
C343 Lab Report 1

Name: Aniruddha Seal

ID Number: 1811022

22 February 2021

1

Vibrational frequency of HCl (ν_H): $2930.2102 \text{ cm}^{-1} = 8790.6306 \times 10^{10} \text{ Hz}$

Vibrational frequency of DCl (ν_D): $2101.5557 \text{ cm}^{-1} = 6304.6671 \times 10^{10} \text{ Hz}$

Zero Point Corrections of HCl (ZPC_H) and DCl (ZPC_D) are

$$ZPC_H = \frac{h\nu_H}{2} = 4.18895 \text{ kcal/mol} \quad (1)$$

$$ZPC_D = \frac{h\nu_D}{2} = 3.00432 \text{ kcal/mol} \quad (2)$$

Bond Dissociation Energies of HCl (DE_H) and DCl (DE_D) are
Zero Point Energy(ZPE) of a molecule is taken as $E_{\text{Electronic}} + E_{\text{Vibrational}}$

1. $\text{HCl} \longrightarrow \text{H} + \text{Cl}$

$$\text{ZPE}(\text{HCl}): -460.7956941 \times 627.5095 + 4.18895 = -289149.48665 \text{ kcal/mol}$$

$$\text{ZPE}(\text{H}): -0.5002728 \times 627.5095 + 0.00000 = -313.92593 \text{ kcal/mol}$$

$$\text{ZPE}(\text{Cl}): -460.1362422 \times 627.5095 + 0.00000 = -288739.86327 \text{ kcal/mol}$$

$$\begin{aligned} DE_H &= \text{ZPE}(\text{H}) + \text{ZPE}(\text{Cl}) - \text{ZPE}(\text{HCl}) \\ &= -313.92593 - 288739.86327 + 289149.48665 \text{ kcal/mol} \\ &= 95.69745 \text{ kcal/mol} \end{aligned} \quad (3)$$

2. $\text{DCl} \longrightarrow \text{D} + \text{Cl}$

$$\text{ZPE}(\text{DCl}): -460.7956941 \times 627.5095 + 3.00432 = 289150.67128 \text{ kcal/mol}$$

$$\text{ZPE}(\text{D}): -0.5002728 \times 627.5095 + 0.00000 = -313.92593 \text{ kcal/mol}$$

$$\begin{aligned} DE_D &= \text{ZPE}(\text{D}) + \text{ZPE}(\text{Cl}) - \text{ZPE}(\text{DCl}) \\ &= -313.92593 - 288739.86327 + 289150.67128 \text{ kcal/mol} \\ &= 96.88208 \text{ kcal/mol} \end{aligned} \quad (4)$$

Percentage change in Bond Dissociation Energy in going from HCl to DCl

$$\begin{aligned} &= \frac{DE_D - DE_H}{DE_H} \times 100\% \\ &= \frac{96.88208 - 95.69745}{95.69745} \times 100\% \\ &= 1.2378\% \end{aligned} \quad (5)$$

2

(a) Thermodynamic Stability at Room Temperature(298.15 K)

- (a) $\text{CHDCl}_2 \xrightarrow{\text{Cl}^*} \text{CDCl}_2^* + \text{HCl}$ -[ppts 1]
Zero Point Energy Calculation of **CDCl₂***:

| S.No. | Vibrational Frequencies of CDCl ₂ * | |
|-------|--|------------------------------|
| | (in cm ⁻¹) | (in Hz) |
| 1 | 303.0270 | 909.0810 × 10 ¹⁰ |
| 2 | 395.1547 | 1185.4641 × 10 ¹⁰ |
| 3 | 721.4403 | 2164.3209 × 10 ¹⁰ |
| 4 | 814.3202 | 2442.9606 × 10 ¹⁰ |
| 5 | 980.6224 | 2941.8672 × 10 ¹⁰ |
| 6 | 2391.4184 | 7174.2552 × 10 ¹⁰ |

$$\begin{aligned}
 ZPC[\text{CDCl}_2^*] &= \frac{1}{2} \sum_{k=1}^6 h\nu_k \\
 &= 8.01416 \text{ kcal/mol} \\
 ZPE[\text{CDCl}_2^*] &= -959.0341081 \times 627.5095 + 8.01416 \text{ kcal/mol} \\
 &= -601794.9994 \text{ kcal/mol}
 \end{aligned} \tag{6}$$

$$\begin{aligned}
 \text{Total Gibbs Free Energy of ppts 1}(G[1]) &= G[\text{CDCl}_2^*] + G[\text{HCl}] \\
 &= -(959.048846 + 460.806911) \times 627.5095 \text{ kcal/mol} \\
 &= -890972.9761 \text{ kcal/mol}
 \end{aligned} \tag{7}$$

- (b) $\text{CHDCl}_2 \xrightarrow{\text{Cl}^*} \text{CHCl}_2^* + \text{DCl}$ -[ppts 2]
Zero Point Energy Calculation of **CHCl₂***:

| S.No. | Vibrational Frequencies of CHCl ₂ * | |
|-------|--|------------------------------|
| | (in cm ⁻¹) | (in Hz) |
| 1 | 304.9139 | 914.7417 × 10 ¹⁰ |
| 2 | 481.1237 | 1443.3711 × 10 ¹⁰ |
| 3 | 755.9114 | 2267.7342 × 10 ¹⁰ |
| 4 | 877.2279 | 2631.6837 × 10 ¹⁰ |
| 5 | 1267.3935 | 3802.1805 × 10 ¹⁰ |
| 6 | 3247.9574 | 9743.8722 × 10 ¹⁰ |

$$\begin{aligned}
 ZPC[\text{CHCl}_2^*] &= \frac{1}{2} \sum_{k=1}^6 h\nu_k \\
 &= 9.91341 \text{ kcal/mol} \\
 ZPE[\text{CHCl}_2^*] &= -959.0341081 \times 627.5095 + 9.91341 \text{ kcal/mol} \\
 &= -601793.1002 \text{ kcal/mol}
 \end{aligned} \tag{8}$$

$$\begin{aligned}
\text{Total Gibbs Free Energy of pdts } \mathbf{2}(G[\mathbf{2}]) &= G[\mathbf{CHCl_2^*}] + G[\mathbf{DCI}] \\
&= -(959.045604 + 460.809466) \times 627.5095 \text{ kcal/mol} \\
&= -890972.545048 \text{ kcal/mol}
\end{aligned} \tag{9}$$

H abstraction Pathway favoured thermodynamically at 298.15 K as $G[\mathbf{1}] < G[\mathbf{2}]$

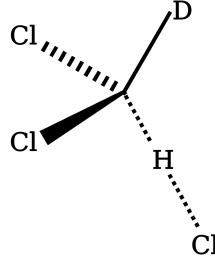
The (thermodynamic) product ratio at room temperature (T=298.15 K)

$$\begin{aligned}
\frac{[\text{pdts } \mathbf{1}]}{[\text{pdts } \mathbf{2}]} &= \exp(-(G[\mathbf{1}] - G[\mathbf{2}])/RT)) \\
&= \exp((890972.9761 - 890972.545048)/(1.987 \times 10^{-3} * 298.15)) \\
&= 2.0701
\end{aligned} \tag{10}$$

(b) **Kinetic Stability at Room Temperature(298.15 K)**

(a) H abstraction Pathway

Zero Point Energy Calculation of the Transition State



Figuur 1: Transition State Structure in H-abstraction

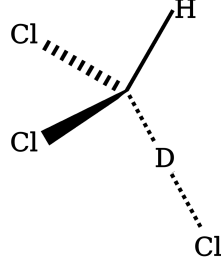
| S.No. | Vibrational Frequencies of TS-H | |
|-------|---------------------------------|-------------------------|
| | (in cm^{-1}) | (in Hz) |
| 1 | -985.5910 | |
| 2 | 85.8395 | 2.5751×10^{12} |
| 3 | 148.6307 | 4.4589×10^{12} |
| 4 | 295.4240 | 8.8627×10^{12} |
| 5 | 381.6423 | 1.1449×10^{13} |
| 6 | 718.4330 | 2.1552×10^{13} |
| 7 | 786.8909 | 2.3606×10^{13} |
| 8 | 871.0385 | 2.6131×10^{13} |
| 9 | 913.5675 | 2.7407×10^{13} |
| 10 | 974.0599 | 2.9221×10^{13} |
| 11 | 1005.3785 | 3.0161×10^{13} |
| 12 | 2342.1960 | 7.0265×10^{13} |

$$\begin{aligned}
\text{Zero Point Energy}[\text{TS}_H] &= -1419.8272383 \times 627.5095 \text{ kcal/mol} + \frac{1}{2} \sum_{k=2}^{12} h\nu_k \\
&= -890942.8960 \text{ kcal/mol}
\end{aligned} \tag{11}$$

$$\begin{aligned}\text{Gibbs Free Energy of } \mathbf{TS_H} &= -1419.839473 \times 627.5095 \text{ kcal/mol} \\ &= -890962.7577 \text{ kcal/mol}\end{aligned}\quad (12)$$

(b) D abstraction Pathway

Zero Point Energy Calculation of the Transition State



Figuur 2: Transition State Structure in D-abstraction

| S.No. | Vibrational Frequencies of TS-D | |
|-------|---------------------------------|-------------------------|
| | (in cm^{-1}) | (in Hz) |
| 1 | -757.3327 | |
| 2 | 85.7568 | 2.5727×10^{12} |
| 3 | 149.9622 | 4.4988×10^{12} |
| 4 | 294.2044 | 8.8261×10^{12} |
| 5 | 396.2160 | 1.1886×10^{13} |
| 6 | 672.4661 | 2.0173×10^{13} |
| 7 | 704.7508 | 2.1142×10^{13} |
| 8 | 767.5210 | 2.3025×10^{13} |
| 9 | 841.9804 | 2.5259×10^{13} |
| 10 | 1031.2673 | 3.0938×10^{13} |
| 11 | 1268.4158 | 3.8052×10^{13} |
| 12 | 3182.9476 | 9.5488×10^{13} |

$$\begin{aligned}\text{Zero Point Energy}[\mathbf{TS_D}] &= -1419.8272383 \times 627.5095 \text{ kcal/mol} + \frac{1}{2} \sum_{k=2}^{12} h\nu_k \\ &= -890941.6488 \text{ kcal/mol}\end{aligned}\quad (13)$$

$$\begin{aligned}\text{Gibbs Free Energy of } \mathbf{TS_D} &= -1419.837485 \times 627.5095 \text{ kcal/mol} \\ &= -890961.5102 \text{ kcal/mol}\end{aligned}\quad (14)$$

H abstraction Pathway is favoured kinetically at 298.15 K as $G[\mathbf{TS-H}] < G[\mathbf{TS-D}]$

The (kinetic) product ratio at room temperature (T=298.15 K)

$$\begin{aligned}\frac{[\text{pdts 1}]}{[\text{pdts 2}]} &= \exp(-(G[\mathbf{TS-H}] - G[\mathbf{TS-D}])/(RT)) \\ &= \exp((890962.7577 - 890961.5102)/(1.987 \times 10^{-3} * 298.15)) \\ &= 8.2133\end{aligned}\quad (15)$$

(c) **Kinetic Isotope Effect**

According to Transition State Theory, rate of a reaction $\mathbf{k(T)}$ is given by:

$$k(T) = \frac{k_B T}{h c^0} e^{-\Delta^\ddagger G / RT} \quad (16)$$

where, the standard Gibbs free energy of activation $\Delta^\ddagger G$, is the change in Gibbs free energy in going from reactants at a concentration c^0 to the transition state at a concentration c^0 . I've taken c^0 as 1 in calculations henceforth.

• **Pathway 1**

$$\begin{aligned} \Delta^\ddagger G(H) &= G[\text{TS-H}] - G[\text{CHDCl}_2] - G[\text{Cl}^*] \\ &= (-1419.839473 + 959.696439 + 460.151919) \times 627.5095 \text{ kcal/mol} \\ &= 5.5754 \text{ kcal/mol} \end{aligned} \quad (17)$$

$$\begin{aligned} k(298.15, \text{H}) &= \frac{k_B T}{h c^0} e^{-\Delta^\ddagger G(H) / RT} \\ &= \frac{1.380662 \times 10^{-23} (298.15)}{6.626176 \times 10^{-34} (1)} \exp \frac{-5.5754 * 1000}{1.987 * 298.15} \\ &= 6.2125 \times 10^{12} e^{-9.4111} \\ &= 5.0825 \times 10^8 s^{-1} \end{aligned} \quad (18)$$

• **Pathway 2**

$$\begin{aligned} \Delta^\ddagger G(D) &= G[\text{TS-D}] - G[\text{CHDCl}_2] - G[\text{Cl}^*] \\ &= (-1419.837485 + 959.696439 + 460.151919) \times 627.5095 \text{ kcal/mol} \\ &= 6.8229 \text{ kcal/mol} \end{aligned} \quad (19)$$

$$\begin{aligned} k(298.15, \text{D}) &= \frac{k_B T}{h c^0} e^{-\Delta^\ddagger G(D) / RT} \\ &= \frac{1.380662 \times 10^{-23} (298.15)}{6.626176 \times 10^{-34} (1)} \exp \frac{-6.8229 * 1000}{1.987 * 298.15} \\ &= 6.2125 \times 10^{12} e^{-11.5169} \\ &= 6.1878 \times 10^7 s^{-1} \end{aligned} \quad (20)$$

$$\begin{aligned} \text{Kinetic Isotope Effect} &= \frac{k(298.15, \text{H})}{k(298.15, \text{D})} \\ &= \frac{5.0825 \times 10^8}{6.1878 \times 10^7} \\ &= 8.2136 \end{aligned} \quad (21)$$