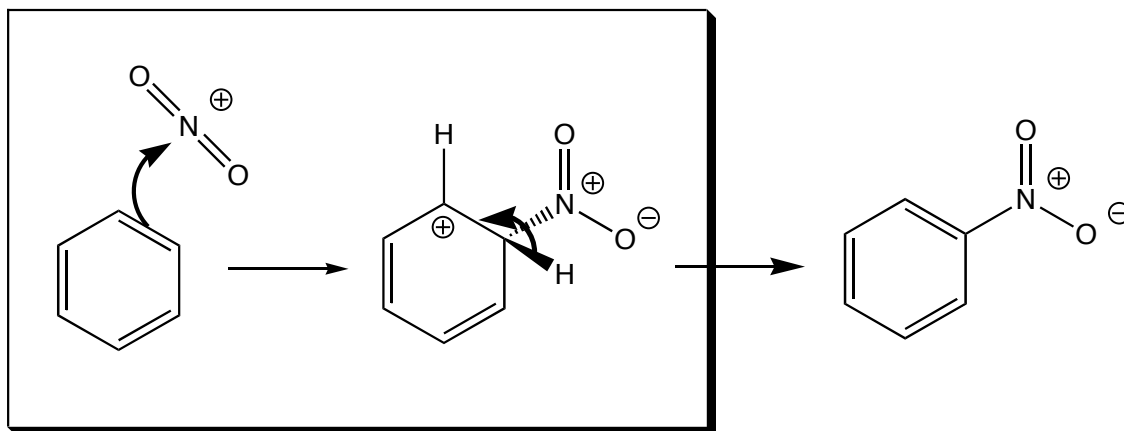


Nitration of Methyl Benzoate. An Experimental and Computational Investigation.

The rate-limiting step in the nitration of an aromatic species involves the addition of an electrophile to an aromatic ring.



For monosubstituted benzenes three products are possible (ortho, meta, and para). The rate-limiting step involves nucleophilic addition of the aromatic species to the nitronium cation. If the most nucleophilic position on the aromatic ring can be determined, the regiochemistry of the reaction can be predicted. Since nucleophilicity is determined by the availability of electrons, a good predictor of this property is electron density, with addition preferred at the position that has the highest electron density (the most negatively charged position).

In this experiment you will be using a semi-empirical calculation (AM1) to predict electron density. Last semester you carried out molecular mechanics calculations (MM), also known as force field calculations. These calculations were based on classical mechanics. Semi-empirical molecular orbital (MO) calculations are based on quantum mechanics. You will determine electron density by calculating the electrostatic charges at the ring carbons in methyl benzoate and from this be able to predict the outcome of the reaction.

Running the calculations on PC SPARTAN '04.

- (1) In the CRC, log onto a PC and launch SPARTAN.
- (2) Under “**File**”, select “**New**”. This will bring up a builder window.

(3) Click on **"Rings"** near the lower right. In the small window, the structure of benzene will appear. Clicking on the main builder window will produce a benzene structure. (Recall that moving the mouse with the left mouse button depressed will rotate the structure. Moving the mouse with the right mouse button depressed will move the structure.)

(4) Add the carboxylic acid function to the ring. Click on **"Groups"** and pull down the menu bar which is next to the Groups and Rings buttons. Choose **"Carboxylic Acid"** and the Carboxylic Acid functional group will appear in the small window. Click on one of the hydrogen atoms on the benzene ring and it will be replaced by the carboxylic acid functional group, making benzoic acid. (Note that each time you click in the box having the carboxylic acid group, a marker will switch back and forth from the carbon to the single-bonded oxygen. Because you want to connect the carbon to the benzene ring be sure that the marker is on the carbon atom of the carboxylic acid group before connecting it to the benzene ring. This is the default setting so unless you accidentally clicked in the box you need not worry about this.)

(5) Add a methyl group to the carboxylic acid to make an ester. Select the tetrahedral carbon in the builder and click on the end of the single-bonded oxygen of the carboxylic acid. This will place a methyl group onto the structure, making the ester, methyl benzoate.

(6) **"Save"** the structure as "methylbenzoate. If necessary rotate the structure for better viewing.

(7) Set up the calculation. Under "Setup", select "Calculations". In the dialog box, "Calculate" should be set to "Equilibrium Geometry" with "Semiempirical: AM1". Click on "Electrostatic Charges" then "Submit".

(8) A confirmation will appear when the job starts and ends. Click on "OK" both times. If necessary rotate the molecule for better viewing.

(9) Under "Display" select "Output". Record the calculated heat of formation of the molecule. Close this window then under "Display", select "Properties" then click on an atom in the structure. You can now click on individual atoms to determine their charges. Record the "electrostatic charges" for the three unsubstituted ring positions.

Under “**Setup**” select “**Surfaces**”. Click on “Add”. Select “Surface: Density” and “Property: Potential”. Rerun the calculation (Setup, Submit). Once the calculation is complete, under Display select Surfaces. Drag the box over to the left and click on the small yellow box next to “density”. Your molecule will appear as a brightly colored blob, with red corresponding to more highly electronegative areas and blue to more electropositive areas. The charges on the ring atoms are generally not different enough to show up as different colors but you can observe the colors of the highly electronegative oxygens and get an idea of what SPARTAN is capable of.

This exercise was developed by Professor Vince Rotello and tweaked by Peter Samal.

(revised 1//08 pws)