Comparative Rates of Electrophilic Aromatic Substitution Reactions

The study of reaction rates is one important component used to determine a reaction mechanism. Once a reaction mechanism is known, comparing reaction rates of slightly different starting materials can provide useful detailed information about the electronic or steric properties of those starting materials.

Electrophilic Aromatic Substitution (EAS) reactions have been well studied and the operating mechanism is well understood.

The electronic properties of the substituent on an aromatic ring will have a large impact on the rate of the addition of any subsequent substituent to that ring. An aromatic ring (Ar) with a strong electron donating group (EDG) will have a faster rate of reaction than the same aromatic ring with a moderate electron donating group. An aromatic ring with a moderate electronic donating group will have faster rates of reaction than the same aromatic ring having no substituents. An aromatic ring with no substituents will have a faster reaction rate than the same aromatic ring with a moderate electron withdrawing group (EWG).

RATES
Ar-Strong EDG > Ar-Moderate EDG > Ar-Weak EDG > Ar > Ar-Weak EWG > Ar-Moderate EWG > Ar-Strong EWG

The stronger the electron donating group, the faster the EAS reaction rate.

By comparing the relative rates of EAS reactions between differently substituted aromatic rings, the relative strength of the electron donating ability of those substituents may be determined. A comparison of the EAS reaction rates of 6 different substituted aromatics will be performed in this experiment. The electron donating ability of these substituents will be ranked based on this information.

From the information learned, projections about relative reaction rates of other substituent may be predicted.

The rates of most reactions are highly dependent on temperature according to the Arrhenius equation with reaction rates approximately doubling for each 10°C rise in temperature. An increase in 50°C will therefore decrease the reaction time by approximately 1/30th. A comparison of reaction rates at two temperatures will be made in this experiment.

PRE-EXPERIMENT ASSIGNMENT
Study the notes pages which accompany this lab. Review this topic from your lecture notes. Do the first parts of your notebook write-up.
A student who has prepared for the Electrophilic Aromatic Substitution experiment should be able to:

1. Define and explain the concepts of rate determining steps and limiting reagents.
2. Define and explain the concept of comparative reaction rates.
3. Be able to write structure given the name, or give the name if provided with the structure of all of the substituted organic materials.
4. Be able to explain the safety concerns of this experiment.
5. Perform the day’s experiment in a safe and competent manner.

After the experiment has been performed a student should be able to do the following.

6. Be able to predict relative rates of Electrophilic aromatic reaction given structures of molecules.
7. Explain relative rates of reactions.
8. Explain the procedure used to determine the rates of reaction.
10. Be able to explain why it was not necessary to calculate the absolute moles of all reagents used.
11. Explain why the time required for a reaction to proceed to completion was reduced when the reaction was run at an elevated temperature.
12. Explain what would happen if the procedure was altered such as changing the temperature of the water bath, increasing the amount of organic reagents used, increasing or decreasing the amount of bromine used.
13. Be able to draw the complete mechanism of the EAS reaction including using correct curved arrow notation and all intermediates and resonance structures.

Safety
Bromine is highly corrosive and causes severe burns. Wear gloves. Handle reagents with care. If any skin contact is made, rinse affected area immediately with running water and soap. Report any spills to the instructor.
90% Acetic Acid is a high concentrated acid. Be careful to not allow skin contact. Wash with soap and running water if contact is made.
All of the organic aromatic molecules possess toxic properties. Phenol is particularly toxic and may be absorbed by the body through skin. Handle with care. Keep away from mouth and eyes.

Comparison of Electrophilic Aromatic Substitution Reaction Rates.
Students will work with partners during this experiment. One student will be given the role as timekeeper during the reactions; the other student will manipulate the chemicals and be responsible for saying “start” and “stop”. The team may want to practice with a ‘dry run’ before combining chemicals. Practice with the stop watch. Be sure start, stop and reset is understood.
Obtain 6 clean test tubes of the same size. If dirty, clean with soap and water and a test tube brush. Rinse with DI. Label each test tube with the following Salicylic Acid, Anisole, Phenol, Toluene, Acetanilide, Phenyl acetate. Place the test tube in a test tube rack. Into each test tube place 1.5 mL of 0.20 M solution of the solution which corresponds to that test tube. Be very careful not to cross contaminate the pipettes or solutions. If you think you may have gotten the pipettes mixed up, then throw them away and get new ones. Pipettes with a line which corresponds to 1.5 mL are available. At this point there should be 6 test tubes with 1.5 mL of liquid in each.

Record the temperature of the room in notebook.

Work in a hood. Place one test tube in a small three prong clamp. To this test tube, quickly and all at once, add 1.5 mL of 0.050 M Bromine in Acetic Acid. (Do not slowly add this dropwise, add entire volume all at one. Do not spill.) Say “Start”. Shake the test tube with a back and forth motion until all of the brown color has disappeared. When the brown color of the solution disappears, say “Stop”. Note the stop point may be slightly complicated if the starting organic reagent is colored.

The time keeper student will hit the start/stop button on the stop watch when “Start” is called. The time keeper student will hit the start/stop button on the stop watch when “Stop” is called.

Record all data including observations and times in the notebook.

Repeat for the other 5 solutions.

Any reaction which is not complete after 10 minutes may be stopped. The reaction time in the notebook may be noted simply as “Greater than 10 minutes” or “>10min”.

Choose one reagent with a moderate reaction time and repeat the reaction two additional times. Compare all three times. How consistent are these three reaction times? What factors could have influenced differences in times?

Higher Temperature Comparison

Take the two slowest compounds from the room temperature series and measure their reaction times, using the same procedure, in a higher temperature hot water bath. Be sure to record the temperature of the water bath in notebook. Test these two materials side by side, until one material reacts. Be sure to record the temperature.

CLEAN-UP

Dispose of all brominated aromatic solution in the “Halogenated Liquid Organic Waste” container. Clean the test tubes with soap and a brush. Wipe up any extraneous messes. Wash hands with soap and water. Dispose of gloves in trash can.

POST-EXPERIMENT ASSIGNMENT
From your data determine the order of reactivity towards bromination. Make a simplified list of the substituents based on strength of electron donation (e.g. A>B>C). Complete provided datasheet.

References
