5.62 Physical Chemistry II
Spring 2008

Transition State Theory. I.

Transition State Theory = Activated Complex Theory = Absolute Rate Theory

$$H_2 + F \rightleftarrows [H_2F]^{\ddagger} \xrightarrow{k} HF + H$$

Assume equilibrium between reactants H_2 + F and the transition state.

$$K^{\ddagger} = \frac{[H_2F]^{\ddagger}}{[H_2][F]}$$

Treat the transition state as a molecule with structure that decays unimolecularly with rate constant k.

$$\frac{d[HF]}{dt} = k\left[H_2F\right]^{\ddagger} = kK^{\ddagger}\left[H_2\right]\left[F\right]$$

k has units of $\sec^{-1}$ (unimolecular decay). The motion along the reaction coordinate looks like an antisymmetric vibration of $H_2F^{\ddagger}$, one-half cycle of this vibration. Therefore k can be approximated by the frequency of the antisymmetric vibration $\nu[\sec^{-1}]$

$k \approx \nu \equiv$ frequency of antisymmetric vibration (bond formation and cleavage looks like antisymmetric vibration)

$$\frac{d[HF]}{dt} = \nu K^{\ddagger}\ [H_2]\ [F]$$

$$\frac{d[HF]}{dt} = \nu\left[\frac{(q^{\ddagger *}/N)}{\left(q^{*H_2}/N\right)(q^{F}/N)}\right] e^{-E^{\ddagger}/kT}\left[H_2\right]\left[F\right]$$

$$K^{\ddagger} = \left[\frac{(q^{\ddagger}_{trans}/N)}{\left(q^{H_2}_{trans}/N\right)}\right]\left(\frac{q^{\ddagger}_{rot}}{q^{H_2}_{rot}}\right)\left(\frac{q^{\ddagger *}_{vib}}{q^{*H_2}_{vib}}\right)\left(\frac{g^{\ddagger}_0}{g^{H_2}_0 g^{F}_0}\right) e^{-E^{\ddagger}/kT}$$

Reaction coordinate is antisymmetric vibrational mode of $H_2F^{\ddagger}$. This vibration is fully excited (high T limit) because it leads to the cleavage of the H–H bond and the formation of the H–F bond. For a fully excited vibration

$$h\nu \ll kT$$

The vibrational partition function for the antisymmetric mode is

$$q_{\text{vib}}^{*\text{asym}} = \frac{1}{1-e^{-h\nu/kT}} \;'\; \frac{kT}{h\nu} \qquad \text{since } e^{-h\nu/kT} \approx 1 - h\nu/kT$$

Note that this is an incredibly important simplification. The unknown ν simply disappears! We do not need to estimate it!

$$K^{\ddagger} = \frac{kT}{h\nu}\left[\frac{q_{\text{trans}}^{\ddagger}/N}{\left(q_{\text{trans}}^{H_2}/N\right)\left(q_{\text{trans}}^{F}/N\right)}\right]\left(\frac{q_{\text{rot}}^{\ddagger}}{q_{\text{rot}}^{H_2}}\right)\left(\frac{q_{\text{vib}}^{\ddagger*\prime}}{q_{\text{vib}}^{*H_2}}\right)\left(\frac{g_0^{\ddagger}}{g_0^{H_2}g_0^{F}}\right)e^{-E^{\ddagger}/kT}$$

where

$$q_{\text{vib}}^{\ddagger*\prime} = \prod_{i=1}^{3n-5-1} \frac{1}{1-e^{-h\nu_i/kT}} \qquad \text{if transition state is linear}$$

or

$$q_{\text{vib}}^{\ddagger*\prime} = \prod_{i=1}^{3n-6-1} \frac{1}{1-e^{-h\nu_i/kT}} \qquad \text{if transition state is nonlinear}$$

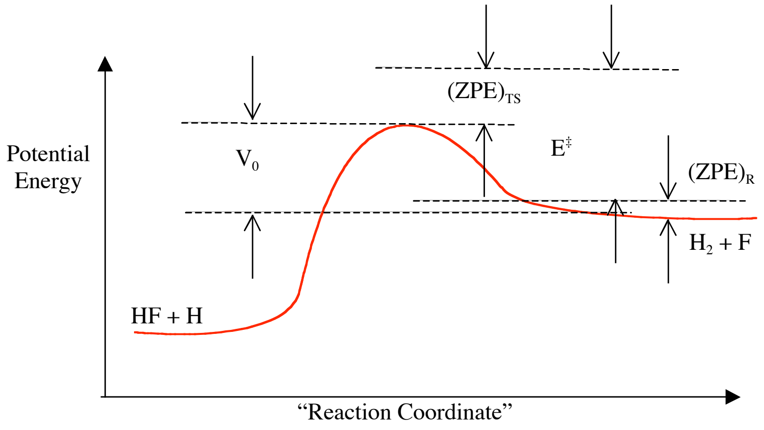
n is # of atoms in transition state

$q_{\text{vib}}^{\ddagger*\prime} \equiv$ partition function from which the antisymmetric vibrational mode is excluded; it has become the *reaction coordinate*

So $$K^{\ddagger} = K^{\ddagger} = \frac{kT}{h\nu}K^{\ddagger\prime}$$

$K^{\ddagger\prime}$ = "special" modification of $K^{\ddagger}$ that excludes the partition function for the antisymmetric vibrational mode

What is $E^{\ddagger}$?



"Reaction Coordinate"

Since a molecule cannot have a vibrational energy lower than its zero point energy, the effective barrier along the reaction coordinate is

$$E^{\ddagger} = V_0 + (\mathrm{ZPE})_{\mathrm{TS}} - (\mathrm{ZPE})_{\mathrm{R}}$$

V_0 is the potential energy difference between the bare barrier (saddle point) and the reactant bare minimum.

For linear $H_2F^{\ddagger}$, n = 3, so 3n–5–1 = 3 regular vibrational modes, thus

$$E^{\ddagger} = V_0 + \underbrace{\frac{1}{2}h\left[\nu^{\ddagger}_{\text{sym.st.}} + 2\nu^{\ddagger}_{\text{bend}} - \nu_{H_2}\right]}_{\text{Difference in ZPE}}$$

FORMULATION of k^{TST}

$$\frac{d[HF]}{dt} = \nu\frac{kT}{h\nu}K^{\ddagger\prime}[H_2][F] = \frac{kT}{h}K^{\ddagger\prime}[H_2][F] = k^{\mathrm{TST}}[H_2][F]$$

so

$$k^{\mathrm{TST}} = \frac{kT}{h}K^{\ddagger\prime}$$

but not all reactant molecules make it all the way to products — some are reflected back to separated reactants.

Thus,

$$k^{\mathrm{TST}} = \kappa\frac{kT}{h}K^{\ddagger\prime} \qquad \text{where } \kappa \equiv \text{transmission coefficient (a fudge factor)}$$

EVALUATION OF k^{TST}

POTENTIAL ENERGY SURFACE KNOWN:

$E^{\ddagger}$ — directly from potential energy surface

$I^{\ddagger}$ — (moment of inertia of transition state)
calculate from geometric structure of transition state

$\nu^{\ddagger}$ — analyze shape of potential in saddle point region

κ — trajectory calculations — consider $\kappa = 1$ for now.

$$H_2 + F \rightarrow HF + H \qquad T = 300K$$

$$m_{H_2} = 2 \qquad m_F = 19$$

Translational part

$$\left[\frac{\left(q^{\ddagger}_{trans}/N\right)}{\left(q^{H_2}_{trans}/N\right)\left(q^{F}_{trans}/N\right)}\right] = \frac{Nh^3}{(2\pi kT)^{3/2}}\left(\frac{m^{\ddagger}}{m_{H_2}m_F}\right)^{3/2} =$$

$$6\times10^{23}\text{mol}^{-1}\frac{(6.63\times10^{-34}\,\text{J}\cdot\text{s})^3}{(2\pi\times1.38\times10^{-23}\text{J/K}\ \times300\text{K})^{3/2}}\left(\frac{6\times10^{23}\times0.021}{0.002\times0.019\text{kg}}\right)^{3/2}$$

$$= 2.52\times10^{-7}\ \text{m}^3\ \text{mol}^{-1}$$

Rotational part

$$\sigma_{H_2} = 2 \qquad \sigma^{\ddagger} = 1 \qquad q_{rot} = \frac{8\pi^2 IkT}{\sigma h^2}$$

$$I_{H_2} = 4.56\times10^{-48}\,\text{m}^2\text{kg} \qquad I^{\ddagger} = 1.24\times10^{-46}\,\text{m}^2\text{kg}$$

(assume linear transition state)

$$\frac{q^{\ddagger}_{rot}}{q^{H_2}_{rot}} = \frac{I^{\ddagger}}{I_{H_2}}\frac{\sigma_{H_2}}{\sigma^{\ddagger}} = 54.4$$

Vibrational Part

$H_2F^{\ddagger}$ is a linear transition state (assumed)

3n–5–1 = 3 vibrational degrees of freedom (one vibration is reaction coordinate)

$\frac{h\nu^{\ddagger}_s}{k} =$ 5771K stretch $\frac{h\nu^{\ddagger}_b}{k} =$ 573K (doubly degenerate) bend

$h\nu_{H_2}/k = 6323K$

$$\frac{q^{\ddagger *\prime}_{vib}}{q^{*H_2}_{vib}} = \frac{\left(1-e^{-h\nu^{\ddagger}_s/kT}\right)^{-1}\left(1-e^{-h\nu^{\ddagger}_b/kT}\right)^{-2}}{\left(1-e^{-h\nu H_2/kT}\right)^{-1}} = 1.38$$

Electronic part

$$g_0^\ddagger = 2(S=1/2) \qquad g_0^F = 6(L=1, S=1/2) \qquad g_0^{H_2} = 1$$

(spin orbit splitting of F $^2P_{1/2} - ^2P_{3/2}$ is 404 cm^{-1})

$$\frac{g_0^\ddagger}{g_0^F g_0^{H_2}} = \frac{1}{3}$$

Calculate $E^\ddagger$

$V_0 = 3.8\,\text{kJmol}^{-1}$ $\quad \nu_s^\ddagger = 1.20\times10^{14}\,\text{s}^{-1}$ $\quad \nu_b^\ddagger = 1.19\times10^{13}\,\text{s}^{-1}$ (reasonable guesses)

(How do we guess values for $\nu_s^\ddagger$ and $\nu_b^\ddagger$?)

$$\nu_{H_2} = 1.32 \times 10^{14}\ \text{s}^{-1}$$

$$E^\ddagger = V_0 + \frac{1}{2}hN\left[\nu_s^\ddagger + 2\nu_b^\ddagger - \nu_{H_2}\right] = 6.1\,\text{kJ mol}^{-1}$$

Calculate kT/h

$$kT/h = \frac{1.38\times10^{-23}\,\text{J/K} \times 300\text{K}}{6.63\times10^{-34}\,\text{J}\bullet\text{s}} = 6.24\times10^{12}\ \text{s}^{-1}$$

Putting it all together:

$$\begin{aligned} k^{TST} &= \kappa\frac{kT}{h}K^{\pm'} \\ &= 1\left(6.24\times10^{12}\text{s}^{-1}\right)\left(2.52\times10^{-7}\,\text{m}^3\text{mol}^{-1}\right)(54.4)(1.38)\frac{1}{3}e^{-6.1/RT} \\ &= 3.93\times10^{7}e^{-6.1/RT} \end{aligned}$$

$$\boxed{k^{TST} = 3.40\times10^6\,\text{m}^3\text{mol}^{-1}\text{s}^{-1} \text{ at 300K}}$$

$k^{EXP} = 2.70 \times 10^6\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ acceptable agreement

Experimental value is smaller because κ is probably not 1. Sometimes k^{TST} will be smaller than k^{EXP} because of tunneling. This model for k^{TST} does not take the quantum mechanical phenomenon of tunneling into account. Tunneling can make the reaction rate become faster than the k^{TST} prediction.

If $k^{TST} < k^{EXP}$, it may mean that there is some tunneling contribution.