.30)

and using the molar volume, the partition function for A becomes

$q_{T,A} = (2\pi m_A k_B T / h^2)^{3/2} V_m^0$

$= V_m^0 / \Lambda_A^3 , \quad \Lambda_A = h / (2\pi m_A k_BT)^{1/2}$ (33.31)

Where V^0_m is the standard molar volume, given by RT/p^0 and Λ_A is called the de Broglie thermal wavelength. For the activated complex, the partition function is the product of translational, vibrational and rotational partition functions, because in our present model, AB is a diatomic. However, we have already considered the vibrational partition function in (33.24) and we need to consider $\bar{q}_{C^{\neq}}$ now which includes only translation and rotation .

This is given by

$$\bar{q}_{C^{\neq}} = V^0_m / \Lambda^3_{C^{\neq}} \cdot (2 I k_B T / \hbar^2)$$

(33.32)

The term in the brackets of eq (33.31) is the rotational partition function of the activated complex. The moment of inertia I is given by μr^2 where r is the "bond length" of the activated complex and $\mu = m_A m_B / (m_A + m_B)$) is the reduced mass. Substituting the values of q_A, q_B and q_C in equations (33.27) and (33.28), we get

$$k_2 = {}^{\kappa} (k_B T / h)(RT /p^0)N_A (\Lambda^3_A \Lambda^3_B / \Lambda^3_{C^{\neq}} V^0_m) (2 I k_B T / \hbar^2) e^{-\Delta U^0/RT}$$

(33.33)

Canceling RT/p^0 and V^0_m (which are equal) and substituting the values of Λ^0_A, Λ^0_B and $\Lambda^0_{C^{\neq}}$, we get

$$k_2 = N_A (8 k_B T / \pi \mu)^{1/2} (\kappa \pi r^2) e^{-\Delta U^0/RT}$$

(33.34)

If we identify the reaction cross section σ^* as $\kappa \pi r^2$, this equation, (33.32) is identical to the equation derived using a simple collision theory of lecture 32. It is indeed remarkable that two very different theories give the same result! Does it mean that this result is more "correct" than the result that is usually obtained from a single theory ? While it would be tempting to say yes, what this means is that we have captured some of the essential features relevant in the dynamics of chemical reactions. Further improvements will come when we consider the cross sections of each of the states of the reacting species and also when we remove the requirement that $C^{\neq}$ is not in equilibrium with A and B. In the next section, we relate k_2 to the activation parameters for the reaction.

33.2 Activation Parameters s

In the Arrhenius theory, the only activation parameter that was introduced was the activation energy. In the transition state theory developed in this lecture, we have related the concentration of the activated complex to the reactant concentrations through an equilibrium constant K. Treating $(p^0/RT) \bar{K}$ of eq (33.27) and (33.28) as an equilibrium constant (although one vibrational mode is removed from $C^{\neq}$), we can define the Gibbs free energy of activation $\Delta G^{\neq}$ as

$$\Delta G^{\neq} = - RT \ln (\bar{K} p^0 / RT)$$

(33.35)

the rate constant k_2 becomes

$$k_2 = {}^{\kappa} k_B T /h (RT / p^0) e^{-\Delta G^{\neq}/RT}$$

(33.36)

The free energy of activation can be divided into enthalpy and entropy terms (analogous to G = H - TS) through

$$\Delta G^{\neq} = \Delta H^{\neq} - T \Delta S^{\neq}$$

(33.37)

For the time being let us either take = 1 or include it in the entropy term. The rate constant then becomes

$$k_2 = B e^{\Delta S^{\neq}/R} e^{-\Delta H^{\neq}/RT} \text{ with } B = (k_B T / h)(R T / p^0)$$

(33.38)

The activation energy of the Arrhenius equation, E_a is defined through $E_a = R T^2 (d \ln k_2 / dT)$. Substituting k_2 into this, we get

$$E_a = \Delta H^{\neq} + 2 RT$$

(33.39)

Substituting this in eq (33.38), we get

$$k_2 = e^{-2} B \, e^{\Delta S^{\neq}/R} \, e^{-E_a/RT} \tag{33.40}$$

and the Arrhenius factor A becomes

$$A = e^{-2} B \, e^{\Delta S^{\neq}/R} \tag{33.41}$$

Usually, when A and B form a complex $(AB)^{\neq}$, more ordering is created and entropy is reduced. $\Delta S^{\neq}$ is thus negative. This is based on a collision complex model for the reaction. In addition to this decrease, there is a further orientational or steric decrease due to the preference of only certain configurations for the activated complex (as illustrated in lecture 32 for the reaction between C_2H_4 and H_2. The steric factor of collision theory may be associated with $e^{\Delta S^{\neq}_{steric}/R}$, i.e.,

$$P = e^{\Delta S^{\neq}_{steric}/R} \quad \text{where} \tag{33.42}$$

$$\Delta s^{\neq} = \Delta s^{\neq}_{\text{collisional}} + \Delta s^{\neq}_{\text{orientational or steric}} \tag{33.43}$$

Similar to activation enthalps and entropy, activation volume can also be defined through $\partial \Delta G^{\neq}/\partial p = \Delta V^{\neq}$. For reactions in solution, these $\Delta V^{\neq}$ values are small, but for gas phase reactions, they may be approximated by the ideal gas values

$$P \Delta V^{\neq} = \Delta n^{\neq} RT \tag{33.44}$$

Example

For the $K + Br_2 \rightarrow KBr + Br$ reaction at 300 K, find the thermodynamic activation parameters $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ of the transition state theory.

Solution :

The Arrhenius parameters for the above reaction are (from Table 32.1) A = 1.0 * 10^{12} m^{-1} s^{-1} and E_a = 0 kJ/ mol

$$\Delta S^{\neq} = R \ln \{ h A \, \bar{p} / N_A \, e^2 \, k^2_B T^2 \}$$

Here h = 6.65 * 10^{-34} Js, $\bar{p}$ = 1 bar = 10^5 J/m^3, N_A = 6.02 * 10^{23} mol^{-1}

k_B = 1.38 * 10^{-23} J/ K, A = 10^{12} M^{-1} s^{-1} = mol^{-1} dm^{+3} s^{-1}

Substitute all these values and show that

h A $\bar{p}$ / N_A e^2 $k^2_B T^2$ = 7.812 * 10^{-11} $(A/M^{-1}s^{-1})$ / $(T/K)^2$

Substituting the above value in the equation for $\Delta S^{\neq}$, we have

$\Delta S^{\neq}$ = R ln { 7.812 * 10^{-11} * 10^{12} * 300^2 }

= - 58 JK^{-1} mol^{-1}

$\Delta H^{\neq}$ = E_a - 2 RT = 0 - 2* 8.314 * 300 J / mol

= -2.5 kJ / mol

$\Delta G^{\neq}$ = $\Delta H^{\neq}$ - T $\Delta S^{\neq}$ = -2.5 - 300 * (-58) / 10^{-3} kJ / mol

= 15 kJ / mol

Recap

In this Lecture you have learnt the following

Summary

In this lecture, you have been introduced to the transition state theory of reaction rates. This theory relates the rate constant to the activation parameters involved in the rate process, namely, the free energy, enthalpy and entropy of activation.

The concentration of the transition state is dependent on the reactant concentrations, and this proportionality constant $K^{\neq}$ is expressed in terms of the equilibrium constant K between the reactants and the transition state. This K is expressed in terms of the partition functions of reactants and the transition state and this equilibrium is rationalized through the population equilibration between the reactants and the transition state. Although the activated complex refers to the region on the potential energy diagram in the vicinity of the transition state (which is one point on the potential energy curve), the two terms are often used synonymously. The decomposition rate of the activated complex is related to a vibrational frequency of the transition state. Through this vibration, the activated complex is converted to the products. The steric factor P encountered in the collision theory is related to the steric or orientational entropy of activation, $P = \exp(\Delta S^{\neq}_{steric}/R)$. The effect of isotopic substation on the kinetics of deuteration is explained using the transition state theory.