Short note

The fate of nitrogen upon nitrite irradiation: Formation of dissolved vs. gas-phase species

Elisa De Laurentiis [a], Marco Minella [a], Silvia Berto [a], Valter Maurino [a], Claudio Minero [a], Davide Vione [a,b,*]

[a] Università degli Studi di Torino, Dipartimento di Chimica, Via P. Giuria 5, 10125 Torino, Italy [1]
[b] Università degli Studi di Torino, Centro Interdipartimentale NatRisk, Via L. Da Vinci 44, 10095 Grugliasco, TO, Italy [2]

ARTICLE INFO

ABSTRACT

Nitrite photochemical transformation is an important sink for nitrite and a source of nitric oxide, which affects the air–water partitioning of $^{\bullet}$NO. It is shown here that aliphatic and aromatic $^{\bullet}$OH scavengers alter the photochemical fate of nitrogen, in addition to enhancing nitrite photodegradation. In aerated solution, the addition of phenol as scavenger induced a significant formation of gas-phase nitrogen species from irradiated nitrite, differently from nitrite alone or in the presence of 2-propanol. Moreover, phenol strongly favoured the photochemical production of gas-phase nitric oxide in aerated solution: an upper limit of about 20% could be established for the nitrite fraction that may be transformed into gas-phase $^{\bullet}$NO under these conditions. The photochemical production of $^{\bullet}$NO was considerably higher in the absence of oxygen, most likely because the scavenging of nitric oxide by superoxide is an important $^{\bullet}$NO sink in aerated systems. These results suggest that the concentration of dissolved oxygen and the nature of the $^{\bullet}$OH scavenger(s) may considerably affect the phototransformation of nitrite into gas-phase nitrogen compounds, and particularly into nitric oxide, in aqueous solution and at water-air interfaces.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The nitrite ion is the least stable but also the most biologically and photochemically active inorganic nitrogen species that can be found in natural waters. From a photochemical point of view, nitrite photolysis is an important source of hydroxyl radicals ($^{\bullet}$OH) that are involved in the transformation of xenobiotics and in the mineralisation of natural organic compounds. Nitrite reaches low concentration values in most surface-water environments and, in oxygenated waters, it is quickly converted to NO_3^- [1]. However, the low $[NO_2^-]$ is compensated for by the ability of nitrite to absorb a significant fraction of sunlight (the UVA absorption maximum of nitrite is around 360 nm) and by the rather elevated photolysis quantum yield [2,3]. Because of its significant photochemical reactivity, nitrite undergoes photodegradation as an important sink in sunlit surface waters [4].

Unlike most other dissolved compounds, the photodegradation of nitrite is enhanced in the presence of $^{\bullet}$OH scavengers. When nitrite is alone in solution, the photochemical production of $^{\bullet}$OH and the subsequent oxidation of NO_2^- by the hydroxyl radical has the effect of triggering the null cycle (1), which regenerates nitrite with no resulting transformation [2].

(1)
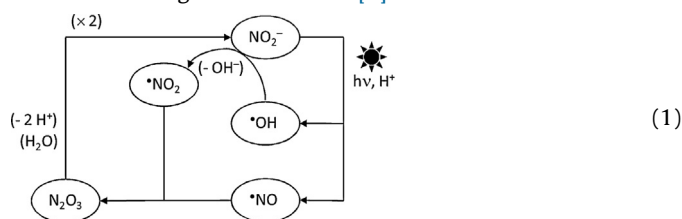
Some photodegradation of nitrite actually takes place, because of the following process [5]:

$$2^{\bullet}NO_2 \leftrightarrows N_2O_4 \quad (2)$$

$$N_2O_4 + H_2O \rightarrow NO_3^- + NO_2^- + 2H^+ \quad (3)$$
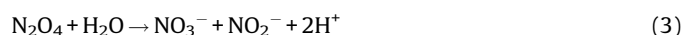
* Corresponding author at: Università degli Studi di Torino, Dipartimento di Chimica, Via P. Giuria 5, 10125 Torino, Italy. Tel.: +39 11 6705296; fax: +39 11 6705242.
E-mail address: davide.vione@unito.it (D. Vione).
[1] http://www.chimicadellambiente.unito.it.
[2] http://www.natrisk.org.

The photodegradation of nitrite is enhanced in the presence of $^{\bullet}OH$ scavengers, which inhibit the oxidation of nitrite to $^{\bullet}NO_2$ and limit the onset of the null cycle, triggered by reaction between $^{\bullet}NO$ and $^{\bullet}NO_2$ to yield N_2O_3 [4]. The $^{\bullet}OH$ scavengers would understandably enhance the occurrence of $^{\bullet}NO$, which could either react to produce dissolved species or be partitioned to the gas phase. In support of the latter issue, irradiation of nitrite in seawater has been reported to produce $^{\bullet}NO$ and to affect as a consequence its air–water partitioning [6,7]. Interestingly, the photochemical formation of nitric oxide from nitrite seems to be poorly affected by inorganic salts, while there is evidence that reactive oxygen species (and most notably $O_2^{-\bullet}$) would be important $^{\bullet}NO$ sinks [7]. The above discussion suggests that $^{\bullet}OH$ scavengers could be involved in the formation of $^{\bullet}NO$, but to our knowledge this issue has not been investigated [7].

Several factors that link nitrite photochemistry with nitric oxide photogeneration are still unclear, including: (i) the effect of $^{\bullet}OH$ scavengers on the generation of gas-phase nitric oxide, and (ii) the effect of the scavengers on the fraction of nitrite that is transformed into different nitrogen species. The present paper has the purpose of providing a preliminary insight into the above knowledge gaps, by closing the balance of dissolved nitrogen upon nitrite photolysis and by assessing the production of gas-phase nitric oxide in the presence of aliphatic (2-propanol) and aromatic (phenol) $^{\bullet}OH$ scavengers.

2. Experimental

2.1. Reagents and materials

KNO_3 (99%), $NaNO_2$ (>99%), K_2CO_3 (>99%), phenol (>99%), 2-propanol (>99%) and methanesulphonic acid (>99%) were purchased from Sigma–Aldrich; zero-grade air was purchased from SIAD (Bergamo, Italy); N_2 (5.0 grade), O_2 (6.0 grade) and Ar (5.5 grade) were purchased from Sapio (Monza, Italy). Water used was of Milli-Q quality.

2.2. Irradiation experiments in solution

A first series of experiments was carried out to assess the fate of dissolved nitrogen upon nitrite irradiation, using the measurement of total dissolved nitrogen (the most important analytical parameter in this context) as a tool to quantify the possible transfer of nitrogen-containing species (including $^{\bullet}NO$) into the gas phase. The experimental set-up, and particularly the initial concentration of nitrite, was optimised to ensure a suitable measurement of total nitrogen, with the goal of minimising the analytical uncertainties. Unfortunately, the need to ensure reliable measures of total nitrogen required the use of nitrite concentration levels (1 mM) that are considerably higher than the environmental ones. The present experimental results give thus insight into photochemical reaction pathways, but the assessment of their environmental significance will require experiments at lower nitrite levels, to be carried out with a different experimental set-up.

Solutions containing 50 mL of 1 mM $NaNO_2$ (alone or spiked with 10 mM phenol or 50 mM 2-propanol) were placed into square Pyrex bottles (100 mL capacity). The concentration values of phenol and 2-propanol were chosen to ensure that the two compounds prevailed over nitrite as $^{\bullet}OH$ scavengers and that they scavenged $^{\bullet}OH$ to a comparable extent [8]. Each bottle was placed with one of its four lateral faces downwards, and irradiated with magnetic stirring under a solar simulator (Solarbox, CO.FO.ME. GRA., Milan, Italy), equipped with a 1500 W Philips xenon lamp and a 320 nm cut-off filter. Lamp radiation was vertically incident over the solutions and the optical path length was 2 cm. The UV irradiance (295–400 nm) reaching the bottles was $30 \pm 2\,W\,m^{-2}$,

measured with a CO.FO.ME.GRA. (Milan, Italy) power meter. Dark runs were carried out by wrapping the bottles with aluminium foil and by placing them under the lamp with magnetic stirring. The temperature of the solutions under the lamp was around 30 °C, the solution pH was 6.5–7.5.

Total nitrogen (TN) was measured with a Shimadzu TN–TOC–V_{CSH} total nitrogen and total organic carbon analyser. The total inorganic nitrogen ($TIN = NO_2^- + NO_3^- + NH_4^+$) was determined by ion chromatography with electrochemical suppression. The adopted apparatus was a Dionex 500 ion chromatograph, equipped with GP40 gradient pump, ED40 electrochemical detector and a Rheodyne injector with 100 μL sample loop. Nitrate and nitrite were eluted on a Ion Pac AG9-HC + AS9-HC (guard column + analytical column), with 9 mM K_2CO_3 at $1.0\,mL\,min^{-1}$ flow rate. Eluent conductivity was suppressed with an ASRS 300 conductivity suppression unit. The analysis of ammonium was carried out with CG12A + CS12A guard column + column, eluting with 20 mM methanesulphonic acid at $1.0\,mL\,min^{-1}$ flow rate and using a CERS 500 conductivity suppression unit. The total organic nitrogen (TON) was determined as $TON = TN - TIN$.

2.3. Assessment of $^{\bullet}NO$ release to the gas phase

The experimental set-up described above was optimised for the measurement of TN, but it was not suitable to determine gas-phase $^{\bullet}NO$. To the latter purpose it was used a NO/NO_x detector, HORIBA APNA mod. 370, which exploits the chemiluminescence produced during the reaction between $^{\bullet}NO$ and O_3. This apparatus needs a continuous airflow at the inlet, which was obtained by using a flow photoreactor built according to the UNI 11,484 norm [9,10]. Inside the reactor, 50 mL of 10 mM $NaNO_2$ were placed in a Pyrex Petri dish (110 mm diameter), alone or in the presence of 100 mM phenol or 500 mM 2-propanol, irradiating with a Philips 9W/2P BLB lamp (maximum emission at 355 nm, UV irradiance of $30 \pm 1\,W\,m^{-2}$). The temperature of the irradiated solutions was around 28 °C. The reactor had an inner mixing flow of $29\,m^3\,h^{-1}$. The gas flow through the reactor and to the detector was provided by a mixture of high-purity N_2 and O_2 in a 79:21 ratio (or by high-purity Ar in the runs without oxygen), at a total flow rate of $1000\,mL\,min^{-1}$, produced with an Entech 4600A dynamic diluter. In the runs without oxygen, the nitrite-containing solutions were degassed with ultra-pure Ar for at least half an hour before irradiation. A photograph and a pictorial scheme of the reactor are reported in Fig. S1 of the Supplementary material.

The nitrite concentration used here was 10 times higher compared to the previous set of experiments, and it was required to obtain measurable values of the gas-phase $^{\bullet}NO$. Unfortunately, an initial concentration of 10 mM $NaNO_2$ would be unsuitable for the monitoring of TN in the previous experimental set-up, in particular as far as possible TN variations within a reasonable irradiation time are concerned. This known inconsistency in experimental conditions (different concentrations, closed vs. flow systems) was taken into account when discussing the results, and coherently only qualitative comparisons were carried out between the two sets of data. Also in this case the irradiation experiments give insight into the photochemical pathways, but the assessment of their environmental significance will require experiments to be carried out at much lower nitrite concentration with a different experimental set-up.

3. Results and discussion

Fig. 1a shows the time trends of the monitored nitrogen species, as a function of the irradiation time in the presence of nitrite alone. For plot readability issues, error bars are only reported for TN. For the other parameters, the repeatability of duplicated experiments