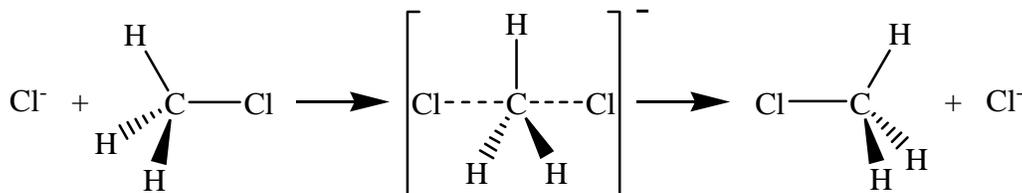


9 Transition States (Spartan)

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



Use the Entry level builder to draw a molecule of methyl chloride. Rotate the molecule so that the orientation matches that of the leftmost molecule shown above.

Click on the “Insert” key located at the bottom right of the screen. Insert a “Cl-“ to the left of the methyl chloride molecule, as shown above.

Use the “Delete” icon (7th across the top) to remove the unfilled valence of the Cl you’ve just added.

Click on the “Add Fragment” icon (6th across the top) to stop the delete mode.

Click on the “View” icon (5th across the top).

Click on the “Transition” icon (curved blue arrow, 23rd across the top).

Click once on the unbound chloride to select it.

Hold down the “Shift” key, click again on the unbound chloride, then on the carbon atom. A curved blue arrow will appear where the new bond will be formed. (You may need to rotate the image to see this clearly).

Click on the C-Cl bond, then click on the bound chlorine. A second blue arrow will appear.

Click on the curved double arrow icon in the lower right corner of the screen. The structure should now match the transition state structure shown in brackets above.

Click on the “Distance” icon (11th across the top), then on the C-Cl bond on the left. Replace the current C-Cl distance in the box (lower right corner of screen) with 4.0 and hit “Enter”. The structure now represents the “reactant”.

Click on the “Constrain Distance” icon (17th across the top), then on the elongated C-Cl bond.

Click on the “Lock” icon in the lower right corner.

Choose Display / Properties, then click on the pink “Constraint” marker at the center of the bond. In the “Constraint Properties” box, click on “Dynamic”, and edit the top line to read “4.00Å – 1.5Å, Steps = 35”. YOU MUST HIT RETURN AFTER CHANGING THE VALUE IN EACH BOX IN ORDER FOR THE CHANGE TO TAKE PLACE.

Close the “Constraint Properties” box.

Choose Setup / Calculations. Choose Energy Profile at Ground State with Semi-Empirical PM3, and change the “Total Charge” to “Anion”.

Click “Submit” and save the file as WaldenPM3.spartan in an appropriate location.

Click “OK” to started message and “OK” to completed message.

Save and Close the file. Open the “WaldenPM3.Profile1”. Rotate the image to match that shown above.

Click on the “Align” icon (Red triple integral, 21st across the top), then click on the three hydrogen in turn. Finally, click on the “Align” button at the bottom right of the screen.

Click on the “View” icon (5th across top). Rotate the image again to match the above orientation. Move the entire image to the upper right corner of the screen.
Choose Display / Spreadsheet. Click on “Add” and choose “E, kcal mol⁻¹”, then click “OK”.
To add the Cl-C distances to the spreadsheet, click on the “Distance” icon (11th across the top), click on the pink ‘Constraint’ marker on the Cl-C bond, then click on the “P” in the lower right corner.
Click on the “View” icon (5th across top).
To add the Cl charge to the spreadsheet, choose Display / Properties. Click on the leftmost Cl atom of the structure. In the “Atom Properties” window, click on the “P” button to the left of “Electrostatic”. Close the “Atom Properties” window.
Choose Display / Plots. For the X-Axis choose “Length”, and choose both E (kcal mol⁻¹) and Electrostatic for the Y-Axis.
You will see two plots of different color, one showing the energy as the reaction proceeds, and the other showing the charge on the Cl. Are the two related? Explain?

Use the “advance” and “reverse” buttons on the lower left to locate the saddle point. The corresponding values will be highlighted in the spreadsheet. Record both the C-Cl bond distance _____ Å (Lit. value 2.38 Å) and the energy _____ kcal mol⁻¹.
Again, use the “advance” and “reverse” buttons to locate one of the minima. Find the highlighted energy in the spreadsheet at the minima and record it here _____ kcal mol⁻¹. Calculate the height of the energy barrier by finding the difference between the two energy values recorded above _____ kcal mol⁻¹ (Lit. value 13 ± 2 kcal mol⁻¹). (Note: Better agreement can be obtained by using a higher level of theory).

Calculations will now be performed that will allow the bond making/breaking process, as well as the migration of negative charge, to be visualized.

Choose Setup / Calculations and choose Single Point Energy at Ground State with Semi-Empirical PM3. Click on “OK”.

Choose Display / Surfaces, and click “Add” in the “Add Surface” window. Choose Surface: density (bond), Property: none, and Resolution: Intermediate. Click on “OK”. In the “Add Surface” window, click on “Add”. Choose Surface: density (bond), Property: potential, and Resolution: intermediate. Click on “OK”. Close the “Surfaces” window.

Choose Setup / Submit.

Click “OK” to started message and “OK” to completed message.

Choose Display / Surfaces and click the box next to “density” in the “Surfaces” window. Animate the image set by clicking on the “Play” button on the lower left. Hit the “Pause” button, and step through the images using the “Advance” and “Reverse” buttons until the saddle point is reached. In terms of bond making/breaking, what is happening in the reaction at this point?

In the “Surfaces” window, click the box next to “density” to uncheck it, then click on the box next to “density potential” to choose it.

Animate the image set by clicking on the “Play” button on the lower left. Hit the “Pause” button, and step through the images using the “Advance” and “Reverse” buttons until the saddle point is reached. Red color indicates negative charge, while blue represents positive charge. In terms of charge distribution, what is happening in the reaction at this point?

Save and close the file.