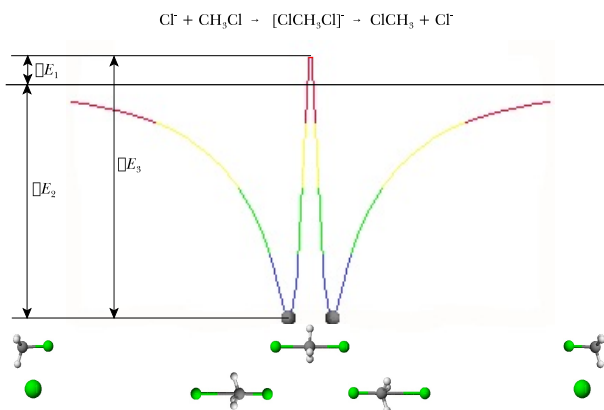


# 9 Transition States

## Exercise 1 Walden Inversion

This laboratory will study the  $S_N2$  reaction between  $Cl^-$  and  $CH_3Cl$  involving a Walden inversion.



Construct  $Cl^-$ . Double click the Draw icon, choose Cl, and draw a Cl atom in the workspace. Click the Select icon and select the Cl atom. Click Build / Set Charge and enter -1. Click OK.

Click Setup / Semiempirical / PM3. Click Options and enter -1 for Total Charge and 1 for Spin Multiplicity. Click OK twice.

Find the  $\Delta_f H$  by clicking Compute / Single Point and record  $\Delta_f H(Cl^-) =$  \_\_\_\_\_ kcal mol<sup>-1</sup>.

Save as cl-pm3.HIN.

Close.

Construct  $CH_3Cl$  and minimize at the PM3 level. Record  $\Delta_f H(CH_3Cl) =$  \_\_\_\_\_ kcal mol<sup>-1</sup>.

Save as ch3clpm3.HIN.

Save as clch3cl-pm3.HIN.

Construct  $ClCH_2Cl^-$  by attaching a  $Cl^-$  to the C atom. Click Build / Allow Arbitrary Valences and draw a Cl atom connected to the C atom on the H side using a long bond. Select the C atom and set the charge as -1.

Minimize at the PM3 level using a charge of -1 and Spin Multiplicity of 1 in the PM3 setup.

Record  $\Delta_f H(ClCH_2Cl^-) =$  \_\_\_\_\_ kcal mol<sup>-1</sup>.

Save.

Save as clch3cl-tspm3.HIN.

Click Select to confirm that Multiple Selections and Atoms are checked. Select the C atom and the three H atoms. Click Select / Name Selection / Other and enter "flat" or some other name. Click OK. Right click in the workspace.

Click Setup / Restraints and Add 4-flat. Click Restrained Value / Other and enter 180 and Force Constant / Other and enter 500.

Minimize at the PM3 level and record  $\Delta_f H(ClCH_2Cl^-)_{ts} =$  \_\_\_\_\_ kcal mol<sup>-1</sup>.

Calculate  $\Delta E_1 =$  \_\_\_\_\_ kcal mol<sup>-1</sup> (literature  $3 \pm 1$  kcal mol<sup>-1</sup>),  $\Delta E_2 =$  \_\_\_\_\_ kcal mol<sup>-1</sup> (literature  $-12 \pm 2$  kcal mol<sup>-1</sup>), and  $\Delta E_3 =$  \_\_\_\_\_ kcal mol<sup>-1</sup> (literature  $13 \pm 2$  kcal mol<sup>-1</sup>). Note better agreement can be obtained by using a higher level of theory.

## Exercise 2 Using Vibrational Motion to Determine the Transition Structure of NH<sub>3</sub> Inversion\*

Construct NH<sub>3</sub> by double clicking the Draw icon to open the Element Table. Choose N and close. Click in the center of the workspace to create a single N atom. Double click the Select icon to all H atoms.

Choose Setup / Density Functional and choose Medium (6-31G\*) as the basis set and click Exchange Correlation. Choose B3-LYP. Click OK / OK.

Choose Compute / Geometry Optimization / OK. Record the energy = \_\_\_\_\_ kcal mol<sup>-1</sup>.

Calculate the vibrational spectrum by choosing Compute / Vibration, Rotation Analysis.

Choose Display / Rendering / Balls and Cylinders / OK.

Choose Compute / Vibrational Spectrum to open the Vibrational Spectrum window. Move the window so that it does not block the molecule.

Click on the lowest energy vibration (farthest to the right). Check the animate vibrations box, enter 25 for the Animation Cycle Frames, and click Apply. The “breathing” normal vibrational mode should appear on the screen.

Click Cancel to close the window and Chose Cancel to stop the animation.

Save as NH3.HIN.

To determine the transition structure, double click the Select icon and choose Compute / Transition State / Eigenvector following / OK. After the vibrational calculation is completed, the Transition State Search window appears.

Click on the lowest energy vibration. Click OK. What is the shape of the transition structure?

Save as NH3TS.HIN.

## Exercise 3 Using a Reaction Path to Determine the Transition Structure of NH<sub>3</sub> Inversion\*

Open NH3.HIN from Exercise 2.

Choose Display / Rendering / Sticks / OK.

Choose Display / Labels / Number / OK.

Click the Draw icon. Hold the Shift key down and click the N atom. The mirror image of the original molecule should appear.

Optimize at the B3-LYP/6-31G\* level and save as NH3m.HIN.

Choose File / Merge and choose NH3.HIN to add the original structure to the workspace.

Select all of the atoms in the original structure by clicking the Select icon and clicking each atom while holding down the Shift key.

Choose Select / Name Structure / Reactant / OK.

Choose Select / Compliment Selection to unselect the original structure and to select the mirror image.

Choose Select / Name Structure / Product / OK.

Right click in the workspace to unselect everything.

Choose Setup / Reaction Map to open the Transition State Mapping window.

Click on 2,1,N / 1,1,N / Add. Repeat carefully matching each pair of H atoms. Click OK.

Choose Compute / Transition State / Synchronous transit / OK. What is the shape of the transition structure? \_\_\_\_\_

Choose Compute / Vibration, Rotation Analysis.

Choose Compute / Vibrational Spectrum. How has the lowest energy vibration changed?

Calculate and record the single point energy using B3-LYP/6-31G\* = \_\_\_\_\_ kcal mol<sup>-1</sup>.

Subtract the two energies to predict the activation energy = \_\_\_\_\_ kcal mol<sup>-1</sup>  
(literature 5.9 kcal mol<sup>-1</sup>).

\*Exercises 2 and 3 are based on those found in *Getting Started*, HyperChem.