THE NITRATION OF BROMOBENZENE

Introduction

An example of an electrophilic substitution is the nitration of aromatic compounds. Thus, benzene reacts with nitric acid to give nitrobenzene. The reactive species in this reaction is the nitronium cation, NO_2^{+1}, (the nitryl cation), which is present in low concentration in nitric acid, HNO_3 …

$$HNO_3 + H_2SO_4 \longrightarrow NO_2^{+1} + H_3O^{+1} + 2\ HSO_4^{-1}$$

Mechanism

The nitric acid accepts a proton from the stronger H_2SO_4

Dissociation occurs to form the nitronium ion…

The nitronium cation is a very strong electrophile and attacks an electron pair available in the π-electron cloud of the aromatic ring. An unstable σ-intermediate, (the Wheland intermediate) is first formed, which undergoes rapid loss of a hydrogen ion (a proton), on one of the ortho carbons to regenerate the aromatic ring, (which retains the stable delocalised ring system), and give the nitrated product…

The mononitro compound formed can, in principle, be attacked a second time by excess NO_2^{+1} ion to give the meta dinitrobenzene, and at much higher temperatures a third time to form 1,3,5,- trinitrobenzenes…

Fortunately, these subsequent substitutions are much slower than the first one (***why?***) and can be suppressed sufficiently by proper choice of reaction conditions: concentration of reagents, and temperature control. If some side-product is formed, it can usually be separated from the main product by physical means such as distillation or recrystallization.

Since both benzene and nitrobenzene are quite toxic, we prefer to study the nitration of less hazardous bromobenzene.
Bromobenzene and its products of nitration may, nevertheless, cause some irritation. Avoid inhaling the vapours and avoid direct contact with the skin. If any liquid is spilled upon the skin, wash immediately with copious amounts of water.

In the case of bromobenzene, mononitration can lead to three positional isomers:
1-bromo-4-nitrobenzene (p-bromonitrobenzene)
1-bromo-2-nitrobenzene (o-bromonitrobenzene)
1-bromo-3-nitrobenzene (m-bromonitrobenzene)

Due to the directive effect of the bromo substituent, the first two of these isomers are formed preferentially, arising in a ratio of about 7:3, whereas the meta isomer is formed in negligible proportion (1%) due to the directive effect of the Br. The ortho-, para- direction can be explained by the conjugation effect : the lone pairs of bromine will stabilize the ortho- and para- intermediates.

In our experiment, use is made of a low solubility of the para- isomer in cold ethanol, to separate it from the ortho- isomer.

Materials
Conc. HNO_3, conc H_2SO_4, ice bath, crushed ice, ethanol (for recrystallization, b.p. 78°C), bromobenzene (mp -31°C, bp 156°C, specific gravity 1.491, molar mass 148 g mol^{-1})

Procedure

1. Cautiously mix 5 cm^3 of conc. HNO_3 with 5 cm^3 of conc. H_2SO_4, in a 50 cm^3 Erlenmeyer flask, with external cooling using the ice bath.
   The mixture with sulphuric acid is extremely corrosive and destroys organic matter (skin, clothes) rapidly. If a spill occurs, flush at once with copious amounts of water.
2. When the mixture has cooled to room temperature, add drop by drop 2.0g of bromobenzene (specific gravity = 1.491; therefore, this corresponds to 1.8 cm^3). Shake well after each drop is added. Place a thermometer in the flask to monitor the temperature.
   Since the two reacting liquids are mutually almost insoluble they react only where their surfaces are in touch. Shaking increases the surface areas and, consequently, the reaction velocity.
   Should the flask become warm, immerse it briefly in an ice-water bath until the contents are cooled to slightly above room temperature before adding more of the bromobenzene. **The reaction proceeds best at 30-35°C**.
3. When all the bromobenzene has been added, allow the flask to stand at room temperature for 10 minutes, with occasional swirling, to complete the reaction.

Isolation of the Product

1. Pour the reaction mixture onto 25 g of crushed ice contained in a beaker, stir until the ice has melted, and collect the solid product by suction filtration using a Buchner funnel.
2. Wash the precipitate with cold water on the funnel and press off excessive water.

Purification of the Product

1. Recrystallise the remaining product from ethanol.
   For this purpose, dissolve it in boiling ethanol (bp 78°C) in an Erlenmeyer flask on the steam bath. Start with a small amount of ethanol and gradually add more until all of the crystals have dissolved.
   Then dilute further with ethanol so that the final volume is increased by ~ 20%

2. Allow the product, p- bromonitrobenzene, to crystallise by cooling the solution in an ice bath.
3. Filter with suction and wash the product with a small amount of chilled ethanol. Suck dry.
4. Mass the p- bromonitrobenzene obtained to determine the % yield.

Note: Poor yield may be due to incomplete separation of the para- from the ortho- isomer during the recrystalliztion step, insufficient ethanol was added to dissolve the ortho product completely.

Questions

1. Calculate the % yield of p- bromonitrobenzene obtained in your experiment.
2. Draw and name the three isomers of bromonitrobenzene. Which of the three would have the highest dipole moment? Explain why.
3. In the nitration of benzene, a second nitro group is introduced much more slowly than the first one. Why?
4. What is the preferred position of the nitration in:

a) benzaldehyde b) benzoic acid c) toluene d) aniline
e) acetophenone

5. In a reaction using 39.0 g benzene (molar mass = 78 g mol^{-1}) and 75.0 cm^3 of 16 mol dm^{-3} concentrated HNO_3 and 75.0 cm^3 H_2SO_4, 40.0 g of nitrobenzene (molar mass = 123 g mol^{-1}) was obtained.

a) Determine the limiting reagent.
b) Calculate the % yield of nitrobenzene.
c) If the reaction was carried out a much higher temperature, give the name and the formula of the expected product.
d) Explain in a few words, by means of an equation, the purpose of the H_2SO_4 in the reaction.