



## Short Communication

# Swift and efficient sono-hydrolysis of nitriles to carboxylic acids under basic condition: Role of the oxide anion radical in the hydrolysis mechanism

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## ABSTRACT

Carboxylic acids are promising candidates for new sustainable strategies in organic synthesis. In this paper, we ascertain the potential of ultrasound for the hydrolysis of nitriles into carboxylic acids through the study of key parameters of the reaction: pH, hydrolysis medium, reaction time and activation technique. The positive influence of ultrasound under basic conditions is due to more than mechanical effects of cavitation. Indeed, the rate of hydrolysis is dramatically increased under sonication in NaOH solutions. A radical mechanism involving the oxide anion radical  $O^{\cdot-}$  is proposed.

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## 1. Introduction

Hydrolysis of nitriles enables the synthesis of amides and carboxylic acids such as aminoacids, acrylamide or adipic acid [1]. Carboxylic acids are promising compounds for sustainable synthesis [2]. Because of their low reactivity, the transformation of starting materials usually requires harsh conditions, such as a strong acidic [3] or basic media [4], leading to the amide intermediate that is generally quickly hydrolysed as described in Fig. 1.

Moreover, these products are rarely stable under these conditions of pH and sustainable development requires softer conditions. Thus, some alternatives have been proposed including enzymatic biocatalysis [5] and heterogeneous organometallic catalysis [6].

Sonochemistry is an alternative to replace these catalysts. Indeed, ultrasound is sometimes considered as a sort of physical catalyst that produces specific physical and chemical effects [7]. Actually, it is known to enhance some processes through a physical phenomenon called cavitation, which is the formation, growth and collapse of bubbles in an elastic liquid [8]. By imploding, these bubbles create locally high pressure (up to 1000 bars) and temperature (up to 5000 K) [9] that lead to high-energy radical mechanisms [10] and also generate some interesting physical effects, such as

micro-mixing, mass transport or reduction of particles size [11]. There exists a growing list of organic reactions which take advantage of this phenomenon, as for example, thiocyanation of aromatic compounds [12], halogenation of alcohol [13] or benzoin condensation [14]. Because of the very harsh environment that is produced upon cavitation in solution, sonochemistry is commonly associated with radical chemistry as it has been observed, for instance, for hydroxystannation of alkenes [15].

In the present paper, we have studied the effect of ultrasound on the hydrolysis of nitriles under both basic and acidic conditions.

## 2. Experimental

### 2.1. Reagent, apparatus and analysis

All reagents, purchased from Aldrich, are of analytical grade and used without further purification.

Concentrated hydrochloric acid and sodium hydroxide (Acros organics) were used to adjust the pH of the solutions.

An ultrasonic horn operating at a frequency of 30 kHz was used for the sonochemical experiments. Its acoustic power of  $1.9 \text{ W mL}^{-1}$  was determined by calorimetry using a procedure described in the literature [16].

A Hewlett-Packard model 1100 HPLC equipped with a UV detector was used for separation and for qualitative and quantitative analyses of the experiments. The products were separated on a  $5 \mu\text{m}$  Interchim C18-ODS2 column and eluted with a phosphoric acid/acetonitrile (80/20) buffer (pH 2.5). The detection wavelength

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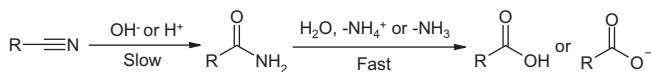


Fig. 1. Hydrolysis of a nitrile in acidic or basic conditions.

of UV detector was set at 220 nm, corresponding to the maximum absorption wavelength of benzonitrile, benzamide and benzoic acid.

The products were isolated and characterized by physical and spectral data.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AMX 300 MHz spectrometer in  $\text{CDCl}_3$  (benzamide and benzoic acid characterization) or  $\text{DMSO}-d_6$  (adipic acid characterization) with chemical shifts ( $\delta$ ) given in ppm relative to tetramethylsilane (TMS). FTIR spectra were recorded using a Perkin-Elmer spectrometer with KBr pellets and reported in  $\text{cm}^{-1}$ . GC-MS spectra were recorded on an Agilent 7973N MS coupled to an Agilent 6890 GC equipped with a HP 5 column. Adipic acid was previously silylated using *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) as derivatization reagent. Melting points were determined on a Kofler bench device (Wagner & Munz) and were not corrected.

## 2.2. Synthesis of benzoic acid

### 2.2.1. Experimental procedure using ultrasonic activation

Hydrochloric acid or sodium hydroxide solution (9.5 mL) with the appropriate pH are sonicated for a determined time with 0.5 mL (5 mmol) of benzonitrile. Argon or air is bubbled in water during sodium hydroxide solution preparation. Control of temperature is ensured by a thermocouple. Reaction is then performed under ambient air or Argon atmosphere.

### 2.2.2. Experimental procedure using thermal activation

Hydrochloric acid or sodium hydroxide solution (40 mL) with the appropriate concentration are mixed with 2.5 mL (25 mmol) of benzonitrile at reflux for 8 h. Control of temperature is insured by a thermal regulator.

**Benzoic acid:** m.p. 122 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta = 7.50$  (m, 2H),  $\delta = 7.64$  (m, 1H),  $\delta = 8.15$  (d ( $J = 7.71$  Hz), 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta = 128.41$  (Csp<sub>2meta</sub>),  $\delta = 130.58$  (Csp<sub>2-COOH</sub>),  $\delta = 130.11$  (Csp<sub>2ortho</sub>),  $\delta = 133.73$  (Csp<sub>2para</sub>),  $\delta = 172.01$  (COOH). FTIR (1% in KBr): O–H: 3405  $\text{cm}^{-1}$ , C=O: 1698  $\text{cm}^{-1}$ , Csp<sub>2</sub>–Csp<sub>2</sub>: 1598, 1452  $\text{cm}^{-1}$ , Csp<sub>2</sub>–H: 3070  $\text{cm}^{-1}$ .

**Benzamide:** m.p. 129 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta = 7.47$  (m, 1H),  $\delta = 7.49$  (m, 2H),  $\delta = 7.86$  (d ( $J = 7.17$  Hz), 2H),  $\delta = 6.10$  (s, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta = 127.59$  (Csp<sub>2ortho</sub>),  $\delta = 128.56$  (Csp<sub>2meta</sub>),  $\delta = 131.48$  (Csp<sub>2para</sub>),  $\delta = 133.25$  (Csp<sub>2-CONH2</sub>),  $\delta = 168.98$  (CONH<sub>2</sub>). FTIR (1% in KBr): N–H: 3369  $\text{cm}^{-1}$ , C=O: 1680  $\text{cm}^{-1}$ , Csp<sub>2</sub>–Csp<sub>2</sub>: 1625, 1464  $\text{cm}^{-1}$ , Csp<sub>2</sub>–H: 3070  $\text{cm}^{-1}$ .

## 2.3. Synthesis of adipic acid

Sodium hydroxide (9.5 mL) with the appropriate concentration are sonicated for 45 min with 0.5 mL (4.4 mmol) of adiponitrile. Control of temperature is insured by a thermal regulator.

**Adipic acid:** m.p. 151 °C.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , 300 MHz):  $\delta = 1.51$  (m, 4H, CH<sub>2</sub>–CH<sub>2</sub>),  $\delta = 2.23$  (m, 4H, CH<sub>2</sub>–COOH),  $\delta = 11.8$  (s, 1H, COOH).  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ , 75 MHz):  $\delta = 24.32$  (CH<sub>2</sub>–CH<sub>2</sub>),  $\delta = 33.12$  (CH<sub>2</sub>–COOH),  $\delta = 173.54$  (COOH). FTIR (1% in KBr): O–H: 3038  $\text{cm}^{-1}$ , Csp<sub>3</sub>–H: 2994, C=O: 1699  $\text{cm}^{-1}$ , Csp<sub>3</sub>–Csp<sub>3</sub>: 1445  $\text{cm}^{-1}$ .

## 2.4. Synthesis of bis(trimethylsilyl)hexanedioate

To 10  $\mu\text{L}$  (0.19 mmol) of adipic acid diluted in 800  $\mu\text{L}$  of diethyl ether are added 100  $\mu\text{L}$  (0.97 mmol) of BSTFA. The mixture is son-

icated for 30 min and bis(trimethylsilyl)hexanedioate is obtained with 100% yield.

**Bis(trimethylsilyl)hexanedioate:** MS (EI)  $m/z$  (%): 275 (19), 247 (2), 231 (2), 217 (6), 204 (4), 185 (6), 172 (14), 159 (11), 147 (38), 141 (22), 129 (10), 117 (12), 111 (62), 99 (4), 83 (17), 73 (100), 67 (4), 55 (41), 45 (20), 29 (5).

## 3. Results and discussion

Benzonitrile was chosen as model compound to enable monitoring of the reaction by UV absorption. Moreover, its degradation products due to sonication have already been determined and their structures have been described previously [17,18].

In order to investigate a possible influence of ultrasound on benzonitrile hydrolysis, two sets of experiments have been performed. In the first set, reactions have been carried out without sonication. In the second set, the reaction has been performed in the same experimental conditions but under sonication. These conditions are summarized in Fig. 2.

In each case, yields have been determined by HPLC with UV detection ( $\lambda = 220$  nm) and after calibration. Results are given in Table 1.

Results show a great influence of pH on the feasibility of the reaction and on its mechanism under ultrasonic conditions since

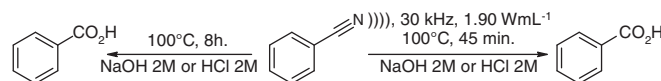


Fig. 2. Experimental conditions for hydrolysis of benzonitrile under thermal or ultrasonic activation in acidic or basic conditions.

Table 1

Conversion percentage of benzonitrile in benzoic acid in basic and acidic conditions, with or without sonication:  $P = 19$  W,  $F = 30$  kHz,  $[\text{HCl}] = 2$  M,  $[\text{NaOH}] = 2$  M.

Entry	Activation method	Catalyst	Time, h	Benzoic acid yield, %
1	Ultrasound	NaOH	0.75	95
2	Thermal	NaOH	8	93
3	Ultrasound	HCl	0.75	0
4	Ultrasound	HCl	1.5	0
5	Thermal	HCl	8	74

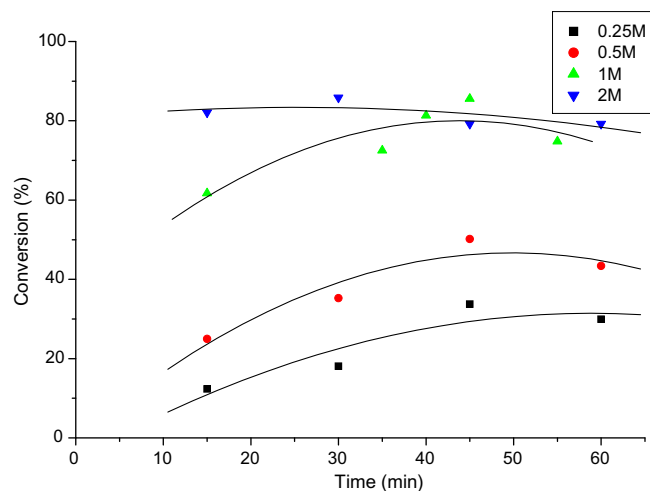


Fig. 3. Influence of time and NaOH concentration on the conversion of benzonitrile in benzoic acid under ultrasonic irradiation in basic conditions, under air atmosphere.  $F = 30$  kHz and  $P = 1.9$  W mL<sup>-1</sup>.

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