12.3: Computational Instructions

To calculate the energetics of the reaction we will need to calculate the starting materials and products for both the opening of oxetane and propylene oxide, as shown in Figure 2. While we have learned to calculate the transition states of substitution reactions in a previous computational exercise, the transition states for these reactions will be provided to help save time.

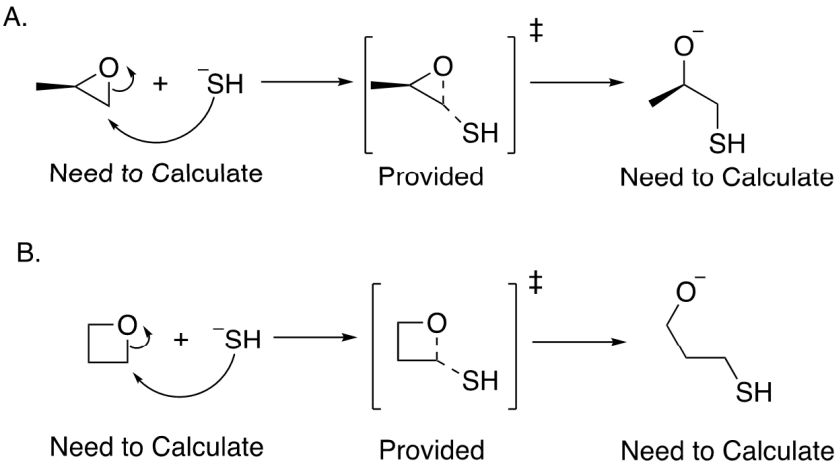

Figure 2A. Opening of propylene oxide with the hydrosulfide anion. **B.** Opening of oxetane with the hydrosulfide anion.

Start by creating a folder on the desktop of your computer and label it as Ether Substitution. Within this folder, please create the following subfolders: SM_Epox, PR_Epox, SM_Oxet, and PR_Oxet. Next you should download the supporting files for this exercise. These files will include a generic input file (denoted by a .inp file extension), and molecular coordinates for the products and starting materials that you will run your calculations upon. Place a copy of the generic input file into each of the nested subfolders and place the appropriate coordinates file into each subfolder. A description of this file structure is shown in Figure 3.

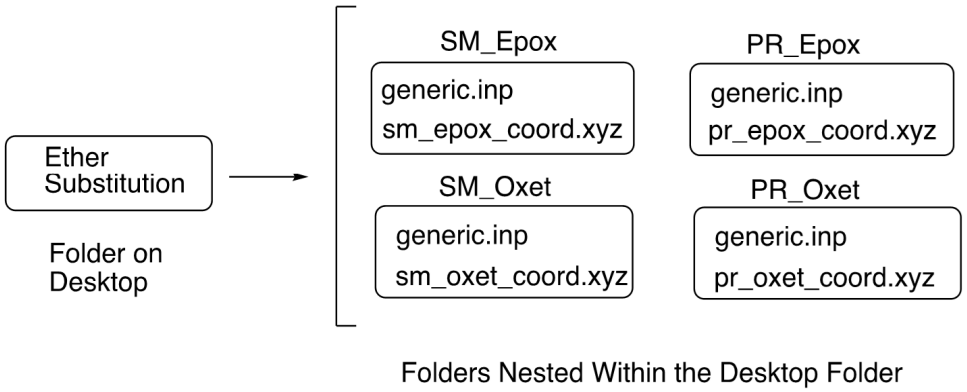

Figure 12.3.1: Copy and Paste Caption here. (Copyright; author via source)

The process for calculating the energy of the products or reactants of the oxetane or epoxide opening is the same for each calculation. To illustrate this process, we will walk through the calculation of the starting materials for the epoxide reaction. Begin by opening the starting coordinates file sm_epox_coord.xyz in Avogadro[4,5] and make sure that it has the starting propylene oxide and hydrosulfide anion as shown in Figure 4.

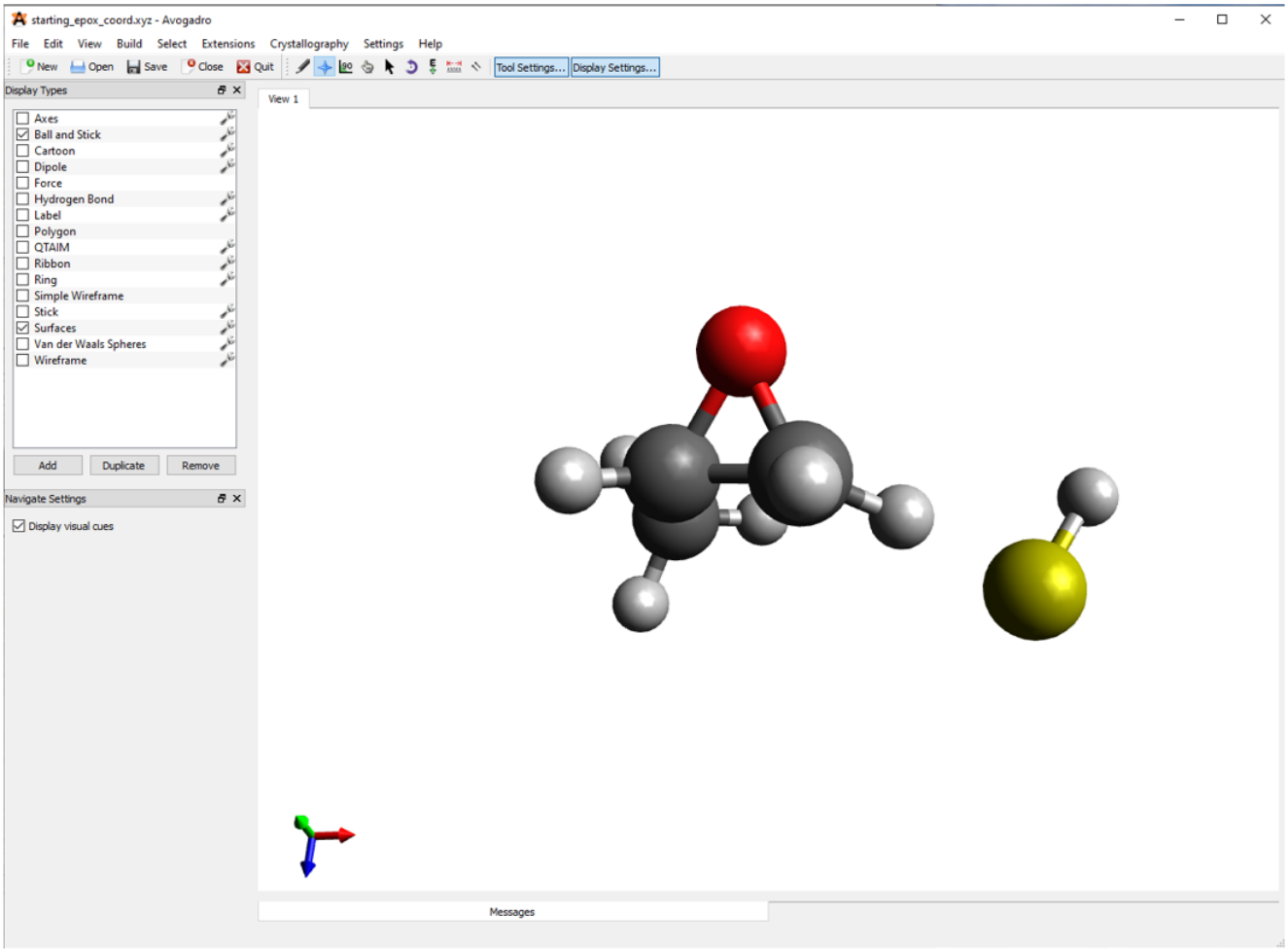

Figure 4. Expoxide opening reaction starting material viewed in Avogadro.

You should then open the generic input file in notepad and save it as sm_epoxide.inp. As shown in Figure 5, please change the name of the file from coord.xyz to sm_epox_coord.xyz so that the computer knows to look for the epoxide starting material coordinates in your folder. Be sure to save your changes.

```
# starting material energy
!PM3 Opt Freq

%geom maxiter 500
End

* xyzfile -1 1 sm_epox_coord.xyz
```

Figure 5. Generic input script for determining the energy values of starting materials or products.

We can now run our calculation using Orca via the command line as we did in previous exercises. Briefly, open the command prompt to your PC by right clicking on the start button and searching for command prompt. First, we need to tell the computer to look on the C drive and we do this by typing C: and hitting enter. Next, we need to tell the computer where the input script and the coordinates file are to run the calculation. We do this by typing cd (space) and pasting the file path. When you hit enter, the computer will paste a new line indicating that the current directory has changed, as shown in Figure 6A. To find the file path of your input script, right click on the input script (sm_epoxide.inp) and select properties. The file path will appear under location, and you can highlight and copy this file path (Figure 6B).

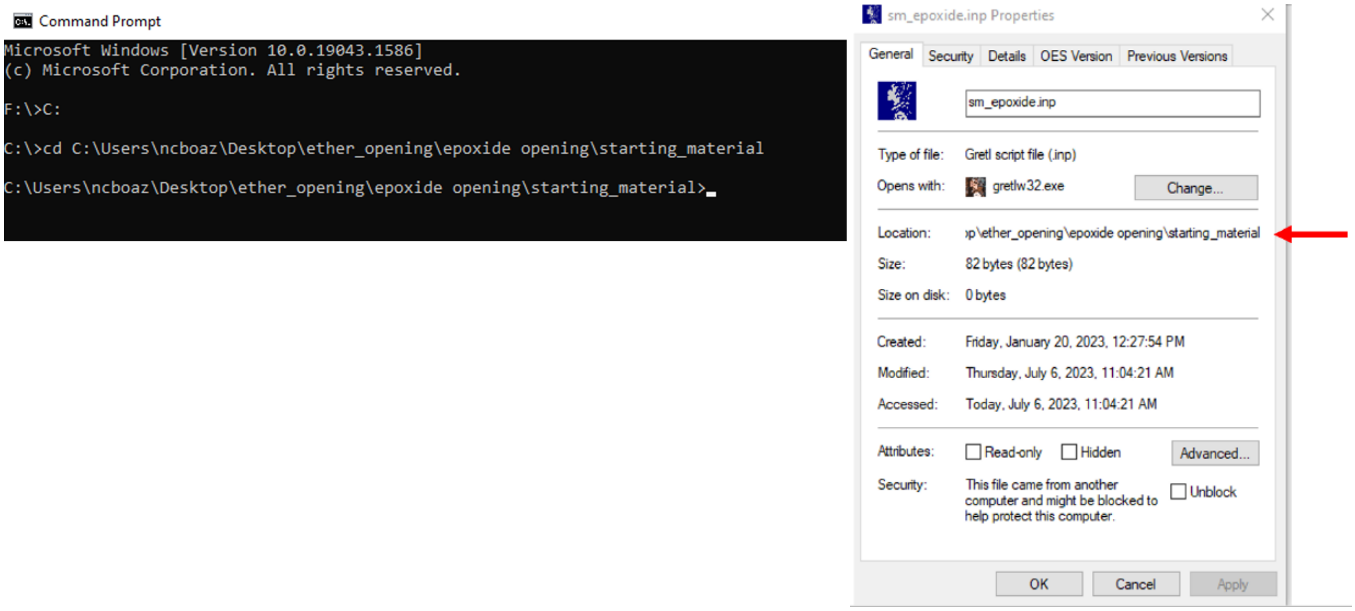

Figure 6A. (**Left**) Changing of the file path in the command prompt to match the location of our input script. **6B. (Right)** Locating the file path on the properties window of the input script (Red Arrow).

Next, we will run the calculation by typing orca sm_epoxide.inp > sm_epoxide.out and pressing enter. After pressing enter it may not appear like much is happening, but the computer is working on your computation and depositing the results in the SM_Epox folder that you created. Depending upon the speed of your computer, the calculation will take about 1-3 minutes, and upon completion the command prompt will print another line indicating that it is ready for the next command (Figure 7).

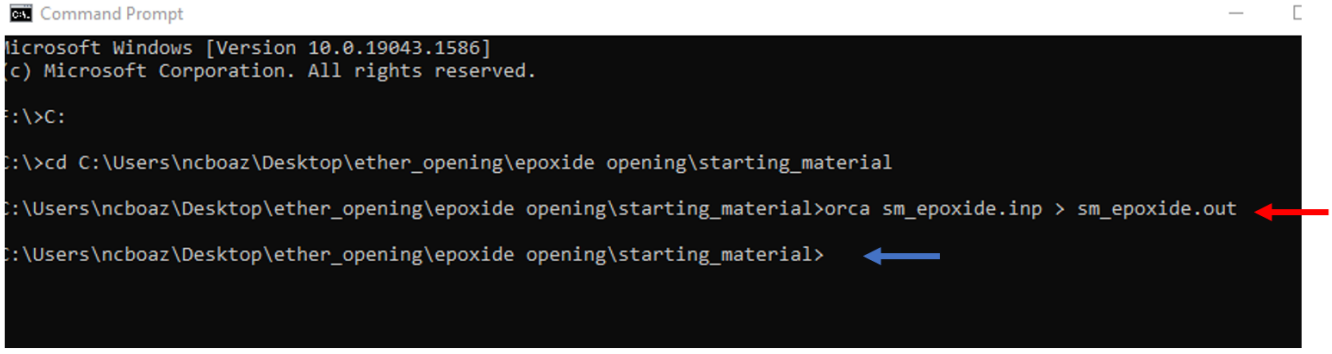

Figure 7. Running the calculation using the command line. The line indicated by the red arrow shows the computer that we want to use Orca to calculate the commands in sm_epoxide.inp and that the results of this calculation should be placed in the output file sm_epoxide.out. The line indicated by the blue arrow is the computer indicating that the calculation is complete, and the command prompt is ready for the next command.

After the Orca job has completed you can access the energy values by opening the output file (sm_expoxide.out) in notepad. At the very end of the file (scroll to the bottom) will be the thermodynamic values that Orca calculated for the starting materials of the epoxide opening reaction. As shown in Figure 8, the value of Gibbs free energy in Hartree (Eh) can be found under the heading of Final Gibbs free energy.

```
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GIBBS FREE ENERGY
------------------

The Gibbs free energy is G = H - T*S

Total enthalpy                  ...    -34.57632764 Eh
Total entropy correction        ...     -0.04005359 Eh    -25.13 kcal/mol
-------------------------------------------------------------------------
Final Gibbs free energy         ...    -34.61638123 Eh

For completeness - the Gibbs free energy minus the electronic energy
G-E(el)                         ...      0.05618773 Eh     35.26 kcal/mol


Total Time for Numerical Frequencies  :       180.476 sec

Timings for individual modules:

Sum of individual times         ...       24.887 sec (=   0.415 min)
STO integral calculation        ...        1.554 sec (=   0.026 min)   6.2 %
SCF iterations                  ...       17.987 sec (=   0.300 min)  72.3 %
SCF Gradient evaluation         ...        1.083 sec (=   0.018 min)   4.4 %
Geometry relaxation             ...        4.262 sec (=   0.071 min)  17.1 %
                           ****ORCA TERMINATED NORMALLY****
TOTAL RUN TIME: 0 days 0 hours 3 minutes 29 seconds 733 msec
```

Figure 8. The Gibbs free energy of the starting material of the epoxide opening reaction (indicated by a red arrow).

Please repeat this process for the products of the epoxide opening, the starting materials of the oxetane opening, and the products of the oxetane opening. After completing these computations use these results to complete the questions at the end of this assignment.

References

1. Neese, F. The ORCA Program System. *WIREs Computational Molecular Science* **2012**, *2* (1), 73–78. https://doi.org/10.1002/wcms.81.
2. Neese, F. Software Update: The ORCA Program System, Version 4.0. *WIREs Computational Molecular Science* **2018**, *8* (1), e1327. https://doi.org/10.1002/wcms.1327.
3. Neese, F.; Wennmohs, F.; Becker, U.; Riplinger, C. The ORCA Quantum Chemistry Program Package. *J. Chem. Phys.* **2020**, *152* (22), 224108. https://doi.org/10.1063/5.0004608.
4. Hanwell, M. D.; Curtis, D. E.; Lonie, D. C.; Vandermeersch, T.; Zurek, E.; Hutchison, G. R. Avogadro: An Advanced Semantic Chemical Editor, Visualization, and Analysis Platform. *J Cheminform* **2012**, *4* (1), 17. https://doi.org/10.1186/1758-2946-4-17.
5. Avogadro: An Open-Source Molecular Builder and Visualization Tool. http://avogadro.cc/.