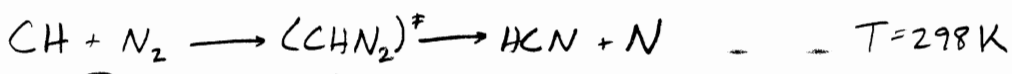


Steinfeld 10.12 (In class, 11/9/07)



each has 3 translational, 1 vibrational (3(2)-5), 2 rotational degrees of freedom. linear -> 2 rotational dof, 3 translational dof, 3(4)-5 = 7 vibrational dof -> one of these is the reaction coordinate.

(experimental k = 7.1 x 10^-14 cm^3 molecule^-1 s^-1)

k = (k_B T / h) * (Q† / (Q_CH * Q_N2)) * e^(-E_0 / k_B T) E_0 = 221 kJ/mol

Q = Q_elect * Q_rot * Q_vib * Q_trans

(eq. 10-58) Q_elect = sum(g_i * e^(-E_i / k_B T)) E_i = electronic energy above the ground state = 0 (for R + X†) g_CH = 2, g_N2 = 1, g_HCN2 = 2

(eq. 10-72) Q_rot = (8 * pi^2 * I * k_B T) / h^2 (for linear) I_CH = 1.935 * 10^-40 g cm^2, I_N2 = 13.998 * 10^-40 g cm^2, I_HCN2 = 73.2 * 10^-40 g cm^2

(eq. 10-69) Q_vib = product(1 / (1 - exp(-h * nu_i / k_B T))) nu_CH = 2733 cm^-1, nu_N2 = 2330 cm^-1, nu_HCN2 = 3130, 2102, 1252, 1170, 564, 401 cm^-1

(eq. 10- V) Q_trans = ((2 * pi * m * k_B T) / h^2)^3/2 M_CH = 13.019 g/mol, M_N2 = 28.018 g/mol, M_HCN2 = 41.032 g/mol

$$Q_{HCN_2}^{\ddagger} : Q_{elect}^{\ddagger} = g_i e^{-E_i/k_B T} = (2) e^{-0} = \boxed{2}$$

$$\frac{kg\ m^2\ J\ K}{K\ J^2\ s^2}$$

$$Q_{rot}^{\ddagger} = \frac{8\pi^2 (73.2 \times 10^{-40} g\ cm^2) (1.38 \times 10^{-23} J/K) (298\ K)}{(6.626 \times 10^{-34} J\cdot s)^2} \left(\frac{1\ m}{100\ cm}\right)^2 \left(\frac{1\ kg}{1000\ g}\right)$$

$$Q_{rot}^{\ddagger} = \boxed{541.4}$$

$$\frac{kg\ m^2\ s^2}{kg\ m^2\ s^2}$$

$$= \text{unitless}$$

$$Q_{vib} : \frac{hc}{k_B T} = \frac{(6.626 \times 10^{-34} J\cdot s) (2.998 \times 10^8\ m/s)}{(1.38 \times 10^{-23} J/K) (298\ K)} = 4.830 \times 10^{-5}\ m$$

$$Q_{vib}^{\ddagger} = \left(\frac{1}{1 - \exp[-4.830 \times 10^{-5}\ m \times 3130\ cm^{-1} \times 100\ cm/m]} \right) \left(\frac{1}{1 - \exp[-4.830 \times 10^{-5}\ m \times 2102\ cm^{-1} \times 100\ cm/m]} \right) \\ \times \left(\frac{1}{1 - \exp[-4.830 \times 10^{-5}\ m \times 1252\ cm^{-1} \times 100\ cm/m]} \right) \left(\frac{1}{1 - \exp[-4.830 \times 10^{-5}\ m \times 1170\ cm^{-1} \times 100\ cm/m]} \right) \\ \times \left(\frac{1}{1 - \exp[-4.830 \times 10^{-5}\ m \times 564\ cm^{-1} \times 100\ cm/m]} \right) \left(\frac{1}{1 - \exp[-4.830 \times 10^{-5}\ m \times 401\ cm^{-1} \times 100\ cm/m]} \right)$$

$$Q_{vib}^{\ddagger} = \left(\frac{1}{1 - \exp(-15.119)} \right) \left(\frac{1}{1 - \exp(-10.1154)} \right) \left(\frac{1}{1 - \exp(-6.0477)} \right) \left(\frac{1}{1 - \exp(-5.6516)} \right) \\ \times \left(\frac{1}{1 - \exp(-2.7244)} \right) \left(\frac{1}{1 - \exp(-1.9370)} \right)$$

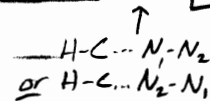
$$Q_{vib}^{\ddagger} = (1.0000) (1.0000) (1.0024) (1.0035) (1.0702) (1.1684) = \boxed{1.2578}$$

$$\frac{g\ kg\ mol\ J\ K}{m\ J\ K\ J\ s^2}$$

$$= \left(\frac{kg\ mol}{kg\ m^2\ s^2} \right)^{3/2} = m^{-3}$$

$$Q_{trans}^{\ddagger} = \left(\frac{2\pi (41.032\ amu) (1.661 \times 10^{-27}\ kg/mol) (1.38 \times 10^{-23}\ J/K) (298\ K)}{(6.626 \times 10^{-34}\ J\cdot s)^2} \right)^{3/2} = \boxed{2.5404 \times 10^{32}\ m^{-3}}$$

$$Q_{HCN_2}^{\ddagger} = (2) (541.4) (1.2578) (2.5404 \times 10^{32}\ m^{-3}) = \boxed{3.4599 \times 10^{35}\ m^{-3}} \times 2 = \boxed{6.9198 \times 10^{35}}$$



$$Q_{CH} : Q_{elect}^{CH} = (2) e^{-0} = \boxed{2}$$

$$Q_{rot}^{CH} = \frac{8\pi^2 (1.935 \times 10^{-40} g\ cm^2) (1.38 \times 10^{-23} J/K) (298\ K)}{(6.626 \times 10^{-34} J\cdot s)^2} \left(\frac{1\ m}{100\ cm}\right)^2 \left(\frac{1\ kg}{1000\ g}\right) = \boxed{14.311}$$

$$Q_{vib}^{CH} = \frac{1}{1 - \exp[-4.830 \times 10^{-5}\ m \times 2733\ cm^{-1} \times 100\ cm/m]} = \boxed{1.0000}$$

$$Q_{trans}^{CH} = \left(\frac{2\pi (13.019\ amu) (1.661 \times 10^{-27}\ kg/mol) (1.38 \times 10^{-23}\ J/K) (298\ K)}{(6.626 \times 10^{-34}\ J\cdot s)^2} \right)^{3/2} = \boxed{4.5402 \times 10^{31}\ m^{-3}}$$

$$Q_{CH} = (2) (14.311) (1.0000) (4.5402 \times 10^{31}\ m^{-3}) = \boxed{1.2995 \times 10^{33}\ m^{-3}}$$

$$Q_{N_2} : Q_{elect}^{N_2} = (1) e^{-0} = \boxed{1}$$

$$Q_{rot}^{N_2} = \frac{8\pi^2 (13.998 \times 10^{-40} g\ cm^2) (1.38 \times 10^{-23} J/K) (298\ K)}{(6.626 \times 10^{-34} J\cdot s)^2} \left(\frac{1\ m}{100\ cm}\right)^2 \left(\frac{1\ kg}{1000\ g}\right) = \boxed{103.5}$$

$$Q_{vib}^{N_2} = \frac{1}{1 - \exp[-4.830 \times 10^{-5}\ m \times 2330\ cm^{-1} \times 100\ cm/m]} = \boxed{1.0000}$$

$$Q_{trans}^{N_2} = \left(\frac{2\pi (28.013\ amu) (1.661 \times 10^{-27}\ kg/mol) (1.38 \times 10^{-23}\ J/K) (298\ K)}{(6.626 \times 10^{-34}\ J\cdot s)^2} \right)^{3/2} = \boxed{1.4330 \times 10^{32}\ m^{-3}}$$

$$Q_{N_2} = (1) (103.5) (1.0000) (1.4330 \times 10^{32}\ m^{-3}) = \boxed{1.4832 \times 10^{34}\ m^{-3}}$$

$$k = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_{CH} Q_{N_2}} e^{-E_0/k_B T}$$

$$\frac{k_B T}{h} = \frac{(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})}{6.626 \times 10^{-34} \text{ J}\cdot\text{s}} = 6.206 \times 10^{12} \text{ s}^{-1}$$

$$k = (6.206 \times 10^{12} \text{ s}^{-1}) \frac{(6.9198 \times 10^{35} \text{ m}^{-3})}{(1.2995 \times 10^{23} \text{ m}^{-3})(1.4832 \times 10^{24} \text{ m}^{-3})} \exp\left(\frac{-221 \text{ kJ/mol} \left(\frac{1000 \text{ J}}{1 \text{ kJ}}\right) \left(\frac{1 \text{ mol}}{6.022 \times 10^{23}}\right)}{(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})}\right)$$

$$k = (6.206 \times 10^{12} \text{ s}^{-1})(3.6013 \times 10^{-32} \text{ m}^3) \exp(-89.239) = 3.9198 \times 10^{-59} \text{ m}^3/\text{s}$$

Pre-exponential factor = $\frac{k_B T}{h} \frac{Q^\ddagger}{Q_A Q_B}$ (from comparison w/ Arrhenius eqn: $k = A e^{-E_a/k_B T}$)

for Q^\ddagger : $Q_{\text{elect}}^\ddagger \propto T^0$; $Q_{\text{rot}}^\ddagger \propto T$; $Q_{\text{vib}}^\ddagger \propto T^0$; $Q_{\text{trans}}^\ddagger \propto T^{3/2}$
 $Q^\ddagger \propto (T)(T^{3/2}) \propto T^{5/2}$

for Q_{CH} : $Q_{\text{elect}} \propto T^0$; $Q_{\text{rot}} \propto T$; $Q_{\text{vib}} \propto T^0$; $Q_{\text{trans}} \propto T^{3/2}$
 and Q_{N_2} $Q \propto (T)(T^{3/2}) \propto T^{5/2}$

so $A \propto \frac{T \cdot T^{5/2}}{T^{5/2} T^{5/2}} \propto \boxed{T^{-3/2}}$