Benzoic acid (n°23)

1. INTRODUCTION

1.1) Purpose

The objective of this experiment is to synthesize the benzoic acid by oxidizing the ethylbenzene.

1.2) Scheme

![Reaction Scheme]

1.3) Mechanism [3]

The exact mechanism of this reaction is still unknown, although it is supposed to be a radical reaction. What is known is that when refluxing a solution of any alkylbenzene with KMnO₄ and afterwards acidifying it, the product will always be benzoic acid and MnO₂.

2. PROCEDURE

2.1) Reaction

<table>
<thead>
<tr>
<th>Reagents</th>
<th>molar mass [g/mol]</th>
<th>wt/vol taken</th>
<th>n [mmol]</th>
<th>equivalence</th>
</tr>
</thead>
<tbody>
<tr>
<td>KMnO₄</td>
<td>158.03</td>
<td>10g</td>
<td>63.3</td>
<td>2.24</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>106.16 (d=0.867)</td>
<td>3.5mL</td>
<td>28.3</td>
<td>1</td>
</tr>
</tbody>
</table>
In a 250mL bottom flask, a solution of 5g of Na$_2$CO$_3$ and 10g of MnO$_4$ in 100mL of water was made. This flask was then equipped with a magnetic agitator and a condenser and 3.5mL of ethylbenzene were added. The solution was refluxed for 90min and then acidified with concentrated HCl in order to protonate the acid and about 6g of Na$_2$SO$_3$ were then added to dissolve the MnO$_2$ deposit. The mixture was then cooled down with an ice bath to complete the benzoic acid crystallization and the product was collected by filtration.

2.2) Isolation

The final product was obtained by recrystallization of the benzoic acid in water. Some of the product was recollected from the mother liquor using the rotary evaporator (not in the yield).

3. DISCUSSION AND RESULTS

3.1) Observations

The solution was initially violet due to the KMnO$_4$, but after being refluxed for enough time, it turned to brown due to the formation of the solid precipitate MnO$_2$.

The addition of HCl was very exothermic and violent, so it had to be done very slowly not to make an explosion of the solution on the table.

When respecting the protocol, the experiment doesn’t work because the crystallization cannot be made properly in the 150mL of initial water.

3.2) Yield

<table>
<thead>
<tr>
<th>molar mass [g/mol]</th>
<th>$n$ [mmol]</th>
<th>$n_{exp}$ [mmol]</th>
<th>yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>122.12</td>
<td>28.3</td>
<td>4.2</td>
<td>15%</td>
</tr>
</tbody>
</table>

0.5113g of pure product were obtained at the end of the crystallization. The yield is very low and could be due to the amount of water used at the beginning. It is still two times bigger than the yield (0.2488g; 7%) obtained when applying the original protocol (150mL H$_2$O).
4. SPECTROMETRY DATA

4.1) NMR \(^1\)H (CDCl\(_3\), 400MHz)

\[
\begin{align*}
\text{bond} & \quad \text{shift } \delta \text{ [ppm]} & \quad \text{multiplicity} & \quad \text{hydrogen} \\
\text{O-H} & \quad 11-13.2 & \quad \text{singlet} & \quad \text{Carboxyl } H_1 \\
\text{C-H} & \quad 7.48-7.66 & \quad \text{multiplet} & \quad \text{benzene } H_3, H_4 \\
\text{C-H} & \quad 8.13-8.815 & \quad \text{multiplet} & \quad \text{benzene } H_2
\end{align*}
\]

The two hydrogens ortho have the biggest shift value (since they are more deshielded by the carboxyl group).

The hydrogen from the carboxyl group (H\(_1\)) is mobile (the acid can be deprotonated), therefore the relaxation is very fast and the peak corresponding to its shift is broad. It should be at 12.7 ppm, but in this spectrum it is almost undistinguishable.

4.2) IR (neat, cm\(^{-1}\))

2831; 2675; 2549; 1685; 1582; 1454; 1420; 1323; 1290; 1179; 1127; 1074; 935-916; 707; 520.

The IR specter shows that the substance, which is analyzed, is the product.

There are peaks for the specific groups corresponding to the product. For example, the peak corresponding to the C=O stretch of the carboxyl group is found at 1685, the value given by the protocol is 1675. This difference might come from the delocalization of the double bond, which overcomes in the molecule. In the IR table, the value given for carboxylic aryl acids is 1700-1680.

There is also a big peak corresponding to the C-O stretch of the carboxylic acid at 1290 (IR table: 1320-1210).

5. REFERENCES

6. QUESTIONS

1) The oxidation of an aromatic compound is always made on the nearest carbon to the aromatic core. Explain this.

The positive charge can be delocalized around the cycle into resonance forms, when it is near the core, which stabilizes the compound:

![Resonance structures for aromatic oxidation](https://via.placeholder.com/150)

2) Compare the acidity of benzoic, acetic and oxalic acids. [4]

So, oxalic acid has a bigger acidity than benzoic acid, which, in its turn, is more acid than the acetic one. Oxalic acid is polyprotic, so it is not surprising that its first Ka is the biggest. Benzoic acid, due to its aromatic ring has a stabilized deprotonated state, so its Ka is at least bigger than acetic’s one.

7. ANNEXES

IR spectrum, NMR spectrum