The Reaction of 4-Nitrotoluene with Chromic Acid

Prelaboratory Exercises:

Based on what you have learned in lecture about oxidations with chromic acid, predict some possible structures of the product of the above reaction.

Cautions:

Sodium dichromate, like other chromium compounds, is a suspected carcinogen. Handle these substances with great care. Use gloves when appropriate. Avoid breathing dust or vapors. Concentrated H₂SO₄ is very corrosive. Wear gloves when handling it.

TLC

You are required to run a TLC to monitor the progress of the reaction. Plates should have three spots (or lanes) on the origin: one for the main organic starting material that is being transformed, one for a cospot (starting material and the reaction mixture), and one for the reaction mixture.

Synthesis:

Place a 1/2-inch magnetic stirring bar in the 5-mL long-neck flask from your microscale kit and clamp it (use 3 prong microclamp) over the magnetic stirrer. Using the small plastic funnel from this kit, add 390 mg of sodium dichromate dihydrate (Na₂Cr₂O₇·2H₂O) and 1 mL water and stir until the sodium dichromate dissolves. In the solution, suspend 137 mg of p-nitrotoluene (m.p. 52-54°C). Drop-wise, add 1.0 g of concentrated sulfuric acid (H₂SO₄ density = 1.84 g/mL) over a period of 15 minutes. A slow enough rate of addition will assure that the reaction doesn’t become so exothermic that it boils out the top of the flask. Then a sand bath is placed under the flask and heating and stirring continued for 45 minutes at a gentle boil so that the vapors reflux and don’t come out the top of the flask. (What is the approximate temperature of the refluxing liquid?) Your solution should turn a dark green color.

Isolation and Purification:

While cooling the reaction in a small beaker of ice water, 3 to 6 small chips of ice are dropped into the reaction mixture, and the reaction is cooled and stirred for 15 to 30 minutes. Filter off the solid product on a Hirsch funnel with a 1.3-cm filter paper disc placed in it. Wash out any solid adhering to the flask walls by adding about 1 mL of cold water to it, swirling rapidly and quickly pouring into the filter funnel. Alternatively, one could wash the product down the sides of the flask using a Pasteur pipet filled with cold water, and withdrawing the solid suspended in water with the same pipet. If dark brown chromate salts remain on the solid, wash with 10 to 20 drops of 1M sulfuric acid.

Dissolve the solid in 1 mL of 1M sodium hydroxide (NaOH) in a small flask containing a stir bar. Heat if needed to dissolve all of the solid. Take a spatula tip full of Celite and place it in a small beaker. Then carefully dampen it with a few drops of water from a Pasteur pipet and transfer the moist clump onto the Hirsch funnel frit. Make sure that none of the Celite runs through the filter into the flask. Then
suction filter this solution through a Hirsch funnel containing a 1/8-inch-deep bed of wetted Celite filter aid. Rinse the flask and filter with a few drops of water. Cool the filtrate on ice, while at the same time chilling 1 mL of 1M sulfuric acid in a small beaker or 20 mL vial. When both solutions have been completely chilled, slowly and carefully add the filtrate dropwise with a Pasteur pipet to the chilled sulfuric acid. After the addition is complete, check that the solution is acidic by testing with pH paper and, if it is not, add a few drops of 1M sulfuric acid until it is. The precipitate is collected by suction filtration using the Hirsch funnel, and the crystals are washed dropwise with cold water. Dry the product by leaving it in an open container until the next period. Weigh the amount of crude product; set aside a small amount for a melting point. If the crystals are brownish and the m.p. is less than 236°C, recrystallize the product from ethanol. Determine the yield and m.p. of both the crude and purified products. Analyze the product using the method given in your Experiment Assignment sheet.

Cleaning Up:
Add saturated sodium bisulfite to the aqueous filtrate from the initial reaction so that all the orange or brownish dichromate ion is reduced to the greenish chromic ion. This may then be flushed down the drain with lots of water (it is equivalent to 21 mg of chromium) or placed in the heavy metals waste container. The remaining aqueous or ethanol/water filtrates can also be flushed down the drain.

Analysis
In addition to TLC analysis, you may be instructed to analyze your final product by IR. Analyze your sample according to your assignment sheet and the instructions on Sample Preparation in the Lab Guide.

Product Determination - Final Report:
There are four conceivable products as shown below:

![Images of four products]

On the basis of your spectral analysis, give the structure of the product in your Results and Discussion section. On the spectrum, draw the correct structure and point out the spectral features that led you to choose that structure.

Postlab Questions:
1. What features of an IR spectrum would be different for the three structures that you ruled out as possible structures for the final product? What evidence is there that the functional groups present are para-substituted? (See the IR section of Ch. 11 of the Lab Guide)
2. Write equations for the reaction of your product with NaOH and for the subsequent reaction with H₂SO₄. Explain why the solubility of the organic species changes with pH.
3. Why are the carbons of the aromatic ring not oxidized by Cr(VI) salts?
4. What is the oxidation state of Cr after it oxidizes the reactant? What is the visual cue that something has been oxidized?