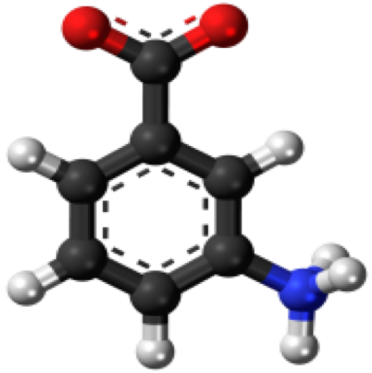
1 st International Electronic Conference on Catalysis Sciences

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

Sarra Tadrent, Christophe Len



Introduction

- 3-aminobenzoic acid is widely considered as promising platform chemicals for the production of dyes, antioxidants, pharmaceuticals and agricultural chemicals.

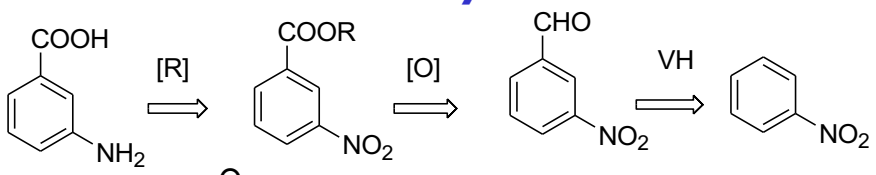
Dyes

Pharmaceuticals

Agricultural chemicals

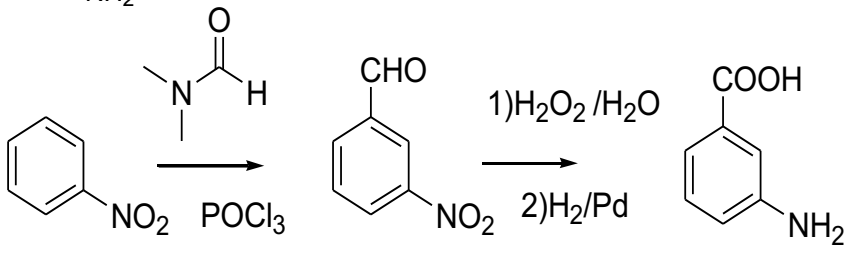
Preparation of 3-aminobenzoic acid from 3-nitrobenzaldehyde

Retrosynthetic scheme:

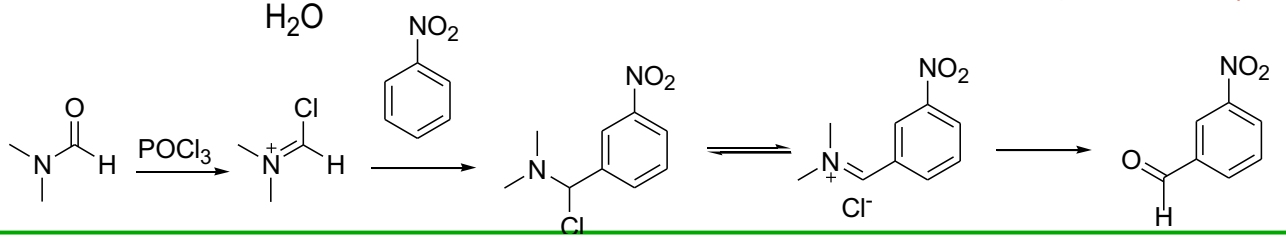


- Three steps
- Metal catalysts
- Organic solvent
- …

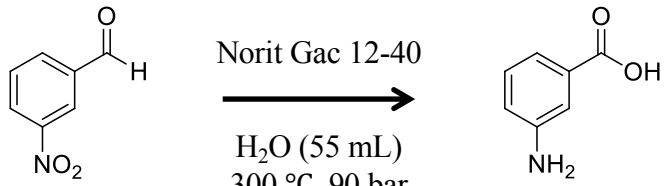
Synthesis diagram:



Vilsmeier-Haak reaction (VH):

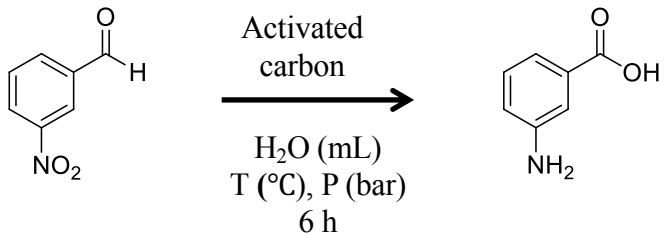


New process :



- One-pot
- Charcoal
- Water

Process optimization



1) Carbonaceous materials loading

NORIT GAC 12-40 (g)	Yield (%)
3	30
6	33
8	15
10	20

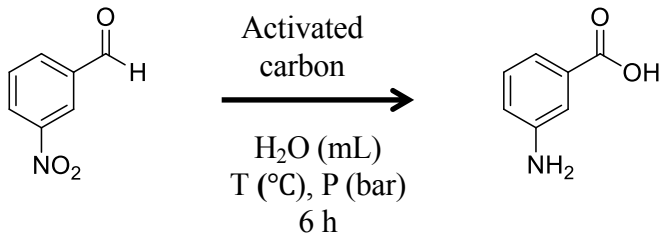
3-nitrobenzaldehyde (10 mmol), NORIT GAC 12-40 (3-10 g), water (55 mL), 310 ° C, 90 bar, 6 hours.

2) Nature of the carbonaceous materials

Type of activated carbon	Yield (%)
NORIT GAC 12-40	33
DACARB PC 1000	1
NORIT A supra	23
NORIT SA2	20

3-nitrobenzaldehyde (10 mmol), charcoal (6 g), water (55 mL), 310 ° C, 90 bar, 6 hours.

Process optimization



3) Water volumes loading

Water volume	Yield (%)
35	15
45	16
55	33
65	26

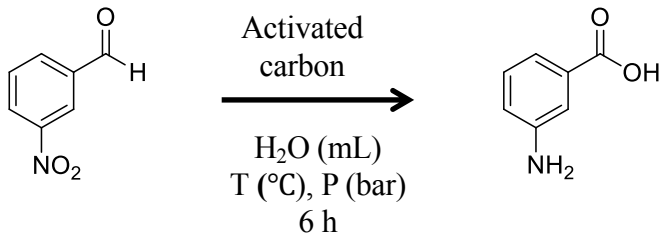
3-nitrobenzaldehyde (10 mmol), NORIT GAC 12-40 (6 g), water (35-65 mL), 310 ° C, 90 bar, 6 hours.

4) Reaction temperature

T (° C)	Yield (%)
250	12
270	36
300	59
310	33
320	21

3-nitrobenzaldehyde (10 mmol), NORIT GAC 12-40 (6 g), water (55 mL), 250-320 ° C, 90 bar, 6 hours.

Process optimization



5) Substrate loading

n (mmol)	Yield (%)
5	20
10	59
20	22
30	30

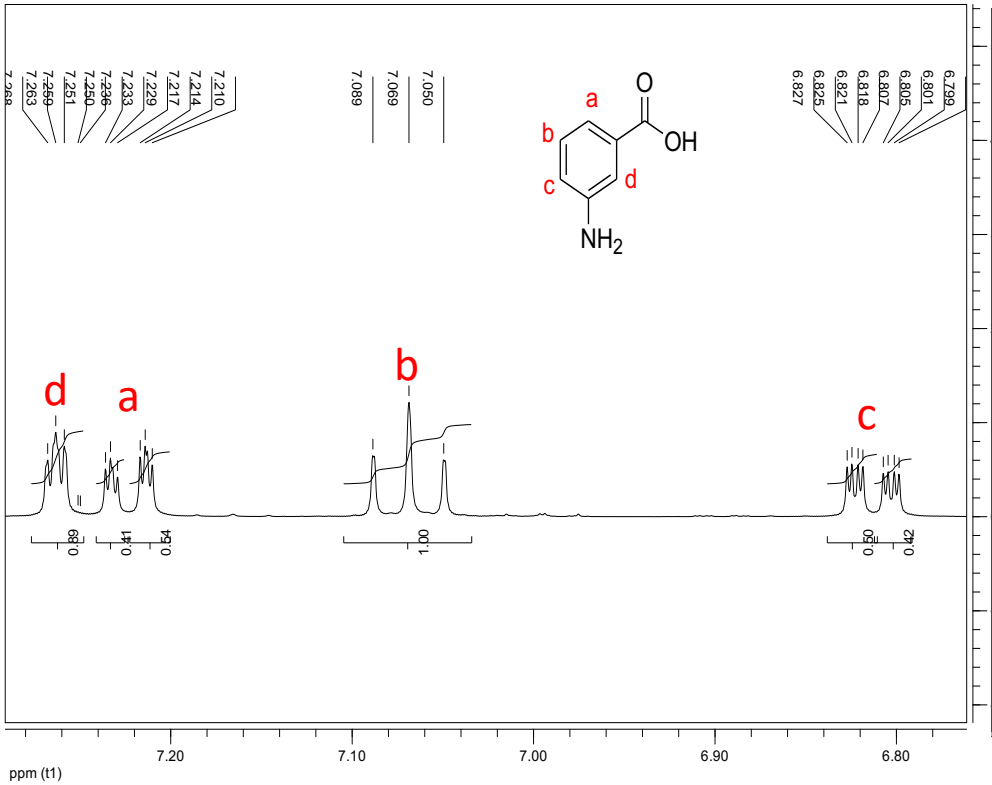
3-nitrobenzaldehyde (5-30 mmol), NORIT GAC 12-40 (6 g), water (55 mL), 300 ° C, 90 bar, 6 hours.

6) Reaction time

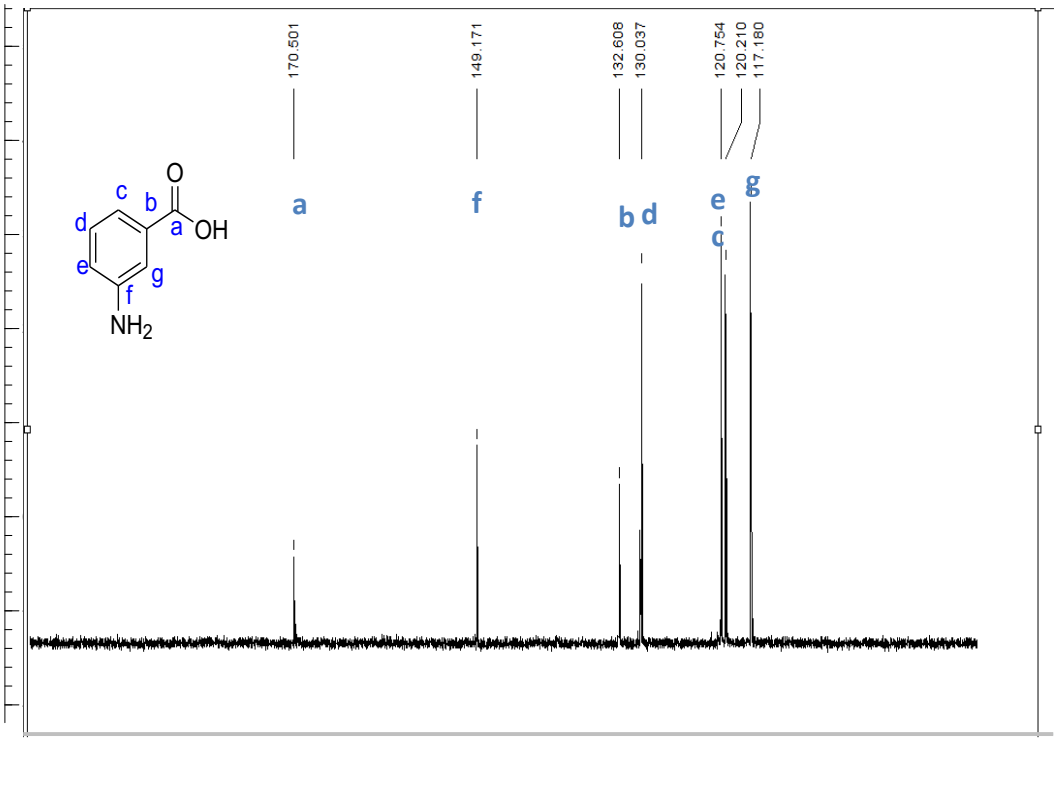
Time (h)	Yield (%)
2	30
4	30
6	30
8	25

3-nitrobenzaldehyde (10 mmol), NORIT GAC 12-40 (6 g), water (55 mL), 300 ° C, 90 bar, 2-8 hours.

NMR analyzes of the finished product

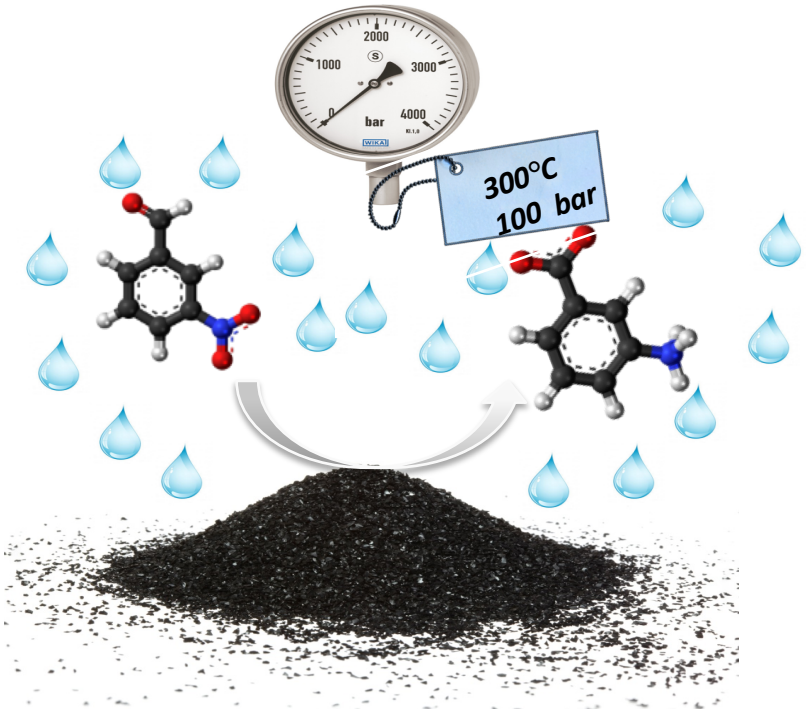


^{1}H NMR experimental spectrum 3-aminobenzoic acid

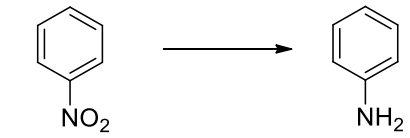


^{13}C NMR experimental spectrum 3-aminobenzoic acid

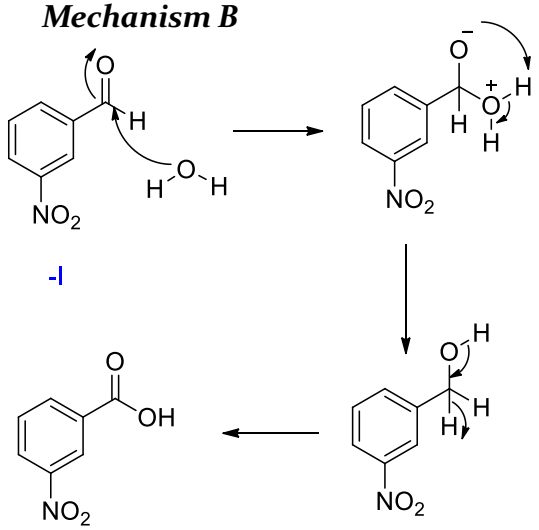
Proposed mechanism for the preparation of 3-aminobenzoic acid



Mechanism A



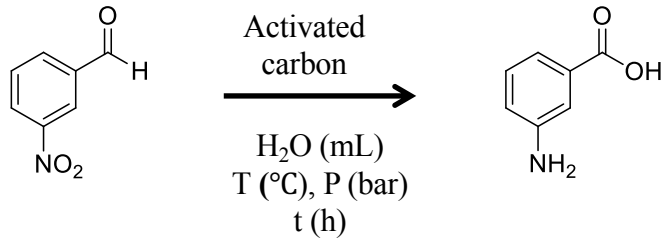
Mechanism B



Activated carbon

Conclusion

- A simple and ecological process of preparation of 3-aminobenzoic acid (3-ABA) based on the redox of 3-nitrobenzaldehyde in a single step called “one pot” has been optimized.



- **The best yield obtained is**: 59%

- **Reaction conditions**:
  - substrate loading (10 mmol)
  - Temperature (300° C)
  - pressure (90 bar)
  - water (55 mL),
  - Norit Gac 12-40 (6 g)
  - Reaction time (6 h)

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