

The Friedel-Crafts Reaction (Thermodynamic Control – part II) : A Discovery Based Lab

This project will involve doing a Friedel-Crafts alkylation of xylene similar to the Friedel-Crafts (Part I) described earlier in this webbook, but at elevated temperature and extended time so that the reaction will be under thermodynamic control. The product mixture will be analyzed using GC/Mass Spectrometry (GCMS). Dr. Nerz will assist you in operating the GC/Mass Spec instrument. You should work in groups of three on this project.

Please do the following to prepare for your project. Please use the time allotted in lab to prepare your plan and to start reading about GCMS.:

1. Go over the Friedel-Crafts procedure in your lab book (Part I – the last lab you did) and adapt it so that the reaction will be done at 50°C in a sand bath for two hours rather than the given time at room temperature. You should also consider using 1-bromobutane in lieu of **1-bromopropane** in the reaction because it gives better resolved products on the GCMS. What control reaction should you run? With your group work out a plan for how you are going to do a thermodynamic reaction (assume the reaction will take much longer than you think to set up, particularly because it takes a long time to regulate a sand bath to 50°C) in a group and a kinetic reaction individually, along with any needed control. Perhaps, one control can be run per section. Please outline what you are doing before you come to lab with your group. Then go over it with your instructor/TA at the beginning of lab.
2. Read up on the mass spectroscopy of aromatic compounds in your textbook (Chapter 12). Take careful notes on the lecture given on mass spectrometry. Read up on the mass spectroscopy of substituted aromatics, in particular propyl, butyl, isopropyl and secbutyl xylenes, on the web. Do this before the conference week – it is expected that you will have thought about it though there will be time in lab to work on it.
3. Write down the monoalkylation products you would expect to obtain if the reaction were under thermodynamic control (there are at least six). Hint: You will only obtain n-butyl and sec-butyl products. Realize that thermodynamic control means that the reaction is in equilibrium. This means the reaction is equilibrating and the major product(s) will be those that are most inherently stable. Remember, carbocation stability relates better to kinetics (what happens fastest) rather than thermodynamics. When the reaction goes backwards methyl groups can come off and reattach in new and exciting locations that are more stable!! Again it is expected that you will have thought about this before the conference week which is next week.
4. You will be given some boiling points of related compounds from a very good reference called. Rossini, Pitzer, Arnett, Braun, Pimentel, Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds. You can use propylxylene boiling points as models for butylxylenes. Using this reference, arrange the proposed isomers in order of boiling points. Realize the compounds should elute of the GC of the GCMS in order of boiling point. It is expected that you will have thought about this before the conference week of the lab next week.
5. After you have carried out your experiment and have interpreted your data, you should propose a mechanism for the formation of the various products. This mechanism should be based on the mechanism for Friedel-Crafts Alkylation that you learned in lecture and in lab. Realize that it is possible for a reaction to go backwards by the same mechanism by which it goes forward (like a movie running backwards). Think about this when you are formulating your mechanism for the formation of the more exotic products you discover.

Again, though you will work most of this out the week after you do the experiment, you really should use the time while your lab is equilibrating to think about the points outlined above.

You will be responsible for the material in this lab so take good notes during the conferences that are next week.

Upon completion of your project, your results will be presented orally to Dr. Nerz or a TA during lab next week (probably in groups of six). Each group will only have thirty or forty minutes for the presentation, so you must prepare. You should not go to the meeting without having done all the following. The presentation will involve answering questions at the marker board. Your presentation should involve the following.

Preparation will entail thinking about the points outlined above ahead of the conference day and then working with your groups, TAs and Dr. Nerz during the first couple of labs the week after completing the lab work. At the end of lab there will be four conference times and you will go over the lab with Dr. Nerz or a TA during that time. That will constitute your conference.

- I.** The structures of all viable products. You should come up with eight isomers.
- II.** The order of their boiling points. You can use the boiling points of propylxylenes as models for butylxylenes.
- III.** The assignment of GC peaks for butylxylenes.
- IV.** The fundamental aromatic GCMS fragmentation of n-butylxylene and sec-butylxylene.
- V.** The ionic chemical mechanism for the formation of the unexpected products (what happened in your lab)

It is expected that all members of the group will have a strong knowledge of all the above areas. The idea is to have the knowledge and understanding of the work, not to make a fancy presentation. The idea is also to cut some of the time you would need to do a write-up so don't get carried away with this. Dr. Nerz or your TA will guide the conference.