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Processes of formation of NH_4^+ and NO_3^- ions during the photocatalyzed oxidation of N-containing compounds at the titania/water interface

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Abstract

Nitrogen-containing substrates such as amino acids, amides, succinimide, imidazole, hydroxylamine and urea were photodegraded in illuminated TiO_2 suspensions, and the temporal course of formation of NH_4^+ and NO_3^- ions was monitored. The hydroxylated nitrogen moiety in a molecule was predominantly converted to NO_3^- ions, whereas a primary amine and/or an amide were exclusively transformed to NH_4^+ ions under the prevailing conditions. Heterocyclic nitrogen groups in imidazole were converted to both NH_4^+ and NO_3^- ions via the intermediates whose structures were the primary amine and hydroxylamine, respectively. The influence of chemical structure on formation of NH_4^+ and NO_3^- ions is discussed from the view point of adsorption behaviours of substrates onto the TiO_2 surface.

Keywords: Photocatalyzed oxidation; NH_4^+; NO_3^-; Titania/water interface; Photodegradation

1. Introduction

The treatment of waste waters using the TiO_2 photocatalyzed oxidative route is one of several promising advanced oxidation technologies for environmental remediation. Many nitrogen-containing compounds (e.g. proteins, nucleic acids, etc.) are found in nature. Most pesticides and herbicides contain one or two nitrogen atoms. The mechanism of photocatalytic mineralization of these nitrogen-containing compounds is an important subject that begs urgent elucidation. Various organic pollutants such as chlorinated compounds [1,2] and heteroatom compounds [3] can be photomineralized by titania. Many researchers report that the hydrocarbon fragment is completely converted to CO_2 and the photoconversion of chlorine, sulfur and phosphorous atoms in the organic compounds produces Cl^-, [4] SO_4^{2-}, [5] and $H_2PO_4^-$, [6] respectively. However, the fate of the N atom(s) in the photomineralization of nitrogen-containing compounds has not yet been clarified [7–11].

The TiO_2 photocatalyzed transformation of such inorganic nitrogen as NH_2OH [12] and NO gas [13] in aqueous media and/or under gaseous conditions in an argon atmosphere generates N_2, N_2O, NO_2, NH_3 and N_2H_4 via either photoinduced reductions or oxidations by electrons or holes generated on the exited TiO_2 surface. Gaseous ammonia was photo-oxidized over TiO_2 particulates to produce only N_2 and N_2O at high oxygen pressure [14]. Low et al. [15] reported on the degradation of organic compounds containing nitrogen in the form either nitrate, nitro, saturated or aromatic ring nitrogens and confirmed the production of NH_4^+ and NO_3^- ions as the ultimate photomineralization species. Ammonium ions formed from the photo-oxidation of *N*-pentylamine, piperidine and pyridine via the immonium cation radical ($RCH{=}NH_2^{\cdot +}$) intermediate. Nitrate ions can be generated from the further oxidation of NH_4^+ ions. However, both NH_4^+ and NO_3^- ions are concomitantly produced in different quantities during the photo-oxidation of nitrogen-containing surfactants [16]. This observation implies that formation of NH_4^+ and NO_3^- ions probably takes place by at least two pathways. In excess oxygen, photocatalytic reductions are less frequently encountered than are oxidations, presumably because the reducing power of photogenerated electrons is significantly lower than the oxidizing power of photoholes, and also because most reducible substrates do not compete kinetically with oxygen in the trapping of conduction band electrons [17]. Thus a reduction of the nitrogen atom in the substrate is unlikely. We tentatively suggest that the formation of both NH_4^+ and NO_3^- ions proceeds through a photo-

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oxidative pathway. Evidently, concomitant formation of both ionic species under photo-oxidative mineralization conditions presents a complex challenge.

In this study, various nitrogen-containing compounds were photodegraded in illuminated TiO_2 aqueous suspensions to measure the concentration of NH_4^+ and NO_3^- ions formed. The dependence of the formation of NH_4^+ and NO_3^- ions on the chemical structure of the substrates are investigated. In particular, the structures which photoconvert easily to give either the NO_3^- ions or the NH_4^+ ions were identified. The mechanism of formation of these ions is discussed from the standpoint of the chemical structure and the adsorption of substrate on the photocatalyst TiO_2 surface.

2. Experimental section

2.1. Materials

8-amino-octanoic acid (8-AOA NH_2–$(CH_2)_7$–COOH) was supplied by Aldrich; 6-aminohexanoic acid (6-AHA NH_2–$(CH_2)_5$–COOH), 3-aminopropanoic acid (3-APA NH_2–$(CH_2)_2$–COOH), butylamide ($CH_3CH_2CH_2CONH_2$), succinimide, imidazole, pyrrole, formaldoxime (CH_2=N–OH), formamide ($HCONH_2$), formamidoxime (HO–N=CH–NH_2), *N*-methylhydroxyamine (CH_3–NHOH), hydroxylamine (HO–NH_2), dimethylglyoxime (CH_3–N=CH–CH=N–CH_3) and urea (NH_2CONH_2) were all supplied by Tokyo Kasei Co. Ltd. *N*-hydroxysuccinimide was a generous gift from Chemie Linz GesmbH. All the reagents employed were not subjected to any further treatment. Water used throughout was deionized and doubly distilled. Fluorescamine was supplied by Fluka Chem.

2.2. Photodegradation procedure

An aqueous dispersion consisting of nitrogen-containing systems (0.1 mM, volume 50 ml; pH = 6.5 to 7.7) and TiO_2 (Degussa P-25; 100 mg) was illuminated under continuous magnetic agitation with a 75 W mercury lamp (Toshiba SHL-100UVQ100) delivering 1.5 to 1.7 mW cm^{-2} at wavelengths greater than 330 nm. Experiments were carried out under an excess oxygen atmosphere. TiO_2 particles were removed by centrifugation and filtration through a Millipore membrane (0.22 μm) prior to the measurement of NH_4^+ and NO_3^- ions.

2.3. Analytical methods

Changes in the concentration of NH_4^+ ions were monitored with a JASCO ion chromatograph equipped with a Y-521 cationic column; the eluent was nitric acid (4 mM). Nitrate ions were also monitored by ion chromatography with an I-524 anionic column using a mixed solution (pH 4, pH 2.2) of phthalic acid (2.5 mM) and tris(hydroxymethyl)-aminomethane (2.3 mM) as the eluent. The primary amine was detected by fluorometric assay with the reagent fluorescamine [18]. The amine solution (0.15 ml) was mixed with 0.15 ml of borate buffer solution (pH 9.0) in a small test tube to which was added a 0.15 ml fluorescamine solution (0.03%) prepared in acetone. The fluorescence signal at 475 nm was recorded one minute after the addition under excitation at 390 nm with a JASCO 660 UV spectrofluorometer. The zeta-potential was measured with a Laser Zee Model 501 equipment [19].

2.4. Computational calculations of molecular orbitals

Molecular orbital (MO) calculations were carried out to the single determinant (Hartree–Fock) level. Optimal geometries for conformational minima were obtained at the AM1 level. All semi-empirical calculations were performed with MOPAC version 6 using the CAChe system (see Appendix) as implemented on a Power Macintosh 8100/100 computer.

3. Results and discussion

Formation of NH_4^+ and NO_3^- ions from the photo-oxidation of 8-amino-octanoic acid, 6-aminohexanoic acid and 3-aminopropanoic acid, all of which possess a primary amine function at the terminal position, and from butylamide is depicted in Fig. 1(a). The primary amine moiety is almost completely converted to NH_4^+ ions via first-order kinetics, irrespective of the number of methylene groups. The amount of NO_3^- ions formed is negligibly small. The amide group is transformed to NH_4^+ ions also by first-order kinetics, but at a rate faster than observed for the primary amino group. The percent conversion of nitrogen atom to NH_4^+ and NO_3^- ions and the first order rates of both ions are shown in Table 1.

We hypothesize that the α-carbon adjacent to the primary amine is initially oxidized to promote the scission of the N–C bond, whereas in the amide moiety the N–C bond is easily and readily cleaved. In the case of the ω-amino acid homologues, both terminal –COOH and –NH_2 groups are photo-oxidized competitively on the titania particle surface, as witnessed by the concomitant evolution of CO_2 and production of NH_4^+ ions. Fig. 1(b) shows the disappearance of the primary amine moiety in 8-amino-octanoic acid and 3-aminopropanoic acid versus irradiation time, followed by fluorometric analysis. The primary amine signal in these substrates decreased inversely with formation of NH_4^+ ions during their temporal photodegradation. Subsequent to cleavage of the C–N bond in the primary amine homologues, formation of NH_4^+ ions is fairly rapid: 3-APA > 6-AHA > 8-AOA reflecting variations in the number of methylene groups or chain length.

Primary and secondary amine functions are photocatalytically oxidized on illuminated TiO_2 powders suspended in acetonitrile to yield *N*-alkylideneamines via a surface-bound R–$NH_2^{+\cdot}$ cation radical intermediate as reported [20]. Concomitantly, this cation radical rapidly transforms to immonium cation followed by oxidation of the α-carbon adja-

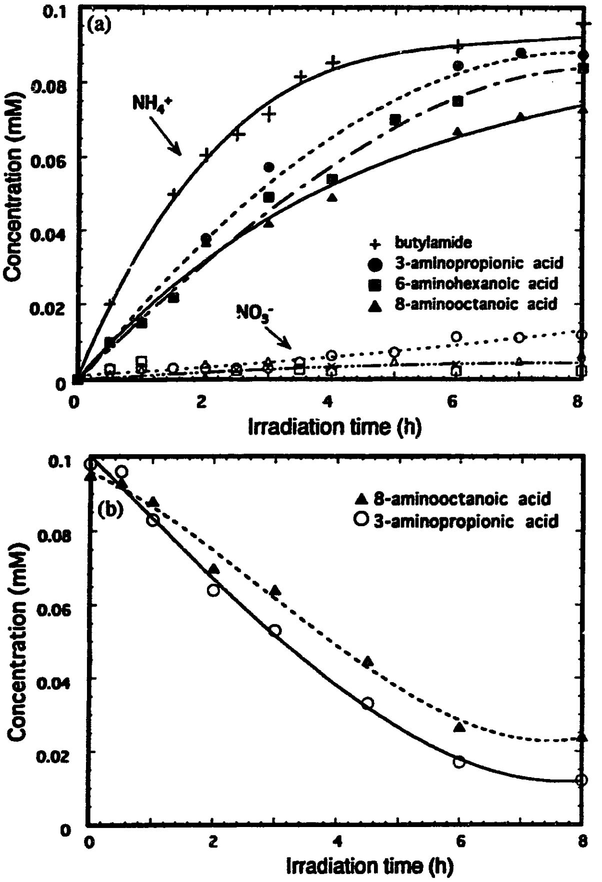


Fig. 1. (a) The relationship between the formation of NH_4^+ and NO_3^- ions and the irradiation time for the photodegraded solution (0.1 mM). NH_4^+: ▲, 8-aminooctanoic acid; ■, 6-aminohexanoic acid; ●, 3-aminopropanoic acid; +, butylamide. NO_3^-: △, 8-aminooctanoic acid; □, 6-aminohexanoic acid; ○, 3-aminopropanoic acid; ×283, butylamide. (b) The disappearance of the primary amine moiety of 8-aminooctanoic acid (▲) and 3-aminopropanoic acid (○) vs. illumination time.

cent to the primary amine by either the $^{\cdot}OOH$ and/or $^{\cdot}OH$ radical to yield an alkylated aldehyde and NH_3. Some researchers have claimed that the immonium radical cation is the precursor to formation of NH_4^+ ions [15]. Although nitrogenous cation radicals produced from direct hole oxidation on the TiO_2 surface have not yet been detected, it is reasonable to infer a mechanism since the rate of C–N bond cleavage in the primary amine moiety is faster than cleavage of either the C–C or C–H bonds in the hydrocarbon residue.

Fig. 2 depicts the formation of both NH_4^+ and NO_3^- ionic species from such cyclic nitrogens as are present in succinimide and in *N*-hydroxysuccinimide. The nitrogen in succinimide is almost totally transformed to NH_4^+ ions (Table 1), whilst that in *N*-hydroxysuccinimide is predominantly converted into larger quantities of NO_3^- ions than NH_4^+ ions (78% versus 13% after 8 h of irradiation). These observations would suggest that nitrate ions are most likely generated from the hydroxylamino group and that ammonium ions arise principally from the amide group formed subsequent to opening of the succinimide ring.

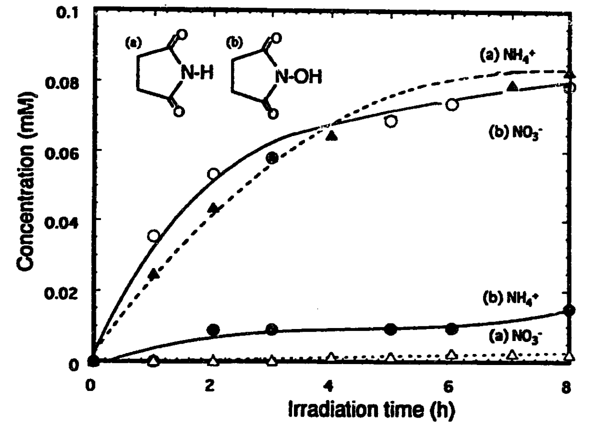


Fig. 2. Formation of NH_4^+ and NO_3^- ions as a function of illumination time in the photomineralization of succinimide: ▲, NH_4^+; △, NO_3^-; and *N*-hydroxysuccinimide: ●; NH_4^+, ○; NO_3^- solutions (0.1 mM).

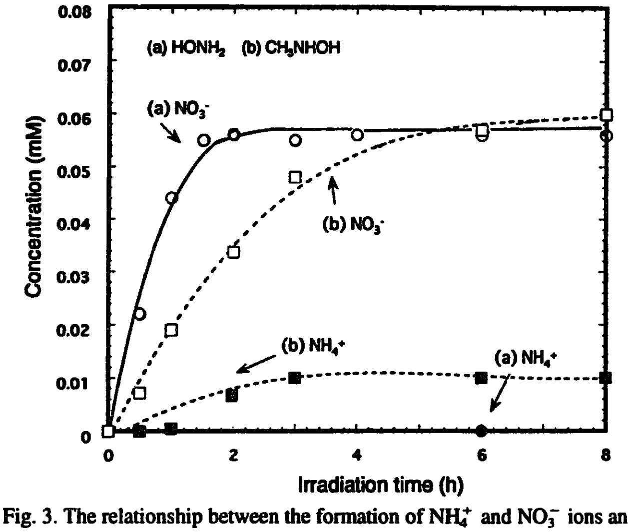


Fig. 3. The relationship between the formation of NH_4^+ and NO_3^- ions and the irradiation time for the photomineralization of hydroxylamine: ●, NH_4^+; ○, NO_3^-; and *N*-methylhydroxylamine: ■, NH_4^+; □, NO_3^-.

Photoconversion of hydroxylamine and *N*-methylhydroxylamine produces mostly NO_3^- ions as shown in Fig. 3, and confirms the above notion. Small quantities of NH_4^+ ions are generated in the photo-oxidation of *N*-methylhydroxyl amine. The extent of conversion of the nitrogen moiety in the two compounds is approximately 60% after 8 h of illumination. The remainder is converted to other inorganic species [12,13,21]; formation of N_2 and/or N_2O gas was not determined in our experiments.

The phototransformation of the hydroxyimino moiety in dimethylglyoxime, formaldoxime and formamidoxime was examined to assess the generation of both ammonium and nitrate ions (Fig. 4). The two nitrogen atoms in dimethylglyoxime are predominantly converted to NO_3^- ions. Small quantities of NH_4^+ ions were detected only after ~2 h of irradiation to reach the maximal value of ca. 0.02 mM. Formaldoxime also generates a greater quantity of NO_3^- ions (~2.5 times) than NH_4^+ ions. Nearly equal quantities of NO_3^- ions are generated for dimethylglyoxime and formam-

Table 1
The rates of conversion of nitrogen atom to NH_4^+ and NO_3^- ions and first-order rates of formation of both ions upon the photo-oxidation of various N-containing substrates

Substance	Conversion (%) after 8 h		Rate constants $\times 10^{-3}$ (min^{-1})[b]	
	NH_4^+	NO_3^-	NH_4^+	NO_3^-
Butylamide	96	3	7.2±1.2	[a]
3-aminopropanoic acid	92	3	5.1±0.3 (4.2±0.2)[c]	[a]
6-aminohexanoic acid	88	3	3.8±0.2	[a]
8-aminooctanoic acid	70	3	2.9±0.1 (3.3±0.2)[c]	[a]
Succinimide	82	3	5.7±0.3	[a]
N-hydroxysuccinimide	13	78	3.7±0.4	9.7±0.9
Hydroxylamine	[e]	56	[a]	23±3
N-methylhydroxylamine	6	58	18±9[d]	6.5±0.8
Dimethylglyoxime	9	85	15±3[d]	4.9±0.4
Formaldoxime	23	56	19±2	19±2
Formamidoxime	68	30	11.8±0.9	7.4±1.5[d]
Urea	9	42	3.7±1.0	3.6±1.1[d]
Formamide	53	47	15±1	16±3
Imidazole	49	26	3.6±0.3	2.1±0.4[d]
Pyrrole	69	17	13±1	2.4±0.7

[a] Negligibly small.
[b] After 8 h of irradiation.
[c] First-order rate of loss of the $-NH_2$ group.
[d] After 1 h induction period.
[e] No formation.

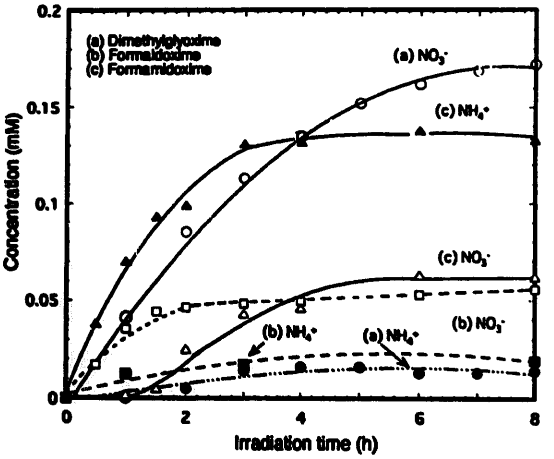


Fig. 4. The temporal formation of NH_4^+ and NO_3^- ions and the irradiation time profile for the photo-oxidized solution (0.1 mM). NH_4^+: ●, dimethylglyoxime; ■, formaldoxime; ▲, formamidoxime. NO_3^-: ○, dimethylglyoxime; □, formaldoxime; △, formamidoxime.

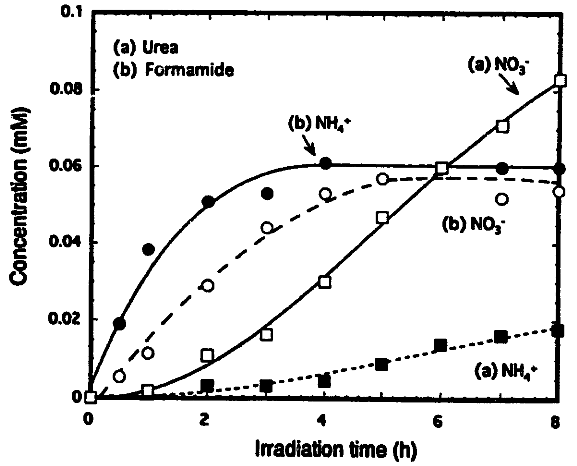


Fig. 5. Formation of NH_4^+ and NO_3^- ions vs. the irradiation time for the photodecomposition of urea: ■, NH_4^+; □, NO_3^-; and formamide: ●, NH_4^+; ○, NO_3^-.

idoxime. With respect to the latter, which possesses both a primary amine function and a glyoxime group, NH_4^+ ions are initially formed followed by NO_3^- ions after ~2 h irradiation. The maximal concentration of NH_4^+ of 0.13 mM is reacted after 3 h irradiation whereas that of NO_3^- ions is 0.06 mM nearly identical to the yield of NO_3^- ions in the photodegradation of formaldoxime. This fact implies formation of NH_4^+ ions arises from the amino group in formamidoxime. By contrast, photo-oxidation of the hydroxyimino moiety yields predominantly leads to NO_3^- ions.

Fig. 5 shows the formation of both NH_4^+ and NO_3^- ions during the photodecomposition of urea and formamide. A larger quantity of NO_3^- ions is produced in the photo-oxidation of urea, though it has the two primary amine functions. Photo-oxidation of urea is five-fold slower than photo-oxidation of formamide (Table 1). Quantities of NH_4^+ and NO_3^- ions formed from formamide are nearly equivalent. At this juncture we can only speculate that direct attack by OH radicals to the amide groups of urea on the TiO_2 surface is somehow facilitated by the two $-NH_2$ groups and leads to a greater yield of NO_3^- ions. With respect to formamide, $^\cdot OH$ radicals attack competitively both amine and carboxyl groups. Evidently, adsorption of the substrate via a nitrogen atom on the TiO_2 surface to form a surface complex may be relevant for the formation of NO_3^- ions.

Imidazole contains two heterocyclic nitrogen atoms and pyrrole which possesses only one nitrogen atom; their photo-oxidative conversion is shown in Fig. 6(a). For imidazole the yield of NH_4^+ ions generated is two-fold greater than NO_3^- ions (49% versus 26% after about 8 h of illumination) which begin to form only after a 2 h induction period at a rate slower than formation of ammonium ions (Table 1). To ascertain that no NO_3^- ion is derived from the oxidation of NH_4^+ we also carried out the oxidation of NH_4Cl under otherwise identical photocatalytic conditions as above. Only about 4% of ammonium chloride is converted to NO_3^- ions after ~15 h [16]. Evidently the rate of this photo-oxidation is relatively slower than those listed in Table 1.

The heterocyclic nitrogen atom in pyrrole is converted predominantly to NH_4^+ ions in a 69% yield (Fig. 6(a)). Formation of NO_3^- ions also shows an induction period; the yield is 17% after 8 h of irradiation. These results imply that formation of NO_3^- ions in the photo-oxidation of imidazole may originates from the conversion of the nitrogen atom at the 3-position, since the equivalent nitrogen in pyrrole (N at 1-position in imidazole) is converted primarily to ammonium ions. Thus, the inference is that photoconversion of the two nitrogen atoms in imidazole occurs via two pathways.

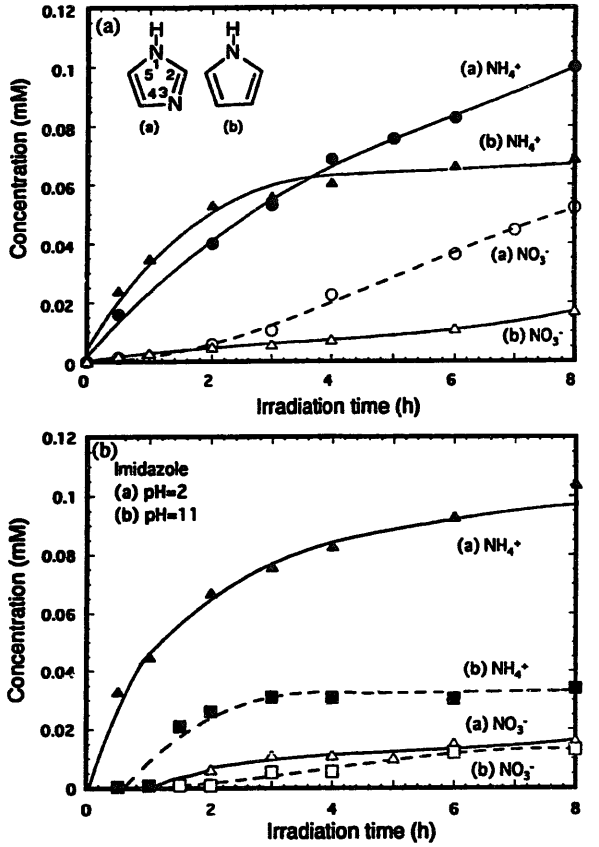


Fig. 6. (a) Time profile of concentration of NH_4^+ and NO_3^- ions for the photo-degradation solutions (0.1 mM) of imidazole; ●, NH_4^+; ○, NO_3^-; and pyrrole; ▲, NH_4^+; △, NO_3^-. (b) The pH dependence of the formation of NH_4^+ and NO_3^- ions for the photodegradation of imidazole solution (0.1 mM) of pH 2: ▲, NH_4^+; △, NO_3^-; and pH 11: ■, NH_4^+; □, NO_3^-.

To clarify these two likely pathways, we examined the pH dependence of the formation of NH_4^+ and NO_3^- ions in the photo-oxidation of imidazole (Fig. 6(b)) at pH 2 and pH 11; HCl and NaOH solutions were used to prepare the solutions. We first note that in the TiO_2 catalyst, the principal amphoteric surface functionality is the "titanol" moiety, ≡Ti–OH. Hydroxyl groups on the TiO_2 surface are known to undergo the following acid–base equilibrium:

$$\underset{\text{(acidic side)}}{\equiv\text{Ti}-\text{OH}_2^+} \underset{\text{H}^+}{\overset{\text{OH}^-}{\rightleftarrows}} \underset{\text{(neutral)}}{\equiv\text{Ti}-\text{OH}} \underset{\text{H}^+}{\overset{\text{OH}^-}{\rightleftarrows}} \underset{\text{(alkaline side)}}{\equiv\text{Ti}-\text{O}^-} \tag{1}$$

The extent of surface sorption of an electron donor to TiO_2 particles plays an important role in the determination of the photoreactivity [22]. The pH dependence of adsorption of an organic substrate to the TiO_2 surface has been examined by several workers [23]. On the acidic side (pH 2), imidazole is rapidly photodegraded and yield a greater quantity of NH_4^+ ions than NO_3^- ions (ratio of ~6.4 to 1). At natural pH (pH 7.8) the concentration of NO_3^- ions formed in an imidazole solution is three-fold greater than in acidic media at pH 2 (see Fig. 6(a)).

It is noteworthy that the concentration of NO_3^- ions formed at pH 11 is not very different from at pH 2. The nitrogen moeity in the photoproduced intermediates of imidazole are largely substituted by protons in acidic solution and thus may favour production of NH_4^+ ions at the expense of NO_3^- ions. In alkaline media (pH 11), the smaller quantities of NH_4^+ ions produced from the photo-oxidation of imidazole is due to significant adsorption on the TiO_2 surface. To verify this notion, when TiO_2 (100 mg) particles were added to the NH_4Cl solution (0.1 mM/50 ml) at pH 11, 75% of ammonium ions is adsorbed on the TiO_2 surface. Furthermore, a few NH_4^+ ions formed is converted to NH_3 gas in the photodegraded solution at pH 11.

Fig. 7 depicts the temporal variation of the fluorescence intensity at 475 nm which is attributed to the presence of a

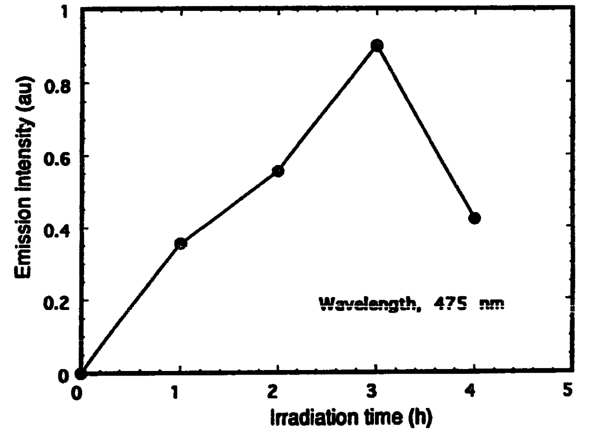


Fig. 7. Increase of fluorescence of the primary amine (475 nm) vs. irradiation time during the photodegradation of the imidazole solution (1 mM).

primary amine moeity in the intermediate products formed during the photodegradation of an imidazole solution (1 mM). No emission was seen at this wavelength before irradiation. Fluorescence intensity increased with irradiation time until 3 h and then gradually decreased. This result suggests that a primary amine is indeed produced and is subsequently decomposed along the photo-oxidative mineralization of imidazole.

The variation of the ζ-potential of TiO_2 particles in illuminated imidazole solutions was determined by the electrophoretic method (Fig. 8). The dynamic change of the TiO_2 surface potential in the photodegraded solution reflects the changes in the electrostatic adsorption of imidazole on the TiO_2 surface. Typically, the surface of the titania particles becomes positively charged under UV illumination because of the production of H^+ ions from the splitting of water [22]. The ζ-potential of TiO_2 in solution in the absence of imidazole (pH 6.3) is rapidly shifted positive after about 1 h of irradiation, following which it remains nearly constant between 3 mV to 8 mV. In the imidazole-containing system, the initial ζ-potential is negative (about −12 mV) in comparison with the potential of the control solution (about −4 mV), which are ascribed to the presence of imidazole in the solution (pH 7.8). the ζ-potential shifts to more positive potential on increasing the irradiation time.

3.1. Mechanism of photodegradation of imidazole

The usefulness of assessing the electrostatic potential is widely recognized for studying molecular structures and interactions in various chemical systems [24]; it expresses the coulombic interaction between the proton and the substrate. The electrostatic potential at a point near the substrate is the potential energy that a proton would have placed at that point. If the potential energy is negative, the proton and the substrate are attributed to each other; a positive potential energy is repulsive. Fig. 9(a) and 9(b) show the electrostatic potential of pyrrole and imidazole. The nitrogen in pyrrole and the nitrogen at the 1-position in imidazole are surrounded by a large spread of positive potential, while the spread of positive potential around the nitrogen at the 3-position is smaller. There is a domain of negative potential near the nitrogen at the 3-position that indicates no interaction with a proton. The surface of the titania particles is positively charged under UV illumination for about 1 h (see Fig. 8). The most negative side of the organic substrate should easily approach the TiO_2 surface electrostatically. Thus approach of imidazole to TiO_2 surface should be facilitated via the nitrogen at the 3-position rather than the nitrogen at the 1-position.

The reaction site of both pyrrole and imidazole can be estimated by the frontier electrodensity; they are illustrated in Fig. 9(c) and 9(d) (the values denote sites for radical reaction). It is clear that the most reactive sites are the two carbons at both the 2- and 5-positions in both heterocycles. Thus, when pyrrole reacts with an ˙OH radical it will do so either at the 2-carbon or at the 5-carbon position. Likewise for imidazole, ˙OH radicals will most likely attack the carbons at both the 2- and 5- positions.

The presently available data and the theoretical calculations of reactive sites permit us to postulate a tentative mechanism for the formation of NH_4^+ and NO_3^- ions in the photodegradation of imidazole, as described in Scheme 1. In the first step, the imidazole molecule approaches the TiO_2 surface from the side of nitrogen at the 3-position; subsequently ˙OH radicals attack the 2-carbon atom. Our results

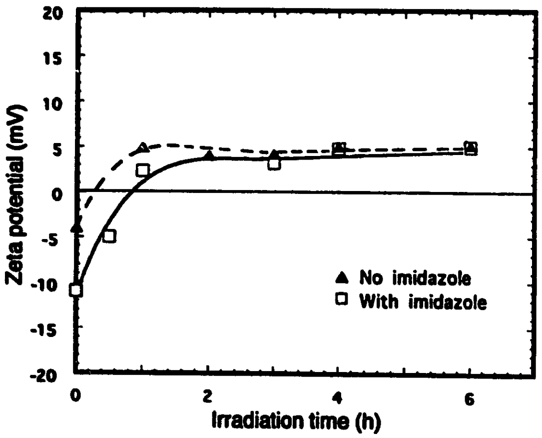


Fig. 8. The change of ζ-potential of TiO_2 particles against the irradiation time for the photodegraded imidazole solution (1 mM) (□) and solution without the imidazole (▲).

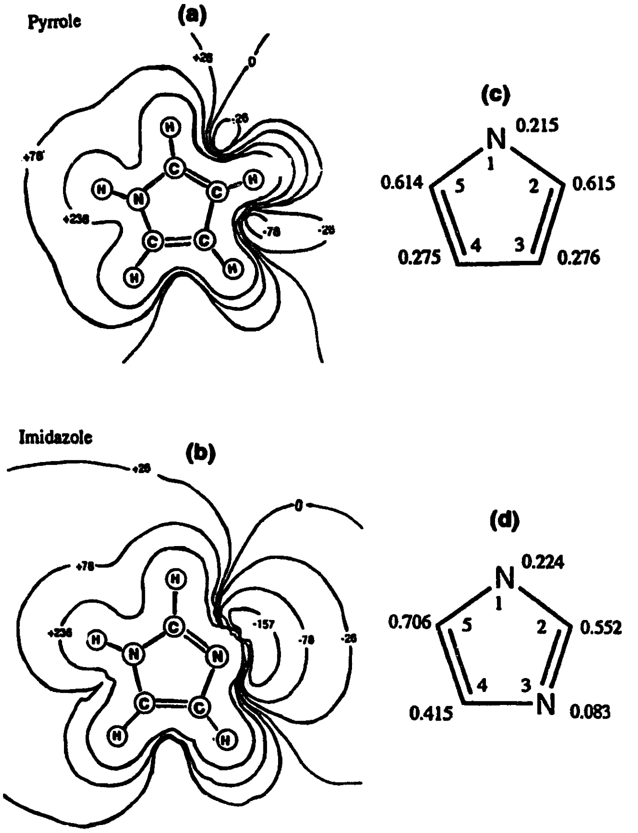
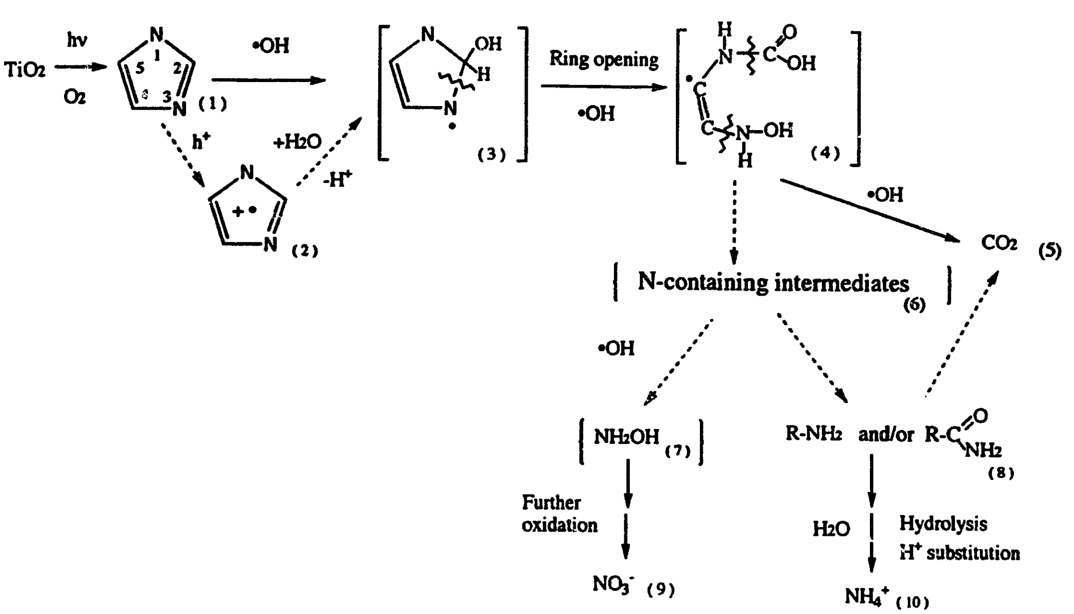


Fig. 9. The electrostatic potential maps of (a) pyrrole and (b) imidazole, where the unit of the value cited is kJ mol^{-1}. Also shown are the frontier electrodensity for (c) pyrrole and (d) imidazole.



Scheme 1. The postulated pathway of formation of NH_4^+ and NO_3^- ions in the photomineralization of imidazole.

are silent and do not preclude a pathway that implicates direct hole oxidation of the imidazole ring to give the imidazole cation radical (species **2**); reaction with water may give intermediate **3**. Further attack by an $^\cdot OH$ radical and subsequent rapture of the C2–N bond produces an intermediate such as (**4**). Continued oxidation then yields carbon dioxide and some N-containing intermediates (**6**). The results illustrated in Fig. 2 for the photo-oxidation of succinimide and *N*-hydroxysuccinimide suggest that conversion of nitrogen to NO_3^- ions likely occurs via a route that involves formation of a hydroxylamino group. Additional oxidation of the latter may yield first nitrite ions and then NO_3^- ions, by analogy with the photodegradation of hydroxylamine (Fig. 3) for which NO_3^- ions are formed almost exclusively. The fate of the nitrogen at the 1-position is to give primary amines and/or amide moieties that ultimately are transformed into ammonium ions, by analogy with the decomposition of amino acids and butylamide (Fig. 1).

4. Conclusions

In TiO_2 photocatalyzed oxidations of nitrogen-containing substances, formation of intermediates possessing a primary amino group or an amide moiety leads predominantly to the production of NH_4^+ ions. Nitrate ions are likely formed via generation of hydroxylamino groups. The chemical structure of the substrate influences the proportion of theses ions formed. Adsorption of and/or the mode of access of substrates to the TiO_2 particle surface are also relevant factors to consider in the ultimate formation of either NH_4^+ or NO_3^- ions.

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Appendix A

The electrostatic potential $V(r)$ at a point r describes the energy of the proton (+ 1 point charge) replaced near the atom A; it can be calculated from Eq. (2) [25];

$$V(r)=\sum_{A}\frac{Z_A}{(r-r_A)}-\int\frac{\rho(r')}{|r-r'|}\,dr' \qquad (2)$$

where Z_A denotes the nuclear charge of atom A, r_A is the position of atom A, and $\rho(r')$ is the electron density function at r' which is expressed as the sum of the density function of molecular orbitals. The first term in Eq. (2) is the contribution of the nucleus in atom A to the positive charge, and the second term is the negative charge of the electron.

Frontier electron density calculations can reveal a reactive site based on the electron distribution for a set of active orbitals near the highest occupied molecular orbital (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) [26]. The frontier electron density $f(x)$ in Eq. (3) is the weighted sum of the squares of the molecular coefficients, and is weighted by the difference in energy from either the HOMO or LUMO frontier orbital.

$$f(x)=\frac{2-\nu}{2}\frac{\sum_{j=1}^{N}\nu_j\phi_j(x)^2\mathrm{e}^{-\lambda(e\mathrm{HOMO}-)}}{\sum_{j=1}^{N}\nu_j(x)^2\mathrm{e}^{-\lambda(e\mathrm{HOMO}-)}}+\frac{\nu}{2}\frac{\sum_{j=1}^{N}(2-\nu_j)\phi_j(x)^2\mathrm{e}^{-\lambda(e\mathrm{LUMO}-e_j)}}{\sum_{j=1}^{N}(2-\nu_j)\mathrm{e}^{-\lambda(e\mathrm{LUMO}-e_j)}} \quad (3)$$

where λ is a number indicating the type of reaction; 0 for an electrophilic reaction, 1 for a radical reaction, and 2 for a nucleophilic reaction; N is the total number of orbitals; V_j is the number of electrons in orbital j which is usually 0, 1 or 2; $\phi_j(x)$ is the coefficient of orbital j at point x, and e_j is the energy of orbital, respectively.

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