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5.62 Physical Chemistry II
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Transition State Theory. II. E^\ddagger vs. E_a . Kinetic Isotope Effect.

Want to get k^{TST} into Arrhenius form

$$k^{\text{TST}} = \kappa \frac{kT}{h} K^\ddagger'$$

but $K^\ddagger' = e^{-G^\ddagger/RT} \longrightarrow -RT \ln K^\ddagger' = \Delta G^\ddagger$

so $k^{\text{TST}} = \kappa \frac{kT}{h} e^{-G^\ddagger/RT} = \kappa \frac{kT}{h} e^{S^\ddagger/R} e^{-H^\ddagger/RT}$

because $G^\ddagger = H^\ddagger - TS^\ddagger$

NOW: $H^\ddagger = E^\ddagger + \Delta n RT$

where $\Delta n = (\# \text{ molecules in TS}) - (\text{molecularity of reaction})$
(molecularity: e.g., unimolecular, bimolecular, etc.)

e.g. $\Delta n = \quad 1 \quad -2 \quad = -1$

So:

$$k^{\text{TST}} = \kappa \frac{kT}{h} e^{S^\ddagger/R} e^1 e^{-E^\ddagger/RT}$$

$$k^{\text{TST}} \equiv \underbrace{\kappa \frac{kT}{h} e^{S^\ddagger/R} e^1}_{\text{BT}^m} e^{-E^\ddagger/RT} \quad \text{where } m = 1$$

Surprisingly, theory predicts a temperature dependence to the pre-exponential factor. This T-dependence is difficult to observe experimentally unless the rate constant is measured over a wide temperature range (at least a factor of 5)

Now:

$$\frac{d \ln k^{\text{TST}}}{dT} = \frac{d \left(\ln \left[\kappa \frac{k}{h} e^{S^\ddagger/R} e^1 \right] + \ln T + e^{-E^\ddagger/RT} \right)}{dT}$$

$$= \frac{1}{T} + \frac{E^\ddagger}{RT^2} \quad (\text{TST})$$

Contrast this to Arrhenius model:

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

$$\frac{d \ln k}{dT} = \frac{d \ln k^{\text{TST}}}{dT}$$

$$\frac{E_a}{RT^2} = \frac{1}{T} + \frac{E^\ddagger}{RT^2}$$

$$\therefore E_a = RT + E^\ddagger$$

Again, the experimental E_a is larger than E^\ddagger because E_a is a difference between the average energy of molecules in the pot and the average energy of molecules that react, while E^\ddagger is a microscopic quantity, a threshold energy along the PES. Notice that E_a is not a barrier along PES.

COMPARISON OF TRANSITION STATE THEORY WITH COLLISION THEORY

Calculate k^{TST} in the limit of the assumptions of collision theory (i.e. simplified TST):

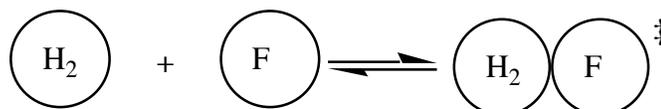
- 1) collisions of hard spheres
- 2) only translational degrees of freedom

Treat H_2 as an atom — a hard sphere of mass 2. [No rotation, no vibration]

Treat $\text{H}_2\text{F}^\ddagger$ as a diatomic molecule



With these assumptions



$$k \approx \frac{kT}{h} \left[\frac{(q_{\text{trans}}^\ddagger / N)}{(q_{\text{trans}}^{\text{H}_2} / N)(q_{\text{trans}}^{\text{F}} / N)} \right] q_{\text{rot}}^\ddagger e^{-E^\ddagger/RT}$$

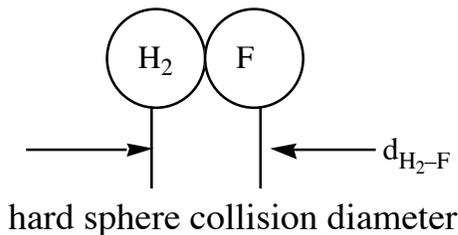
Note: no vibrational partition function for $\text{H}_2\text{F}^\ddagger$ is included because the one vibrational mode for the pseudo-diatom transition state has become the reaction coordinate. Also, no rotational partition function for H_2 is included because we are treating H_2 as an atom.

$$k \approx \frac{kT}{h} \left[\frac{\frac{(2\pi(m_{\text{H}_2} + m_{\text{F}})kT)^{3/2}}{h^3 N}}{\frac{(2\pi m_{\text{H}_2} kT)^{3/2}}{h^3 N} \frac{(2\pi m_{\text{F}} kT)^{3/2}}{h^3 N}}}{\frac{8\pi^2 I^\ddagger kT}{\sigma h^2}} e^{-E^\ddagger/RT} \right]$$

The reason there is no rotational or vibrational partition function for H_2 is not that we are assuming the high-T limit, but rather that we are treating H_2 as if it were an atom.

Now: $I^\ddagger = \mu d_{\text{H}_2-\text{F}}^2$

where $\mu = \frac{m_{\text{H}_2} m_{\text{F}}}{m_{\text{H}_2} + m_{\text{F}}}$



$$k \approx N \left[\frac{8kT}{\pi} \left(\frac{m_{\text{H}_2} + m_{\text{F}}}{m_{\text{H}_2} m_{\text{F}}} \right) \right]^{1/2} \frac{\pi d_{\text{H}_2-\text{F}}}{\sigma} e^{-E^\ddagger/RT}$$

This looks identical to the collision theory result, and collision theory is not based on thermodynamics.

$$k^{\text{CT}} = \left(\frac{8kT}{\pi\mu} \right)^{1/2} \pi d_{\text{AB}}^2 e^{-E_0/RT}$$

Calculate value for k^{TST} in limit of collision theory assumptions (i.e. what fraction of collisions are effective because they have sufficient translational energy along the line of centers?):

$$\sigma = 1 \quad \pi d_{\text{H}_2-\text{F}}^2 = 3 \times 10^{-19} \text{ m}^2$$

$$k \approx 3.4 \times 10^8 e^{-E^\ddagger/RT} \text{ m}^3/\text{mol} \cdot \text{s}$$

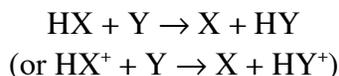
Compare to k^{TST}

$$k^{\text{TST}} = 3.9 \times 10^7 e^{-E^\ddagger/RT} \text{ m}^3/\text{mol} \cdot \text{s}$$

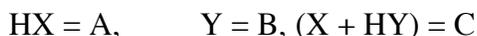
k^{TST} is smaller because it reflects the more restrictive co-linear steric requirement. k^{CT} is an upper bound because collision theory treats reactants as spheres with no favored direction of approach (but with an explicit requirement on the effective collision energy).

TRANSITION STATE THEORY AND KINETIC ISOTOPE EFFECT

Consider the H atom (or proton) transfer reaction



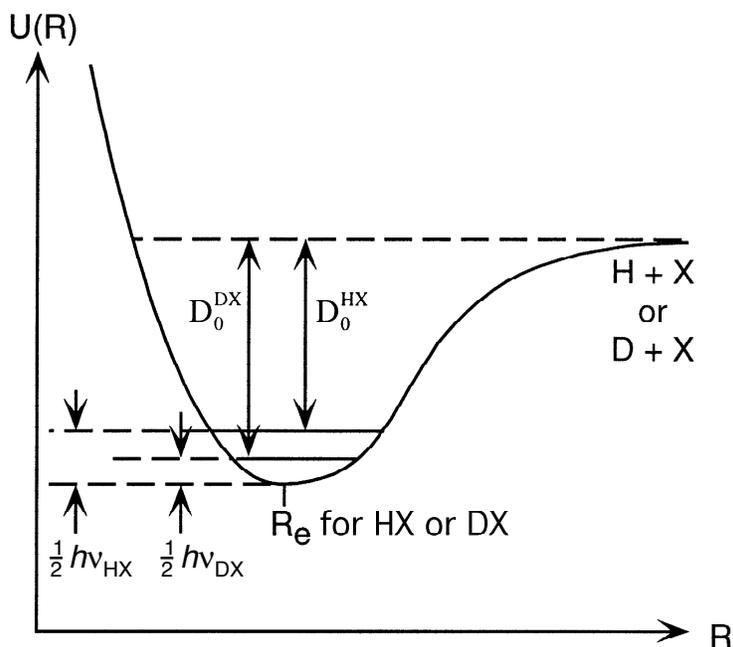
where the original HX bond is broken and a new HY bond is formed



So the key question is *how do we know whether breaking and making a bond to H occurs in the transition state region of the reaction coordinate?* The size of the HD kinetic isotope effect tells us whether the H transfer occurs at or before/after the transition state.

Kinetic isotope effect — reaction rates are slower if deuterium is substituted for hydrogen *and a hydrogen bond is involved in the reaction.*

Why? Potential energy of interaction the same for HX and DX (Born-Oppenheimer approximation).



Because zero point energy of DX is smaller than for HX

Since $\nu \propto \left(\frac{k}{m}\right)^{1/2}$ where k = force constant

$$\frac{v_{\text{HX}}}{v_{\text{DX}}} \propto \left(\frac{m_{\text{DX}}}{m_{\text{HX}}} \right)^{1/2} \quad \text{because } k_{\text{HX}} = k_{\text{DX}}$$

Intramolecular potentials are the same. The “shape” of potential curve doesn’t change upon isotopic substitution.

$$v_{\text{DX}} = v_{\text{HX}} \left(\frac{m_{\text{DX}}}{m_{\text{HX}}} \right)^{1/2}$$

Since $m_{\text{DX}} > m_{\text{HX}}$

$$\text{So } \frac{1}{2} h v_{\text{DX}} < \frac{1}{2} h v_{\text{HX}}$$

$$\text{So } D_0^{\text{DX}} > D_0^{\text{HX}}$$

dissociation energy to break D—X bond is larger than that to break H—X

$$\text{Kinetic Isotope Effect} \equiv \frac{k_{\text{H}}}{k_{\text{D}}}$$

Calculate this using transition state theory

$$\frac{k_{\text{H}}}{k_{\text{D}}} = \frac{\frac{kT}{h} \left[\frac{q_{\ddagger}^{\text{H}} / N}{(q_{\text{H}}^{\text{A}} / N)(q_{\text{H}}^{\text{B}} / N)} \right] e^{-E_{\ddagger}^{\text{H}}/RT}}{\frac{kT}{h} \left[\frac{q_{\ddagger}^{\text{D}} / N}{(q_{\text{D}}^{\text{A}} / N)(q_{\text{D}}^{\text{B}} / N)} \right] e^{-E_{\ddagger}^{\text{D}}/RT}}$$

$$\frac{k_{\text{H}}}{k_{\text{D}}} = \left(\frac{q_{\ddagger}^{\text{H}}}{q_{\ddagger}^{\text{D}}} \right) \left(\frac{q_{\text{D}}^{\text{A}} q_{\text{D}}^{\text{B}}}{q_{\text{H}}^{\text{A}} q_{\text{H}}^{\text{B}}} \right) e^{(-E_{\ddagger}^{\text{H}} + E_{\ddagger}^{\text{D}})/RT}$$

$$-E_{\ddagger}^{\text{H}} + E_{\ddagger}^{\text{D}} = -V_0^{\text{H}} - \frac{1}{2} h \sum_i v_i^{\ddagger \text{H}} + \frac{1}{2} h \sum_i v_i^{\text{H}} + V_0^{\text{D}} + \frac{1}{2} h \sum_i v_i^{\ddagger \text{D}} - \frac{1}{2} h \sum_i v_i^{\text{D}}$$

But $V_0^{\text{H}} = V_0^{\text{D}}$

$$\frac{k_{\text{H}}}{k_{\text{D}}} = \left(\frac{q_{\ddagger}^{\text{H}}}{q_{\ddagger}^{\text{D}}} \right) \left(\frac{q_{\text{D}}^{\text{A}} q_{\text{D}}^{\text{B}}}{q_{\text{H}}^{\text{A}} q_{\text{H}}^{\text{B}}} \right) e^{-\frac{1}{2} h \left(\sum_i v_i^{\ddagger \text{H}} - \sum_i v_i^{\ddagger \text{D}} - \sum_i v_i^{\text{H}} + \sum_i v_i^{\text{D}} \right) / RT}$$

Most of the isotope effect is in the difference between the zero point energies of the deuterated vs. hydrogenated reactants. Can use isotope effect to determine whether a hydrogen bond was involved in the transition state. Standard diagnostic in kinetics!