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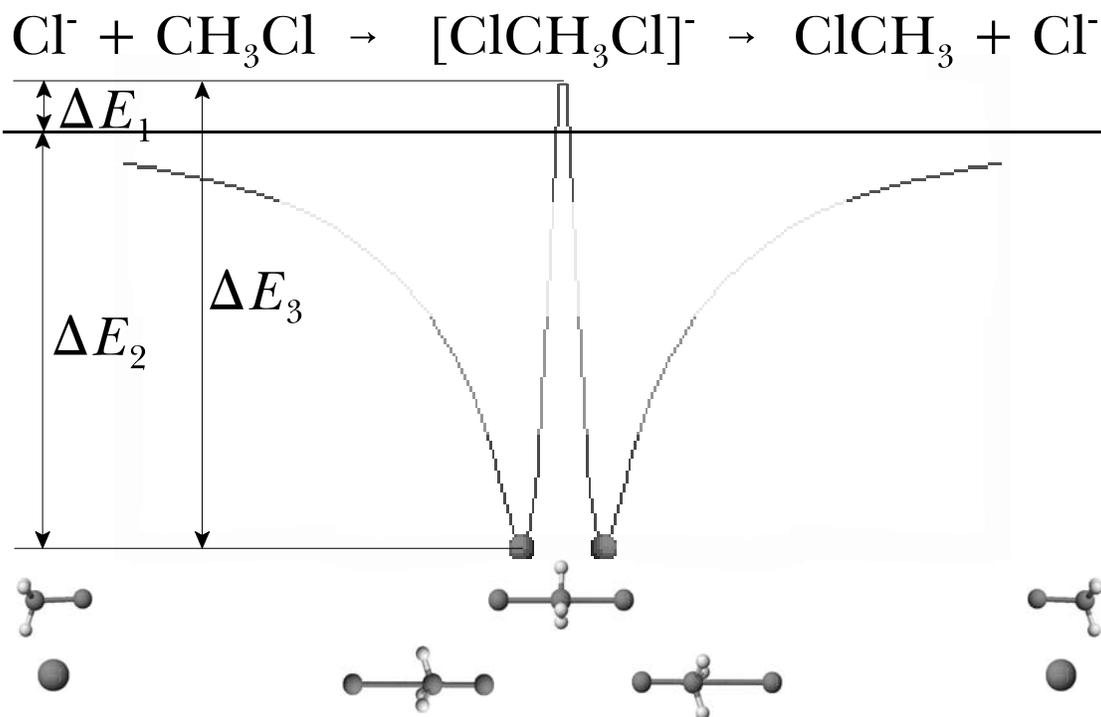
This laboratory will study the S_N2 reaction between Cl^- and CH_3Cl involving a Walden inversion.

$$Cl^- + CH_3Cl \rightarrow [ClCH_3Cl]^- \rightarrow ClCH_3 + Cl^-$$

Construct Cl^- and calculate $\Delta_f H$.

      Use sp^3 Cl with -1 charge. Save as Cl-.csf.

      Experiment / New / Chemical Sample, Heat of Formation, PM3. Record $\Delta_f H(Cl^-)$
          = _____ kcal mol^{-1}.

Construct CH_3Cl and optimize.

      Use sp^3 C, sp^3 Cl, beautify comprehensive. Save as CH3Cl.csf.

      Experiment / New / Chemical Sample, Optimize Geometry, PM3. Record
          $\Delta_f H(CH_3Cl)$ = _____ kcal mol^{-1}.

Construct $ClCH_3Cl^-$ and calculate $\Delta_f H$.

      Open CH3Cl.csf, use sp^3 Cl with -1 charge, single bond. Save as ClCH3Cl-.csf.

      Define the two C-Cl bond length labels.

          Select the left Cl and C atoms; adjust, atom distance, define geometry
             label, search 5.0 to 1.5 using 35 steps.

Repeat for the C and the right Cl atoms.

Experiment / New / Reaction and transition state, map reaction, PM3 reaction coordinate (two labels).

The PES should appear with the "ball" indicator at one of the van der Waals complexes. Record the C-Cl distances _____ Å and _____ Å (literature 3.27 Å and 1.83 Å).

Rotate the PES and move the indicator to the saddle point. Record the C-Cl distances _____ Å (literature 2.38 Å).

Construct the left half of the reaction coordinate diagram.

Open ClCH3Cl-.csf; select the left Cl and C atoms; adjust; atom distance, search between 10.0 and the value of the distance at the saddle point determined above using a sufficient number of steps to generate 0.2 Å changes.

Select the C and right Cl; adjust; atom distance; unselect define geometry label.

Experiment / New / Chemical Sample Conformation, optimized map, PM3 (1 label).

The reaction coordinate diagram should appear with the indicator at the van der Waals complex and record $E =$ _____ kcal mol^{-1} (choose calc_energy in the drop down menu at the bottom of the reaction coordinate window).

Move the indicator to the transition structure and record $E =$ _____ kcal mol^{-1}.

Calculate $\Delta E_1 =$ _____ kcal mol^{-1} (literature 3 ± 1 kcal mol^{-1}), $\Delta E_2 =$ _____ kcal mol^{-1} (literature -12 ± 2 kcal mol^{-1}), and $\Delta E_3 =$ _____ kcal mol^{-1} (literature 13 ±2 kcal mol^{-1}). (Note better agreement can be obtained by using a higher level of theory.)