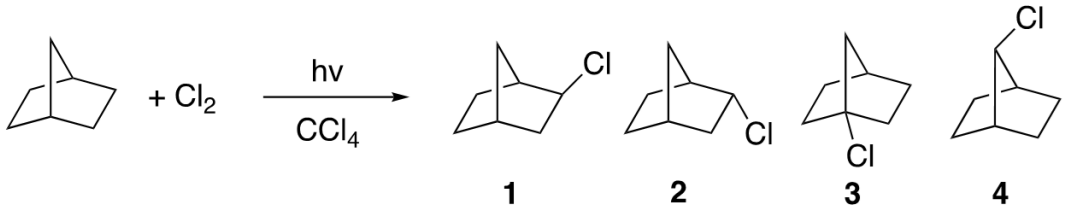
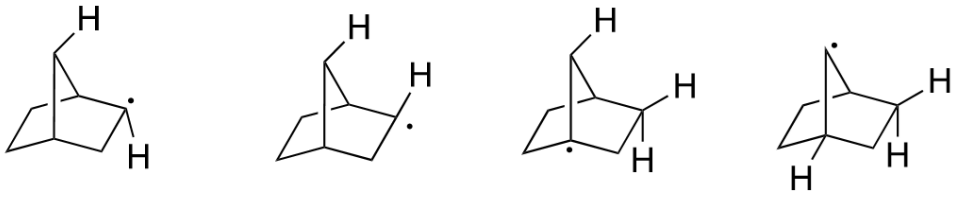
9.4: Exercise Questions

1. Using the relative reactivity table shown in figure 2, please calculate the expected ratio of products for the radical halogenation of norbornane. Does your estimated product ratio's match those found experimentally (see Figure 3)? For full credit please show your work. (Hint: Remember that each unique *[Math Processing Error]* bond is present in different numbers)



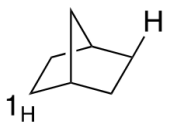
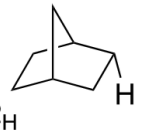
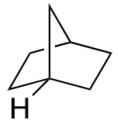
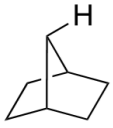
2. Use the computational data that you have generated to complete the table below for each of the norbornyl radicals that can be formed under reaction conditions. There are 627.5 kcal/mol for every 1 Hartree (Eh). Please rank the formed radicals in order of increasing stability (Low Ranking (e.g., 1) =least stable, High Ranking= most stable). Hint: *[Math Processing Error]* and *[Math Processing Error]* have extremely similar enthalpy values you should give them the same number.

Radical	Enthalpy, H (EH)	Enthalpy, H (kcal/mol)
1_{rad}		
2_{rad}		
3rad		
4_{rad}		

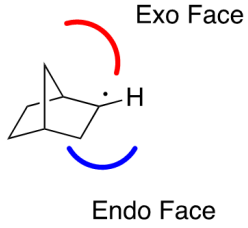


3. Using the equation provided below and the data that you calculated, please determine the bond dissociation enthalpy for each distinct type of *[Math Processing Error]* bond in norbornane. Please show you work. *[Math Processing Error]*

Species	Enthalpy, H (EH)	Enthalpy, H (kcal/mol)
Hydrogen Atom	-0.49764	-312.119808
Norbornane	-273.3914137	-171553.11

C-H Bond				
BDE (kcal/mol)				

4. Because 1rad and 2rad have the same enthalpy values, the *[Math Processing Error]* bonds broken to form these radicals will have the same BDE. Examine the structure of both optimized radicals and propose why they should have the same stability.
5. Examine the structure of 3rad. Why do you think that it is so much less stable than we would have expected?
6. Do the *[Math Processing Error]* BDE values and radical structures explain the experimental selectivity of the chlorination of norbornane?
7. Examine the structure of 1rad or 2rad in Avogadro in space filling mode. To do this click the Van der Waals Spheres option in the left “display types” window. Pay special attention to the accessibility of the exo and endo face of the radical. Using this structure, propose a reason why the exo chlorinated product is produced in higher yield than the endo product.



8. Norbornane can also be halogenated using bromine. Using your data indicating *[Math Processing Error]* BDE values, predict the product distribution yielded by reaction of norbornance with a less reactive bromine radical. How would this product distribution compare to the chlorination product distribution?
