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Photocatalytic interconversion of nitrogen-containing benzene derivatives

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The role of the electrons and holes at the surface of semiconductor oxides (TiO_2 and WO_3) in heterogeneous photocatalysis has been investigated in aqueous media for the reactions involving the series: nitrobenzene, nitrosobenzene, phenylhydroxylamine, aniline, and the related compound, 4-nitrosophenol. Qualitative and quantitative evaluation of most intermediates and their time evolution suggest that the reductive pathways are important and even predominant under a variety of experimental conditions. This aspect is not only true at the beginning of the process or for the readily reducible structures, but also during the entire degradation process.

Each compound of the series is converted to all the others, even though in widely different amounts. In the early part of the photocatalytic process, with nitrosobenzene and with phenylhydroxylamine, even in the presence of oxygen, the nitrogen substituent undergoes simultaneous oxidation and reduction at comparable rates, so that very little change in the mean oxidation state of the system is observed. This suggests that photogenerated electrons have a controlling role, particularly for some compounds in the early steps of the photocatalytic transformation. For 4-nitrosophenol and *p*-benzoquinone, in the early steps of degradation the reductive pathways represent the main route, even in the presence of oxygen. As a consequence, for some compounds the presence of an excess of oxygen in the reacting atmosphere decreases the degradation rate, instead of promoting it, as is commonly observed in photocatalysis. It is also remarkable that, for some compounds examined, the redox reactions at the nitrogen-containing substituent have a comparable or even more important role than the hydroxylation of the aromatic ring, which was the predominant degradation pathway for most of the other aromatic compounds.

Introduction

Light-induced electron-transfer reactions on semiconductor oxides represent a very active research area for the implications that these reactions have on environmental processes and on the construction of devices for energy production. Heterogeneous photocatalytic processes have proved capable of converting solar energy into chemical or electrical energy, provided new synthetic routes to organic chemistry and have offered valuable alternatives to conventional methods for the removal of organic pollutants from waste- and ground water.[1]

In the last domain, titanium dioxide-mediated photocatalytic processes in aerated aqueous slurries were shown to attack even highly refractory compounds, which could be totally converted into carbon dioxide and inorganic ions. The possible mechanisms for the overall oxidation process have been considered in detail, although some questions remain unanswered.[1–6]

Organic compounds containing nitrogen atoms are extremely common in nature (amino acids and proteins) and several classes of man-made substances of environmental concern have nitrogen atoms in their structure (herbicides and pesticides, drugs, explosives, dyes *etc.*). As a consequence, increasing attention has been addressed to the photocatalytic degradation mechanism of nitrogen-containing functional groups and the ultimate fate of the nitrogen moiety.[7–16] The reduction of substituted nitrobenzenes has been carefully investigated, both for its ecotoxicological importance in the subsurface environment and for the treatment of hazardous wastes and contaminated soils.[17–19]

The reaction pathways by which nitrobenzene, nitrosobenzene, phenylhydroxylamine, aniline and a few related derivatives are transformed in oxygenated and deoxygenated aqueous solution by the action of irradiated semiconductors have been investigated and, in the present report, particular attention is addressed to the transformation of the nitrogen functional groups and to the interconversion of the compounds in the series as a function of experimental conditions. Investigation of further degradation steps leading to mineralization into carbon dioxide and inorganic nitrogen compounds will be presented in a forthcoming study. Nitrobenzene has been studied in detail recently,[12,13] so only a few further experiments involving it are presented here as a basis for comparison with the other substrates.

Experimental

Reagents

Nitrobenzene (NB), *o*-, *m*- and *p*-nitrophenols (NP), nitrosobenzene (NOB), 4-nitrosophenol (4-NOP), aniline (A), *o*-, *m*- and *p*-aminophenols (AP), hydroquinone (HQ), *p*-benzoquinone (BQ) and hydroxylamine were 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 zinc dust[20] and recrystallized twice from cold water.

Titanium dioxide TiO_2 P25 (BET area 55 $m^2\ g^{-1}$, 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. Titania loaded with 1% of platinum (Pt^0) was prepared by photocatalytic reduction of hexachloroplatinate ions. The aqueous TiO_2 slurry was added to Na_2PtCl_6 (Aldrich) and illuminated until H_2 was detected. The powder was recovered and washed with deionized, bidistilled water. WO_3 of BET surface area 1 $m^2\ g^{-1}$[21] was purchased from Ventron.

Irradiation experiments

Suspensions of the catalyst were prepared at different 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 ppm) of organics and 200 mg l^{-1} (ppm) of TiO_2. The cells containing the reaction slurry were kept in a water bath in the dark until they reached the working temperature of the lamp housing (*ca.* 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. Irradiation conditions have been described elsewhere.[22,23] Total photon flux (340–400 nm) in the cell was 1.35×10^{-5} ein min^{-1} (1 ein = 1 mole of photons). 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 analysed without further clean-up. In the experiments carried out in the absence of oxygen, the cells were purged with helium for 0.5 h before the organic substance was added and subsequently irradiated.

Analytical procedures

The aqueous solutions obtained upon filtration of the reaction slurry were extracted three times with CH_2Cl_2. The organic extracts were concentrated to small volume under vacuum and then to *ca.* 300 µl in conical vials under a stream of argon. The concentrated extracts were analysed by gas chromatography–mass spectrometry (GC–MS) in electron impact (EI) mode, from which the semivolatile products were identified. Qualitative and quantitative determinations were carried out using authentic standards. Benzoquinonemonoimine, hydroxybenzoquinonemonoimine and hydroxybenzoquinone were identified only on the basis of their mass spectra. Aniline and hydroxylamine were determined using GC–MS, after derivatization with hexylchloroformate.[24] GC–MS experiments were performed on a Finnigan-MAT 95 Q hybrid instrument, with magnetic, electrostatic and quadrupole analysers. Ions were collected at the first detector, located after the electrostatic sector. Samples were injected splitless into a Varian 3400 gas chromatograph equipped with a J&W DB-5MS 30 m × 0.25 mm capillary column, 0.25 µm film thickness. The oven temperature was programmed as follows: isothermal at 50 °C for 3 min, from 50 °C to 300 °C at 12 °C min^{-1}, isothermal at 300 °C for 10 min.

Qualitative and quantitative determinations of initial compounds and reaction intermediates were carried out by high-performance liquid chromatography (HPLC) using authentic standards. Determinations were performed by UV detection (model L6200 and model 6000 Hitachi-Merck pumps with model L4200 UV) and using an RP-18 column (Lichrocart 5 µm, 150 mm long). Different eluents were used, depending on the analytes under study: acetonitrile–phosphate buffer 5×10^{-2} M, pH 2.8 (eluent A); acetonitrile–1-hexanesulfonic acid 1×10^{-2} M in phosphate buffer 5×10^{-2} M, pH 2.8 (eluent B). The buffer was used for eluting acid compounds in their undissociated form and to avoid peak tailing. Solutions of pure authentic standards were used for quantitative assessment, whenever commercially available.

Nitrobenzene and nitrophenols were detected at 210 nm using either eluent A or B at 35/65 v/v ratio; nitrosobenzene was determined at 307 nm using the same eluents; 4-nitrosophenol was also detected at 307 nm using both eluent A and B at 13/87 v/v ratio; phenylhydroxylamine and aniline at 197 nm using eluent B at 14/86 v/v ratio; 2- and 3-aminophenol were determined at 208 nm using eluent B at 7/93 v/v ratio; 4-aminophenol at 208 nm with eluent B at 5/95 v/v ratio; BQ at 246 nm using eluent A at 10/90 v/v ratio; HQ at 195 nm using eluent A at 5/95 v/v ratio. The wavelength selection was based on maximum analytical sensitivity. Under these conditions, retention times were (in parentheses, min): NB (7.91), 2-NP (6.34), 3-NP (3.98), 4-NP (3.64), NOB (9.04), 4-NOP (4.33), PHA (4.55), A (3.28), 2-AP (7.30), 3-AP (5.80), 4-AP (4.40), BQ (4.35), HQ (3.48), respectively.

Results and Discussion

Primary events and reactive species at irradiated TiO_2

The reactions and species, occurring at the surface of irradiated semiconductors, have been discussed in detail elsewhere.[1–6] In the forthcoming paragraphs reactions of hydroxyl radical and aquated electrons in aqueous homogeneous solutions are referred to for comparison. However, heterogeneous photocatalytic processes involve reactions at the surface/solution interfaces where (i) the oxidizing species can be either holes (more oxidizing than aqueous hydroxyl radical)[25] or trapped holes (*i.e.* $^{\bullet}OH_{ads}$, less oxidizing than aqueous hydroxyl radical); (ii) the reducing species can be conduction band electrons or trapped electrons, both being much less reducing than aqueous hydrated electrons. For the sake of simplicity, the photocatalytic process is usually depicted by considering only the main processes, where the organic substrates (initial and intermediates) can react through direct interaction with the carriers and with the trapped holes (hereafter called $^{\bullet}OH$ radicals). Photogenerated electrons and hydroxyl radicals concurrently promote the reduction and the oxidation of the nitrogen-containing group and induce the hydroxylation of the aromatic moiety. Oxidative steps are presented both as hydrogen abstraction and OH addition, but these are only symbolic representations of the actual two-step mechanisms involving surface-bound species. However, besides the solvent, other species present at the interface or in solution (*e.g.* $HO_2^{\bullet}/O_2^{\bullet-}$, O_2, H_2O_2) may participate in the degradation scheme leading finally to mineralization of the organics.

All the starting structures involved, and the initial intermediates, detected by GC–MS and HPLC are considered in Scheme 1 that will be discussed in detail later. Although not quantified precisely, benzoquinone, benzoquinonemonoimine, hydroxybenzoquinonemonoimine and hydroxybenzoquinone were clearly identified by GC–MS.

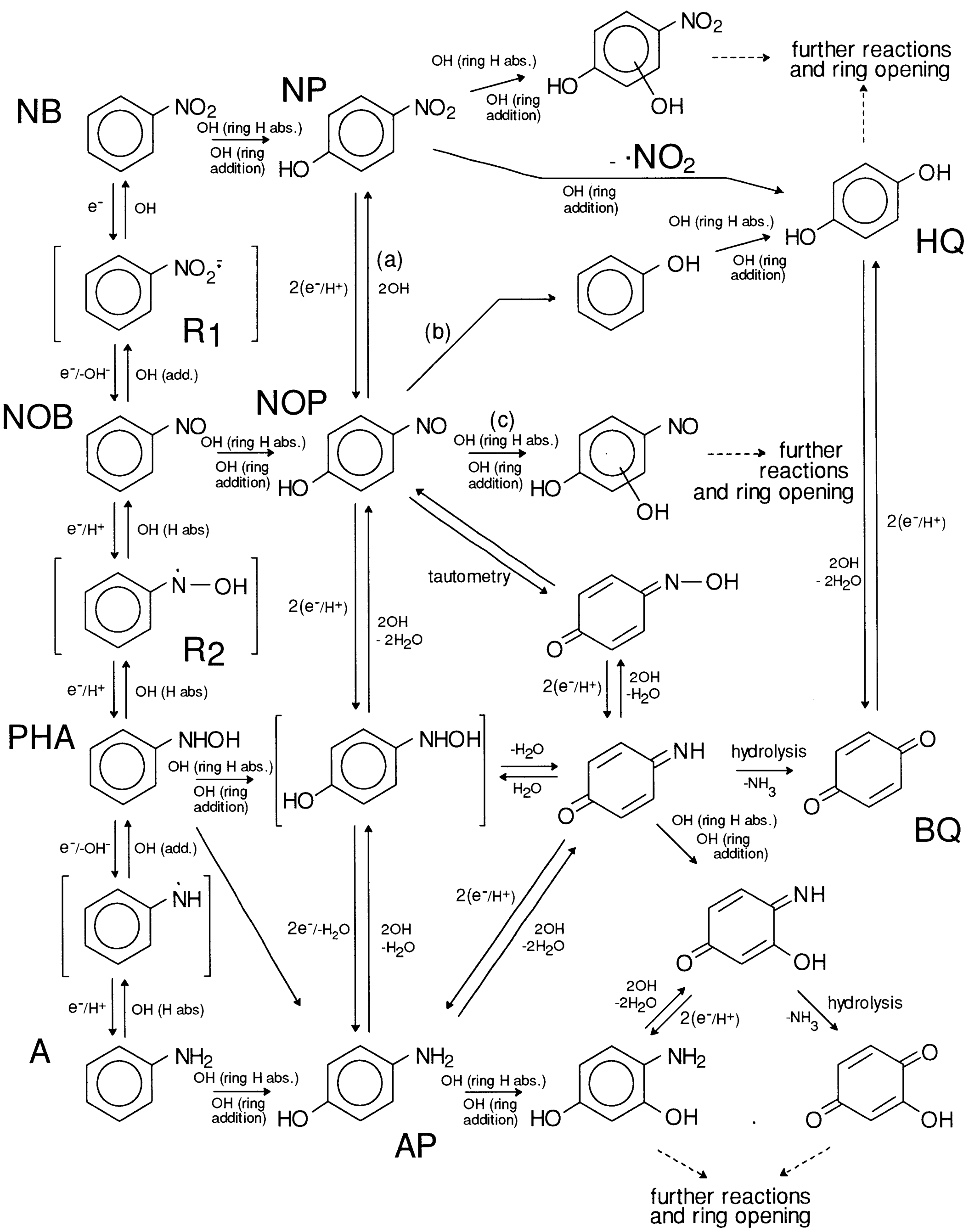
Interconversion of the functional groups

Nitrosobenzene. In the investigations reported previously,[12,13] only small amounts of reduced species (NOB, PHA, A) were found to be produced from the photocatalytic degradation of nitrobenzene and 4-nitrophenol (4-NP). During the degradation of 4-NP, 4-aminophenol was produced at a maximum concentration of 2% of the initial substrate concentration (after 2 min irradiation). The high degradation rate constants found for NOB and PHA in the present study under identical conditions justify such low concentrations of reduced compounds. High rate constants for the decomposition of the reduced species can account for the attainment of low steady-state concentrations in the degradation of NB and 4-nitrophenol, even in the case when reduction is the major degradation path.

The photolysis of NOB has been reported in non-aqueous solvents (freon,[26] ethanol[27]), assuming, for the initial step:

$$C_6H_5NO \xrightarrow{h\nu} C_6H_5^{\bullet} + NO \qquad (1)$$

Owing to the small amount of phenol (<0.01%) found in the present experiments and the slow degradation of NOB in



Scheme 1 Early steps of oxidative and reductive photocatalytic pathways proposed for degradation of NB, NOB, PHA, A, NOP, NP, AP, BQ and HQ. Only the *para*-isomer is shown for clarity (when applicable). The ring hydroxylation is illustrated by two consecutive OH attacks, initially leading to H abstraction and subsequently to OH addition onto the radical formed.

the absence of the photocatalyst (15% of NOB was decomposed after 5 h irradiation), the contribution of direct photolysis [eqn. (1)] appears to be modest in the overall degradation process.

In the presence of a small amount of TiO_2 (200 mg l^{-1}) and UV light, nitrosobenzene disappears very rapidly (see Fig. 1). Table 1 reports the NOB decay rate constants as a function of both the catalyst and initial substrate concentrations. The behaviour is saturative, as usually reported for photocatalytic transformations. As proposed and verified recently,[28,29] the saturative behaviour as a function of catalyst and substrate concentration can be ascribed to primary photochemical processes, independent of the adsorption of substrates. The effects of temperature, pH, catalyst loading and composition of the gas phase on the decay rate constant are reported in Table 2. Fig. 1 shows the evolution of major and minor detected intermediates corresponding to NOB degradation. Although not comprehensive, the species reported account, after 1 min irradiation, for *ca.* 80% of the organic matter present in the system.

The analysis of product evolution at short irradiation times under photocatalytic conditions reveals that a large part of the photocatalytic reactions takes place at the nitrogen-

Table 1 Monoexponential decay rate constant (min^{-1}) for different concentrations of NOB and TiO_2 under air-saturated conditions

	NOB concentration			
TiO_2 /mg l^{-1}	9.3×10^{-5} M	1.9×10^{-4} M	4.7×10^{-4} M	9.3×10^{-4} M
50	0.66 ± 0.07	—	—	—
100	1.21 ± 0.10	—	—	—
200	1.39 ± 0.18	0.81 ± 0.03	0.39 ± 0.02	0.24 ± 0.01
500	1.39 ± 0.09	—	—	—
1000	1.49 ± 0.11	—	—	—

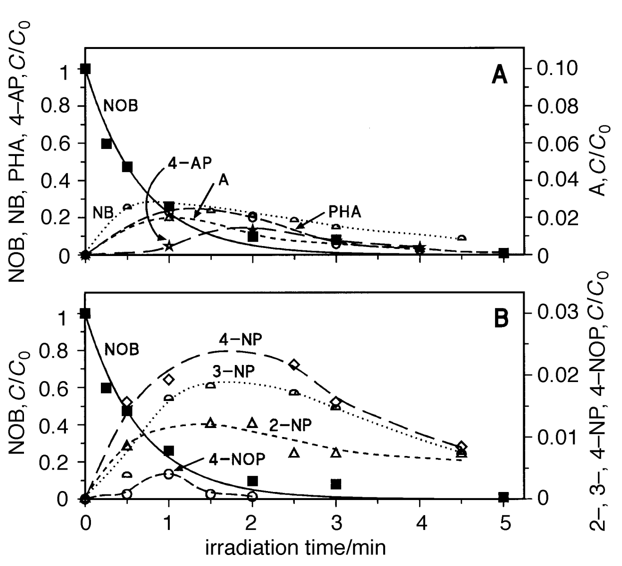


Fig. 1 Photocatalytic degradation of NOB (9.3×10^{-5} M) on TiO_2 (200 mg l^{-1}) at pH 5.8 as a function of irradiation time: (A) NOB and time evolution of the main intermediates, NB, PHA, 4-AP and A; (B) time evolution of minor intermediates, NP, 4-NOP

containing substituents and involves e^- and h^+ in comparable extents. For NCB degradation, NB and PHA (peaks after *ca.* 1 min) account for *ca.* 25% each of the initial concentration of NOB (75% degraded). The symbolic reaction (2) exemplifies this reaction course.

$$2C_6H_5NO \xrightarrow{+H_2O} C_6H_5NO_2 + C_6H_5NHOH \qquad (2)$$

The average oxidation number of nitrogen, in the organic compounds present in the reaction mixture, as a function of irradiation time, is quite significant. The value of the average nitrogen oxidation number (by assuming +3 for NB, +1 for NOB, −1 for PHA, −3 for A) is varying in the range ±0.5 in the initial 30 min of reaction.

These considerations and the nature of the intermediates detected suggest the occurrence of the reactions depicted in the upper part of Scheme 1 as viable early steps in the oxidative degradation process. Among the possible oxidative routes accounting for NOB degradation, the conversion of NOB to NB and further oxidation of the latter appears to be the most favourable. However, the direct hydroxylation of the NOB aromatic ring, yielding three nitrosophenol isomers, is also likely to represent an important competing process, as suggested by the detection of 4-NOP, despite its fast degradation kinetics (see later) and its consequent low tendency to accumulate.

The degradation route represented by the oxidation of the functional group (from nitroso to nitro) is peculiar to this class of compounds, since previous investigations on benzene derivatives indicated the hydroxylation of the aromatic ring to be the most important process. It is worth noting that exposure of dilute NOB solution to ^{60}Co γ-rays under N_2O atmosphere led to nitrobenzene formation.[30] It has been reported that, under pulse radiolytic conditions, ˙OH radicals in homogeneous solutions give $C_6H_5NO_2^{\cdot -}$ from NOB ($k = 1 \times 10^{10}$ l mol^{-1} s^{-1}).[30] This radical (radical R_1 in Scheme 1) is a weak acid ($pK_a = 3.2$). Further reactions of this radical in homogeneous solution are either: (i) direct e^- abstraction by ˙OH radical to give NB; (ii) disproportionation in the presence of NOB[30] to produce NB and nitrosobenzene radical ($C_6H_5NOH^{\cdot}$, a very weak acid with $pK_a = 11.7$, reported in Scheme 1 as R_2);[30] radical R_2 can, in turn, (iii) undergo electron exchange with $C_6H_5NO_2^{\cdot -}$ (R_1) to give NB and PHA ($k = 5 \times 10^5$ l mol^{-1} s^{-1} for the dismutation)[30] or (iv) directly acquire an electron to give PHA.

The reductive reactions of NOB are reported in the lower part of Scheme 1. NOB reacts with electrons in homogeneous solution at a rate slightly higher than with ˙OH radicals ($k = 4 \times 10^{10}$ l mol^{-1} s^{-1})[30] giving the nitrosobenzene radical ($C_6H_5NOH^{\cdot}$, R_2). Further reduction of this radical by electron capture and charge neutralization (addition of one proton) produces PHA. As cited above, radical R_2 can exchange electrons with other species in solution, whose concentrations possibly influence the reaction kinetics.

In the electrochemical reduction of NOB pH appears to be the most important factor controlling the route of reduction, although the products may be influenced by the nature of the cathode.[31] In weakly acidic media, as in the present experiments, aromatic hydroxylamines and nitroso components are formed. However, the aromatic hydroxylamines are not readily reduced (at least at the metallic cathode) and may rearrange to *p*-AP (see Scheme 1). PHA and 4-AP give rise to formation of quinonemonoimine or to further hydroxylation, oxidation and ring opening.

Table 2 Monoexponential decay rate constants (min^{-1}) for NOB (9.3×10^{-5} M), PHA (9.2×10^{-5} M) and A (1.1×10^{-4} M) in the presence of TiO_2 (200 mg L^{-1}) as a function of different temperatures, gaseous phases and pH

	temperature			
compound	20 °C	35 °C		50 °C
NOB	0.73 ± 0.07	0.80 ± 0.07		0.90 ± 0.17
	gas phase			
	air	O_2	He	He +0.1 M *tert*-butanol
NOB	1.39 ± 0.18	0.86 ± 0.05	2.45 ± 0.40	3.04 ± 0.33
PHA	0.88 ± 0.08	—	0.12 ± 0.02	0.43 ± 0.03
	pH			
	3.2	5.8	6.3	11.1
NOB	0.99 ± 0.11	1.39 ± 0.18	—	1.03 ± 0.17
A	0.12 ± 0.01	—	0.15 ± 0.01	0.45 ± 0.01

The compound concentration was followed as a function of the irradiation time. The photocatalytic disappearance of the starting materials can be reasonably represented by pseudo-first-order kinetics:[25] $C = C_0 \exp(-kt)$. The reported first-order degradation constants refer to experiments in which the decrease of C with time followed monoexponential decay law with good correlation at least to $C_0/2e$.

Apart from the preliminary transformations of the substrates, mainly involving their functional group, the progressive attack of the aromatic ring of NB,[13] phenol,[32] NOPs, PHA and 4-AP by means of photocatalytic reactions is indicated by the detection of several hydroxylic and quinonoid derivatives.

In the present photocatalytic study, the change from air atmosphere to pure oxygen decreased the NOB disappearance rate (see Table 2), contrasting with the expectation for an oxidation-driven degradation process. The slight detrimental effect on the rate of NOB disappearance is probably due to the competition of oxygen with organics for reduction by conduction band electrons. 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.[33]

In our experiments, when He was substituted for O_2 (Fig. 2), the initial NOB disappearance increased substantially (Table 2), and PHA became by far the major product, with almost 70% yield after 2 min irradiation. Interestingly, the rate of NOB disappearance is very close to the initial PHA formation rate. NB was formed to a much lower extent (only 3%) than in air-saturated conditions, while aniline tended to accumulate slowly. The absence of an antagonist for electrons, such as O_2, increased the reduction pathway rate, as indicated by the high PHA concentration. However, the comparison between Fig. 1(A) and Fig. 2(A) indicates that holes (h^+) or trapped holes (formally $^{\bullet}OH_{ads}$), are both kinetically inadequate oxidizers for NOB, while O_2 molecules may participate in the initial oxidation step as photoadsorbed species according to the following reaction:

$$\text{R-NO} + O_{2(ads)} + 2H^+ + 2e^-_{CB} \rightarrow \text{R-NO}_2 + H_2O \qquad (3)$$

This kinetic inhibition (see Table 2) is less pronounced for PHA (which is more easily oxidized than NOB, see later), although in this case also the absence of oxygen makes the reductive pathways more important than the oxidative ones. The scavenging of holes or trapped holes may proceed through the formation of surface peroxo-species[34] or by hydroxylation of the PHA aromatic ring (accounting for 20% of the organic carbon content not detected).

The relative significance of reduction pathways (see Scheme 1) is enhanced by the presence of an $^{\bullet}OH$ scavenger such as *tert*-butanol [Fig. 2(B)]. Under these experimental conditions, nitrobenzene was not produced during the degradation while phenylhydroxylamine reached *ca.* 40% of the initial NOB concentration after 30 s irradiation and rapidly converted to aniline, which became the major product reaching 55% after 6 min. As in the case of Fig. 2(A), the rate of NOB disappearance was very close to the initial rate of PHA formation. These results can be rationalized by considering that the conduction band electrons are completely available for reacting with the organic substrate, while $^{\bullet}OH$ radicals are trapped by *tert*-butanol.

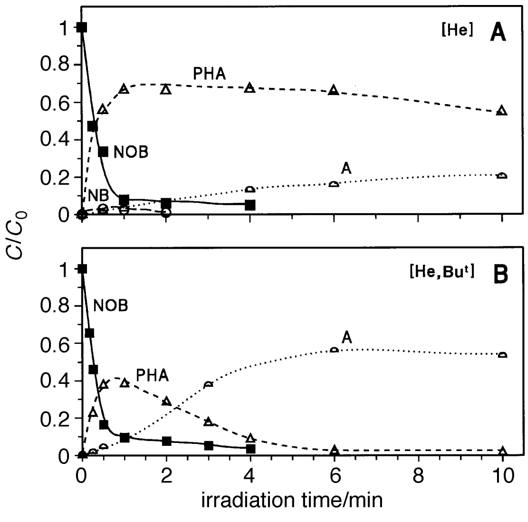


Fig. 2 Disappearance of NOB and formation of intermediates in the photocatalytic degradation carried out (A) under helium atmosphere and (B) under helium atmosphere and in the presence of 0.1 M *tert*-butanol (other conditions as in Fig. 1)

The deposition of Pt^0 onto TiO_2 [Fig. 3(A)] slightly decreases the NOB degradation rate ($k = 0.86 \pm 0.08$ min^{-1}) and modifies the product distribution for reduced species, such as PHA, and the time evolution of nitrophenols. The platinum islands were reported to act as pools of electrons.[35] For example, they lead to hydrogen evolution in the so-called 'sacrificial systems' for photocatalytic water cleavage.[36] They also produced a more efficient reduction of oxygen.[37,38] This effect decreases the availability of electrons for the reduction of the organic compounds.

The temperature at which the photocatalytic degradation was carried out showed little effect on the degradation rate of NOB (Table 2). While some authors have obtained data exhibiting an Arrhenius type behaviour and activation energies ranging from 10 to 16 kJ mol^{-1},[6] other studies report very low values of activation energy and even a decrease in the disappearance rate with the increase of the temperature.[39] These activation energies are comparable with those measured for the reactions of both $^{\bullet}OH$ radicals and e_{aq}^- with several organic substrates in homogeneous phase. It has been reported that E_{act} ranges from 11 to 18 kJ mol^{-1} for the reaction of e_{aq}^- with nitrobenzene and 4-nitrophenol, and from 5 to 10 kJ mol^{-1} for the reaction of $^{\bullet}OH$ with formate and 2-methyl propan-2-ol.[40]

A variation in pH is likely to affect both the charge of the TiO_2 surface and the speciation of the organic substrate. In the case of NOB, no major effect is expected because of the aprotic character of the organic (in the investigated pH range). Although TiO_2 P25 has a pH_{zc} of 6.25,[34] no dramatic variation of the NOB degradation rate is observed in the pH 3–11 range (Table 2). This is the usual behaviour reported for neutral molecules.

The photocatalytic activity of another semiconductor oxide, WO_3,[41] was compared with TiO_2. WO_3 presents a +0.3 V increment in the reduction potential of the conduction band

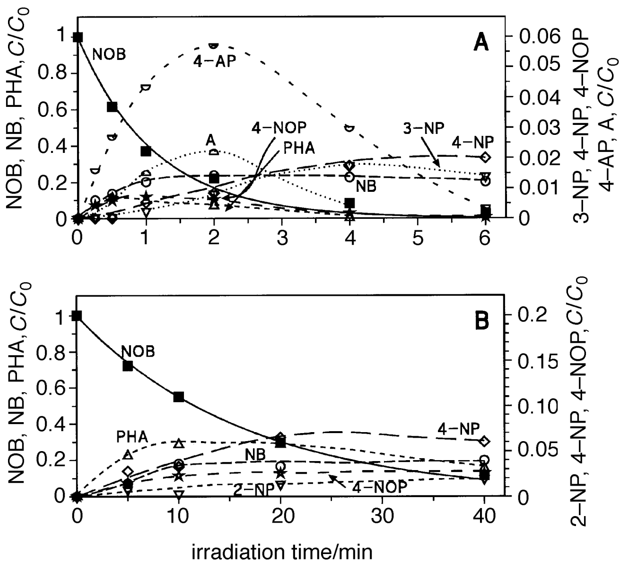


Fig. 3 Photocatalytic degradation of NOB (9.3×10^{-5} M at pH 5.8) and time evolution of intermediates: NB, PHA, 4-AP, A, 4-NOP and NP: (A) on TiO_2 loaded with 1% of Pt (200 mg l^{-1}) and (B) on WO_3 (1 g l^{-1})

with respect to TiO_2. The degradation rate of NOB in the presence of 1 g l^{-1} WO_3 is slower [see Fig. 3(B)]. As for titanium dioxide, NB and PHA are the most important intermediates, reaching 20% and 35% of the initial NOB concentration, respectively. Despite the different reduction potential of the conduction band, the reductive pathways still play the predominant role, as proved by large PHA formation. 4-NOP, 2- and 4-NP are formed in lower abundances, ranging from 2% to 7% of the initial NOB concentration.

Phenylhydroxylamine. The photodegradation of phenylhydroxylamine occurs by both oxidative and reductive pathways to comparable extents. This deduction is based on the observation [Fig. 4(A)] that oxidation and reduction intermediates are formed approximately in the same amount ([4-AP] + [A] *vs.* [NOB] + [NOP]).

Under He atmosphere [Fig. 4(B)], the PHA degradation rate decreased considerably in comparison to the standard conditions (Table 2). Concurrently, aniline formation increased considerably, reaching 15% instead of 1% as in the presence of oxygen, while 4-aminophenol became the predominant intermediate reaching *ca.* 30% with respect to the initial PHA concentration after 15 min. Conversely, the abundance of oxidized products declined. Nitrosobenzene concentration rose to 15%, as in air, but after 15 min irradiation reached a constant 8% value, while it kept decreasing in air atmosphere until it disappeared. Nitrobenzene showed very similar behaviour.

The addition of *tert*-butanol [Fig. 4(C)] consistently favoured the formation of aniline (*ca.* 80%). Nitrobenzene and nitrosobenzene reached only 5% of the initial PHA concentration. The degradation rate constant for PHA (see Table 2) was intermediate between those obtained in air and in helium atmosphere. Note that the degradation rate reached its minimum value when both electron and hole scavengers are absent. This observation can be easily rationalized by the kinetic model proposed recently.[28] From these results we can also deduce that oxygen plays an important role, not only as an electron scavenger, but also in the oxidative chain (reactions not reported in Scheme 1).

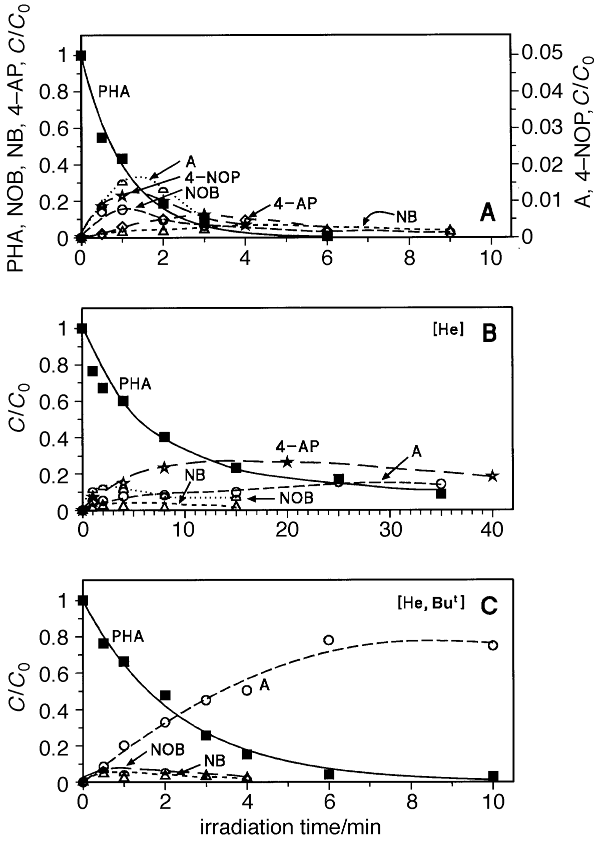


Fig. 4 Photocatalytic degradation of PHA (9.2×10^{-5} M, 200 mg l^{-1} of TiO_2 at pH 5.8) and formation of intermediates (A) under air, (B) under He atmosphere and (C) under He and in the presence of 0.1 M *tert*-butanol

The degradation pathways of PHA are depicted within the general Scheme 1. The initial oxidative attack on the molecule could either involve the nitrogen-containing group, giving nitrosobenzene (see the preceding discussion), or the aromatic ring, giving hydroxyphenylhydroxylamine isomers. The detection of these species is problematic as discussed previously. When the oxidative path is limited by *tert*-butanol scavenging, only the reduction of the nitrogen-containing group remains accessible, and consequently the overall degradation rate is decreased.

Aniline. Aniline proved much more stable than the other substrates studied so far. In fact, it was virtually unaltered when irradiated in the absence of the catalyst, while it degraded slowly under photocatalytic conditions (Table 2). During photodegradation, 2-aminophenol was the predominant intermediate [Fig. 5(A)] reaching a maximum of 10%, with respect to the initial aniline concentration, after 3 min. Nitrobenzene and 4-aminophenol were formed at trace level.

The effect of pH on the degradation rate constant is different from that observed for NOB (Table 2), as the rate increased in moving to more basic solutions. Since, in aniline phototransformation, the oxidative pathways are predominant, an improved transfer of photogenerated holes to OH^-, adsorbed at an increased density onto the surface, can account for the results. The primary oxidation products, aminophenols, can undergo further oxidation at the nitrogen-containing group or ring hydroxylation (Scheme 1). As already found in the preceding experiments on phenylhydroxylamine, very low amounts of aminophenols are observed, confirming that these species are extremely reactive under photocatalytic conditions.

Effect of organic compound structure: the 4-nitrosophenol case

To assess the influence of related structures on the photocatalytic transformation pathways, the process involving 4-nitrosophenol has been investigated. Under the conditions typically adopted in our experiments, direct photolysis halves

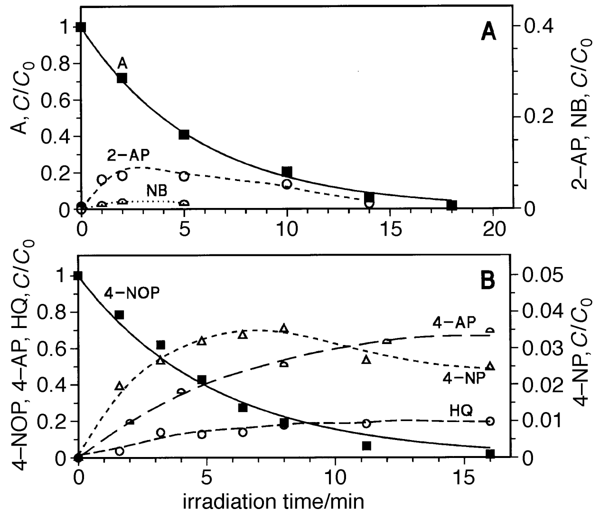


Fig. 5 (A) Disappearance of A (1.1×10^{-4} M) and formation of intermediates in the photocatalytic degradation in the presence of 200 mg l^{-1} TiO_2 at pH 6.3. (B) Disappearance of 4-NOP (4.4×10^{-5} M) and formation of intermediates in the photocatalytic degradation in the presence of 10 mg l^{-1} of TiO_2 at pH 5.8.

Table 3 Monoexponential decay rate constants (min^{-1}) for the degradation of BQ (9.2×10^{-5} M), HQ (9.2×10^{-5} M) and BQ in the presence of HQ (4.6×10^{-5} M) using TiO_2 at different concentrations as catalyst

	TiO_2 (50 ppm) in water	TiO_2 (200 ppm) in water	TiO_2 (200 ppm) 0.1 M *tert*-butanol	TiO_2 (200 ppm) 0.1 M NaCl
BQ	2.07 ± 0.20	4.43 ± 0.44	2.71 ± 0.29	1.28 ± 0.08
HQ	—	0.18 ± 0.02	—	—
BQ (+HQ)	—	3.17 ± 0.23	—	—

4-NOP concentration after 16 min and under photocatalytic conditions 4-NOP disappears in less than 1 min. To follow the photocatalytic degradation, the catalyst concentration had to be drastically diminished; in the presence of as little as 10 mg l^{-1} of TiO_2 the half-life of 4-NOP is reduced to *ca.* 4 min [$k = 0.19 \pm 0.03$ min^{-1}, see Fig. 5(B)]. The detected intermediates are 4-aminophenol (4-AP), HQ and 4-nitrophenol (4-NP). These species, together with 4-NOP, account for 97% of the initial organic content at 5 min of irradiation. Traces of phenol, BQ and quinonemonoimine were also detected. Their involvement in the degradation mechanism will be discussed later. From the detected intermediates, the reductive and oxidative pathways depicted in Scheme 1 can be proposed for the degradation process. 4-Hydroxyphenylhydroxylamine was not available as an authentic standard nor was clear evidence of its presence found, possibly because of its labile structure. If this species was formed, as our attribution of HPLC peaks suggests, its maximum concentration did not exceed some 2–3% of the initial NOP amount. The same applies also to dihydroxynitrosophenol isomers [through path (c)], which are evident in HPLC profiles, but difficult to quantify. The reduction process yielding 4-AP represents the most important degradation path for NOP. Oxidative paths lead to the formation of hydroquinone and, in lower abundance, to 4-NP [path (a)]. However, paths (b) and (c) are likely to account for small fractions of the overall NOP degradation.

In aqueous solution, 4-NOP is present principally in the benzoquinonemonoxime tautomeric form.[42] 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 (forthcoming paper) and the very low concentration of 4-nitrophenol formed, in comparison with the much more relevant production of nitrobenzene from the NOB degradation.

To check the importance of the reductive processes further, the transformation process of BQ was also investigated (see Fig. 6). HQ was formed with an 80% yield (with respect to the initial BQ concentration) after 1 min irradiation. BQ half-life decay in these conditions was as low as 0.25 min (see Table 3). When the experiment was carried out in the presence of 0.01 M *tert*-butanol, the same amount of HQ was formed, but consecutive HQ depletion was significantly reduced. Similar results were found when 0.1 M sodium chloride was added to act as a hole scavenger.[43] In separate experiments on HQ and phenol, HQ was mainly degraded by oxidative processes, yielding trihydroxybenzenes and products of ring opening, but only traces of BQ. This implies that the scavenging of $^{\bullet}OH$ radical decreases the rate of HQ disappearance, as here reported.

When an equimolar mixture of HQ and BQ was irradiated in the presence of titanium dioxide (see Table 3), the HQ concentration increased to 160% of its initial value after 1 min and decreased to 60% after 6 min, while the *p*-benzoquinone disappearance rate was unaffected by the simultaneous presence of HQ. Quinonoid structures appear to be efficient e^-_{CB} scavengers, even in aerated solutions. Interestingly, generation of $^{\bullet}OH$ and $^{\bullet}H$ radicals in sonolysis experiments on aqueous solutions of BQ also produced HQ in considerable yield.[44]

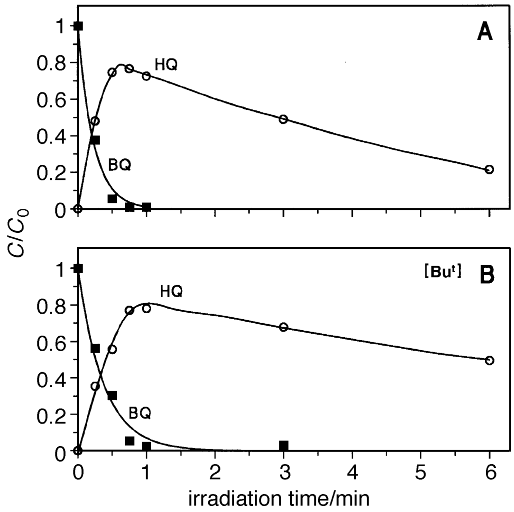


Fig. 6 Disappearance of BQ (9.2×10^{-5} M) and time evolution of HQ during the photocatalytic degradation (A) on TiO_2 (200 mg l^{-1}) at pH 5.8; (B) on TiO_2 (200 mg l^{-1}) at pH 5.8 in the presence of 0.01 M *tert*-butanol

These results support the prominent role of reductive paths in the degradation of compounds which may exist in a quinonoid tautomeric form.

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