



Modeling the photochemical transformation of nitrobenzene under conditions relevant to sunlit surface waters: Reaction pathways and formation of intermediates



Davide Vione^{a,*}, Elisa De Laurentiis^a, Silvia Berto^a, Claudio Minero^a, Arzu Hatipoglu^b, Zekiye Cinar^b

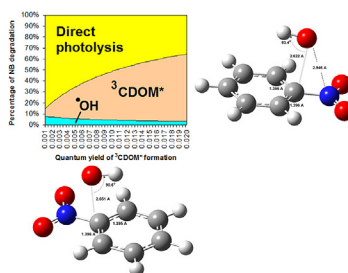
^a Università degli Studi di Torino, Dipartimento di Chimica, Via P.Giuria 5, 10125, Torino, Italy

^b Yildiz Technical University, Department of Chemistry, 34220, Istanbul, Turkey

HIGHLIGHTS

- Nitrobenzene is mainly photo-transformed by direct and triplet-sensitized photolysis.
- Reaction with $\cdot\text{OH}$ proceeds via a pre-reactive complex and has low energy barrier
- Phenol and nitrophenols are the main phototransformation intermediates.
- Phenol is mainly formed upon reaction between nitrobenzene and $\cdot\text{OH}$.
- Transformation of nitrobenzene into phenol would be a potential $\cdot\text{OH}$ probe reaction.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 9 October 2015

Accepted 12 November 2015

Available online 11 December 2015

Handling Editor: Klaus Kümmerer

Keywords:

Nitrobenzene

Hydroxyl radical

Photo-oxidative degradation

DFT calculation

COSMO

ABSTRACT

Nitrobenzene (NB) would undergo photodegradation in sunlit surface waters, mainly by direct photolysis and triplet-sensitized oxidation, with a secondary role of the $\cdot\text{OH}$ reaction. Its photochemical half-life time would range from a few days to a couple of months under fair-weather summertime irradiation, depending on water chemistry and depth. NB phototransformation gives phenol and the three nitrophenol isomers, in different yields depending on the considered pathway. The minor $\cdot\text{OH}$ role in degradation would make NB unsuitable as $\cdot\text{OH}$ probe in irradiated natural water samples, but the selectivity towards $\cdot\text{OH}$ could be increased by monitoring the formation of phenol from NB+ $\cdot\text{OH}$. The relevant reaction would proceed through *ipso*-addition of $\cdot\text{OH}$ on the carbon atom bearing the nitro-group, forming a pre-reactive complex that would evolve into a transition state (and then into a radical addition intermediate) with very low activation energy barrier.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Nitrobenzene (NB) is a nitroaromatic compound used in several industrial applications, mostly as an intermediate in the synthesis of aniline to finally produce rubber chemicals, pesticides, azo dyes, explosives and pharmaceuticals (including paracetamol)

* Corresponding author.

E-mail address: davide.vione@unito.it (D. Vione).

(Bhatkhandea et al., 2003).

The nitro group makes NB fairly resistant to biological degradation. Because of incomplete removal by wastewater treatment plants (Chen et al., 2014; Xia et al., 2014), NB may occur in surface waters up to $\mu\text{g L}^{-1}$ levels (Jin et al., 1998; Kang et al., 2001; Wang et al., 2002, 2003; He et al., 2006; Gao et al., 2013). Among the natural attenuation processes, biodegradation is possible but predictably slow (Jin and Rolle, 2014; Liu et al., 2014). Alternatively, photodegradation may occur by both direct photolysis (absorption of sunlight by NB, triggering degradation) and indirect photochemistry. In the latter, sunlight is absorbed by photosensitizers (chromophoric dissolved organic matter -CDOM-, nitrate and nitrite) to produce reactive transients such as the hydroxyl ($\cdot\text{OH}$) and carbonate ($\text{CO}_3^{\cdot-}$) radicals, singlet oxygen ($^1\text{O}_2$) and CDOM triplet states ($^3\text{CDOM}^*$) (Canonica et al., 2006; Canonica, 2007; Richard et al., 2007; Fenner et al., 2013). In addition to reacting with pollutants, $\cdot\text{OH}$ and $\text{CO}_3^{\cdot-}$ are mainly scavenged by DOM (either chromophoric or not), $^1\text{O}_2$ is deactivated by collision with water, and $^3\text{CDOM}^*$ is scavenged by O_2 to yield $^1\text{O}_2$ (Vione et al., 2014). Photochemistry might be an important pathway for NB degradation (Vialaton and Richard, 2002), but very limited evidence is available concerning the NB lifetime in natural settings.

NB is also a satisfactory $\cdot\text{OH}$ probe in simplified laboratory systems (Vione et al., 2009), while its use as probe in irradiated surface waters is problematic because of interference by photolysis and $^3\text{CDOM}^*$ reactions (Vialaton and Richard, 2002; Vione et al., 2010).

The present paper aims at: (i) assessing by modeling, for the first time to our knowledge, the photochemical NB lifetime in surface-water environments, as a function of water chemistry and depth; (ii) elucidating the mechanism of NB reaction with $\cdot\text{OH}$, and (iii) assessing whether the selectivity of NB as $\cdot\text{OH}$ probe may be improved by taking into account the formation of intermediates.

2. Methods and procedures

2.1. Irradiation experiments

Samples to be irradiated (5 mL total volume) were introduced into cylindrical Pyrex glass cells (diameter 4.0 cm, height 2.5 cm), tightly closed with a screw cap on the side neck. The samples were magnetically stirred during irradiation. The direct photolysis of NB was studied under a Philips TL 01 UV-Vis lamp, with emission maximum at 313 nm. Hydrogen peroxide was used as $\cdot\text{OH}$ source under UVA irradiation (lamp Philips TL K05, emission maximum at 365 nm), to limit the NB direct photolysis. The same UVA lamp was used to irradiate NB in the presence of anthraquinone-2-sulphonate (AQ2S). Emission (lamp) and absorption spectra are reported in Fig. SM1 of the Supplementary Material (hereafter SM). After irradiation, the time evolution of NB, phenol and nitrophenols was monitored by liquid chromatography (see SM for further details).

2.2. Kinetic data treatment

The reported concentration vs. time data of NB and its transformation intermediates are the average results of triplicate runs. The NB time evolution data were fitted with equation (1):

$$C_t = C_0 \exp\left(-k_{\text{NB}}^d t\right) \quad (1)$$

where C_t is NB concentration at the time t , C_0 its initial concentration, and k_{NB}^d the pseudo-first order degradation rate constant. The initial NB transformation rate is $R_{\text{NB}} = k_{\text{NB}}^d C_0$. The time

evolution of each transformation intermediate was fitted with equation (2):

$$C_{\text{int},t} = \frac{k_{\text{int}}^f C_0 \left[\exp\left(-k_{\text{NB}}^d t\right) - \exp\left(-k_{\text{int}}^d t\right) \right]}{k_{\text{int}}^d - k_{\text{NB}}^d} \quad (2)$$

where C_0 , k_{NB}^d and t are as above, $C_{\text{int},t}$ is the concentration of the intermediate at the time t , and k_{int}^f , k_{int}^d are its pseudo-first order formation and transformation rate constants, respectively. The initial formation rate of each intermediate is $R_{\text{int}} = k_{\text{int}}^f C_0$, which is also the slope of the tangent to the relevant time evolution curve ($C_{\text{int},t}$ vs. t) at $t \rightarrow 0$. The intermediate yields were derived as the ratio of their initial rates to that of NB, $\eta_{\text{int}} = R_{\text{int}} R_{\text{NB}}^{-1}$.

2.3. Photochemical modeling

The NB phototransformation kinetics under conditions relevant to surface waters was modeled with the APEX software (Aqueous Photochemistry of Environmentally-occurring Xenobiotics). It predicts photochemical half-life times of pollutants, formation kinetics and yields of intermediates as a function of water chemistry and depth, for compounds with known direct photolysis quantum yields and second-order reaction rate constants with transient species (Vione, 2014; Bodrato and Vione, 2014). APEX results have been validated by comparison with field data of photo-transformation kinetics in surface freshwaters (Maddigapu et al., 2011; Vione et al., 2011; De Laurentiis et al., 2012; Marchetti et al., 2013). APEX applies to well-mixed water bodies, including the epilimnion of stratified lakes.

2.4. Computational set-up and methodology

Quantum mechanical modeling techniques were employed to determine the reaction mechanism of NB+ $\cdot\text{OH}$. The relevant calculations were carried out with the DFT method, within the GAUSSIAN 03 package (Frisch et al., 2003). The DFT calculations used the hybrid B3LYP functional, which combines Hartree-Fock and Becke exchange terms with the Lee–Yang–Parr correlation functional. Concerning the choice of the basis set, optimizations were performed at the B3LYP/6-31G(d) level followed by single-point energy calculations at the B3LYP/6-311 + G(d,p) level (Wong and Radom, 1998; Ozen et al., 2003). Zero-point vibrational energies (ZPEs) were calculated at the B3LYP/6-31G(d) level, and the same ZPEs were used for B3LYP/6-311 + G(d,p)//B3LYP/6-31G(d) calculations.

The solvent effect on the reaction was taken into account with the COSMO solvation model, which describes the solvent reaction field by means of apparent polarization charges distributed on the cavity surface (Barone and Cossi, 1998; Hush et al., 2005).

3. Results and discussion

3.1. Photochemical reactions of NB

The second-order reaction rate constant between NB and $\cdot\text{OH}$ is reported in the literature ($k_{\text{NB},\cdot\text{OH}} = 3.9 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$; Buxton et al., 1988). No data are available for the NB reactivity with $^1\text{O}_2$, but electron-poor aromatics have $^1\text{O}_2$ reaction rate constants around $10^3 \text{ M}^{-1} \text{ s}^{-1}$ (Wilkinson and Brummer, 1981). Reaction between electron-poor NB and $^1\text{O}_2$ should thus be unimportant in surface waters, and Vialaton and Richard (2002) have excluded it upon irradiation of surface water samples or humic acids. NB would also be unreactive with $\text{CO}_3^{\cdot-}$ (Vione et al., 2009). Among the remaining photoreactions of environmental significance, direct photolysis and

Download English Version:

<https://daneshyari.com/en/article/6307032>

Download Persian Version:

<https://daneshyari.com/article/6307032>

[Daneshyari.com](https://daneshyari.com)