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Photocatalytic mineralization of nitrogen-containing benzene derivatives

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Abstract

The photocatalytic mineralization of nitrobenzene, nitrosobenzene, phenylhydroxylamine, aniline and 4-nitrosophenol has been investigated in aerated conditions. In slightly acidic TiO_2 suspensions, all these compounds proved to undergo quantitative formation of carbon dioxide, whereas nitrogen is converted into nitrate and ammonium ions.

The mechanism of ammonium ion release is suggested. Ammonium ions are not generated by reduction of nitrate or nitrite ions, but directly from partly oxidized and unstable intermediates, such as, for example, quinonemonoimine and aliphatic imines. Ammonium ions are formed from nitro- and nitroso-derivatives through reduction of the nitrogen-containing substituent. The reductive pathway prevents detachment of nitro- and nitroso-groups as either nitrate or nitrite ion from the organic moiety. Quite specularly, from phenylhydroxylamine, aniline and aminophenol, ammonium ions are released by means of a partially oxidative pathway. Thus, the temporal evolution of the $[NO_3^-]/[NH_4^+]$ concentration ratio, besides other experimental conditions (pH, photon flux, reactant concentrations), depends largely on both the initial oxidation state of the nitrogen and the nature of the starting organic substrate (e.g. 4-nitrosophenol vs. nitrosobenzene).

Keywords: Photocatalysis; Nitrogen-containing organics; Mineralization; Detoxification; Degradation of organics

1. Introduction

Heterogeneous photocatalytic processes involving organic compounds have been extensively investigated as a possible route for the removal of pollutants [1–6] as well as for gaining information on naturally occurring transformations [7,8].

Quantitative formation of carbon dioxide and inorganic ions from several organic compounds has been reported in exhaustive reviews [4–6].

Most heteroatoms present in the organic compounds are converted to only one type of inorganic ion, e.g. sulfur to sulfate, phosphorous to phosphate, halogens (F, Cl, Br) to halides [6]. In contrast, nitrogen-containing compounds show more complex transformations. Extensive work on the photocatalytic degradation of a wide range of nitrogen-containing compounds reported the formation of nitrate and ammonium ions as the final species [9], but the relative concentration of these two ions was shown to depend largely on the nature of the nitrogen atom in the organic substrate as well as on some experimental conditions, such as substrate concentration, pH and illumination time.

The comprehension of all the possible processes involved in the natural evolution of nitrogen-contain-

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ing compounds is extremely important, not only because nitrogen constitutes a key element of the nutritional cycle and its speciation determines the actual uptake by the living organisms, but also because a large number of anthropogenic compounds widely produced throughout the world (herbicides, pesticides, dyes, drugs, explosives) contain one or more nitrogen atoms. Among these processes, the transformations induced by photocatalytic activation of nitrogen-containing functional groups in a variety of organic compounds have been studied extensively, together with the final formation of inorganic nitrogen species [9–19]. Detoxification of substituted nitrobenzenes by reductive degradation processes have been investigated in association with global treatments of hazardous wastes and contaminated soils [20–22].

In a previous paper [23], the early reaction pathways by which nitrobenzene, nitrosobenzene, phenylhydroxylamine, aniline and a few related derivatives are transformed into one another (retaining the aromatic moiety) in oxygenated aqueous solution by the action of irradiated semiconductors, have been reported. In the present study, particular attention is devoted to the mechanism of formation and distribution of the final inorganic products.

2. Experimental

2.1. Reagents

Nitrobenzene (NB), nitrosobenzene (NOB), 4-nitrosophenol (4-NOP), aniline (A), and hydroxylamine were all purchased from Aldrich (Steinheim, Germany) at the highest purity available and were used without further purification. Phenylhydroxylamine (PHA) was synthesized by reduction of nitrobenzene with dust zinc [24] and recrystallyzed twice from cold water.

Titanium dioxide TiO_2 P25 (BET area 55 m^2/g, Degussa A.G., Frankfurt, Germany) was irradiated in aerated aqueous suspension for at least 12 h and washed with deionized-bidistilled water in order to eliminate both organic impurities and inorganic ions possibly adsorbed on the photocatalyst. WO_3 of BET surface area 1 $m^2\ g^{-1}$ [25] was purchased from Ventron and used as supplied.

2.2. Irradiation experiments

Suspensions of the catalyst were prepared at different catalyst concentrations and then mixed with aqueous solutions of the organic substrates directly in the cells used for the irradiation experiments (final volume, 5 ml). Typical concentrations were 10 mg l^{-1} (10 part per million, ppm) of organics and 200 mg l^{-1} (ppm) of TiO_2. The cells containing the reaction slurry were preliminarily thermostatized in a water bath in the dark until they reached the working temperature of the lamp housing ($\approx$50°C). Irradiation was carried out in cylindrical Pyrex glass cells (4.0 cm diameter, 2.5 cm height), containing 5 ml of aqueous suspension and the desired amount of photocatalyst and substrate. A 1500 W Xenon lamp (Solarbox, CO.FO.MEGRA, Milan, Italy) was utilized, which was equipped with a 310 nm cut-off filter and simulated AMl solar light. The cut-off filter was used to avoid direct UV photolysis of samples. The irradiance spectrum and the cells have been described elsewhere [26,27]. Total photonic flux (340–400 nm) in the cell during irradiation was 1.35×10^{-5} Ein min^{-1}. During the irradiation time, samples were magnetically stirred. At fixed time intervals the irradiation was stopped, the whole sample was filtered through 0.45 μm cellulose acetate membranes (Millipore HA), and the filtrates were analyzed without further clean-up.

2.3. Analytical procedures

Non-purgeable organic carbon (NPOC), total organic carbon (TOC) and inorganic carbon (IC) were measured on filtered suspensions by a Shimadzu TOC-5000 analyzer (catalytic oxidation on Pt at 680°C). Calibration was obtained by injecting potassium phthalate standards.

Nitrate was determined by ion chromatography using a Biotronic IC-5000 instrument equipped with a BT1AN separation column, a chemical suppression column and a 1.5 mM K_2CO_3/1.5 mM $NaHCO_3$ eluent. Alternatively, it was also analyzed by non-suppressed ion chromatography on a Metrohom apparatus using a 4 mM benzoic acid/sodium 4-hydroxybenzoate buffer (pH 8.5). Nitrite was determined using the Griess reagent (Merck) and photometric determination at 543 nm. Ammonium ion was quantified by: (i) suppressed ion chromatography with HNO_3 2 mM as eluent; (ii) non-suppressed ion chromatography using HNO_3 4 mM, methanol/water at 30/70 v/v ratio eluent; (iii) the Nessler reagent (Merck) and the spectrophotometric determination at 410 nm; (iv) the Berthelot reagent (Merck kit) and spectrophotometric determination at 690 nm. Different methods have been used depending on the composition of solutions (chromatographic and spectral interferences, side-reactions) and to assure the reliability of measurements. Hydroxylamine were determined using GC/MS, after derivatization with hexylchloroformate [28].

Benzoquinonemonoimine, hydroxybenzoquinonemonoimine benzoquinone and hydroxybenzoquinone and other initial and produced organic molecules were clearly identified by GC/MS. The analytical procedure was previously reported [23]. Owing to the absence of stable standards, benzoquinonemonoimine and hydroxybenzoquinonemonoimine have been identified only qualitatively.

3. Results and discussion

The basic principles of photocatalysis have been discussed extensively elsewhere [6,29,39]. For the purpose of the present paper, the organic substrates (initial and intermediates) are considered to react through direct interaction with the carriers (conduction band electron and valence band holes) and with the trapped holes (hereafter called $^\bullet OH$ radicals). Besides the solvent, other species are present at the interface or in solution (e.g. $HO_2^\bullet/O_2^{\bullet -}$, O_2, H_2O_2) which can participate in the complex degradation scheme leading to final mineralization of the organics.

Since each compound of the series investigated here is converted in variable extent to all the others [23], it stems that photogenerated electrons and hydroxyl radicals simultaneously promote the reduction and the oxidation of the nitrogen-containing group and induce the hydroxylation of the aromatic moiety.

3.1. Carbon mineralization rate

The mineralization of organic carbon into CO_2 has already been reported for NB [14] and A [31]. We have focussed our attention on the TOC variation during photocatalytic experiment for NOB, a compound for which nitrogen is at an intermediate oxidation state. The results are shown in Fig. 1.

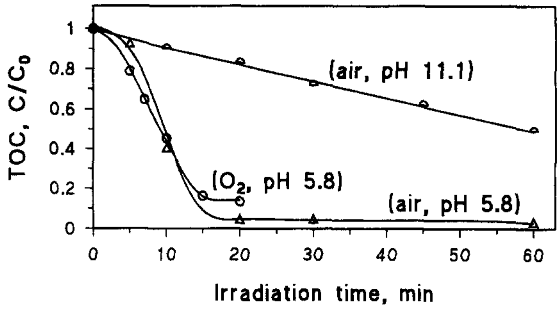


Fig. 1. Total organic carbon disappearance as a function of irradiation time, in oxygen atmosphere at pH 5.8 and at two pHs under air saturated conditions for the photocatalytic degradation of nitrosobenzene (NOB, 9.3×10^{-5} M) on TiO_2 (200 mg l^{-1}).

3.1.1. pH dependence

A remarkable pH effect is observed on TOC profiles, whereas NOB disappearance rate is only slightly affected by pH in the range 3–11 [23]. At pH 5.8 the TOC is less than 5% of the initial value after 20 min irradiation, whereas at pH 11 the TOC is reduced by one half only after 60 min irradiation. It seems that at basic pH, the evolution of the reaction intermediates is considerably slowed. The formation of organic species bearing a negative charge as the result of acid–base equilibria (i.e. phenols and carboxylic acids) is likely to reduce drastically the photocatalytic rate of degradation, since these species at basic pH are repelled by the negatively charged TiO_2 surface [32].

TOC measurements confirmed that the organic carbon content in the degradation of NOB was quantitatively (>95%) converted into carbon dioxide in short times when operating at pH<6.

3.1.2. Oxygen dependence

The slight detrimental effect of oxygen reported for NOB disappearance [23] is also observed in the related TOC measurement (Fig. 1). These results are quite unusual in photocatalysis, where a strong direct dependence of the photocatalytic degradation rate on the oxygen partial pressure has been reported for most compounds, as a result of the prevalence of oxidative processes [6].

The role of oxygen proved crucial for the complete mineralization (CO_2 formed) of the organics [33]. Its effect on the reaction rate has been described in terms of simple Langmuir adsorption isotherm or an equivalent functional form (Eq. (1)) giving the Langmuirian shape without requiring the hypotheses of surface adsorption and competition for the substrate and oxygen [34]:

$$\frac{-\mathrm{d}[D_\mathrm{s}]}{\mathrm{d}t} = \frac{k_\mathrm{f}\phi k_\mathrm{r}[A_\mathrm{s}]k_\mathrm{o}[D_\mathrm{s}]}{k_\mathrm{s}k_\mathrm{f}\phi + k_\mathrm{r}[A_\mathrm{s}]k_\mathrm{o}[D_\mathrm{s}]}, \qquad (1)$$

where the electron donor D (an oxidizable substrate) and the electron acceptor A (like oxygen) are at the surface s, k_f ϕ is the absorbed photon flux leading to the primary charge separation, k_r is the rate constant for the reaction of an electron with A, k_o is the rate constant for the oxidation of D with $^{\bullet}\mathrm{OH}$ or h^+ and k_s is the rate constant for $\mathrm{e}^-/\mathrm{h}^+$ recombination. Although obtained under some stringent hypotheses [34], Eq. (1) clearly indicates the role of electron donors and scavengers in semiconductor catalysis. Eq. (1) suggests that increasing the surface concentration of oxygen, the oxidation rate grows up with a saturative behavior. Electron scavengers other than oxygen have the same effect. Recent studies on photocatalyzed oxidation of organic compounds suggested that the quantum efficiency of the process can be limited by the kinetics of oxygen reduction [35], i.e. the value of k_r. A beneficial effect was observed in the degradation of dichloropropionic acid by incorporating Pd^0 at the surface of the catalyst, acting as a co-catalyst for electron transfer to oxygen. In another recent contribution concerning 4-chlorophenol it was reported that the use of an anodic bias obviates for the need of oxygen as an electron acceptor; however, the molecular oxygen itself plays an important role in the degradation course [36].

Generalization of Eq. (1) to more competing processes is trivial. It follows that at fixed $[D_\mathrm{s}]$ competing electron scavengers have each other an inhibitory effect. Indeed, this is shown in Fig. 1. The TOC parameter is the result of transformations involving different parent and intermediate structures. Thus, the experimental results suggest that (i) oxygen competes with some organic compounds; or, in turn, (ii) the mineralization of starting material implies some reductive pathways (in which some organic molecules take conduction band electrons in competition with oxygen). However, when reductive pathways characterize part of the overall degradation process, the dependence of TOC degradation rate on oxygen concentration is not straightforward. Some examples involve tetrachloromethane [37] and tetranitromethane [38] in which C and N are at their high oxidation state.

3.2. *Fate of nitrogen*

The distribution of ammonium and nitrate ions varies with irradiation time and type of initial organic substrate. The time evolution of nitrate, nitrite and ammonium ions for the photocatalytic transformation of NOB, PHA and A are reported in Figs. 2–4. The corresponding data for NB have been already reported [15]. Several forming and disappearing organic intermediates have been detected during the course of the mineralization process [23]. Besides the dependence on the very nature of the initial compound, the different final distributions of ammonium and nitrate ion

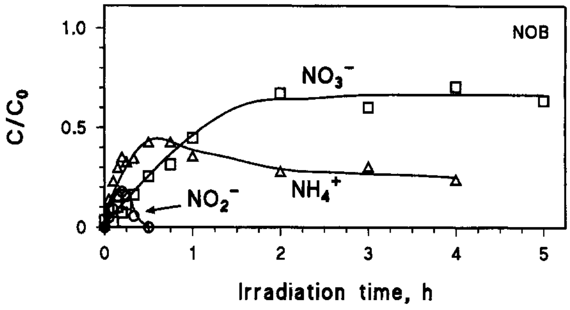


Fig. 2. Time evolution of nitrate, nitrite and ammonium ions at pH 5.8 under air saturated conditions for the photocatalytic degradation of nitrosobenzene (NOB, 9.3×10^{-5} M) on $\mathrm{TiO_2}$ (200 mg l^{-1}).

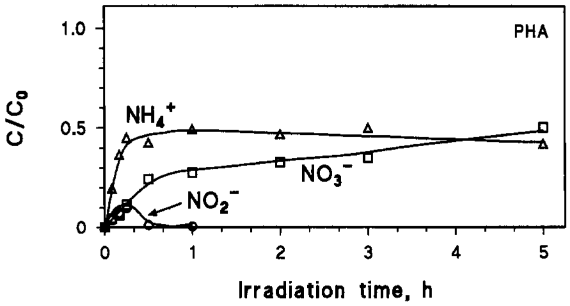


Fig. 3. Time evolution of nitrate, nitrite and ammonium ions for the photocatalytic degradation of phenylhydroxylamine (PHA 9.2×10^{-5} M, 200 mg l^{-1} of $\mathrm{TiO_2}$ at pH 5.8, under air).

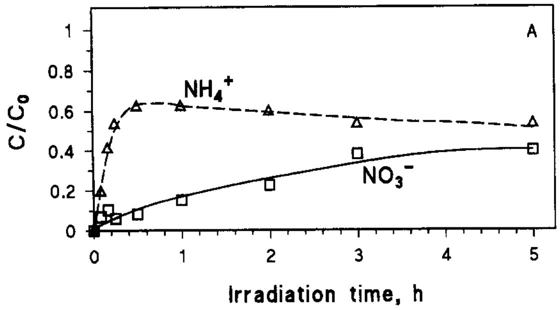


Fig. 4. Time evolution of nitrate, nitrite and ammonium ions in the photocatalytic degradation of aniline (A, 1.1×10^{-4} M, 200 mg l^{-1} of illuminated TiO_2 at pH 6.3 under air).

Table 1
Nitrate/ammonium ratio measured at $t=t_{TOC1/4}$ in the presence of 200 mg l^{-1} of TiO_2.

Compound (nitrogen oxidation state)	$[NO_3^-]/[NH_4^+]$ (mean oxidation state ±0.4)
Nitrobenzene (+3)	4:1 ($\cong$+3)
Nitrosobenzene (+1)	1:2 ($\cong$0)
Phenylhydroxylamine (−1)	1:4 ($\cong$−1)
Aniline (−3)	1:6($\cong$−2)

Initial concentrations of organic substrates (in parentheses) were: (NB) 8.1×10^{-5} M, (NOB) 9.3×10^{-5} M, (PHA) 9.2×10^{-5} M, (A) 1.1×10^{-4} M, respectively. In parenthesis is indicated the mean oxidation state, as averaged from the abundance ratio of nitrate (+5) and ammonium (−3) ions.

concentration observed may depend also on the photocatalytic interconversions of ammonium, nitrite and nitrate ions under the present experimental conditions.

3.2.1. Interconversion of inorganic nitrogen species

The irradiation of 5×10^{-4} M ammonium fluoride in aerated suspensions of 0.2 g l^{-1} of TiO_2 led to the slow formation of nitrate ions, which reach 13% of the initial ammonium concentration in 5 h. Nitrite ion was not detected even at very short irradiation times. Although chloride is known to have an inhibitory effect [39], whereas fluoride does not [32], no difference was observed when ammonium chloride was used as the starting material, probably because of the very low concentration of chloride.

The irradiation of 2×10^{-4} M sodium nitrite in aerated suspensions of 0.2 g l^{-1} of TiO_2 led to the rapid conversion of nitrite into nitrate ions. Stationary final concentrations (96% nitrate) were reached in about 30 min. Ammonium grew up to 6–8% in the first 10 min, then stabilized to 4% after 0.5–5 h.

The irradiation under photocatalytic conditions of 1.6×10^{-4} M sodium nitrate in aerated solutions did not produce nitrite even after 5 h of illumination. Only traces of ammonium ions are formed. Thus, nitrate ions can be considered as a stable product.

Although ammonia formation has been observed when nitrate solutions are photocatalytically treated in the presence of 2-propanol [40] or *tert.*-butanol [9] in deaerated conditions, the addition of 10 mg l^{-1} of phenol to nitrate, nitrite and equimolar solutions of nitrate/nitrite (1.0×10^{-4} M each) solutions had no significant effect on the concentration profiles described above and on ammonium formation from nitrate and nitrite. All the transformations referred to above produced significant changes neither in the rate nor in final ratios of the species by increasing TiO_2 concentration up to 1 g l^{-1}.

3.2.2. Inorganic nitrogen species formed from organics

The ratio $[NH_4^+]/[NO_3^-]$ after 75% TOC reduction is reported for four initial substrates in Table 1. The irradiation time for 75% TOC reduction is arbitrary, although corresponding to the time at which the initial substrate has completely disappeared and the concentration of the first produced intermediates starts to decline. At this time, after the disappearance of most of the initial parent molecules, the interconversion of inorganic nitrogen species is limited, except for nitrite to nitrate. The ratio $[NH_4^+]/[NO_3^-]$ depends on the very nature of the initial compound. Table 1 shows that there is a strong correlation between the oxidation state of nitrogen in the initial compound and the mean oxidation state of the final products.

Nitrite and nitrate are likely to be formed through nitrite radical release from nitroaromatics [15] or nitroaliphatics [41]. Radical $^\bullet NO_2$ can (i) react with hydroxyl radical [42] (rate constant 1.2×10^{10} M^{-1} s^{-1} in homogeneous solution)

$$^\bullet NO_2 + {}^\bullet OH \rightarrow HO_2NO \rightarrow H^+ + NO_3^-; \qquad (2)$$

(ii) compete with other species for the conduction band electrons, since the reaction

$$^\bullet NO_2 + e^- \rightarrow NO_2^- \qquad (3)$$

has been estimated to have a rate constant of $3\times10^{10}\,M^{-1}\,s^{-1}$ with aquated electrons [43]; (iii) disproportionate according to [44]

$$^{\bullet}NO_2 + {}^{\bullet}NO_2 + H_2O \rightarrow NO_3^- + NO_2^- + 2H^+ \qquad (4)$$

with a reaction rate constant of $1\times10^{8}\,M^{-1}\,s^{-1}$.

The sequence (2)–(4) and the above mentioned experiments on the photocatalytic oxidation of nitrite to nitrate account for the concentration profiles of nitrite and nitrate reported in Figs. 2–4. Nitrite forms and rapidly disappears, while nitrate concentration is monotonically increasing. As mentioned above, for longer irradiation time a contribution of ca. 10% can arise from ammonium conversion to nitrate.

More intriguing is the observed formation of ammonium ions in non-negligible amount during the photocatalytic degradation of nitro- and nitroso-compounds in aerated solutions [9,15]. Since only traces of ammonium ions were found in photocatalytic-treated nitrate solutions, ammonium ions could arise directly neither from nitrate nor from nitrite, at least not to the extent observed in nitrobenzene and nitrosobenzene degradation.

Closer inspection of the evolution rate of ammonium ions during NOB degradation (Fig. 2) reveals that formation of NH_4^+ predominates up to 1 h irradiation. It is worth noting that the oxidation state of nitrogen in NOB is +1, intermediate between +5 of nitrate and −3 of ammonia. Owing to the preceding discussion, nitrate ions, initially originated from nitrite, do not form ammonium ions (except for a small contribution).

In order to verify the possible influence of the nature of the semiconductor oxide, the degradation of NOB in the presence of WO_3 was compared to that occurring with TiO_2. WO_3 presents a +0.3 V increment in the reduction potential of the conduction band with respect to TiO_2 [45]. The evolution of nitrate, nitrite and ammonium ions arising from NOB degradation in the presence of WO_3 is depicted in Fig. 5. The comparison with their time evolution in the presence of TiO_2 shows that at the same irradiation time they are formed in lower amount and are far from the stoichiometric value. However, the ratios between [ammonium ion]/[nitrate]/[nitrite] do not differ significantly from those observed with TiO_2 in the first 10 min. Thus, at least for small changes in the positions of conduction and valence band potentials, the ratio of evolution of inorganic nitrogen species would not depend on the specific nature of the semiconductor, but on the nature of organic intermediates.

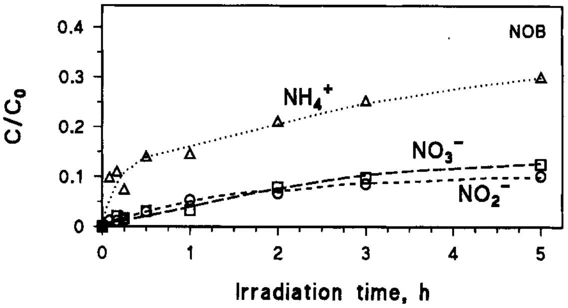


Fig. 5. Time evolution of nitrate, nitrite and ammonium ions at pH 5.8 under air saturated conditions for the photocatalytic degradation of nitrosobenzene (NOB, 9.3×10^{-5} M) on WO_3 ($1\ g\,l^{-1}$).

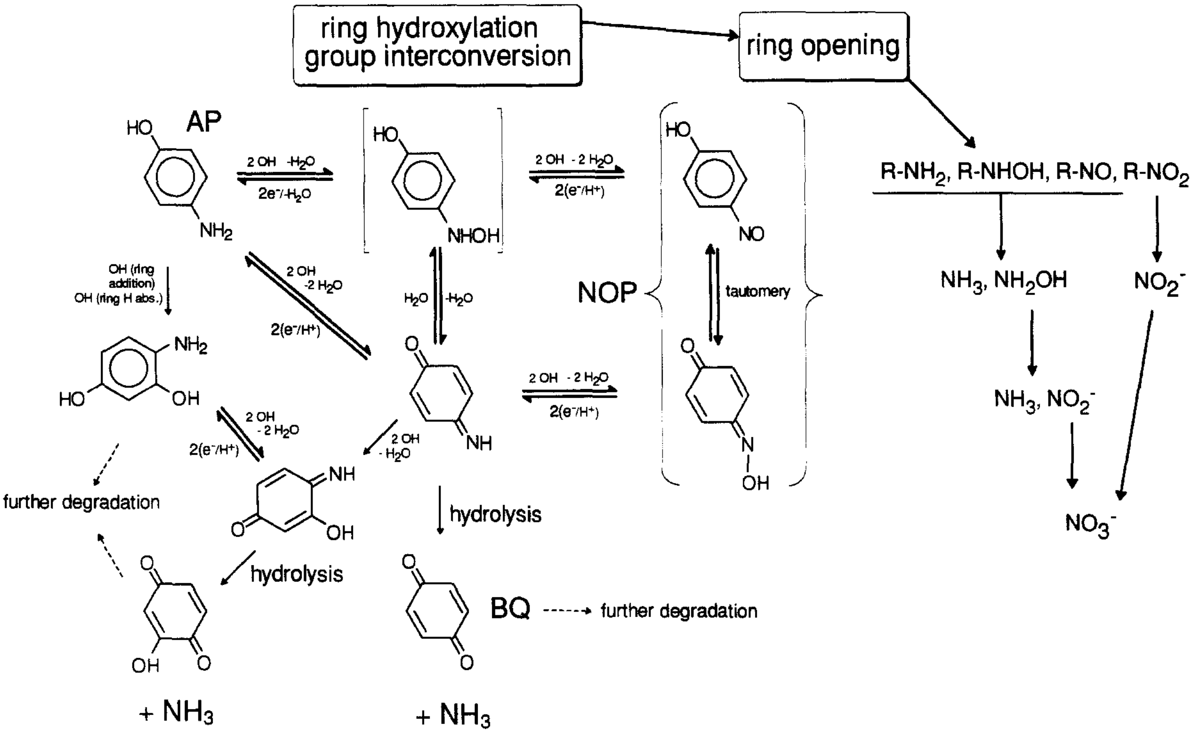
Ammonium ions may be mainly formed by reductive reactions involving the nitrogen-containing functional group of the organics. Since NB produces mainly nitrate, the reaction pathways that produce ammonia have to involve nitroso (and nitro) groups reduction. The remarkable variations of nitrite evolution as a function of the substrate supports this hypothesis. For example, in the photocatalytic degradation of NOB, nitrite ion concentration reaches 20% of the initial nitrogen while in the case of nitrobenzene reaches 40% [15]. For ammonium and nitrate this is also evidenced by the $[NO_3^-]/[NH_4^+]$ ratios observed for the four compounds under study after 75% TOC mineralization ($t_{TOC\ 1/4}$) (see Figs. 2–4 and Table 1). Table 1 shows also that there is a strong correlation between the oxidation state of the initial substrate and inorganic products formed before ammonia and nitrite to nitrate conversion.

Moreover, there is a correlation between the detected intermediates of degradation [23] and the type of final inorganic species. For example, for NOB the largest concentrations observed for major intermediates (given as mole percent of the initial compound) in the very initial steps of degradation are [NB]≈[PHA]≈[A] (18–25%)>[4-aminophenol] (15%)≫[nitrophenols] (1–2.5%); for PHA, [A] (30–35%)>[4-NOP] (25%)>[NOB] (15%)>[4-AP] (10%)>[NB] (5%); for A, [2-AP] (10%)≫[NB] (1.5%). These data show that as more concentration of reduced organic species is observed, more ammonium is released. The photodegradation of phenylhydroxylamine occurs by both oxidative and reductive pathways in comparable extent, and also NH_4^+ and NO_3^- are produced in equivalent abundances (see Fig. 3).

The trend of the average oxidation number of nitrogen, as calculated from the organic and inorganic compounds concentrations in the reaction mixture, as a function of irradiation time was previously highlighted [23]. The initial values of the nitrogen oxidation number (+3 for NB, +1 for NOB, −1 for PHA, −3 for A) are varying in the range ±0.5 in the initial 30 min of reaction. However, at longer times and in oxygenated solutions the conversion of ammonia to nitrate moves the average nitrogen oxidation number towards higher values (+5 for NO_3^-). If this view is extended to the compounds in Table 1 and to the ultimate fate of nitrogen, it could be concluded that in the early part of the process (up to $t_{\mathrm{TOC1/4}}$,), the photocatalytic transformations of aromatics with nitrogen-containing substituents involves transformations without significant modification of the mean oxidation state of nitrogen in the system, also including the inorganic species.

As far as the release of ammonia is concerned, it has to come out from reduced forms of organic nitrogen. Hydrolytic loss of ammonium ions was demonstrated from structures such as benzoquinoneimines [46,47], giving benzoquinone. Although not quantified precisely, benzoquinonemonoimine, hydroxybenzoquinone-monoimine, benzoquinone and hydroxybenzoquinone were clearly identified by GC/MS. The possible pathways are exemplified in Scheme 1.

In the case of aniline large amounts of ammonium ions are in fact detected at the very early steps of the degradation process (Fig. 4). The primary oxidation products, aminophenols, can easily undergo further oxidation or ring hydroxylation. Both reaction pathways can easily lead to (hydroxy)-quinonemonimine



Scheme 1. Formation of ammonia via (hydroxy)quinonemonoimine hydrolysis for the photocatalytic degradation of nitrobenzene, nitrosobenzene, phenylhydroxylamine, aniline, nitrosophenol (NOP), nitrophenols, and aminophenol (AP). Pathways of benzoquinone (BQ) formation is also shown. Nitrate and nitrite ions are formed from $^{\bullet}NO_2$ through reactions (2)–(4) reported in the text. Only the *para*-isomers are shown for clarity.

from which ammonia and quinone are released. Interestingly, ammonia release follows aniline oxidation. Similarly, oxidative treatment of anilines and 4-aminophenol by ClO_2 are reported to give ammonia through the fast quinonemonoimine hydrolysis in slightly acidic media [47]. For PHA the ring hydroxylation followed by water loss can easily give quinonemonimine and ammonia, justifying the observed sustained production of ammonia versus nitrite (nitrate). For NOB, oxidation to NOP or reduction to PHA, followed by reduction or oxidation, respectively, to quinonemonoimine lead to a rate of ammonia production larger than nitrite (nitrate) in early steps of degradation.

The nitrogen fate in the degradation of 4-NOP is different from that observed for NOB. After 1 h irradiation in the presence of 10 mg l^{-1} TiO_2 the concentration ratio $[NH_4^+]/[NO_3^-]$ is as high as 5 and tends to 1 only after 5 h irradiation (Fig. 6). This result suggests that the reductive processes are predominant in the photocatalytic degradation of 4-NOP, even more than for NOB. In aqueous solution, 4-NOP is principally present in the benzoquinonemonoxime tautomeric form [48]. From our data, it appears that this structure can be more easily reduced than oxidized under photocatalytic conditions. This assumption explains both the predominant production of ammonium ions and the very low concentration of 4-nitrophenol formed, in comparison with the much more relevant production of nitrobenzene from the NOB degradation [23].

It sorts out that under aerated photocatalytic conditions, the initial redox steps occur largely at the nitrogen substituents. Nitrate ions are formed rapidly through nitrite and more slowly from ammonium ions. Ammonium ions are released in oxygenated solutions even from organic compounds in which nitrogen is initially at high oxidation number. For these compounds, reductive pathways operate on the nitrogen substituent and ammonia is released from unstable intermediates, probably imino derivatives either quinonoid or aliphatic. In contrast, from highly reduced compounds (e.g. aniline) the release goes through an initial oxidation step. The balance of these paths depends on the initial nature of the organic compound and is responsible for the $[NH_4^+]/[NO_3^-]$ ratio in the early degradation process.

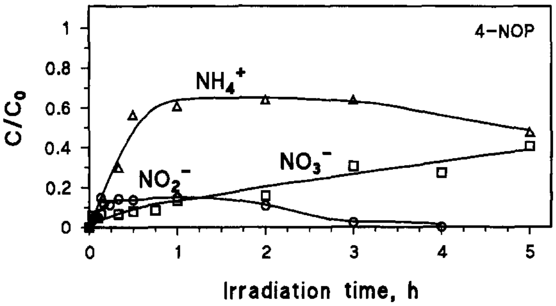


Fig. 6. Formation of nitrate, nitrite and ammonium ions in the photocatalytic degradation of 4-nitrosophenol (NOP, 4.4×10^{-5} M) in the presence of 10 mg l^{-1} of TiO_2 at pH 5.8 under air.

Since inorganic nitrogen species are formed also after the disappearance of the aromatic intermediates, it follows that aliphatic compounds containing nitrogen substituents are formed and subsequently release these ions (see Scheme 1, right). Oxidative release of ammonia from aliphatic amines has been reported in electrochemical oxidation through imino-intermediates [49]. The mechanism of photocatalytic release of nitrogen inorganic species from aliphatic derivatives is under investigation.

Finally, the fast evolution of ammonia suggests that under photocatalytic conditions a possible assisted hydrolysis could operate on benzoquinoneimine structures. The photocatalytically assisted hydrolysis would consist of sequences of $^\bullet OH$, e^-/H^+ reactions (equivalent to H_2O addition), with null redox change on the substrate. This process would accelerate the hydrolysis step [46,47] responsible for ammonia release.

For further reading

Refs. [30,45]

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