Reactions of benzene

A. Dehydrogenation of cyclohexane to form benzene

In this exercise you will calculate the change in energy as cyclohexane is stepwise dehydrogenated to form benzene.

Open Chemcraft and select **Edit→Add fragment**. Select molecules→rings and find cyclohexane. Left-click on the main Chemcraft window to create the cyclohexane (point group D3d) molecule. Set up a Hartree-Fock geometry optimization using the 3-21G basis set on Elja (i.e. create a directory, make an ORCA input file and copy a jobscript to the directory) and run the calculation.

When the calculation has finished, open the output file with ChemCraft and select the equilibrium geometry, i.e. select the last 'image' on the list (the lowest energy point) found in the panel to the left of the main window. If you scroll through the 'images' you will see how the equilibrium structure search (also called geometry optimization) proceeded. The optimized geometry should look similar to the initial structure. Record the ground state energy from the output file. Now, remove two hydrogen atoms by clicking on them, one from each of two neighboring carbon atoms, and select **Edit→Delete selected** (or simply press the Del key). Now copy the coordinates and set up a new calculation in a new directory for this intermediate configuration with the same settings as before.

When the calculation has finished, visualize the equilibrium structure. You should see a planar −CH−CH− unit in the molecule. If the molecule lacks such a unit, a local minimum has been found rather than the global minimum. In this case, repeat the last step, but choose different hydrogen atoms.

Now, repeat the procedure of dehydrogenation. Make sure that you remove hydrogen atoms in such a way that the two carbon atoms that are next to each other and still bonded to two hydrogen atoms. Run the calculation. You should now see two of the (nearly) planar −CH−CH− units.

Repeat the dehydrogenation procedure so that each C-atom becomes bonded to only one H-atom.

Q1: *Write balanced chemical equations for each one of the three dehydrogenation steps in your report. What other products are involved?*

For calculating the reaction energy of each step, the ground state energy of all the reactants and products has to be calculated. Calculate the equilibrium structure of the other molecules involved in the reactions. Make sure you use the same level of theory in each case.

Q2: *Write the calculated ground state energy of each molecule in your report.*

Q3: *Calculate the reaction energy for each of the three steps in the dehydrogenation of cyclohexane. Draw an energy diagram showing the three steps of the reaction. Note that it is essential that all numbers that get added or subtracted are obtained from calculations that use the same level of approximation.*

Now check whether the reaction energy is converged with respect to the basis set. Repeat the aforementioned calculations using a larger basis set, 6-31G. To make the calculations faster, use the previously calculated equilibrium geometry of each molecule as an initial guess for the new calculations (using the larger basis set).

Q4: *Make a table of the reaction energy in the three steps of the dehydrogenation and compare the results obtained from the two basis sets.*

Q5: *Draw an energy diagram based on the numbers obtained using the second basis set.*

Q6: *Are the reaction steps exothermic or endothermic? What is the energy change during hydrogenation of benzene? How well do the calculated results agree with experimental observations?*

B. Reaction of nitronium cation with benzene

The nitronium ion, NO_2^+, is a commonly used active reagent for the nitration of benzene and other aromatics.

To construct the nitronium ion, do the following: Open Chemcraft, **Edit**→Add atom and select nitrogen in the periodic table. Then, select oxygen. Click on the nitrogen atom. Repeat for the second oxygen atom. Now we need to make sure that the molecule is bent. Select the three atoms O−−N−−O and assign it an angle of 109° in the geometrical editor (bottom-right in the Chemcraft window). Do a geometry optimization (equilibrium structure search) of the cation using Hartree-Fock and the 6-31G basis set. Remember to set the charge of the molecule to **1**.

Make sure that the geometry optimization converged properly, i.e. can you find the following message:

```
**********************HURRAY********************
***        THE OPTIMIZATION HAS CONVERGED     ***
************************************************
```

If you are unable to converge your initial configuration of NO_2^+ start by increasing the number of allowed iterations in the geometry optimziation. Create a 'geom block' and define a larger 'maxiter' for example:

```
%geom
maxiter = 150
end
```

When the calculation has finished, open the output file with ChemCraft and make a figure of the optimized geometry. Also, plot the progress of the optimization. Click **Optimization steps** and select **Show optimization convergence →Energy vs step N**. You will see a plot of how the energy changes during the optimization. Select eV as the units. Copy the data into Matlab/Excel and create a plot. Include the plot in your report. Also, if you click individual optimization steps, you can select 'show forces' and 'label force value' to inspect the magnitude and direction of the atomic forces . Now click the last optimization step and use the geometric editor to view the bond lengths and the angle.

Q7: *What is the ground state energy of the nitronium cation? Is the molecule bent or linear? Are the N-O bond lengths identical or different?*

To understand the reactions of the nitronium cation it is good to know how the charge is distributed in the molecule. From this information, one can predict possible reaction mechanisms. Often it is useful to create a figure showing the electron density isosurface colored according to the electrostatic potential. This is actually not straightforward to do with ORCA / ChemCraft.

To begin, make a new directory, copy a job-script to the new directory. Create a new input file that calculates the single point energy (i.e. no 'OPT') using HF/6-31G on the optimized molecular geometry of NO_2^+ (found in the previous calculation). Furthermore, it is essential to add the keyword 'keepdens' to the simple-input line (this makes ORCA store the density matrix in the given basis on the disk). This will make ORCA print one more file with the extension '.densities' that we need to create the electrostatic potential. Run the calculation.

We now need to create a '.cube' file format of the electrostatic potential that can be visualized in ChemCraft. For this purpose, we need to use a python tool that will generate a '.cube' file. Copy the python script 'electro_potgen.py' to the directory where you performed the single point energy calculation on the optimized nitronium-ion (">> cp /users/home/share/CompChem/lab4/electro_potgen.py ."). Verify that the current working directory contains the python script and the two files 'orca.gbw' and 'orca.densities' using the 'ls' command. Also, copy the 'orca.xyz' from the previous optimization job to the current working directory.

Now before we can execute the python script and generate our .cube file, we need to make sure python is loaded. Type; ">> ml load Python/3.9.6-GCCcore-11.2.0". Now to verify that the correct python is loaded, type ">> which python". You should see the following lines printed to the terminal window:

```
/hpcapps/libsci-gcc/software/Python/3.9.6-GCCcore-11.2.0/bin/python
```

Now we can use the electro_potgen script to generate a '.cube' file of the electrostatic potential that can be inputted into ChemCraft. To execute the script type:

>> python electro_potgen.py xyz=file.xyz npts=80 offset=7.0

where 'file.xyz' needs to be a '.xyz' file containing the equilibrium geometry of the nitronium cation (i.e. orca.xyz). Also, the files from the single point energy run with extensions '.gbw' and '.densities' have to be included in the same directory. The 'npts' is the number of grid points in one dimension. 'offset' allows the grid to extend beyond the molecule (unit in Bohr). If the script executed normally, a file with the extension '.cube' should have been generated in your working directory. Copy this file to your local machine and open it with ChemCraft.

Click 'Show mapped spheres' and select a value range from 0.4 to 0.6. Do not change the 'Scale' from 1. Select 'Values range' from 0.4 to 0.6. Here you might need to press 'Clear all' and again 'Show mapped spheres'. You can slightly adjust the values if you want. Typically in chemistry and physics a region of positive charge is depicted by blue and a region of negative charge by red. However, in ChemCraft it is the opposite. If you want to turn this around, you can click "Style"and change the "Map colors"to go from 'red' to 'blue'. This will 'correct' the surface. Also, you can play around with the options 'Points', 'Lines' and 'Surface' within the 'Style' option. Save an image of the surface and include the picture into your report.

Q8: *Where is the positive charge mostly located? Based on your calculation, draw the Lewis dot structure that best represents the nitronium cation.*

Calculate the benzene molecule at the same level of approximations (i.e. HF/6-31G). You can generate a reasonable initial geometry for the benzene molecule from the fragment database of ChemCraft or use the geometry from your calculations in part A. Start by performing an equilibrium structure search and then do a single point energy calculation on the optimized geometry using HF/6-31G with the additional keyword 'keepdens'. Display the electrostatic potential in the same way you did for the nitronium cation. Find a good 'value range' to display the electrostatic potential (e.g., 0.01 to 0.1). If you want you can reverse the color scheme. Save a picture of the electrostatic potential surface of benzene and include in your report.

Q9: *Judging from the electrostatics, how do you expect the nitronium ion to react with the benzene molecule (which part of the nitronium ion will most likely collide with what part of the benzene molecule?). Draw a Lewis structure of the nitronium/benzene adduct.*

The adduct is metastable, i.e. corresponds to a local minimum on the energy surface so its structure and energy can be calculated with a minimization starting close enough to the minimum energy structure. Build the $(NO_2/\text{benzene})^+$ adduct by first loading the equilibrium structure of benzene into ChemCraft. Now add a single nitrogen atom bound to one of the carbon atoms. Add two oxygen atoms to the nitrogen. ChemCraft offers an excellent method based on chemical informatics to improve the initial guess of the geometry. Select **Edit →Clean... →Set all**. All of the structural parameters will be displayed as well. To remove the display of the structural parameters select **View →Structural parameters →Clear**. Copy the coordinates and set up a Hartree-Fock geometry optimization using the 6-31G basis set. Remember to set the charge to **1**. The calculation will take a few minutes.

Q10: *Place a picture of the optimized structure in your report. How do you describe the bonding (get the C-C bond lengths in the ring)?*

Q11: *What is the binding energy of the adduct (energy of the adduct minus the energy of reactants, i.e. isolated nitronium ion and benzene molecule).*

Now create a picture of the electrostatic potential surface for the adduct. Play with the 'Scale' and 'Value range' to get a reasonable physical picture of the charge distribution.

Q12: *Show a picture of the electrostatic potential map of the adduct in your report.*

Since the adduct is charged, disproportion to a cation and a neutral molecule might reduce the total energy. One possibility is to have the back reaction, removal of NO_2^+ from the ring, to form the reactants again. Another option is the removal of H^+ from the adduct.

Q13: *Which proton would you expect to be easiest to remove? Why?*

Load the adduct into ChemCraft and remove the hydrogen atom you expect will be easiest. Since you effectively want to remove a proton, the charge needs to be set to zero. Carry out a geometry optimization. It might be a good idea to use 'Set all' again, to improve the bond lengths.

Q14: *Do you have to run a calculation on the single proton to determine its energy? Is the total energy of your product and the proton higher or lower than that of the charged adduct?*

Q15: *Can you name another (quite well known) aromatic compound containing nitro groups that has similar properties regarding thermodynamical stability?*