

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

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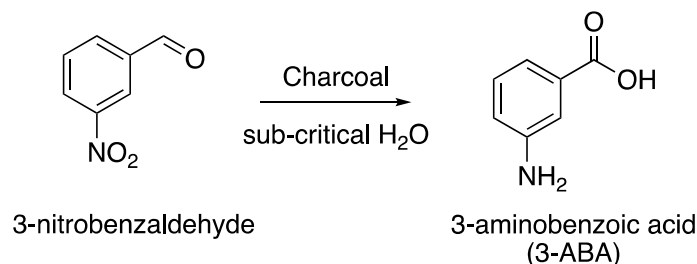
**Abstract:** A green and sustainable approach for the production of 3-aminobenzoic acid (3-ABA) from 3-nitrobenzaldehyde promoted by NORIT GAC 12-40 as a carbonaceous bio-based material was successfully achieved in subcritical water. The process involves two successive reactions: reduction of the nitro 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

## 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, and harsh conditions and expensive hydride sources are used. Among the different functionalized aminoarenes, 3-aminobenzoic acid (3-ABA), with 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 hazardous reagents, a new “one-pot” oxo-reduction process of 3-nitrobenzaldehyde catalyzed by carbonaceous bio-based materials in subcritical water without added metal and H<sub>2</sub> has been developed for the production of 3-ABA (Scheme 1).



**Scheme 1.** Synthesis of 3-aminobenzoic acid (3-ABA) starting from 3-nitrobenzaldehyde in the presence of commercial charcoal in subcritical water.

## 2. Experimental

### 2.1. Reagents

Substrates and solvents were purchased from Acros (3-nitrobenzaldehyde, 3-aminobenzoic acid, ethyl acetate, 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 was of 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 Subcritical Water

In a typical experiment, a batch reactor (100 mL) was charged with water (55 mL), nitrobenzene (1.23 g, 30 mmol), NORIT GAC 12-40 (6 g). The autoclave was sealed, placed in the heating collar and heated at 300 °C and 90 bar for 2 h. The temperature in the autoclave was measured by a probe. At the end of the reaction, the 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 (PolyTetraFluoroEthylene (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 were performed on a PerkinElmer gas chromatograph (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<sup>-1</sup>. The column was heated at 150 °C for 2 min, and then warmed to 350 °C with a temperature gradient of 15 °C min<sup>-1</sup> before being held at that temperature for 4.67 min. Each sample of the reaction mixture was analyzed separately. The 3-nitrobenzaldehyde conversion ( $X$ ) (Equation (1)) and 3-ABA yield ( $Y_i$ ) (Equation (2)) were calculated using standard equations.

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

$$Y_i = \frac{\text{Final 3-ABA amount (mol)}}{\text{Initial 3-nitrobenzaldehyde amount (mol)}} \times 100 \quad (2)$$

## 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 a 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 led to a low efficiency (1%). This result is surprising because DACARB PC 1000 allowed the reduction of nitrobenzene to the corresponding aniline with 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 study, 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 (gas chromatography analysis)<sup>1</sup>.

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

<sup>1</sup> 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 on 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 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), the temperature of the reaction was optimized for the reduction of 3-nitrobenzaldehyde (Table 2, entries 3 and 5–8). The yield of 3-ABA increases with temperature to an optimum of 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 was 59% for a 3-nitrobenzaldehyde amount of 10 mmol. As the objective was to obtain a higher productivity, the loading of 30 mmol (Table 2, entry 11) was chosen to continue the study. Kinetic studies of the reaction were aimed to optimize the reaction times for the reduction of 3-nitrobenzaldehyde (Table 2, entries 11–14). The maximum yield of 30% was obtained for 2, 4 or 6 h of reaction. For reasons of energy saving, the duration of the reaction of 2 h was chosen.

**Table 2.** Variation of parameters for the transformation of 3-nitrobenzaldehyde to 3-ABA (GC analysis)<sup>1</sup>.

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

<sup>1</sup> 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. Conclusions

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 subcritical water obtained 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. A study of the mechanism pathway with a successive reduction of the nitro group and oxidation of formyl group is underway and will be published shortly.

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