Dependence on chemical structure of the production of NH_4^+ and/or NO_3^- ions during the photocatalyzed oxidation of nitrogen-containing substances at the titania/water interface

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Received 30 June 1995; accepted 20 September 1995

The dependence of the formation of NH_4^+ and/or NO_3^- ions on chemical structure has been examined in TiO_2 photocatalyzed oxidations of various amino acids, amides, and nitrogen-heterocyclic compounds. The primary amino groups and the amide moiety are converted photocatalytically and predominantly to NH_4^+ ions, whereas the hydroxylamino group in N-hydroxysuccinimide is photoconverted predominantly to NO_3^- ion. Results show that the nitrogen at the 1-position in imidazole is mainly photoconverted to NH_4^+ ion by analogy with the equivalent nitrogen atom in pyrrole; the nitrogen at the 3-position is transformed into NO_3^- ion. Formation of ammonium ions is faster than formation of nitrate ions in all but the N-hydroxysuccinimide substrate.

Keywords: photooxidation; titanium dioxide; heterogeneous catalysis; imidazole; succinimide; amino-acids

1. Introduction

Although photocatalyzed oxidations of a variety of organic compounds in the presence of titania catalysts have been examined rather extensively in the past few years [1], parallel studies on the photooxidation of nitrogen-containing molecules (e.g., benzamide [2], pyridine [3], atrazine and s-triazines [4]) have been relatively scarce. Nitrogen moieties in organic compounds can be transformed photocatalytically to ammonium and nitrate ions [5,6]. These few studies have shown that the nitro group is converted predominantly to NO_3^-. By contrast, the nitrogen in heterocyclic aromatic rings is transformed into both NH_4^+ and NO_3^- species. Related to this, secondary, tertiary and quaternary nitrogens, as well as the peptide group in surfactants are photoconverted predominantly to NH_4^+ ions [7,8]. Differences in the proportion of NH_4^+ to NO_3^- ions appear to be related to the chemical structure of the nitrogen-containing substrates.

Mechanistic details of the formation of ammonium and nitrate ions remain to be established. It is known that gamma radiolysis of aqueous amino acids generates NH_3 exclusively by reduction with solvated electrons [9]. At this time, formation of NH_4^+ in the photocatalyzed mineralization of nitrogenous substances by a reductive path appears to us somewhat unlikely since the electrons photogenerated on the TiO_2 surface should be scavenged predominantly by the excess oxygen present in solution under our experimental conditions. Formation of both NH_4^+ and NO_3^- ions appears to proceed through a photooxidative pathway. This concomitant formation of both ionic species under photooxidative mineralization conditions is indeed puzzling.

In this study we report the photocatalyzed transformation of various nitrogen-containing organic materials by illuminated TiO_2 aqueous suspensions. In particular we examine how the chemical structure of 8-aminooctanoic acid, 6-aminohexanoic acid, 3-aminopropionic acid, butylamide, succinimide, N-hydroxysuccinimide, imidazole, and pyrrole substrates influences the nature and the extent of formation of NH_4^+ and NO_3^- species. We show, for example, that all except one substrate yield predominantly NH_4^+ ions; the N-hydroxysuccinimide system, by contrast, yields predominantly NO_3^- ions.

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2. Experimental

An aqueous TiO_2 (Degussa P-25; 100 mg) dispersion containing nitrogen-containing systems (0.1 mM, volume 50 ml; pH = 6.5–7.7) of 8-aminooctanoic acid (99%; Aldrich), 6-aminohexanoic acid, 3-aminopropionic acid, butylamide, succinimide, imidazole, pyrrole (all from Tokyo Kasei Co. Ltd.), and N-hydroxysuccinimide (Chemie Linz GesmbH) was illuminated under continuous magnetic agitation with a 75 W mercury lamp (Toshiba SQ100) delivering 1.5–1.7 mW cm^{-2} at wavelengths greater than 330 nm [10,11]. Formation of NH_4^+ ions was monitored with a JASCO ion chromatograph equipped with a Y-521 cationic column; the eluent was nitric acid (4 mM). Nitrate ions were likewise monitored by ion chromatography with an I-524 anionic column using a mixed solution (pH 4) of phthalic acid (2.5 mM) and tris(hydroxymethyl)aminomethane (2.3 mM) as the eluent.

3. Results and discussion

Formation of NH_4^+ and NO_3^- ions from the photooxidation of 8-aminooctanoic acid, 6-aminohexanoic acid and 3-aminopropionic acid, all possessing a primary amine at the terminal position, and of butylamide is depicted in fig. 1. The primary amine moiety is nearly quantitatively converted to NH_4^+ ions via first-order kinetics (table 1). The rate is fastest for butylamide and slowest for the amino acid with the longest CH_2 chain. The •OH radicals generated on the TiO_2 surface by hole oxidation of OH^- or H_2O [1,12] can competitively attack the thermal –COOH and NH_2 groups, as witnessed by concomitant evolution of CO_2 with the production of NH_4^+ ions. For the slowest oxidizable amino acid, 8-aminooctanoic acid, such oxidized intermediate products as formic acid and acetic acid are formed to a greater extent than is observed for the 3-aminopropionic acid [13]. We speculate that further photooxidation of these aliphatic species of increased oxygen-to-carbon ratio competes with the conversion of the terminal amino moiety. The quantities of NO_3^- ions formed from the amide and the three amino acids are negligibly small. The amide group is also transformed to NH_4^+ ions by first-order kinetics but at a rate faster (by a factor of ~ 1.5–2.6) than observed for the primary amino groups in the amino acids. We infer that the α-carbon adjacent to the primary amine is initially oxidized to promote the scission of the N–C bond to yield carboxylic acid groups and ultimately production of NH_4^+ ions in acid media. The kinetic data of table 1 infers the N–C bond in the amide moiety is more easily cleaved than in the amino acids.

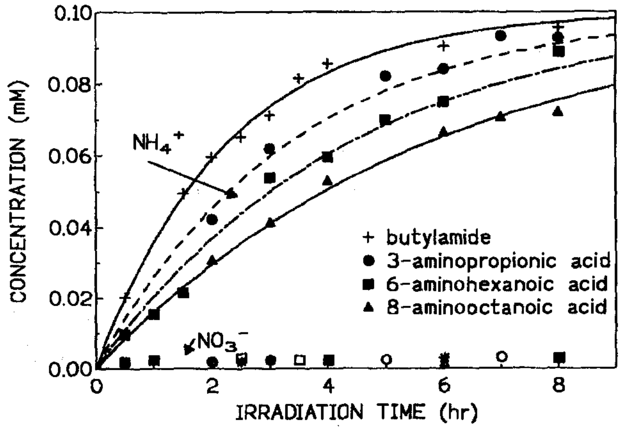

Fig. 1. Formation of NH_4^+ and NO_3^- ions as a function of irradiation time for the photocatalyzed oxidation of various amino acids and butylamide in irradiated TiO_2 aqueous dispersions (0.1 mM in organic substrate). NH_4^+: (▲) 8-aminooctanoic acid; (■) 6-aminohexanoic acid; (●) 3-aminopropionic acid; (+) butylamide. NO_3^-: (△) 8-aminooctanoic acid; (□) 6-aminohexanoic acid; (○) 3-aminopropionic acid; (*) butylamide.

Fig. 2 depicts the evolution of both NH_4^+ and NO_3^- ionic species from such heterocyclic nitrogens as in succinimide and in N-hydroxysuccinimide. The nitrogen in succinimide is totally transformed to NH_4^+ ions contrary to N-hydroxysuccinimide in which photooxidation produces larger quantities of NO_3^- ions than NH_4^+ ions. These observations suggest that formation of nitrate ions likely implicate a hydroxylamino group as an intermediate and that ammonium ions arise principally from the amide group formed on •OH radical opening of the succinimide ring.

The photooxidative conversion of imidazole which contains two heterocyclic nitrogen atoms and of pyrrole with one nitrogen atom, taken as a model compound for comparison, is shown in fig. 3. Photooxidation of imidazole yields both ammonium and nitrate ions in a proportion of 2 to 1, respectively, after about 8 h of illumination. Nitrate ions begin to form only after a 2 h induction period at a rate slower than formation of ammonium ions (table 1).

The available data suggest that conversion of nitrogen to NO_3^- ions likely occurs initially by •OH radical attack of the nitrogen atom in the organic compound as the first step giving a hydroxylamino group; further oxidation proceeds to form nitrite first and subsequently NO_3^- ions. To ascertain that the latter did not evolve 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 of irradiation [8]. Evidently the rate of this photooxidation is relatively slower than those reported in table 1.

The heterocyclic nitrogen atom in pyrrole is converted predominantly to NH_4^+ ions (fig. 3). Concomitantly, NO_3^- ions are also gradually produced in smaller quantities (~ 0.017 mM) after 8 h of irradiation. These results imply that formation of NO_3^- ions in the photooxidation of imidazole likely originates from the conversion of the nitrogen atom at the 3-position, since the

Table 1
Kinetic data in the formation of NH_4^+ and NO_3^- ions during the photooxidation of various N-containing substances

Substance	10^3k (min^{-1})		Percent conversion of N to $\{NH_4^+ + NO_3^-\}$
	NH_4^+	NO_3^-	
butylamide	7.4 ± 0.2	[a]	99 [b]
3-aminopropionic acid	5.1 ± 0.3	[a]	96
6-aminohexanoic acid	3.8 ± 0.2	[a]	92
8-aminooctanoic acid	2.9 ± 0.1	[a]	75
succinimide	5.7 ± 0.3	[a]	84
N-hydroxysuccinimide	3.7 ± 0.4	9.7 ± 0.9	89
imidazole	3.6 ± 0.3	2.1 ± 0.4	75
pyrrole	13.0 ± 1.1	2.4 ± 0.7	85

[a] Negligibly small.
[b] After 8 h irradiation; for experimental details see text.

equivalent nitrogen in pyrrole (N at 1-position in imidazole) is converted primarily to ammonium ions (see below). Thus, the photoconversion of the two nitrogen atoms in imidazole must occur via two pathways. In the first of these, direct •OH radical attack of the nitrogen at the 3-position yields the corresponding hydroxylamino group which, by analogy with the N-hydroxysuccinimide (fig. 2), is ultimately and mostly converted to nitrate ions (0.052 mM or 34% of total nitrogen converted after 8 h; fig. 3). In the second path, attack of •OH radicals elsewhere on the imidazole ring leads to ring cleavage to produce, after a sequence of steps, an amino group (or amide) that is subsequently transformed into ammonium ions (0.099 mM or 65% after 8 h; fig. 3), by analogy with the amino acids and the butylamide (fig. 1), and by analogy with the photooxidative consequences of pyrrole, an equivalent and model substrate, for which ammonium ions account for about 80% of the total nitrogen converted (fig. 3). Conversion of nitrogen to NO_3^- in imidazole and in pyrrole is a relatively slower process (see table 1).

In the formation of nitrate, electrostatic adsorption of the substrate via its most electronegative atom to the titania surface is probably one of several important factors that influence the outcome of the photooxidative pathway to mineralization. Generally, the surface of the titania particle becomes positively charged under UV illumination because of the production of H^+ ions from the splitting of water [14]. AM1 (Austin model 1) molecular orbital calculations carried out semi-empirically using the MOPAC system (a quantum mechanical molecular modeling program) [15] indicate that the nitrogen at the 3-position in the imidazole ring bears the largest negative charge and therefore interacts the most electrostatically with the photocatalyst surface. We conclude that this nitrogen is more readily attacked by the electrophilic •OH radicals on the TiO_2 surface, and that NO_3^- ions are most probably produced from this point

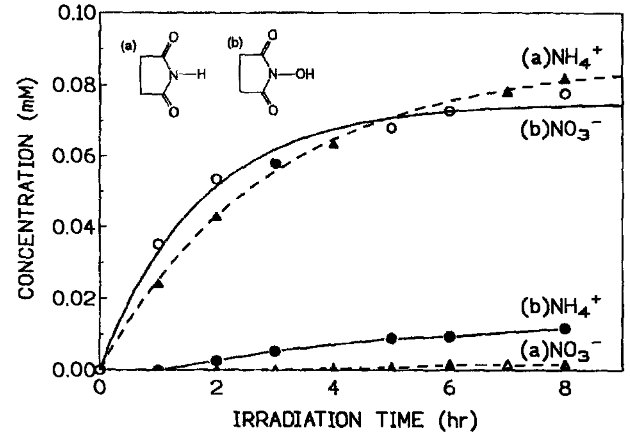

Fig. 2. Temporal course of the formation of NH_4^+ and NO_3^- ions as a function of irradiation time for the photocatalyzed oxidation of succinimide and N-hydroxysuccinimide (0.1 mM in organic substrate). (a) Succinimide: (▲) NH_4^+; (△) NO_3^-. (b) N-hydroxysuccinimide: (●) NH_4^+; (○) NO_3^-.

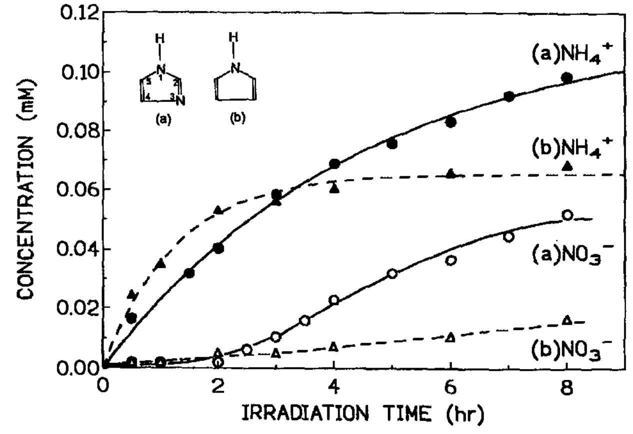

Fig. 3. Time profile of the concentration of NH_4^+ and NO_3^- ions during the photocatalyzed oxidation (0.1 mM in organic substrate) of (a) imidazole: (●) NH_4^+; (○) NO_3^-; and (b) pyrrole: (▲) NH_4^+; (△) NO_3^-.

rather than from the less negatively charged nitrogen atom at the 1-position. Details of these calculations shall be reported at a later date [13].

4. Conclusions

Amino acids and amides are easily photooxidized in irradiated TiO_2 aqueous dispersions; the primary amine and the amide groups are predominantly converted to NH_4^+ ions. Formation of a hydroxylamino group in an intermediate product is exclusively photoconverted to NO_3^- ions as witnessed by the fate of the nitrogen in N-hydroxysuccinimide. The nitrogen at the 3-position in imidazole is photocatalytically oxidized by the surface •OH radicals to give NO_3^- ions; by comparison with succinimide, the nitrogen at the 1-position in imidazole is converted mostly to NH_4^+ ions. The chemical structure of the substrate has an influence on the nature and relative quantities of NH_4^+ and NO_3^- species formed.

Acknowledgement

One of us (KN) thanks the Japanese Science Society for financial support and Dr. P. Pichat of the Ecole Centrale de Lyon, France, for his hospitality during a brief stay in his laboratory (summer 1994).

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