

C343 Experiment I

Kinetic Isotope Effect

1. HCl and DCl

Geometry Optimisation followed by Frequency Calculation was done for both HCl and DCl using B3LYP/6-31G* level of Theory.

Molecule/Atom	Frequency	Electronic Energy (EE)	Zero Point Energy (ZPE)	Enthalpy Correction	Gibbs Correction
HCl	2927.99	-460.795694	0.006670	0.009975	-0.011223
DCl	2099.97	-460.795694	0.004784	0.008089	-0.013776
H	-	-0.500273	0.000000	0.002360	-0.010654
Cl	-	-460.136242	0.000000	0.002360	-0.015677

The Vibrational Frequency of HCl and DCl are 2927.99 cm^{-1} and 2099.97 cm^{-1} respectively.

The Zero Point Energy (ZPE) of HCl and DCl are 0.00667 Hartree (17.5 kJ/mol) and 0.004784 Hartree (12.5 kJ/mol) respectively. As we expect the ZPE of DCl is lower than HCl.

Energy Calculation for a Reaction:

Bond dissociation Energy is the difference between sum of Energy of Products and sum of Energy of reactants

$$\Delta_r E^\circ = \Sigma \Delta_f E_{prod}^\circ - \Sigma \Delta_f E_{reac}^\circ$$
$$\Delta_r E^\circ = \Sigma (EE + ZPE)_{prod} - \Sigma (EE + ZPE)_{reac}$$

(i) Energy Calculation for the Reaction: $\text{HCl} \rightarrow \text{H} + \text{Cl}$

For HCl Dissociation:

$$\Delta_r E^\circ = (EE + ZPE)_H + (EE + ZPE)_{Cl} - (EE + ZPE)_{HCl}$$
$$= (-0.500273) + (-460.136242) - (-460.795694 + 0.006670)$$
$$= 0.157229 \text{ Hartree}$$
$$= 412.8047709458 = \mathbf{412.805 \text{ kJ/mol}}$$

(ii) Energy Calculation for the Reaction: $\text{DCl} \rightarrow \text{D} + \text{Cl}$

For DCl Dissociation:

$$\Delta_r E^\circ = (EE + ZPE)_D + (EE + ZPE)_{Cl} - (EE + ZPE)_{DCl}$$

$$\begin{aligned} &= (-0.500273) + (-460.136242) - (-460.795694 + 0.004784) \\ &= 0.159115 \text{ Hartree} \\ &= 417.756464323 = \mathbf{417.756 \text{ kJ/mol}} \end{aligned}$$

Change in Total Bond dissociation Energy when going from HCl to DCl
Percent Change from HCl to DCl = (DCl - HCl)/HCl *100
= (417.756464323 - 412.8047709458)/412.8047709458 * 100
= **1.1995 %**

2. d-Methylene Chloride

Geometry Optimisation followed by Frequency Calculation was done for all Products and Reactants using B3LYP/6-31G* level of Theory.

Molecule/Atom	Frequency	Electronic Energy(EE)	Zero Point Energy(ZPE)	Enthalpy Correction	Free energy Correction
CHDCl ₂	281.87 683.77 712.63 793.07 912.22 1269.72 1328.99 2338.35 3187.31	-959.696354	0.026217	0.030819	-0.000087
CHCl ₂	304.95 484.44 756.00 876.70 1267.47 3247.42	-959.034108	0.015804	0.020394	-0.011489
CDCl ₂	303.11 397.89 721.28 814.08 980.37 2391.01	-959.034108	0.012775	0.017498	-0.014732
Cl	-	-460.136242	0.000000	0.002360	-0.015677

Thermodynamically favourable product will be determined by the change in free energy of the reaction. The lower the free energy, the more feasible the reaction is. So, Free energy of a reaction can be calculated by:

$$\Delta_r G^\circ(298K) = \Sigma \Delta_f G^\circ_{prod}(298K) - \Sigma \Delta_f G^\circ_{reac}(298K)$$

$$\Delta_r G^\circ(298K) = \Sigma (EE + G^\circ_{corr})_{prod} - \Sigma (EE + G^\circ_{corr})_{reac}$$

(i) Free Energy for H abstraction: $\text{CHDCl}_2 + \text{Cl} \longrightarrow \text{CDCl}_2 + \text{HCl}$

$$\Delta_r G^\circ = (EE + G^\circ_{corr})_{\text{CDCl}_2} + (EE + G^\circ_{corr})_{\text{HCl}} - (EE + G^\circ_{corr})_{\text{CHDCl}_2} - (EE +$$

$$\begin{aligned} & G^\circ_{corr})_{\text{Cl}} \\ &= (-959.034108-0.014732) + (-460.795694-0.011223) - (-959.696354-0.000087) - \\ & (-460.136242-0.015677) \\ &= -0.007397 \text{ Hartree} \\ &= \mathbf{-19.420 \text{ kJ/mol}} \end{aligned}$$

(ii) Free Energy for D abstraction: $\text{CHDCl}_2 + \text{Cl} \longrightarrow \text{CHCl}_2 + \text{DCl}$

$$\Delta_r G^\circ = (EE + G^\circ_{corr})_{\text{CHCl}_2} + (EE + G^\circ_{corr})_{\text{DCl}} - (EE + G^\circ_{corr})_{\text{CHDCl}_2} - (EE +$$

$$\begin{aligned} & G^\circ_{corr})_{\text{Cl}} \\ &= (-959.034108-0.011489) + (-460.795694-0.013776) - (-959.696354-0.000087) - \\ & (-460.136242-0.015677) \\ &= -0.006707 \text{ Hartree} \\ &= \mathbf{-17.609 \text{ kJ/mol}} \end{aligned}$$

Hence, ΔG for H abstraction is lower than D abstraction. So, Hydrogen abstraction is more favorable than Deuterium abstraction thermodynamically.

Thermodynamic Product ratio will be governed by Boltzmann Distribution, given by the formula:

$$\frac{N_i}{N_j} = \frac{g_i}{g_j} e^{\frac{-\Delta E}{kT}}$$

Using the above equation, the product ratio will be:

$$\frac{N_H}{N_D} = e^{\frac{(-17.609+19.420)}{2.479}}$$

$$\frac{N_H}{N_D} = \mathbf{2.076}$$

Thus, the product ratio at 298K will be in ratio of 2:1 for Hydrogen and Deuterium abstraction pathway respectively.

3. Transition State

Geometry Optimisation followed by Frequency Calculation was done for all Transition States and Reactants using B3LYP/6-31G* level of Theory.

Kinetically favourable product will be determined by the Rate of the reaction.

Mol/TS	Frequency	Electronic Energy (EE)	Zero Point Energy (ZPE)	Enthalpy Correction	Free energy Correction
TS1 (H)	-990.37 86.07 152.29 299.80 417.29 778.67 828.88 895.62 955.69 1109.62 1270.60 3183.06	-1419.827238	0.019417	0.025731	-0.012235
TS2 (D)	-757.01 85.78 149.91 294.19 396.27 672.39 704.76 767.51 842.01 1031.02 1268.50 3183.00	-1419.827238	0.021404	0.027763	-0.010247

According to transition state theory, the Rate of a reaction in turn depends on Gibbs free energy change between Transition state and Reactant (Activation Energy). The Rate of a reaction can be calculated by:

$$k(T) = \frac{k_b T}{h c_0} e^{-\Delta G^\ddagger / RT}$$

$$\begin{aligned}
 \text{Reactant Free Energy} &= (EE + Gcorr)_{CHDCI_2} + (EE + Gcorr)_{CI} \\
 &= (-959.696354 - 0.000087) + (-460.136242 - 0.015677) \\
 &= -1419.84836 \text{ Hartree} \\
 &= -3727812.153 \text{ kJ/mol}
 \end{aligned}$$

(i) H abstraction Pathway(TS1) Free Energy:
 TS1 Free energy = $EE(TS1) + Gcorr(TS1)$
 = -1419.827238-0.012235
 = -1419.839473 Hartree
 = -3727788.820 kJ/mol

(ii) D abstraction Pathway(TS2) Free Energy:
 TS2 Free energy = $EE(TS2) + Gcorr(TS2)$
 = -1419.827238-0.010247
 = -1419.837485 Hartree
 = -3727783.600 kJ/mol

$$\Delta G^\ddagger(TS1) = \mathbf{23.333 \text{ kJ/mol}}$$

$$\Delta G^\ddagger(TS2) = \mathbf{28.553 \text{ kJ/mol}}$$

Hence, Kinetically also TS1 is favourable (H ABSTRACTION) as it has lower ΔG^\ddagger (ie, Activation Energy) as compared to TS2 .

The Kinetic Product ratio is given by ratio of the rate constants of the reaction. The rate constant of the reaction can be calculated according to the formula from Transition State Theory.

$$k_1 = 0.37425 * 10^{34} * e^{-23.333/2.479}$$

$$k_1 = 30.582 * 10^{28} s^{-1}$$

$$k_2 = 0.37425 * 10^{34} * e^{-28.553/2.479}$$

$$k_2 = 3.724 * 10^{28} s^{-1}$$

$$\text{So, Kinetic Product ratio will be} = \frac{k_1}{k_2} = \frac{30.582}{3.724} = \mathbf{8.212}$$

4. Kinetic Isotope Effect

Kinetic Isotope effect is defined as the ratio of rate constants of the reactions.

$$\text{So, Kinetic Isotope Effect} = \frac{k_H}{k_D} = \mathbf{8.212}$$