

The fate of organic nitrogen in photocatalysis: an overview

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Abstract

Photocatalytic processes taking place on TiO_2 have been widely employed and investigated. However, nitrogen-containing substances have not received the same attention as other substrates. Mineralization of such compounds is expected to lead to the formation of N_2 gas, ammonium and/or nitrate ions through photooxidative and/or photoreductive pathways. Herein, we will focus the attention on how the chemical structure may influence both the ratio and the extent of formation of the inorganic nitrogen. This review will consider heteroaromatic compounds, containing two or three-nitrogen in the ring, and small molecules, that could be formed as intermediate during the degradation of more complex substrates (i.e. pesticides), such as amino-alcohols, and molecules containing amide groups and nitriles. The final fate of the nitrogen in all these structures has been rationalized on the basis of the nature of N–N and C–N bonds in which the organic nitrogen is involved.

1. Introduction

Photocatalytic degradation with irradiated semiconductors involving oxidation and reduction reactions [1–4] has been established to be effective not only for degradation and final mineralization of several organic compounds, but also for gaining information on naturally occurring transformations. Some examples of the feasibility of this method are represented by reactions occurring in the environment [5] and in living organisms [6, 7]. In both cases, some of the intermediates identified through a photocatalytic process have been found in soil samples [5] and in the animal liver [6, 7].

Even if the fate of the nitrogen has been widely studied, the evolution of N_2 gas in the photooxidation of N-containing compounds is better established than that of NH_4^+ and NO_3^- ion formation, for which the detailed mechanism of formation is not been fully elucidated. This is due to the difficulty of identifying the final intermediate products in the photocatalytic degradation of nitrogen-containing materials.

An understanding of all the possible processes involved in the natural evolution of nitrogen-containing compounds is important, not only because nitrogen constitutes a key element of the nutrient cycle, but also because a large number of anthropogenic compounds, i.e. pesticides, drugs and dyes, contain one or more nitrogen atoms. Thus, it is of great concern to answer to the question on what is the fate of the nitrogen in the mineralization of nitrogen-containing compounds.

Nitrogen moieties in organic compounds can be transformed photocatalytically to either N_2 , $\text{NH}_3/\text{NH}_4^+$ and/or nitrite and nitrate ions, whose ratio depends on the different features of the N-containing structure [8–15]. The final fate of organic nitrogen under photocatalytic processes has been reported to be related essentially to the initial oxidation state of nitrogen in the organics, to the presence/absence of oxygen and, in few cases, to the structure of the organic molecules. Moreover, the ratio between ammonium and nitrate formation is symptomatic of the initial transformation mechanism. Being the transformation of ammonium into nitrate negligible [16], ammonium ions is formed directly from the release of nitrogen as ammonia, when the oxidation state of the bound nitrogen is -3 . Differently, nitrate formation can be achieved either through the release of a nitro-group [17], with the formation of nitrite ions, further oxidised to give nitrate formation, or through a sequence of oxidative steps, i.e. from the hydroxylamine.

A wide range of studies have focused on benzenic derivatives [16–22]. Piccinini et al. [19] have studied the interconversion of nitrogen-containing benzenic derivatives by investigating nitrobenzene, nitrosobenzene, phenylhydroxylamine, aniline and 4-nitrosophenol. Besides the hydroxylation of the aromatic ring, each compound of the series is converted to all the others, even if in widely different amounts.

Nitro- and nitroso-groups are converted predominantly to NO_3^- ions [12, 16]; by contrast, the nitrogen

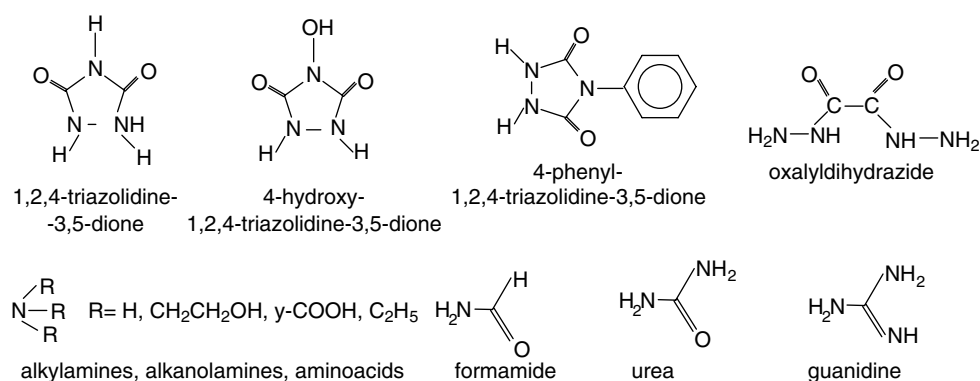
in heterocyclic aromatic rings can be transformed to both NH_4^+ and NO_3^- species, while secondary, tertiary and quaternary nitrogen atoms are photoconverted predominantly to NH_4^+ ions [9, 23]. A particular case in which complete transformation into inorganic ions is not realized is represented by the class belonging to the s-triazine derivatives [24], for which the formation of a stable intermediate (cyanuric acid) does not permit a further degradation and the complete mineralization.

Heteroaromatic structures are building-blocks of numerous anthropogenic compounds and recognized as intermediates during pollutants degradation. Among them, aminopyrimidines have been found as metabolic compounds of different-belonging classes molecules, such as sulfonylic herbicides and sulphamides, widely used synthetic antibacterial agents [25]. The persistence of residues in food are of great concern, in particular because of their potential carcinogenic character. Both sulphonamides and aminopyrimidic derivatives show the formation of intermediates with different photochemical stability. The fate of nitrogen is deeply influenced by these factors. It was evidenced that the presence of a substructure $\text{—N—C(NH}_2\text{)—N—}$ in the molecule leads to a negligible conversion of the organic nitrogen into inorganic ions in the investigated times [26]. Mepanipyrim, a fungicide widely adopted in agriculture, represents another example where, as well as the organic carbon is mostly transformed into CO_2 , a large amount of the organic nitrogen results still bound.

By considering the different factors influencing both the ratio $[\text{NH}_4^+]/[\text{NO}_3^-]$ and the extent of their formation, and the different N-containing molecules we have found a rationalization based on the nitrogen bond configuration, as reported below.

2. Nitrogen with single bonds

Within this class of compounds, there are molecules containing the N—N or C—N bonds, with or without H extractable atoms. As typical representatives of this class, we have chosen the structures indicated in Scheme 1.



Scheme 1. Molecular structures of the reviewed single bonds nitrogen-containing compounds.

2.1. Structures with hydrogen extractable

Characteristic cases of structures containing —NH—NH— bonds are hydrazine and triazolidine derivatives (see Scheme 1, row 1). Heterocycles with two or three nitrogen-containing moieties exist in numerous natural and anthropogenic compounds. They have been shown to release nitrogen, depending on the structure, alternatively as N_2 , NH_4^+ and/or NO_3^- ions.

In hydrazine derivatives (Waki et al. [28]), the hydrazo groups are transformed mainly into N_2 gas (70% of the stoichiometric amount) and only partially into NH_4^+ (approximately 10%). The release of nitrogen from triazolidine derivatives has been investigated by Guillard et al. [27] and it was reported, in all cases, the N_2 gas formation from the beginning of the degradation. The —NH—NH— moiety is mainly converted into N_2 gas, in agreement with what was also observed [28] on hydrazine derivatives. In the case of triazolic structures (1,2,4-triazolidine-3,5-dione, 4-hydroxy-1,2,4-triazolidine-3,5-dione and 4-phenyl 1,2,4-triazolidine-3,5-dione), about 17% of the nitrogen is transformed into N_2 . By considering the ratio between NH_4^+ and NO_3^- ions, ammonium quickly appears, while NO_3^- shows an induction period, so underlining that several steps of nitrogen oxidation had to occur before nitrate ions are formed. In all cases, the stoichiometric amount of inorganic ions is not achieved, with percentages of approximately 50%.

Among the structure containing C—N bond, typical molecules are indicated in Scheme 1, row 2. The degradation of several alkyl- and alkanol-amines have been studied by Klare et al. [29] and Horikoshi et al. [30]. Alkanolamines exhibit shorter half-times than the analogous alkylamines. Through the degradation of $(\text{C}_2\text{H}_5)_2\text{NH}$ the mono-substituted $\text{C}_2\text{H}_5\text{NH}_2$ is formed as intermediate, while nitrogen is prevalently converted into ammonium in all cases.

Horikoshi et al. [30] have followed the cases of mono, di and triethanolamines. In all cases, the overall yield of NH_4^+ ions produced was greater than the corresponding amount of NO_3^- ions and no evolution of N_2 gas was detected. The ratio $[\text{NH}_4^+]/[\text{NO}_3^-]$ in the photo-conversion of the amine nitrogen was, after 8 h of irradiation,

6:1, 3:1, 3:1 respectively for mono-, di- and tri-ethanolamines. While for di- and tri-ethanolamine nitrate formation is immediate, for mono-ethanolamine an induction period of 1–1.5 h exists before nitrate ions are detected. In contrast, formation of ammonium ions from mono-ethanolamine is rapid, whereas evolution from di- and tri-ethanolamines occur after a short induction time (ca. 0.5 h).

Similarly to what observed by Klare et al. [29], both diethanolamine and triethanolamine decompose through the formation of a primary amine function. This behaviour was rationalized by an absorption mechanism [30] and quantum-mechanistic calculation, determining which atoms carries the largest negative point charge. Oxygen atoms in the alcoholic function are the most negatively charged atoms and they are inferred to be the major point of contact between the positively charged TiO_2 surface and ethanolamines. The nitrogen atoms of the three ethanolamines are the positions of richest frontier electron density. Ethanolamines chemisorbs dissociatively through the alcoholic function and the preferred points of attack by the $\bullet\text{OH}$ radicals are the nitrogen atoms, if they are closed to the particle surface where redox chemistry occurs [30].

The described results are in agreement with the occurrence of the mechanism of transformation proposed [29] and briefly resumed in Scheme 2. The reaction scheme accounts for an $\bullet\text{OH}$ attack on the $\alpha\text{-CH}$ bond with an hydrogen extraction. Through a further $\bullet\text{OH}$ attack, giving an $\bullet\text{OH}$ addition, the cleavage of the C–C bond occurs with the break of the molecule into a carbonylic compound and an amine. Through a further hydrogen extraction and $\bullet\text{OH}$ addition, the nitrogen is finally released as ammonium ions. This mechanism is able to explain the formation of primary amines detected both by Klare [29] and Horikoshi [30] and the preferential formation of ammonium. Closely related to alkylamines are the aminoacids, that have been deeply discussed [31].

Looking closer to the ratio $[\text{NH}_4^+]/[\text{NO}_3^-]$ formed from ethanolamines and keeping in mind the Scheme 2, some consideration arises. When a primary amine is involved, NH_4^+ is easily released, in accordance with the mechanism proposed. When considering the case of a tertiary amine, ammonium is released only at the end of the cycle, i.e. when more than one sequence of H abstraction/OH addition occur and lateral residues are lost. This leads to

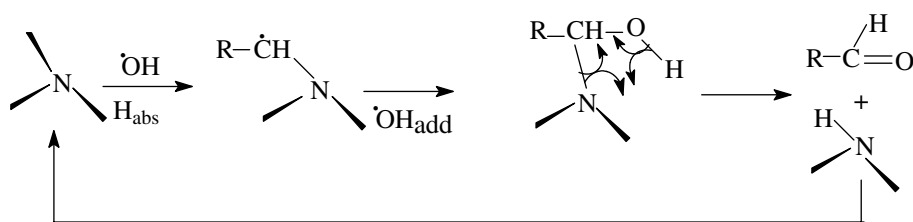
the existence of an induction period, as evidenced in the case of triethanolamine, and to the formation of ammonium at a minor ratio (3:1 instead 6:1).

Nitrate formation can not be explained on the basis of the mechanism described in Scheme 2. In this case, probably the $\bullet\text{OH}$ attack occurs on the nitrogen instead of the carbon atom. For the aromatic rings, amino group is generally oxidized, passing from aniline to nitroso- and nitrobenzene, with the further release of nitrogen as nitrite ions [19]. For aliphatics, this attack, usually concurrent with the preceding mechanism, is probably slow and is only evidenced when no extractable hydrogen are available. This hypothesis is consistent with the existence of an induction period before nitrate formation. In the case of a primary amine, the fast release of ammonia impedes the formation of NO_3^- (see the ratio 6:1 evidenced above). For a tertiary amine, the long way to NH_4^+ relatively favours the production of NO_3^- ions. Some more details will be considered in the section 3.2.

A further case is represented by formamide. The photocatalysed degradation of formamide has been studied by Pelizzetti et al. [32]. The temporal profiles are shown in Figure 1a. In the case of HCONH_2 , for which the carbon oxidation state is +2, the presence of C–H bond is presumably favouring the $\bullet\text{OH}$ attack on the carbon atom, in agreement with the consideration above (see also Scheme 2), generating $\bullet\text{CONH}_2$ radical, followed by carbamic acid formation; the nitrogen is finally released as ammonium ions, as shown in Scheme 3. Carbamic acid hydrolysed more quickly under photocatalytical conditions, suggesting that a “*photo-assisted hydrolysis*” would take place, as was evidenced for halomethanes [33]. By hydrolysis, only ammonium would be formed. The ratio $[\text{NH}_4^+]/[\text{NO}_3^-] = 2:1$ suggests, according to the above hypothesis of OH attack on N, that this pathway is also operating, and it is partially concurrent with the photo-induced hydrolysis. A lack of $\sim 10\%$ of the stoichiometric nitrogen amount is observed, similarly to the cases of cyanate, hydrazine and azo-derivatives [15, 28], indicating that other pathways could also be operating.

2.2. Structures without hydrogen extractable on carbon

As example of these structures, urea and guanidine will be described (see structures in Scheme 1, row 2). The



Scheme 2. Transformation pathways followed by alkyl- and alkanol-amines. The mechanism is operating until CH_i ($i = 1,2$) groups are present in α -position. For $i = 1$ and $i = 2$ a ketone or aldehyde are released, respectively. Final fate of N is ammonia.

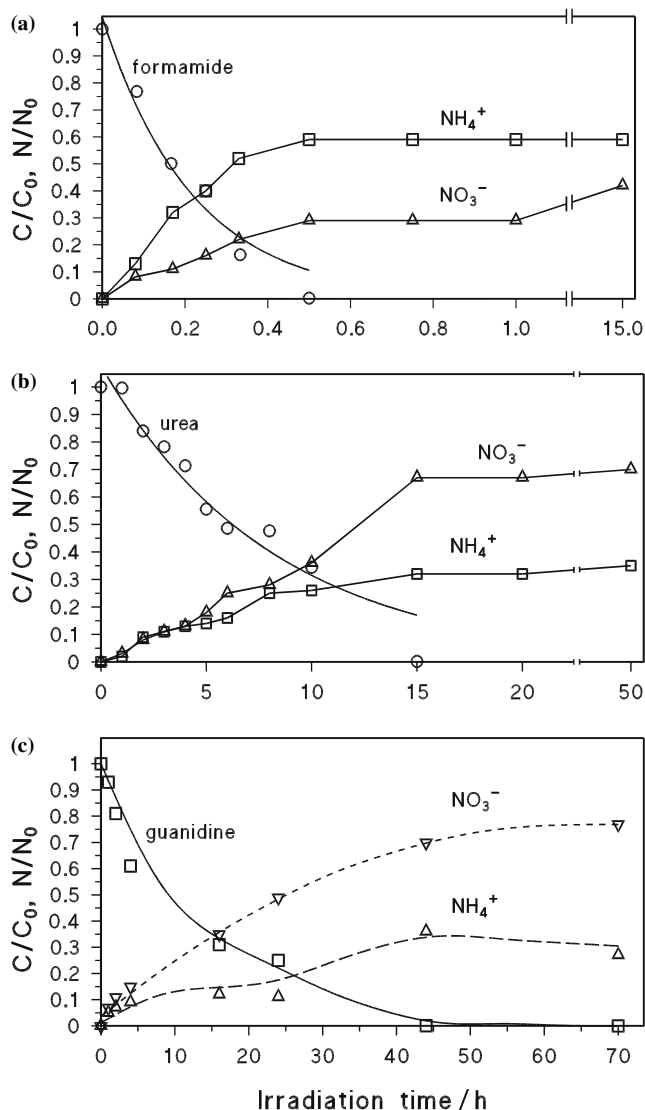


Fig. 1. The photocatalytic transformation of formamide (a), urea (b) and guanidine (c) on TiO_2 200 mg L^{-1} as a function of irradiation time. Disappearance of primary compounds and formation of nitrate and ammonium ions (adapted from ref. [26] and [32]).

photocatalysed degradation of urea and guanidine have been studied by Pelizzetti et al. [32] and Calza et al. [26], whose profiles are shown in Figure 1b and c. These compounds ensue particularly stables (for guanidine, $t_{1/2}$ 8 h). If compared with formamide, several interesting analogies/differences come up. While formamide is easily degraded ($t_{1/2} = 0.2$ h), urea is slowly decomposed ($t_{1/2} = 5$ h). Moreover, the ratio $[\text{NH}_4^+]/[\text{NO}_3^-]$ changes from 2:1 to 1:2 for formamide to urea. Being the nitrogen oxidation state -3 in all cases, the remarkable differences in the degradation rate and in the final nature of nitrogen, both originating from an amido group, can be rationalized by considering carbon oxidation state or, alternatively, the presence/absence of extractable hydrogen. The described differences could be clarified on the basis of the pathways proposed in Scheme 3.

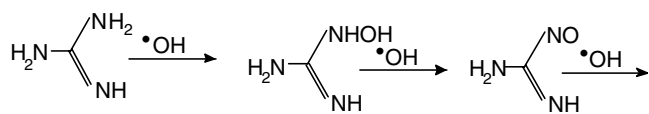
Noting that C atom in the urea structure has $+4$ oxidation state (and no extractable C—H bond are present), $\bullet\text{OH}$ attack is forced at the $-\text{NH}_2$ moiety. This

first pathway is very slow, as deduced above for formamide, and determines the slow rate of urea disappearance. It leads, probably, to the transformation of an amino group into a nitrous group, followed by the detachment of nitrite ions, rapidly oxidized to nitrate [16–18].

Beyond the nitrate formation, 30% of the nitrogen is converted into ammonium ions. Since a negligible formation of ammonium from nitrite and nitrate is reported under these conditions, the ratio $[\text{NH}_4^+]/[\text{NO}_3^-]$ suggests that, after the (slow) attack on the N atom, an $\bullet\text{OH}$ attack on the carbon atom could occur, probably leading to carbamic acid formation. Carbamic acid could then support both an oxido/reductive sequence on the carbon atom, as discussed above. By assuming carbamic acid as key intermediate, after the detachment of the first amino group (giving nitrate formation in stoichiometrical amount, i.e. 50% of the organic nitrogen conversion), the second amino group should follow the same fate of formamide. This would imply that the second N atom would form approximately 30% of ammonium and 15% of nitrate of the stoichiometric amount (2:1 ratio on 50%). This accounts for the ratio observed for urea (30:65 \approx 1:2).

In the case of guanidine photocatalytical degradation, whose temporal profiles are shown in Figure 1c, after 24 h of irradiation 25% of the initial compound is still present and only 60% of the nitrogen has been released as inorganic ions, mainly as nitrate ions, while the complete mineralization is achieved only after 70 h of irradiation. In agreement with the discussion above (both the initial oxidation state of carbon ($+4$) and the absence of extractable C—H bond) the $\bullet\text{OH}$ attack is on the amino group with the release of nitrogen mainly as nitrite, suddenly transformed into nitrate ions.

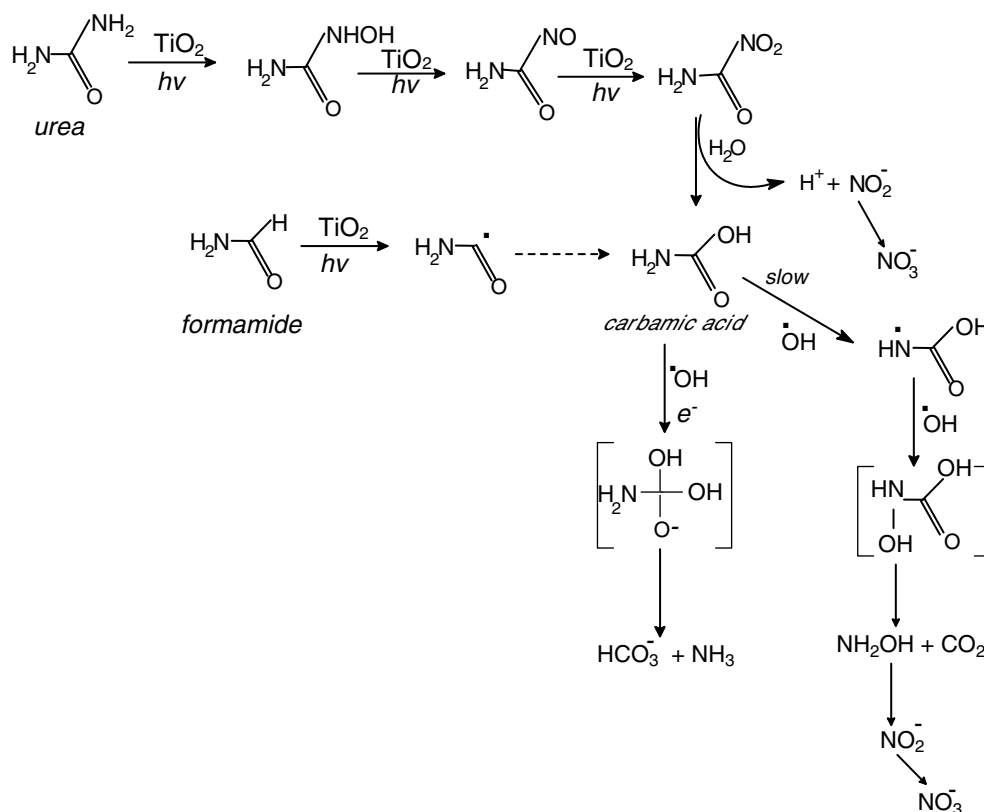
The formation of nitrate ions could be reached through the sequence (1), followed by a sequence of reactions similar to those presented in Scheme 3.



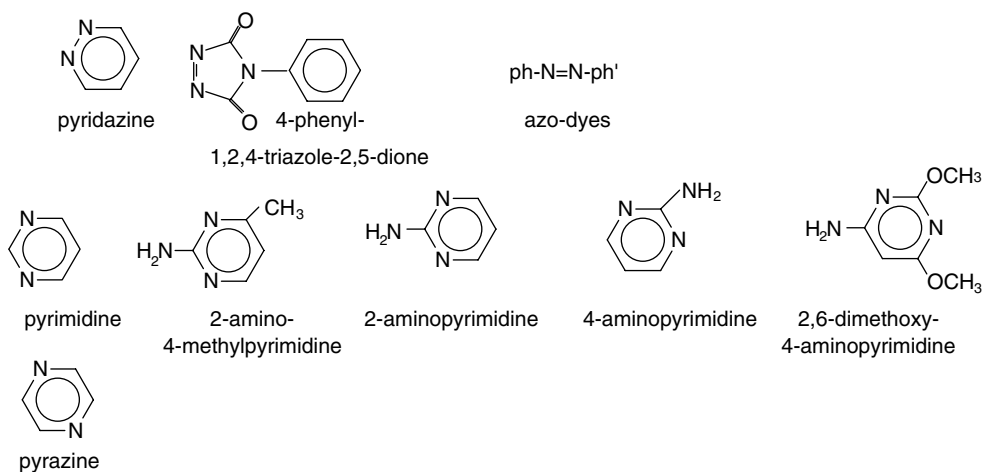
At 70 h the ratio $[\text{NH}_4^+]/[\text{NO}_3^-]$ is $\sim 1:3$. It implies that the nitrogen released through a sequence like (1), probably involves also the other amino groups. The detection of urea as intermediate supports the proposed pathways; further transformation of urea mainly gives the formation of nitrate ions through the mechanism described above (see Scheme 3). In this case, the increase in nitrate yield at long irradiation times could be imputed to the conversion of ammonium into nitrate rather than to a direct formation of nitrate from guanidine.

3. Nitrogen with double bonds and heteroaromatics

As representative of this class, the structures containing $\text{N}=\text{N}$ or $\text{C}=\text{N}$ bonds, indicated in Scheme 4 are



Scheme 3. Transformation pathways followed by urea and formamide (adapted from reference [32]).



Scheme 4. Molecular structures of the reviewed double bonds nitrogen-containing compounds.

considered. Actually, most compounds are heteroaromatics. They are here considered as their resonance structures could be associated to $\text{N}=\text{N}$ or $\text{C}=\text{N}$ class. Formally, to this class belong also pyridine [34, 35] quinoline [36], and their derivatives (see for example haloquinolines [37] and triclopyr [38]). Pyridine degrades by giving aliphatic intermediates with one to five C atoms, all containing $\text{C}=\text{O}$ groups, and whenever the N atom subsists, it is as an amide, so following the same fate as described above in section 2.1. and Scheme 2 with the formation of ammonium and nitrate. In the case of triclopyr, the main degradation product

originating from nitrogen is the ammonium ion. The absence of nitrate ions seems linked to the low oxidation state of the nitrogen. Studies on quinoline [36] have been performed with the aim to demonstrate that oxidative steps in TiO_2 photocatalysis do not involve only OH radicals but also hole transfer.

3.1. $\text{N}=\text{N}$ containing structures

The fate of the nitrogen of $\text{N}=\text{N}$ containing structures closely resemble the case of $-\text{NH}-\text{NH}-$ moiety. The release of nitrogen from triazole derivatives was

investigated by Guillard et al. [27] and had shown N_2 gas formation from the beginning of the degradation, in even a more significant amount (27%) than in the case of triazolidinic derivatives (see section 2.1.). Here, complete mineralization is achieved.

Horikoshi and Hidaka [15] have studied the photocatalysed transformation of six-membered heteroaromatic structures. The photodegradation of these heteroaromatic structures resulted closely related to the position of nitrogen in the heteroring. By considering pyridazine (OP), the $-N=N-$ moiety is converted into N_2 gas, in accordance with Guillard [27] and Waki [28] results. No formation of NH_4^+ and NO_3^- ions in the photodegradation of OP was recognized even after 10 h of irradiation, and nitrogen is stoichiometrically converted into N_2 gas.

Several azo-dyes photocatalytic degradations have also been studied mainly for application purposes. From a mechanistic point of view, the formation of N_2 was evidenced [39, 40]. Gaseous dinitrogen evolved stoichiometrically corresponded to the mineralization of the central $N=N$ azo-group.

3.2. C=N containing structures

Pyrimidine (MP) and pyrazine (PP), containing a $-N=C-N-$ moiety, yield to the predominant formation of NH_4^+ and to a slight amount of NO_3^- ions, while no traces of N_2 have been detected [15]. The final intermediate recognized before final conversion into inorganic ions is formamide in both cases. In the considered time of irradiation (10 h), the photomineralization of pyrimidine ends in the predominant formation of NH_4^+ ions and a slight amount of NO_3^- (at the ratio 5:1), while PP was characterized by an even higher conversion into ammonium (ratio $[NH_4^+]/[NO_3^-]$ of 12:1). Complete mineralization is not achieved; for MP and PP only 42% and 57% of the photomineralization is respectively accomplished.

A closer inspection on the transformation pathways leading to the nitrogen conversion was done by Calza et al. [26], considering MP derivatives differently substituted (2-aminopyrimidine (2-AP), 4-aminopyrimidine (4-AP), 4-methyl-2-aminopyrimidine (2-AMP), 2,6-dimethoxy-4-aminopyrimidine (4-ADMP), see Scheme 4). Their transformation pathways (especially the fate of the bound-nitrogen) seem to be closely related to the position of the amino group in the heterocyclic ring [26]. The temporal evolution of NH_4^+ and NO_3^- ions for the photocatalytic transformation of the differently substituted pyrimidines is depicted in Figure 2, where the part A shows the nitrogen released from 4-amino derivatives and part B from the 2-amino derivatives. It results that both the ratio $[NH_4^+]/[NO_3^-]$ and the extent of their formation are linked to the nature of the substituents and to the amino group position in the heteroaromatic ring. When the amino group is located in C^4 , the transformation pathways proceed mainly through the cleavage of the C-N bonds,

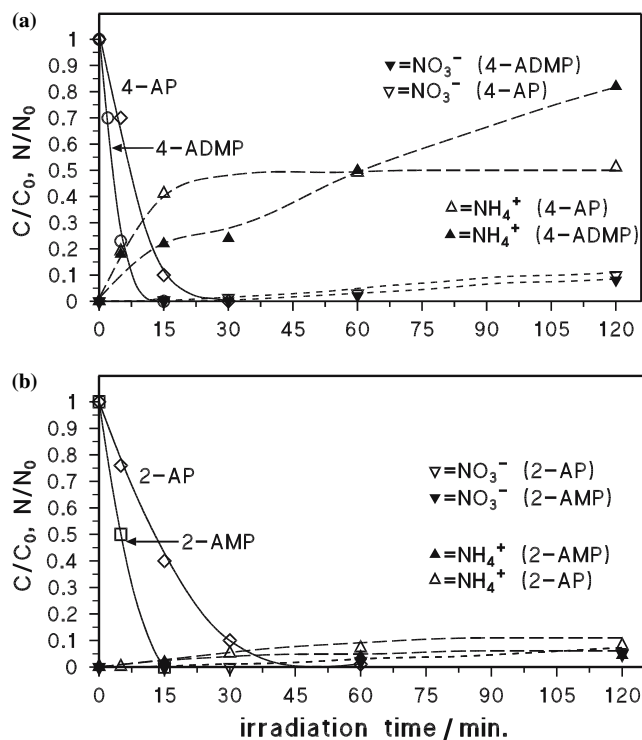
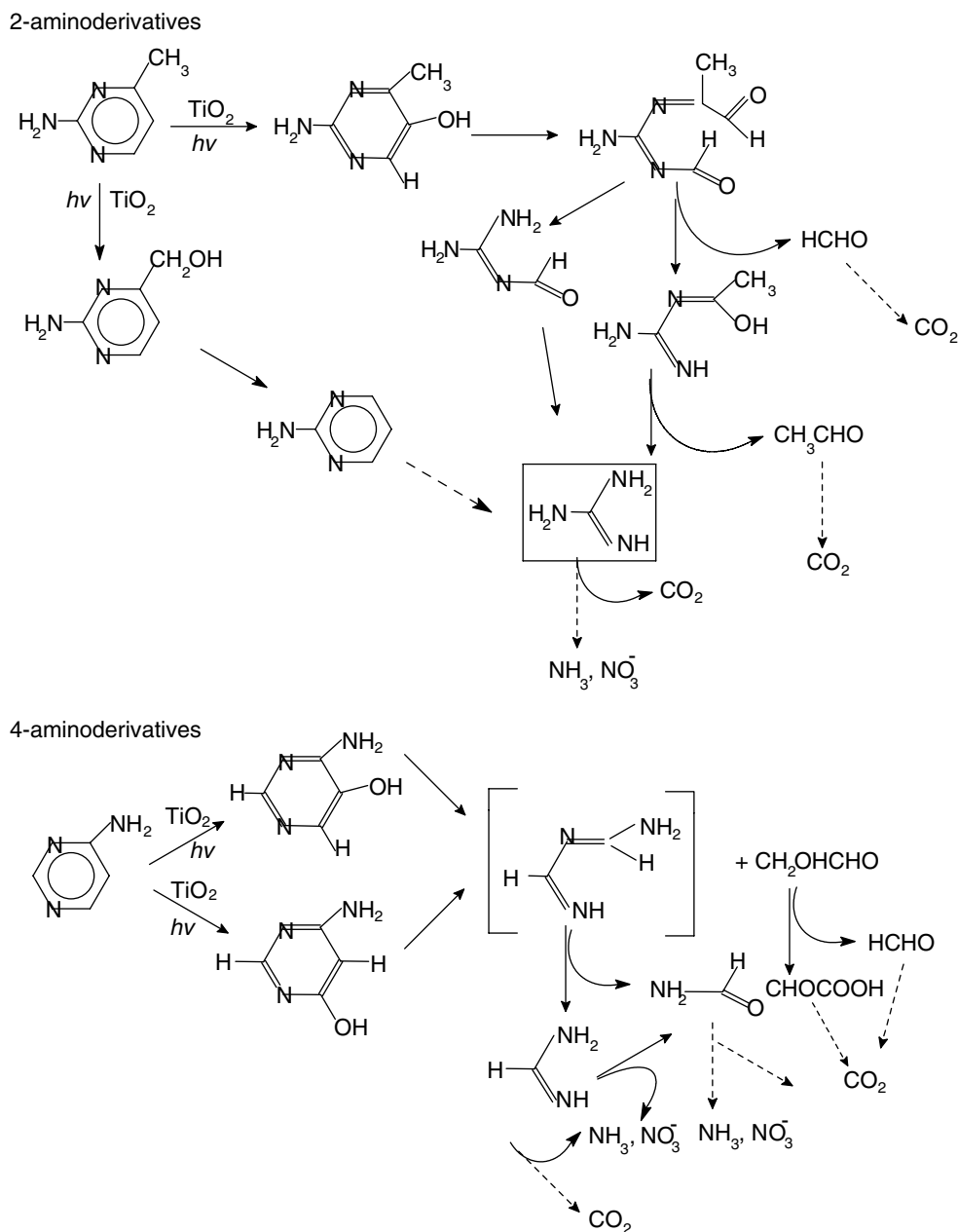


Fig. 2. Disappearance of aminopyrimidines and formation of nitrate and ammonium from the decomposition of aminopyrimidines. (a) 4-aminopyrimidines (b) 2-amino-pyrimidines (adapted from ref. [26]).

with formation of oxygenated structures as intermediates and the release of nitrogen mainly as ammonium ions. In this case, almost all the nitrogen has been mineralised until 2 h of irradiation, both in the structure bearing on C^2 a methoxy group (4-ADMP) and the one in which this position is free (see Figure 2a). In both cases, the nitrogen of N-C moiety was mainly converted into ammonium ions; the ratio $[NH_4^+]/[NO_3^-]$ is 8:1 and 5:1 for 4-ADMP and 4-AP, respectively.

In Scheme 5 (top) are shown the main transformation pathways [26]. Deeper inspection of 4-ADMP profiles shows that, until 2 h of irradiation, the nitrogen is probably released from the formamide, mainly as ammonium, in agreement with the literature data [10–12, 18, 30]. The defective nitrogen yield observed after 2 h of irradiation seems due to the presence of bound-nitrogen as formamide (around 40%).

In contrast, when the position 2 on the heteroaromatic ring is occupied by an amino group, a restricted mineralization of the organic nitrogen occurs (see Figure 2b). For both 2-AP and 2-AMP, after 2 h of irradiation just a small percentage of the organic nitrogen has been released. Besides, for longer irradiation time (16 h) the nitrogen is barely released and the ratio $[NH_4^+]/[NO_3^-]$ is approximately 1:1.5, so indicating the existence of a different mechanism of cleavage. In the case of 2-aminopyrimidine (2-AP), 45% of NO_3^- and 30% of NH_4^+ ions have been formed, while for 2-amino-6 methyl-pyrimidine (2-AMP) only 30% and



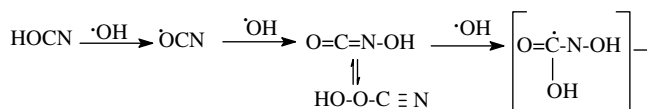
Scheme 5. Transformation pathways followed by 2-aminoderivatives (top) and 4-aminoderivatives (bottom) (adapted from reference [26]).

20% of NO_3^- and NH_4^+ ions respectively have been detected.

In Scheme 5 (bottom) are reported the main pathways involved in the transformation of 2-aminoderivatives. The lack of nitrogen mineralization evidenced in 2-AP and 2-AMP is linked to the stoichiometric conversion of the $\text{N}-\text{C}(\text{NH}_2)-\text{N}$ moiety into guanidine, whose degradation rate has been illustrated on section 2.2. The existence of a slow-rate initial pathway clarifies both the residue of bound-nitrogen detected from aminopyrimidinic structure [26] and mepanipyrim, when as far as aromatic intermediates degradation is concerned, TOC disappearance is fast and almost complete. However, a residual organic carbon, consistent with the guanidine formation [26], is observed.

4. Nitrogen with triple bonds

Frank et al. [41] have investigated the fate of cyanide ion, a rather frequent pollutant, in aqueous solution. Valence band holes cause the oxidation of CN^- to CNO^- . The occurrence of this oxidation is confirmed by Augugliaro et al. [42] which reported, in concomitance to the disappearance of cyanide, the specular formation of cyanate ion. This underlines that cyanate is the first photo-oxidation product during cyanide degradation. The subsequent cyanate oxidation could lead to nitrite (and finally nitrate) formation. Nevertheless, Augugliaro et al. have noted a lack of nitrogen mass balance. This could be explained by supposing that a sequence like (2) occurs.



Through the proposed sequence, NO gas could be formed as intermediate during the nitrite formation, so that the lack of mineralization observed may be linked to a partial loss of nitrogen as NO gas before the formation of nitrite could occur.

The photo-oxidation of acetonitrile adsorbed on TiO₂, both in liquid and gas phase, was studied by Lichtin et al. [43]. They have demonstrated that acetonitrile is much more reactive in the gas phase than in the aqueous phase. The production of cyanogen (CN)₂ as intermediate has been reported, thus indicating the formation of [•]CN radical, which dimerizes. The authors suggest that this radical formation is due to the interaction of a hole (or CH₃=CN^{•+} radical cation) with an adsorbed CH₃CN^{•-} radical anion, thus causing the CH₃CN dissociation. Presumably, the resulting (CH₃)[•] radical reacts rapidly with O₂, while at least some of the (CN[•]) radical undergoes dimerization. In parallel to cyanogen formation, also NO₂ was identified as product, in agreement with the formation of NO reported above in the sequence 2. In the liquid phase, acetonitrile degradation was quite slow. OH radical attack occurs on (CH₃)[•] radical, giving formic acid and HOCN, as observed by Augugliaro et al. [44]. Also, OCN⁻ is slowly photo-oxidised, through the mechanism reported in the sequence 2.

5. Conclusions

In the TiO₂ photo-induced degradation of nitrogen-containing compounds, the fate of the organic carbon can be classified on the basis of the nitrogen bond configuration. While HN—NH (and N=N) moieties are mainly transformed into N₂ gas, more intriguing is the fate of C—N bonds.

For alkyl and alkanol amines, containing extractable H, the formation of NH₄⁺ ions predominates over NO₃⁻ ions with ratio ranging from 3 to 6, depending on the nature of the structure. On the other hand, urea and guanidine, not containing extractable H, are slowly transformed into nitrate ions. This behaviour is linked to the existence of a different initial degradation step. As long as carbon holds an extractable hydrogen, the degradation proceeds mainly through an OH attack on carbon atom, finally leading to ammonium release, while when the carbon does not bind hydrogen, the radical attack occurs on the nitrogen atom, so favouring the detachment of nitrate ions. The latter pathway would be very slow because the rate of disappearance becomes very slow.

Cyanide and acetonitrile, two structures characterized by the presence of C≡N moiety, are predominantly transformed into cyanate. Cyanate is then slowly oxidized, finally giving nitrate ion formation.

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