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One-Pot Green Catalytic Preparation of 3-Aminobenzoic Acid in the Presence of Carbonaceous Bio-Based Materials in Subcritical Water †

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Abstract: A green and sustainable approach for the production of 3-aminobenzoic acid (3-ABA) from 3-nitrobenzaldehyde promoted by NORIT GAC 12-40 as carbonaceous bio-based material was successfully achieved in subcritical water. The process involves two successive reactions: reduction of the nitro group and oxidation of the formyl group. At 300 °C under 90 bar for 6 h, the yield of 3-ABA is 59%.

Keywords: aromatic amine; nitroarene; subcritical water; metal-free reduction

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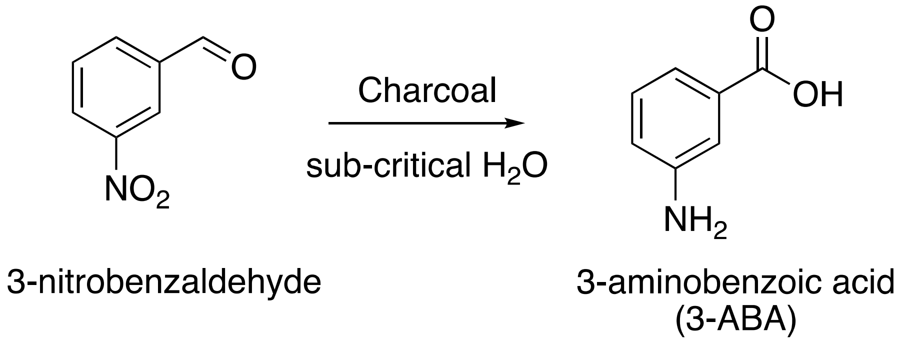
1. Introduction

Functionalized aminoarenes are important intermediates in industry as fine chemicals (pharmaceuticals, dyes and pigments, agrochemicals) and as bulk chemicals (polymers). Among all the processes for the production of aromatic amine, hydrogenation of the corresponding nitro derivatives is mainly applied [1–3]. Whatever the process used: (i) non-catalytic reaction with stoichiometric amount of reducing agents [4] or (ii) catalytic hydrogenation using noble metals or non-noble metals [5], reduction of nitroarenes is not a sustainable process as large amounts of toxic waste are created, harsch conditions and expensive hydride sources are used. Among the different functionalized aminoarenes, 3-aminobenzoic acid (3-ABA) having an amino group and a carboxylic acid group is an interesting industrial chemical [6–8].

In order to limit the use of expensive, toxic and hazardeous reagents, new "one-pot" oxydo-reduction process of 3-nitrobenzaldehyde catalyzed by carbonaceous bio-based materials in subcritical water without added metal and H_2 has been developed for the production of 3-ABA.



Scheme 1. Synthesis of 3-ABA starting from 3-nitrobenzaldehyde in the presence of commercial charcoal in sub-critical water.

2. Experimental

2.1. Reagents

Substrates and solvents were purchased from Acros (3-nitrobenzaldehyde, 3-aminobenzoic acid, ethylacetate, methanol, ethanol, propan-1-ol, butan-1-ol and pentan-1-ol). All materials were used without further purification. The water used in all experiments had a Millipore Milli-Q grade. Charcoals were purchased from Acros (NORIT GAC 12-40, NORIT SA2, NORIT A SUPRA) and DACARB (DACARB PC 1000).

2.2. Synthesis of 3-Aminobenzoic Acid in the Presence of NORIT GAC 12-40 in Sub-Critical Water

In a typical experiment, a batch reactor (100 mL) charged with water (55 mL), nitrobenzene (1.23 g, 30 mmol), NORIT GAC 12–40 (6 g). Autoclave was sealed, placed in the heating collar and heated at 300 °C and 90 bar for 2 h. Temperature in the autoclave was measured by probe. At the end of the reaction, autoclave was cooled down to 40 °C. The aqueous phase was diluted with ethyl acetate (100 mL) under magnetic stirring (500 rpm). The organic phase was filtered prior to analysis through a syringe filter (PTFE, 0.45 μm, VWR). All experiments were repeated at least three times, and the deviation was lower than 5%.

2.3. Gas Chromatography Analysis

Gas chromatography analyses are performed on a PerkinElmer gas chromatography (Autosystem XL GC), using an Altech AT HT column, with a detector at 300 °C, an injector at 340 °C, and a constant flow of nitrogen of 1 mL min^{-1}. The column is heated at 150 °C for 2 min, and then warmed to 350 °C with a temperature gradient of 15 °C min^{-1} before being hold at that temperature for 4.67 min. Each sample of the reaction mixture was analyzed separately. 3-Nitrobenzaldehyde conversion (X) (Equation (1)) and 3-ABA yield (Yi) (Equation (2)) were calculated using standard equations.

$$X = \frac{(Initial\ 3{-}nitrobenzaldehyde\ amount\ (mol){-}Final\ 3{-}ABA\ amount\ (mol))}{Initial\ 3{-}nitrobenzaldehyde\ amount\ (mol)}\ x\ 100, \quad (1)$$

$$Yi = \frac{Final\ 3{-}ABA\ amount\ (mol)}{Initial\ 3{-}nitrobenzaldehyde\ amount\ (mol)}\ x\ 100, \quad (2)$$

3. Results and Discussion

Initial studies were performed for 3-nitrobenzaldehyde conversion (10 mmol) using NORIT GAC 12–40 (3–10 g) in water (55 mL) at 310 °C under 90 bar for 6 h as the model reaction (Table 1, entries 1–4). In the presence of NORIT GAC 12–40, the best yield of 3-ABA (33%) was obtained with a mass of activated carbon equal to 6 g. A decrease of NORIT GAC 12–40 (3 g) gave similar yield (30%) while an increase afforded the target amine in lower yield. This phenomenon can be explained by the formation of aggregates leading to a reduction in the contact surface between the aromatic compound and the carbon. In order to vary the nature of the material, other commercial charcoals: NORIT SA2, NORIT A supra and DACARB PC 1000 were tested in the same conditions (Table 1, entries 5–7). Contrary to our expectations, DACARB PC 1000 leads to a low efficiency (1%). This result is surprising because DACARB PC 1000 allowed the reduction of nitrobenzene to the corresponding aniline with a 100% efficiency under similar conditions [9]. This low yield in the presence of DACARB PC 1000 can be linked to its intrinsic properties (high adsorption capacity, large specific surface area and large mesoporous volume) which gives it a low capacity to desorb organic molecules. In our hands, the best performance was obtained with NORIT GAC 12–40 as activated carbon.

Table 1. Effect of charcoal nature and loading on transformation of 3-nitrobenzaldehyde to 3-ABA (GC analysis).[1]

Entry	Material	Material (g)	Yield (%)
1	NORIT GAC 12-40	3	30
2	NORIT GAC 12-40	6	33
3	NORIT GAC 12-40	8	15
4	NORIT GAC 12-40	10	20
5	DACARB PC 1000	6	1
6	NORIT A supra	6	23
7	NORIT SA2	6	20

[1] Reaction conditions: 3-nitrobenzaldehyde (10 mmol), charcoal (3–10 g), water (55 mL), 310 °C, 90 bar, 6 h.

Using NORIT GAC 12–40, variations of the nature of the solvent, concentration of starting nitroarene and material, temperature, reaction time were studied. The nature of the solvent and the concentration of the reagents have a remarkable influence in reaction yields especially near the critical point. In this regard, variation of the volume of water (35–65 mL) was studied at 310 °C for 6 h in the presence of NORIT GAC 12–40 (6 g) (Table 2, entries 1–4). The higher yield of 3-ABA was obtained starting from 3-nitrobenzaldehyde (10 mmol) in water (55 mL). Other green solvents such as such as methanol, ethanol, propan-1-ol, butan-1-ol and pentan-1-ol were tested but 3-ABA has never been observed; this oxo-reduction is specific and only water allows this synthesis. Using the nitro derivative (10 mmol) in the presence of NORIT GAC 12–40 (6 g) and water (55 mL), temperature of the reaction was optimized for the reduction of 3-nitrobenzaldehyde (Table 2, entries 3 and 5–8). Yield of 3-ABA increases with temperature to an optimum at 300 °C and then decreases at higher temperature. A temperature of 300 °C was therefore chosen for the rest of the optimization.

The effects of the substrate loading (5–30 mmol) were studied to optimize the preparation of 3-ABA from 3-nitrobenzaldehyde at 300 °C for 6 h (Table 2, entries 7 and 9–11). The highest yield of 3-ABA obtained is 59% for a 3-nitrobenzaldehyde amount of 10 mmol. The objective being to have a higher productivity, the loading of 30 mmol (Table 2, entry 11) was chosen to continue the study. Kinetics studies of the reaction were aimed to optimize reaction times for the reduction of 3-nitrobenzaldehyde (Table 2, entries 11–14). The maximum yield of 30% is obtained for 2, 4 or 6 h of reaction. For reasons of energy savings, the duration of the reaction of 2 h was chosen.

Table 2. Parameters variation for the transformation of 3-nitrobenzaldehyde to 3-ABA (GC analysis).[1]

Entry	3-Nitrobenzaldehyde (mmol)	Water (mL)	Temperature (°C)	Time (min)	Yield (%)
1	10	35	310	6	15
2	10	45	310	6	16
3	10	55	310	6	33
4	10	65	310	6	26
5	10	55	250	6	12
6	10	55	270	6	36
7	10	55	300	6	59
8	10	55	320	6	21
9	5	55	300	6	20
10	20	55	300	6	22
11	30	55	300	6	30
12	30	55	300	2	30
13	30	55	300	4	30
14	30	55	300	8	25

[1] Reaction conditions: 3-nitrobenzaldehyde (5–30 mmol), NORIT GAC 12–40 (6 g), water (35–65 mL), 250–310 °C, 90 bar, 2–8 h.

4. Conclusion

A simple and ecological process for the direct production of 3-ABA starting from 3-nitrobenzaldehyde in a "one pot" reaction has been optimized (3-nitrobenzaldehyde (30 mmol), NORIT GAC 12–40 (6 g), water (55 mL), 300 °C, 90 bar, 2 h). Our metal-free and solvent-free process in the presence of carbonaceous material in sub-critical water gave 3-ABA in 59% yield starting from 10 mmol of 3-nitrobenzaldehyde. Nevertheless, a higher productivity is obtained starting with 30 mmol even if the yield was lower. The study of the mechanism pathway with a successive reduction of nitro group and oxidation of formyl group is under way and will be published shortly.

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