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Phototransformations of Nitrogen Containing Organic Compounds over Irradiated Semiconductor Metal Oxides. Nitrobenzene and Atrazine over TiO_2 and ZnO.

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Abstract

The photocatalytic behaviour of nitrobenzene and atrazine over titanium dioxide and zinc oxide has been compared. Whereas the final products are the same, the intermediate distribution depends on the semiconductor nature. Both nitrate and ammonium ions are formed; nitrite represents a noticeable product in the early part of nitrobenzene degradation.

1. INTRODUCTION

Interface between metal oxides and aqueous phase play a crucial role in the transformations of organic and inorganic molecules. In particular many hydrophobic organic substances of environmental concern are concentrated in the interphase between the solid and aqueous or gaseous phase.

The adsorbed molecule behaves differently than in homogeneous phase particularly toward photo transformations. In fact under light exposure reactions involving reactive intermediates originated at the surface by a semiconductor-type mechanism and reactions involving electronically excited surface species may take place [1-3].

Recently an increasing interest has been devoted to heterogeneous photocatalytic reactions over semiconductor oxides. Besides the contribution of these processes to the abiotic transformations in the environment [3-5], they could represent a viable method

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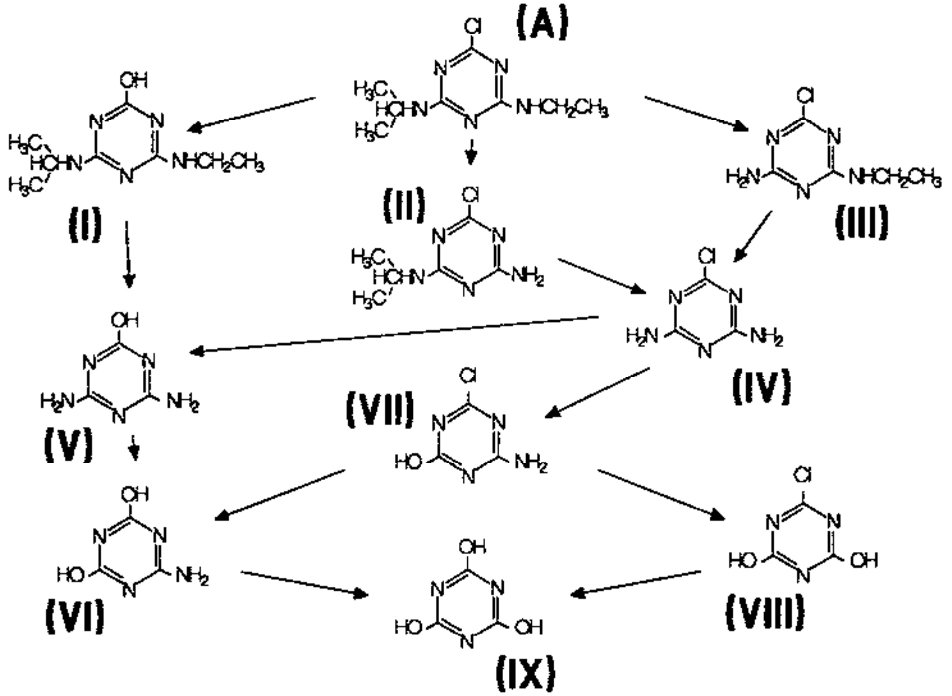
for waste water and ground water treatment [1,6]. This interest originates mainly from the observed "mineralization" (i.e. conversion of the organics into carbon dioxide and, when heteroatoms are present, into the corresponding inorganic ions) of the organic contaminants under mild experimental conditions.

However the photocatalytic behaviour of nitrogen-containing organic compounds has revealed some peculiar aspects [7]. The aim of the present contribution is the comparison of the fate of two different classes of nitrogen-containing compounds representative of two important classes of contaminants: (a) nitrobenzene, the simplest of the nitroaromatic compounds and (b) atrazine, a widely used herbicide, whose molecule contains three nitrogen atoms in the s-triazine ring and two amino nitrogen in the ring substituents (see compound A in Scheme I).

The photodegradation was investigated over two semiconductor oxides (TiO_2 and ZnO) in order to obtain also information on the behaviour of different photocatalysts. The experimental setup and procedure has been previously reported [8].



Scheme 1. Main degradation pathways of atrazine (A).

2. PHOTOCATALYSIS. PRIMARY EVENTS AND REACTIVE SPECIES

When a semiconductor oxide is irradiated with light having energy higher than the band gap (E_{bg}) a pair of conduction band electron (e^-) and valence band hole (h^+) is generated (reaction 1). After this primary event, the charge carriers either recombine within the bulk of the material or migrate to the particle surface where they can also recombine or can be trapped at some defect site (in ca. a few nanoseconds), eventually as subsurface-bound $O^{-\cdot}$ radicals [9]. They are then poised to be implicated in surface redox processes: reduction by the trapped electrons and oxidation by the trapped holes. In the case of TiO_2, the most investigated oxide, the significant events that ensue these photophysical steps at the surface are adsorption of molecular oxygen on the Ti(III) sites which reduce O_2 to the superoxide radical anion, $O_2^{-\cdot}$ (reaction 2), while the positive charge carrier, Ti(IV)-$O^{-\cdot}$-Ti(IV), can oxidise the surface hydroxyl groups or the surface-bound water (reactions 3) to surface-bound $\cdot OH$ radicals. It is relevant to note that recent pulse radiolytic studies were unable to distinguish between the surface-bound $\cdot OH$ radicals and the Ti(IV)-$O^{-\cdot}$-Ti(IV) species [10].

$$TiO_2 + h\nu(> E_{bg}) \xrightarrow{\phi I_a^n} e^- + h^+ \qquad (1)$$

At low light fluxes, n = 1.

$$(O_2)_{ads} + e^- \longrightarrow (O_2^{-\cdot})_{ads} \qquad (2)$$

$$Ti(IV)\text{-}OH^- + h^+ \Longleftrightarrow Ti(IV)\text{-}\cdot OH \qquad (3a)$$

$$Ti(IV)\text{-}OH_2 + h^+ \Longleftrightarrow Ti(IV)\text{-}\cdot OH + H^+ \qquad (3b)$$

It is worth noting that the presence of molecular oxygen and water is essential during the photomineralization process [11]. The trapping of charge carriers (eqns 2 and 3) plays the additional role of suppressing somewhat electron/hole recombination, thereby increasing the competitiveness of the light-induced redox processes.

The currently available evidence suggests the $\cdot OH$ radical, whether "free" [12] or "surface-bound" [10,13], to be the active oxidising species in these and analogous photo-oxidative degradations on TiO_2 [14-18]. The evidence has involved the observations, by a number of workers, that several hydroxylated species are formed during the course of the mineralization of aromatic substrates [19-22]. Electron paramagnetic resonance studies on irradiated TiO_2 have identified the $\cdot OH$ radical by spin-trap techniques and no other radical species under ambient conditions in aqueous dispersions [23,24] and in gas/solid systems [25]. In a kinetic isotope study that examined the photo-oxidation of 2-propanol with TiO_2 and ZnO, the rate-determining step was identified as formation of OH or OD radicals [26].

In aqueous acidic media, as employed in the presently reported degradations (pH 3), $O_2^{-}\cdot$ protonates to form the hydroperoxide radical $HO_2\cdot$, which is subsequently converted to H_2O_2 [15,17,27-28]. Where the light source has a significant UV component (250-300 nm), absorption of these wavelengths by hydrogen peroxide, and/or its interaction with the photo formed electrons can yield ·OH radicals [16,21,27]. However, it would appear that the major source of ·OH radicals is reactions 3 or their equivalents [29]. It should also be emphasised that oxidation may also occur by interaction of the organic substrate with the superoxide radical anion.

Photocatalytic transformations over ZnO also appears to be mainly due to hydroxyl radicals; whereas singlet oxygen does not contribute significantly to the progress of the reaction, direct oxidation by positive holes seems to be operating [30].

3. NITROBENZENE PHOTOCATALYTIC DEGRADATION

Under irradiation over TiO_2 and ZnO nitrobenzene disappears quite rapidly in the case of TiO_2 (half life ca. 3 min) and at slower rate on ZnO (half life ca. 80 min) (see Fig. 1 and 3). Conversion into inorganic carbon has been monitored through TOC analysis and > 90% of organic content was mineralised after 1 hour in the presence of TiO_2, whereas ca. 100 hours are required on ZnO [31].

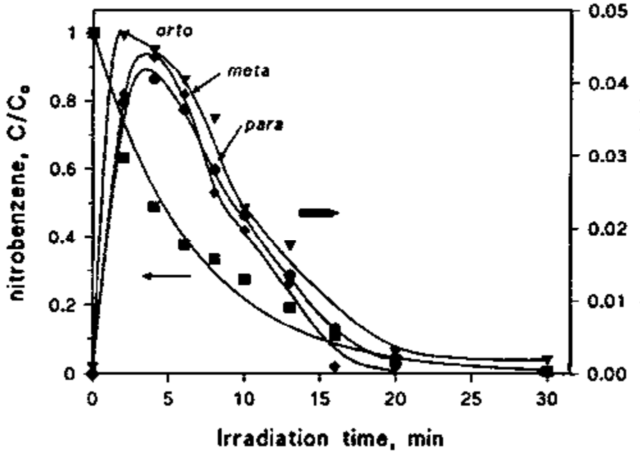


Figure 1. Degradation of nitrobenzene and evolution of 2-, 3- and 4-nitrophenol on TiO_2. Conditions: Solarbox, 1500 W Xenon lamp, 340 nm cut-off filter, 200 mg /l TiO_2, 10 mg/l nitrophenol. Right scale reports quantitative evaluation for intermediates.

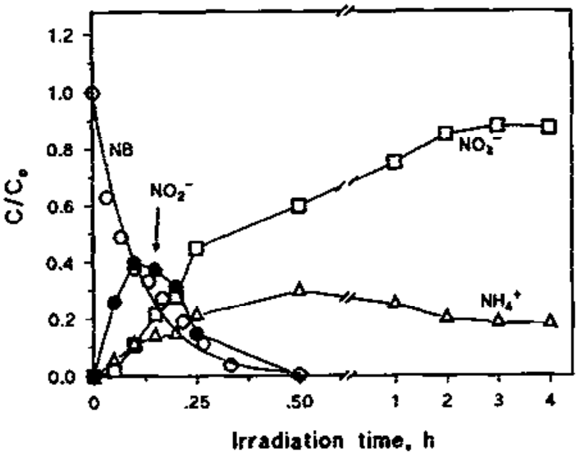


Figure 2. Evolution of inorganic species containing nitrogen during the photocatalytic degradation of nitrobenzene on TiO_2. Conditions as in Fig.1.

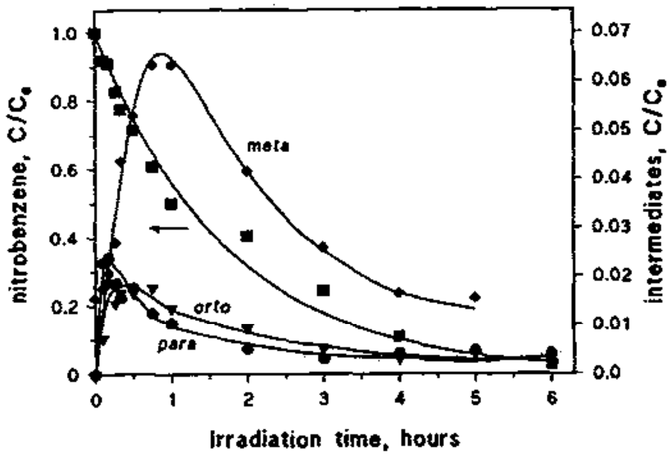


Figure 3. Degradation of nitrobenzene and evolution of 2-, 3- and 4-nitrophenol on ZnO. Conditions: Solarbox, 1500 W Xenon lamp, 340 nm cut-off filter, 200 mg /l ZnO, 10 mg/l nitrophenol.

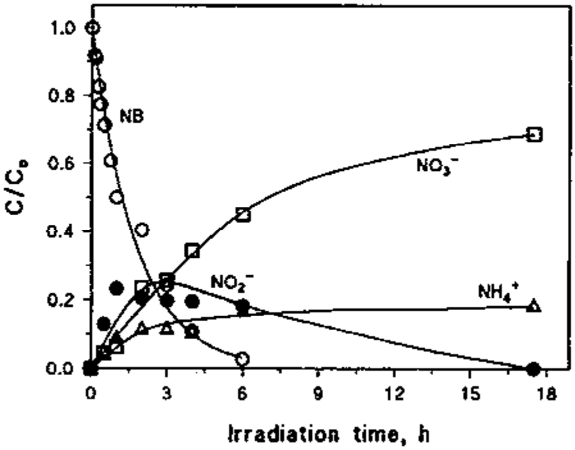


Figure 4. Evolution of inorganic species containing nitrogen during the photocatalytic degradation of nitrobenzene on ZnO. Conditions as in Fig.3.

In Fig. 1 and 3 are also reported the fate of the first stable intermediates, i.e. the three nitrophenols [32]. It is noteworthy that in the case of ZnO, the meta isomer is the predominant intermediates, whereas comparable quantities are observed on TiO_2 [33].

Fig. 2 and 4 show the evolution of inorganic nitrogen containing species. Besides nitrite and nitrate also ammonium ion is detected in non negligible amount.

4. ATRAZINE PHOTOCATALYTIC DEGRADATION

Photocatalytic degradation of atrazine occurs through a series of competitive-consecutive pathways. Many intermediates have been identified, the most important being depicted in Scheme I [34,35]. The most striking feature is the formation of trihydroxy-s-triazine (cyanuric acid, IX) as the main final product (see Fig. 5 and 7). The two remaining nitrogens present as alkylamino substituents in the parent molecule, give rise to the formation of nitrate after long irradiation time and, in much less extent, to ammonium ions (see Fig. 6).

The distribution of the intermediates differs with different semiconductors. Dealkylating route seems to prevail on ZnO since either compounds II and III are formed in larger extent in the initial part of the degradation and compound IV reaches ca. 60% of the stoichiometric value after ca. 30 hours of irradiation [36]. Only little formation of ammelide (VI), i.e. a compound obtained by substitution of an amino group with an hydroxyl group is observed.

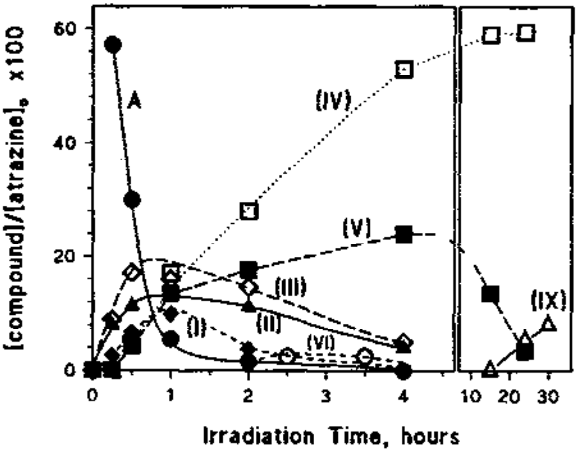


Figure 5. Evolution of selected intermediates in the photocatalytic degradation of atrazine on TiO_2. Roman numbers correspond to compounds of Scheme I. Conditions: Solarbox, 1500 W Xenon lamp, 340 nm cut-off filter, 0.5 g /l TiO_2, 10 mg/l initial atrazine.

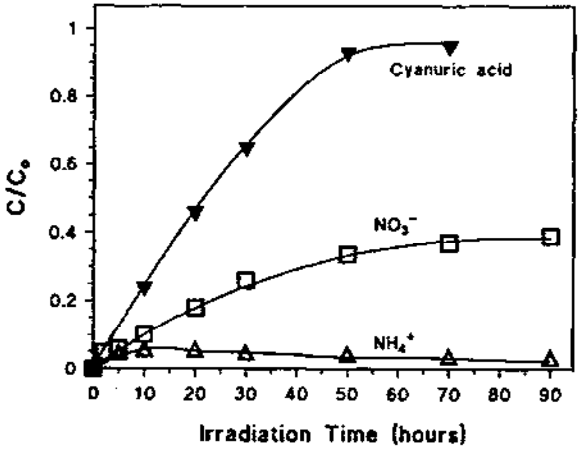


Figure 6. Evolution of final products in the atrazine photocatalytic degradation on TiO_2. Conditions as in Fig.5 .

5. FINAL CONSIDERATIONS

Several interesting features emerge from the presently reported degradation processes involving two peculiar representatives of nitrogen-containing molecules on two different semiconductors.

5.1. Nature of Semiconductor Oxide

Although comparison between the two semiconductors may be complicated by the difference in the surface characteristics of the materials, it appears that TiO_2 is by far superior both in the rate of disappearance of the initial compound as well as, and even more important, in the rate of formation of the final product (i.e. carbon dioxide in the case of nitrobenzene and cyanuric acid for atrazine).

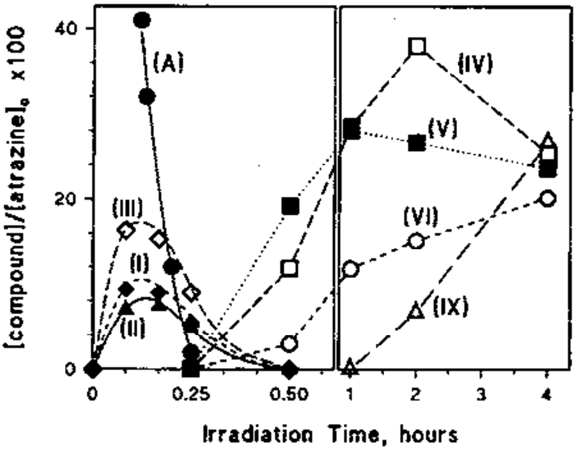


Figure 7. Evolution of selected intermediates in the photocatalytic degradation of atrazine on ZnO. Roman numbers correspond to compounds of Scheme I. Conditions: Solarbox, 1500 W Xenon lamp, 340 nm cut-off filter, 1 g /l ZnO, 10 mg/l initial atrazine.

This difference may arise from several factors depending on intrinsic properties (life-time of active species, molecular energy levels for interfacial reactions) or on specific composition and surface structure (surface area and hydroxyl group density, dopants, light absorption efficiency, adsorption) [1].

An issue often raised in photocatalyzed degradation of organic substrates is whether the initial oxidation of the organic substrate occurs on the surface of the catalyst or in solution. Whereas kinetic dependence is not conclusive on the mechanism [37], several studies (by means of EPR [38], pulse radiolysis [10], photoelectrochemistry [39], experiments with scavengers [30], exchange between different supports [40]) gave conflicting conclusions. Since the degradation over TiO_2 and ZnO have shown different intermediate distribution, both with nitrobenzene and with atrazine, this is supportive of an important role of the surface in these processes.

5.2. Behaviour of Nitrogen Containing Organic Compounds

Under irradiation over semiconductor oxides, complete mineralization (formation of carbon dioxide and inorganic ions) was obtained for nitrobenzene, whereas for atrazine almost stoichiometric cyanuric acid and only partial conversion into inorganic nitrogen containing ions was observed. In the case of nitrobenzene the detected intermediates disappear with comparable or even faster rate in respect to the initial compound; on the contrary in the degradation of atrazine, while its disappearance occurs in very short time, the main intermediates (depicted in Scheme I) become more stable to further degradation. Nitrogen containing compounds then exhibit a quite complex behaviour toward photocatalytic degradation [7].

As far as the nitrogen fate is concerned, in the case of nitrobenzene during the early part of the process nitrite and nitrate are formed, the first virtually disappearing after long irradiation period. Non trivial amounts of ammonium ion reaching ca. 20% of the stoichiometric nitrogen were also detected both on TiO_2 and ZnO. In the case of atrazine, being the three nitrogens in the ring retained in the cyanuric acid, the two monoalkyl substituted amino groups finally give rise to nitrate and ammonium ions. These results confirm that semiconductor oxide mediated illumination of nitrogen containing organic compounds gave both nitrate and ammonium ions, irrespective of the nature of the nitrogen atom in the initial compound [7].

6. ACKNOWLEDGEMENTS

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