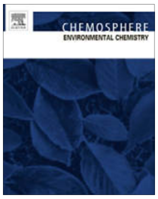
Chemosphere 80 (2010) 340–345

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere



Nitration of nitrobenzene in Fenton's processes

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A R T I C L E   I N F O

Article history:
Received 30 December 2009
Received in revised form 22 March 2010
Accepted 23 March 2010
Available online 24 April 2010

Keywords:
Nitration
Nitroaromatic compounds
Fenton's reagent
AOTs

A B S T R A C T

Previous studies of nitrobenzene (NB) degradation by Fenton and photo-Fenton technologies have demonstrated the formation and accumulation of 1,3-dinitrobenzene (1,3-DNB) as a highly toxic reaction intermediate. In the present study, we analyze the conditions that favor 1,3-DNB formation during NB degradation by Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, UV/Fe^{3+}/H_2O_2 or UV/H_2O_2 processes. Nitration yields in Fenton, Fenton-like and photo-Fenton techniques were much higher than those observed in UV/H_2O_2 systems. Besides, several tests showed that 1,3-DNB formation increases with the initial iron concentration and decreases as the initial H_2O_2 concentration increases.

In order to asses the key species involved in NB nitration mechanism, additional experiments were performed in the presence of NO_2^- or NO_3^-. In dark systems, 1,3-DNB yield significantly increased with increasing $[NO_2^-]_0$, while it was not affected by the presence of NO_3^-. In contrast, 1,3-DNB yields were higher and more strongly affected by the additive concentration in UV/NO_3^- systems than in UV/HNO_2/NO_2^- systems. Dark experiments performed at pH 1.5 in excess of HNO_2 along with UV/NO_3^- tests conducted in the presence of 2-propanol show that hydroxyl radicals play an important role in NB nitration since NB molecule does not react with the nitrating agents ONOOH, $^{\cdot}NO$ or $^{\cdot}NO_2$. The results indicate that, in the experimental domain tested, the prevailing NB nitration pathway involves the reaction between the $^{\cdot}OH$–NB adduct and $^{\cdot}NO_2$ radicals.

1. Introduction

In recent years, significant progress has been made in the implementation of oxidative treatments for the degradation of pollutants in wastewaters that are refractory to traditional methods. These treatments, known as advanced oxidation technologies (AOTs), are based on the generation of highly reactive species such as hydroxyl radicals ($^{\cdot}OH$) that degrade most pollutants yielding less harmful compounds (Legrini et al., 1993; Andreozzi et al., 1999; Pera-Titus et al., 2004). Among the AOTs, the Fenton's reagent (Fe^{2+}/H_2O_2), the Fenton-like reagent (Fe^{3+}/H_2O_2), the photo-Fenton process (UV/$Fe^{2+,3+}/H_2O_2$) and the photolysis of H_2O_2 (UV/H_2O_2) have been proven to be effective methods for the removal of a wide range of organic pollutants (Cater et al., 2000; García Einschlag et al., 2002b; Pignatello et al., 2006). The production of $^{\cdot}OH$ radicals in Fenton and UV/H_2O_2 systems has been discussed extensively by several authors (De Laat et al., 2004; Pignatello et al., 2006; Von Sonntag, 2008). A summary of the key reactions involved in the production of $^{\cdot}OH$ radicals, in acidic solutions (pH = 3.0) and in the absence of organic ligands, is given below

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + HO^- + {}^{\cdot}OH \quad [k_1 = 63\,M^{-1}\,s^{-1}] \qquad (1)$$

$$Fe(III) + H_2O_2 \rightarrow Fe(II) + HO_2^{\cdot} + H^+ \quad [k_2 = 0.002\,M^{-1}\,s^{-1}] \qquad (2)$$

$$Fe(III) + H_2O + h\nu \rightarrow Fe(II) + {}^{\cdot}OH + H^+ \quad [\Phi_{3,313\,nm} = 0.14 - 0.19] \qquad (3)$$

$$H_2O_2 + h\nu \rightarrow 2\,{}^{\cdot}OH \quad [\Phi_{4,254\,nm} = 0.5] \qquad (4)$$

where Fe (II) and Fe (III) represent all soluble species corresponding to each oxidation state.

The complete mineralization of the organic substrates by these treatments may usually become too expensive due to the relatively high H_2O_2 concentrations needed and the high electrical power consumption required to operate the UV lamps for prolonged treatments. For this reason, AOTs have been proposed as "pretreatment" stages in order to reduce the effluent toxicity to secure levels before bio-oxidation application (Muñoz et al., 2006; Ballesteros Martín et al., 2008; Farré et al., 2008). Therefore, in-depth studies concerning oxidation pathways are critical since highly toxic reaction intermediates may be formed and accumulated during intermediate treatment stages. A particularly interesting example is the formation of 1,3-dinitrobenzene (1,3-DNB) in the oxidation of nitrobenzene (NB) by using Fenton and photo-Fenton techniques (Carlos et al., 2008, 2009) since toxicity studies have shown that 1,3-DNB is about 30 times more toxic than NB (Saçan et al., 2007). Furthermore, given that 1,3-DNB is more

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0045-6535/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2010.03.034

resistant to $^{\cdot}OH$-mediated oxidation than NB (García Einschlag et al., 2003) much longer treatment periods are needed for toxicity removal. Hence, the knowledge of the experimental variables that affect the formation of 1,3-DNB is of great importance for the design of efficient processes.

Numerous authors have focused on the nitration of aromatic compounds (including phenolic derivatives, azaarenes and polycyclic aromatic hydrocarbons) setting out several nitration mechanisms that involve different nitrating agents such as NO^+, NO_2^+, N_2O_3, HNO_2, $^{\cdot}NO_2$, $^{\cdot}OH + {}^{\cdot}NO_2$, N_2O_4, and ONOOH (Milligan, 1983; Machado and Boule, 1995; Beitz et al., 1999; Dzengel et al., 1999; Vione et al., 2004, 2005a,b; Matykiewiczová et al., 2007; Shankar et al., 2007). Although the formation of nitro derivatives in aqueous phase has been studied by various research groups, several points concerning the key species involved and the nitration mechanisms of aromatic compounds with electron-withdrawing groups are still unclear.

The nitration of NB in aqueous phase has been extensively studied in strong acidic solutions ($pH < 1$) using HNO_3–H_2SO_4 mixtures or nitronium salts in H_2SO_4 and HF as solvent (Kilpatrick et al., 1965; Fujiwara et al., 1980). However, there are only a few studies reporting the nitration of NB under mild conditions similar to those used for AOTs (García Einschlag et al., 2009).

Previous studies have shown that, as NB is oxidized by Fenton, photo-Fenton, and UV/H_2O_2 techniques, NO_2^- and NO_3^- are formed as the inorganic nitrogen-containing products (García Einschlag et al., 2002b; Carlos et al., 2008, 2009). It has been shown that the nitro group is gradually released from the aromatic ring in the form of NO_2^- as a result of the $^{\cdot}OH$ radical attack on the ipso position (O'Neill et al., 1978; Kotronarou et al., 1991; Carlos et al., 2008). In the darkness and at pH 3, the released HNO_2/NO_2^- (pKa = 3.3) can lead to the formation of different nitrating agents such as peroxynitrous acid (ONOOH) and the $^{\cdot}NO_2$ radical through the following reactions (Fischer and Warneck, 1996; Merenyi et al., 2003):

$$HNO_2 + H_2O_2 + H^+ \rightarrow HOONO + H_2O + H^+ \quad [k_5 = 9.6\ M^{-1}\ s^{-1},\ pH = 3.0] \tag{5}$$

$$HNO_2/NO_2^- + {}^{\cdot}OH \rightarrow {}^{\cdot}NO_2 + H_2O/HO^- \quad [k_6 = 2.6 \times 10^9/1 \times 10^{10}\ M^{-1}\ s^{-1}] \tag{6}$$

The ONOOH formed is unstable in acid media and quickly decomposes following two main reaction pathways, yielding 72% of $NO_3^- + H^+$ and 28% of $^{\cdot}NO_2 + {}^{\cdot}OH$, respectively (Gerasimov and Lymar, 1999). Subsequently, $^{\cdot}NO_2$ can lead to the formation of NO_3^- as stable product through a series of thermal reactions (Mack and Bolton, 1999).

In addition, under UV irradiation both HNO_2/NO_2^- and NO_3^- photolysis may also contribute to the production of reactive nitrogen species through the following photolytic processes (Mack and Bolton, 1999; Goldstein and Rabani, 2007):

$$HNO_2/NO_2^- + h\nu \rightarrow {}^{\cdot}NO + {}^{\cdot}OH/O^{\cdot-} \quad [\Phi_{7,\,360\,nm} = 0.32/0.025] \tag{7}$$

$$NO_3^- + h\nu + H^+ \rightarrow {}^{\cdot}NO_2 + {}^{\cdot}OH \quad [\Phi_{8,\,205\,nm} = 0.13] \tag{8}$$

$$NO_3^- + h\nu + H^+ \rightarrow ONOOH \quad [\Phi_{9,\,205\,nm} = 0.28] \tag{9}$$

Taking into account the formation of NO_2^- and NO_3^- during NB degradation, it is reasonable to assume that the set of Eqs. (5)–(9) summarizes the main pathways leading to the formation of nitrating agents, particularly $^{\cdot}NO_2$ and ONOOH, that are potentially capable of participating in the formation of 1,3-DNB under the reaction conditions used in the different AOTs.

The objective of this paper is to study the conditions that favor the formation of 1,3-DNB during NB treatment using Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, UV/Fe^{3+}/H_2O_2 or UV/H_2O_2 processes. In addition, we analyze the influence of NO_2^- and NO_3^- ions in the production of 1,3-DNB both in the dark and in UV-irradiated systems.

2. Materials and methods

2.1. Reagents

2-Nitrophenol, 3-nitrophenol and 4-nitrophenol were purchased from Riedel de Haën; NB from Fluka; 1,3-DNB, $CuSO_4 \cdot 5H_2O$ and H_2O_2 (30%) from Merck; phenol, $Fe(ClO_4)_2 \cdot H_2O$ and $Fe(ClO_4)_3 \cdot H_2O$ from Aldrich; and $NaNO_2$ and KNO_3 from Carlo Erba. All reagents were used as received without further purification.

2.2. Analytical techniques

Quantification of NB and its oxidation products was performed by HPLC using a Shimadzu instrument (solvent delivery module LC-20AT, on-line degasser DGU-20A5, UV–vis photodiode array detector SPD-M20A, column oven CTO-10 A5 VP and autosampler SIL-20AAT) equipped with a Lichrospher column (RP-C18, 4 mm i.d. × 125 mm long). The column temperature was maintained at 25 °C. Elution conditions: mobile phase composed of 30/70 v/v acetonitrile and an aqueous solution ($[H_3PO_4] = 0.01$ M and [triethylamine] = 0.01 M, pH 3.0); flow rate: 1 mL min^{-1}.

Absorption spectra were recorded on a double-beam Cary 3 spectrophotometer using quartz cells of 1.0 cm optical path length.

2.3. Experimental procedures

All the solutions were prepared daily using deionized water of Milli-Q quality. The pH was adjusted to a value of 3.0 using H_2SO_4. Dark experiments were conducted at room temperature with continuous stirring using a 200 mL batch reactor covered with an aluminum foil to avoid radiation effects. Photochemical experiments were performed in an annular reactor (DEMA, Mangels, Bornheim-Roisdorf, Germany) of 750 mL capacity. The solution was continuously bubbled with analytical air and the temperature of the system was kept at 25 ± 1 °C. A medium-pressure mercury arc lamp (Philips HPK 125 W), positioned in the axis of the reactor in a quartz well, was used as radiation source. The incident photon rate (P_0), measured using potassium ferrioxalate as actinometer (García Einschlag et al., 2002a), was 1.96×10^{-4} Eins s^{-1} L^{-1}. Further details about experimental conditions and procedures can be found in the Supplementary material.

2.4. Evaluation of 1,3-DNB formation

In the present work we used different experimental approaches in order to analyze the formation of 1,3-DNB. In Section 3.1, the formation of 1,3-DNB in different AOTs was characterized by the relative 1,3-DNB production (expressed as $100 \times [1,3\text{-DNB}]/[NB]_0$) evaluated at a conversion degree of 0.8. This value was chosen taking into account that relative 1,3-DNB productions reach their maximum at conversion degrees between 0.8 and 0.9 (see below). On the other hand, for the Fe^{2+}/H_2O_2 experiments of Section 3.2, performed in the presence of initially added NO_2^- or NO_3^-, the formation of 1,3-DNB was evaluated by the relative 1,3-DNB production after 30 min of reaction time. Finally, 1,3-DNB yields ($\eta^{1,3\text{-DNB}}$) were used in Sections 3.3 and 3.4 in order to assess 1,3-DNB formation in UV/HNO_2/NO_2^- and UV/NO_3^- systems. Since the yields of the primary products (η^i) may depend on the elapsed reaction time, we compared initial yields (η_0^i) calculated with the following expression (Carlos et al., 2008):