University of Washington
Department of Chemistry
Chemistry 453
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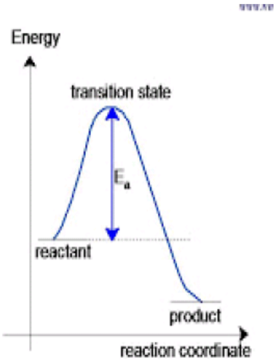
Lecture 20: Transition State Theory. ERD: 25.14

A. Transition State Theory

- Transition State Theory (TST) or Activated Complex Theory (ACT) is a reaction mechanism originally developed to describe gas phase collision reactions. It has the general reaction scheme:

$$A+B \overset{K^\dagger}{\rightleftharpoons} (AB)^\dagger \xrightarrow{k^\dagger} AB \qquad (20.1)$$

Where the reactants A and B collide to first form a transition state or activated complex which is designated $(AB)^\dagger$. The idea behind TST is that the transition state is an unstable, short-lived complex. In the case of a simple diatomic collision the transition state $(AB)^\dagger$ consists of the A-B pair joined by a very weak bond. The colliding molecules A and B are assumed in "equilibrium" with the transition state where



$$K_C^\dagger = \frac{[AB]^\dagger}{[A][B]} \qquad (20.2)$$

- This equilibrium notation however involves the transition state which actually exists at a energy maximum and is thus transitory in nature, as its name implies.
- For the diatomic reaction mechanism the rate is given by

$$rate = k^\dagger\left[AB^\dagger\right] = k^\dagger K_C^\dagger [A][B] = k_2 [A][B] \qquad (20.3)$$

  - To evaluate the rate constant k_2, we can apply statistical methods to $K^\dagger$

$$K_C^\dagger \approx \frac{\dfrac{q_{AB}^\dagger}{V}}{\dfrac{q_A}{V}\dfrac{q_A}{V}} = \frac{q_{AB}^\dagger V}{q_A q_A} = K^\dagger V \qquad (20.4)$$

where the partition functions of A, B, and $AB^\dagger$ are q_A, q_B, $q^\dagger_{AB}$, respectively .

  - The treatment of $q_{AB}^\dagger$ requires some explanation. It is assumed that when A and B form the transition complex the complex acquires translation, rotational, vibrational and electronic motions, which all must be reflected in the partition function, i.e.

$$\begin{aligned} q^{\dagger}_{AB} &= q^{\dagger}_{trans} q^{\dagger}_{rot} q^{\dagger}_{vib} q^{\dagger}_{elec} \\ &\frac{\left(2\pi m^{\dagger} k_B T\right)^{3/2}}{h^3} \frac{8\pi^2 I^{\dagger} k_B T}{\sigma h^2} \frac{e^{-h\nu^{\dagger}/2k_BT}}{1-e^{-h\nu^{\dagger}/k_BT}} g^{\dagger}_1 e^{D^{\dagger}_e/k_BT} \\ &= \frac{\left(2\pi m^{\dagger} k_B T\right)^{3/2}}{h^3} \frac{8\pi^2 I^{\dagger} k_B T}{\sigma h^2} \frac{1}{1-e^{-h\nu^{\dagger}/k_BT}} g^{\dagger}_1 e^{D^{\dagger}_0/k_BT} \end{aligned} \tag{20.5}$$

- In 20.5 the mass of the transition state in the translational partition function is just $m^{\dagger} = m_A + m_B$. In the rotational partition function where the reduced mass $\mu = \dfrac{m_A m_B}{m_A + m_B}$, $I^{\dagger} = \mu\left(R^{\dagger}\right)^2$ is the moment of inertia of the transition complex and . The term $g^{\dagger}_1$ is the degeneracy of the ground electronic state of the transition complex and $D^{\dagger}_0 = D^{\dagger}_e - \frac{h\nu^{\dagger}}{2}$ is the dissociation energy of the transition complex.
- The vibrational motion is treated in the following way. We assume as A and B come together to form the transition complex that translational motion along the reaction coordinate is eventually converted in part to a vibrational motion of the bond also directed along the reaction coordinate. We use the notation

$$K^{\dagger} = \frac{q^{\dagger}_{AB,trans} q^{\dagger}_{AB,rot} q^{\dagger}_{AB,vib}}{q_A q_B} g_1 e^{D^{\dagger}_0/k_BT} \tag{20.6}$$

  where $q^{\dagger}_{AB,vib} = \dfrac{1}{1-e^{-h\nu^{\dagger}/k_BT}}$ is a reduced vibrational partition function.

- Now the vibrational of the bond in the transition complex is assumed to occur at a very low frequency such that

$$q^{\dagger}_{AB,vib} = \frac{1}{1-e^{-h\nu^{\dagger}/k_BT}} \approx \frac{1}{1-\left(1-h\nu^{\dagger}/k_BT\right)} = \frac{k_BT}{h\nu^{\dagger}} \tag{20.7}$$

- In other words the bond vibration is calculated in the high temperature limit. Now we also assume that the transition complex is converted to product AB within a vibrational period so that $k^{\dagger} \approx \nu^{\dagger}$. Using this expression and equation 20.7 we obtain

$$\begin{aligned} k_2 &= k^{\dagger} K^{\dagger}_C = k^{\dagger} K^{\dagger} V \approx \nu^{\dagger} \frac{q^{\dagger}_{AB,trans} q^{\dagger}_{AB,rot}}{q_A q_B} \frac{k_BT}{h\nu^{\dagger}} g^{\dagger}_1 V e^{D^{\dagger}_0/k_BT} \\ &= \frac{q^{\dagger}_{AB,trans} q^{\dagger}_{AB,rot}}{q_A q_B} \frac{k_BT}{h} g^{\dagger}_1 V e^{D^{\dagger}_0/k_BT} \end{aligned} \tag{20.8}$$

- This is called the Eyring equation. To equation 20.8 is added ad hoc a constant $\kappa < 1$. This is called the transmission coefficient and expresses the fact that not all collisions result in the formation of the transition complex. Normally $0.5 < \kappa < 1$, but κ can be quite small for atomic collisions. The final form for the Eyring equation is

$$k_2 \approx \kappa \frac{k_B T}{h} \bar{K}^\dagger V \tag{20.9}$$

where $\bar{K}^\dagger = \frac{q^\dagger_{AB,trans} q^\dagger_{AB,rot}}{q_A q_B} g_1^\dagger e^{D_0^\dagger / k_B T}$ is absent the degree of vibrational freedom treated in the high temperature limit and giving rise to the factor of $\frac{k_B T}{h}$.

- Reaction rates are normally measured as per mole quantities so equation 20.9 is multiplied by Avagadro's number

$$k_{2,m} = N_A \kappa \frac{k_B T}{h} \bar{K}^\dagger V = \kappa \frac{RT}{h} \bar{K}^\dagger V \tag{20.10}$$

B. Examples of Diatomic Transition State Calculations

- For the collision of two atoms we have

$$\begin{aligned} q^\dagger_{AB,trans} q^\dagger_{AB,rot} g_1^\dagger &= \frac{V\left(2\pi\left(m_A + m_B\right)k_B T\right)^{3/2}}{h^3} \frac{8\pi^2 \mu \left(R^\dagger\right)^2 k_B T}{h^2} g_1^\dagger \\ q_A &= \frac{V\left(2\pi\left(m_A\right)k_B T\right)^{3/2}}{h^3} g_1^A \\ q_B &= \frac{V\left(2\pi\left(m_B\right)k_B T\right)^{3/2}}{h^3} g_1^B \end{aligned} \tag{20.11}$$

- Then we obtain for the rate constant

$$\begin{aligned} k_2 = \frac{\kappa k_B T}{h} e^{D_0^\dagger / k_B T} \frac{\left(2\pi\left(m_A + m_B\right)k_B T\right)^{3/2}}{h^3} \frac{8\pi^2 \mu \left(R^\dagger\right)^2 k_B T}{h^2} \times \\ \frac{h^3}{\left(2\pi\left(m_A\right)k_B T\right)^{3/2}} \frac{h^3}{\left(2\pi\left(m_B\right)k_B T\right)^{3/2}} \frac{g_1^\dagger}{g_1^A g_1^B} = \sqrt{\frac{8\pi k_B T}{\mu}} \kappa \left(R^\dagger\right)^2 \frac{g_1^\dagger}{g_1^A g_1^B} e^{D_0^\dagger / k_B T} \end{aligned} \tag{20.12}$$

- If $D_0^\dagger$ is reported in units of Joules per mole we must write:

$$k_2 = \sqrt{\frac{8\pi k_B T}{\mu}} \kappa \left(R^\dagger\right)^2 \frac{g_1^\dagger}{g_1^A g_1^B} e^{D_0^\dagger / RT} \tag{20.13}$$

C. More Complicated reactions: Ternary Complexes

- The simplest example of a ternary transition complex is the isotope exchange

$$H_2 + D \rightarrow HD + H \tag{20.14}$$

- The transition complex has linear form $H \cdots H \cdots D$ where the bonds lie along the reaction coordinate. The rate constant has the form:

$$k_2 \approx \kappa \frac{\bar{q}^\dagger_{HHD}}{q_D q_{H_2}} \frac{k_B T}{h} e^{\Delta D_0^\dagger / k_B T} \tag{20.15}$$

where $\Delta D_0^\dagger = D_0^\dagger - D_0^{H_2}$. The partition functions for q_D and q_{H2} are obtained as usual for atomic and diatomic species. The transition complex partition function $\bar{q}_{HHD}^\dagger$ is treated as follows. The transition complex is linear so it has a single moment of inertia and rotations are calculated by the same procedure used for a linear triatomic like CO_2 except that σ=1 for HHD.

- The vibrational partition function is treated as follows. Note for a linear triatomic there are four vibrational modes in the partition function corresponding to symmetric and asymmetric stretches and two equivalent bending modes

$$\underset{\leftarrow}{H}\cdots\underset{\rightarrow}{H}\cdots\underset{\leftarrow}{D} \qquad \underset{\leftarrow}{H}\cdots H\cdots\underset{\rightarrow}{D} \qquad \underset{\downarrow}{H}\cdots\overset{\uparrow}{H}\cdots\underset{\downarrow}{D}$$

$$\begin{matrix} \textit{asymmetric} & \textit{symmetric} & \textit{Doubly degenerate} \\ \textit{stretch} & \textit{stretch} & \textit{bend} \end{matrix}$$

- The asymmetric stretch contributes to the reaction coordinate, is therefore treated in the high temperature limit and yields the $k_B T/h$ term in the Eyring equation. The other three vibrational modes remain in the transition complex partition function

$$\bar{q}_{HHD}^\dagger = \frac{\left(2\pi\left(2m_H + m_D\right)k_B T\right)^{3/2}}{h^3}\frac{8\pi^2 I_{HHD} k_B T}{h^2} g_1^\dagger \prod_{j=1}^{3} \frac{1}{1 - e^{-h\nu_j/k_B T}} \qquad (20.16)$$

.C. Gibbs Energy of Activation

- Returning to the general expression for the reaction rate $k_2 = \kappa \frac{k_B T}{h}\bar{K}_C^\dagger$, we define formally the Gibbs energy of activation

$$\Delta G^\dagger = -RT \ln \bar{K}_C^\dagger \qquad (20.17)$$

- Using equation 28.15 we now define the kinetic constant as:

$$k_{2,m} = \kappa \frac{k_B T}{h} e^{\Delta G^\dagger/RT} \qquad (20.18)$$

- Using the corresponding relationship between the Gibbs energy, enthalpy and entropy... $\Delta G^\dagger = \Delta H^\dagger - T\Delta S^\dagger$ we further obtain:

$$k_2 = \kappa \frac{k_B T}{h} e^{\Delta G^\dagger/RT} = \kappa \frac{k_B T}{h} e^{\Delta S^\dagger/R} e^{-\Delta H^\dagger/RT} \qquad (20.19)$$

- Now for an ideal gas

$$\begin{aligned} &\Delta G = \Delta U + \Delta\left(PV\right) - T\Delta S = \Delta U + RT\Delta n - T\Delta S = -RT\ln K \\ &\therefore \frac{\partial \ln K}{\partial T} = \frac{\Delta U}{RT^2} \end{aligned} \qquad (20.20)$$

- We can now apply equation 20.20 to the equation $k_2 = \kappa \frac{k_B T}{h}\bar{K}_C^\dagger$ to obtain

$$\frac{\partial \ln k_2}{\partial T} = \frac{\partial}{\partial T}\ln\left(\kappa \frac{k_B T}{h}\right) + \frac{\partial \ln \bar{K}_C^\dagger}{\partial T} = \frac{1}{T} + \frac{\Delta U^\dagger}{RT^2} \qquad (20.21)$$

- Also for ideal gases $\Delta H = \Delta U + \Delta\left(PV\right) = \Delta U + RT\Delta n$. For the reaction $A + B \to AB$, Δn=-1. Therefore

$$\frac{\partial \ln k_2}{\partial T} = \frac{1}{T} + \frac{\Delta U^\dagger}{RT^2} = \frac{RT}{RT^2} + \frac{\Delta H^\dagger + RT}{RT^2} = \frac{\Delta H^\dagger + 2RT}{RT^2} \tag{20.22}$$

- The Arrhenius/van’t Hoff equation is for comparison

$$\frac{\partial \ln k_2}{\partial T} = \frac{E_a}{RT^2} \tag{20.23}$$

- We conclude $E_a = \Delta H^\dagger + 2RT$ for Δn=-1. More generally

$$E_a = \Delta H^\dagger + \left(1 - \Delta n\right) RT \tag{20.24}$$

- Using 20.24 we write out the Arrhenius rate law for Δn=-1:

$$k_2 = \kappa \frac{k_B T}{h} e^{\Delta S^\dagger / R} e^{-\left(E_a - 2RT\right)/RT} = \kappa e^2 \frac{k_B T}{h} e^{\Delta S^\dagger / R} e^{-E_a / RT} \tag{20.25}$$