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Photooxidation mechanism of nitrogen-containing compounds at TiO_2/H_2O interfaces: an experimental and theoretical examination of hydrazine derivatives

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Abstract

The photocatalytic oxidation of oxalyldihydrazide, N, N'-bis(hydrazocarbonyl)hydrazide, N, N'-bis(ethoxycarbonyl)hydrazide, malonyldihydrazide, N-malonyl-bis[(N'-ethoxycarbonyl)hydrazide] was examined in aqueous TiO₂ dispersions under UV illumination. The photomineralization of nitrogen and carbon atoms in the substrates into N₂ gas, NH₄⁺ (and/or NO₃⁻) ions, and CO₂ gas was determined by HPLC and GC analysis. The formation of carboxylic acid intermediates also occurred in the photooxidation process. The photocatalytic mechanism is discussed on the basis of the experimental results, and with molecular orbital (MO) simulation of frontier electron density and point charge. Substrate carbonyl groups readily adsorb on the TiO₂ surface, and the bonds between carbonyl group carbon atoms and adjacent hydrazo group nitrogen atoms are cleaved predominantly in the initial photooxidation process. The hydrazo groups were photoconverted mainly into N₂ gas (in mineralization yields above 70%) and partially to NH₄⁺ ions (below 10%). The formation of NO₃⁻ ions was scarcely recognized. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The photodegradation of a series of nitrogen-containing compounds has been investigated in our previous papers (Hidaka et al., 1994, 1996; Waki et al., 1995; Nohara et al., 1996, 1997) and other publications (Low et al., 1989, 1991; Pellizzetti et al., 1989, 1992, 1993). The photomineralized products of nitrogen atoms in those N-containing compounds examined were found to be NH_4^+ and/or NO_3^- ions. The ratio of NH_4^+ to NO_3^- formation is dependent on the molecular structure of the substrate. The photocatalytic decomposition of compounds containing one or more hydrazo moieties has rarely been reported.

TiO₂ particles absorb UV light with an energy greater than the bandgap (ca. 3.2 eV) to generate electron/hole pairs. The holes (h⁺) are ultimately trapped by HO⁻ or H₂O at the TiO₂ particle surface to yield •OH radicals and H⁺. Concomitantly, dioxygen molecules react with electrons (e⁻) in the conduction band to produce superoxide radical anions, O₂⁻, which combine with protons to generate hydroperoxy radicals (•OOH). The

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charge of the TiO₂ particle surface becomes positive due to an excess of protons from H₂O or from the solution upon irradiation. Accordingly, the negatively charged atoms of organic compounds may be adsorbed easily on the surface of TiO₂ particles due to Coulombic forces, and the •OH radicals photogenerated on the TiO₂ surface are expected to attack predominantly at the positions having the highest frontier electron density.

In this study, the photocatalytic mineralization of compounds containing one or more hydrazo moieties, oxalyldihydrazide, N, N'-bis(hydrazocarbonyl)i.e., hydrazide, N, N-bis(ethoxycarbonyl)hydrazide, malonyldihydrazide and *N*-malonyl-bis[(*N*'-ethoxycarbonyl) hydrazide] was examined under UV irradiation in aqueous TiO_2 dispersions. The formation of NH_4^+ (or $NO^{3^{-}}$) ions, the evolution of CO_2 and N_2 gases, and the generation of carboxylic acid intermediates were monitored during the photodegradation process. Simulation of frontier electron density and point charge was also carried out. Mechanistic steps are discussed from the standpoint of the chemical structure of the substrates, the point charges and the frontier electron densities. The compounds investigated in this work are commonly used as gas-generating agents. They have characteristic molecular structures, and therefore studies of their photooxidation should provide much information enabling the details of the photocatalytic mechanism for N-containing compounds to be understood.

2. Experimental

2.1. Chemicals and reagents

Oxalyldihydrazide was supplied by Tokyo Kasei Ind. and was recrystallized from water. N, N'-bis(hydrozocarbonyl)hydrazide was synthesized by addition of bis(ethoxylcarbonyl) hydrazide to an excess of hydrazine (10 times by weight) under slow agitation for 24 h (yield, 55%, m.p. 214°C). N, N'-bis(ethoxycarbonyl)hydrazide was prepared by elimination of HCl from hydrazine (1 mol) and ethyl chloroformate (2 mol) in the presence of NaOH (2 mol). The precipitate was washed with iced water to remove NaCl and then was dried (yield 80%). The obtained powder was recrystallized twice from ethanol (m.p. 214°C). Malonyldihydrazide was prepared by the reaction of malonodiethyl ester with an excess of hydrazine under stirring for 24 h. Recrystallization was from water (m.p. 156°C). N-malonyl-bis[(N'-ethoxycarbonyl)hydrazide] was prepared by elimination of HCl from malonodihydrazide (1 mol) and ethyl chloroformate (2 mol) in the presence of NaOH (2 mol). The sample was recrystallized with ethanol and tetrahydrofuran (yield 19%, m.p. 190°C). The purities of all compounds prepared were checked by elemental analysis of C, H and N atoms, which were found to be within

0.6% of the calculated values. The photocatalyst titanium dioxide was Degussa P-25 (particle size, 20–30 nm by TEM; 83% anatase and 17% rutile by X-ray diffraction; surface area, 53 m² g⁻¹ by BET method).

2.2. Photodegradation procedures and analytical methods

For the photocatalyzed conversion of the gas-generating agents, an aqueous dispersion (50 ml) of the substrates (1 mM) and 100 mg of TiO₂ particles were placed in a 124 ml pyrex reactor; the mixture was then dispersed by sonication for 5 min and then was illuminated with a 75 W Hg lamp under continuous agitation, which gave a light intensity of 2.01 mW cm⁻² in the wavelength range 310–400 nm (the maximum emission: $\lambda = 365$ nm). The headspace volume in the reaction vessel was purged with oxygen for 15 min prior to irradiation.

The temporal evolution of N_2 and CO_2 gases was monitored by gas chromatography with an Ookura Riken chromatograph (model 802; TCD detector) through a Molecular sieve 5A (for N_2 gas) or a Porapack Q (for CO_2 gas) column with helium as the carrier gas. The concentration of NH_4^+ and NO_3^- ions formed was assayed with a JASCO HPLC equipped chromatograph with a CD-5 conductivity detector using a Y-521 cationic column or an I-524 anionic column.

Molecular orbital (MO) calculations were carried out at the single determinant (Hartree–Fock) level with the optimal conformation having minimum energy obtained at the AM1 level (Nohara et al., 1997). All semiempirical calculations were performed with MOPAC version 6 in the CAChe package implemented on a Power Macintosh system. All MO calculations were simulated for the initial processes of \cdot OH radical attack and adsorption of molecules on the TiO₂ surface.

3. Results and discussion

The formation of CO_2 , N_2 , NH_4^+ and NO_3^- during photodegradation of the substrates and the detected intermediates of carboxylic acids in the photodegradation of hydrazine substrates is summarized in Table 1.

The photomineralization in the photodegradation of oxalyldihydrazide is illustrated in Fig. 1. The apparent first-order rate constant of N₂ gas formation $(k = 1.1 \times 10^{-2} \text{ min}^{-1})$ was higher than that of CO₂ gas $(k = 6.0 \times 10^{-3} \text{ min}^{-1})$.

The two hydrazo moieties of oxalyldihydrazide were converted to N₂ gas with a yield of 81% after 4 h of illumination. NH₄⁺ ions were also generated in a small amount (ca. 10%) and no formation of NO₃⁻ ions was observed in the photodegradation process. The fronter electron densities and point charges for oxalyldihydrazide were calculated to estimate the position adsorbed of the substrates over TiO₂ catalyst as well as the

Table 1

Formation of NH_4^+ and NO_3^- ions, CO_2 and N_2 gases, and intermediate carboxylic acids in the photodegradation of hydrazine derivatives (1 mM) in aqueous TiO₂ (100 mg) dispersions (50 ml)^a

Substrates Products (mM) after 4 h			Products (mM) after 8 h				Detected		
	N_2	CO_2	NH_4^+	NO_3^-	N_2	CO_2	NH_4^+	NO_3^-	carboxylic acids
Oxalyldihydrazide	1.64	1.20	0.37	0.01	1.68	1.32	0.44	0.02	HCOOH (COOH) ₂
N, N'-bis(hydrazocarbonyl) hydrazide	1.50	0.53	0.25	0.02	2.52	1.36	0.58	0.20	HCOOH
<i>N</i> , <i>N</i> '-bis(ethoxycarbonyl) hydrazide	0.58	2.42	0.01	0.001	0.68	3.89	0.01	0.002	HCOOH CH ₃ COOH
Malonyldihydrazide	1.66	0.84	0.30	0	1.68	2.80	0.30	0.01	HCOOH CH ₂ (COOH) ₂
<i>N</i> -malonyl-bis[(<i>N</i> '-ethoxy- carbonyl) hydrazide]	0.75	1.74	0.03	0	1.87	3.37	0.05	0.02	HCOOH CH ₂ (COOH) ₂ CH ₃ COOH

^a The amount of N₂ and CO₂ formed was calculated as moles from a liter of the dispersion.



Fig. 1. Mineralization yield into CO_2 , N_2 , NH_4^+ and NO_3^- in the photocatalyzed decomposition of oxalyldihydrazide (1 mM) in aqueous TiO₂ (100 mg) dispersion (50 ml) under UV-illumination.

position attacked by \cdot OH radicals. The atoms with the largest negative point charges are O3 and O4, and the two carbonyl moieties have the highest frontier electron density (see Table 2). The O3 and O4 atoms are easily adsorbed on the positive TiO₂ surface in the initial photoreaction. The subsequent reaction is attack of \cdot OH radicals on the two carbonyl moieties to generate formic acid and oxalic acid, and finally to evolve CO₂ gas. It was presumed that the abstraction of hydrogen atoms from the two nitrogen atoms by OH radicals occurs to generate N₂ gas after the cleavage of C–N bonds.

Fig. 2 shows the photomineralization of N, N'bis(hydrazocarbonyl)hydrazide. Since N, N'-bis(hydrazocarbonyl)hydrazide has an additonal hydrazo moiety between the two carbonyl groups, N, N'-bis(hydrazocarbonyl)hydrazide produced about 1.5 times more N₂ gas than oxalyldihydrazide by photooxidation after 8 h Table 2 Frontier electron densities and point charge calculations of the oxalyldihydrazide using the MOPAC system in the CAChe package



Atom	Point charge	Frontier electron density
Cl	0.256	0.298
C2	0.257	0.295
O3	-0.347	0.282
O4	-0.347	0.282
N5	-0.293	0.223
N6	-0.291	0.218
N7	-0.185	0.150
H9	0.269	0.017
H10	0.268	0.018
H11	0.146	0.014
H12	0.154	0.020
H13	0.146	0.014
H14	0.154	0.020

of irradiation as shown in Table 1. The mineralization yield into N_2 gas was about 90% after illumination of 8 h.

The total mineralization yield of the N-atoms in N, N'-bis(hydrazocarbonyl)hydrazide into N₂ gas and NH₄⁺ ions (no NO₃⁻ ions) was almost 100% and no other N-containing organic intermediates were detected in the degraded TiO₂ dispersion. The MO calculation indicated that the adsorption of N, N'-bis(hydrazocarbonyl) hydrazide on the TiO₂ surface occurs preferentially via the two oxygen atoms (O5 and O6), and the two carbons (C3 and C4) in the carbonyl group are easily attacked by OH radicals. It seems that the initial evolution of N₂ gas

is from the decomposition of the two terminal hydrazo moieties, and subsequently the central hydrazo group is to be converted into N₂ because the frontier electron density of the central N–N atoms is lower than that of the terminal hydrazo moieties (see Table 3). The evolution of CO₂ from N, N'-bis(hydrazocarbonyl)hydrazide was slower than that from oxalyldihydrazide within 6 h of irradiation, but the final amount of CO₂ evolved from



Fig. 2. Photomineralization of N, N'-bis(hydrazocarbonyl)hydrazide. (The experimental conditions are the same as in Fig. 1.)

Table 3

Frontier electron densities and point charge calculations of the hydrazocarbodihydrazide using the MOPAC system in the CAChe package



Atom	Point charge	Frontier electron density
N1	-0.230	0.171
N2	-0.229	0.169
C3	0.633	0.335
C4	0.633	0.345
O5	0.654	0.270
O6	-0.653	0.269
N7	-0.238	0.161
N8	-0.340	0.040
N9	-0.237	0.161
N10	-0.340	0.042
H11	0.221	0.003
H12	0.219	0.003
H13	0.219	0.004
H14	0.198	0.005
H15	0.191	0.006
H16	0.218	0.004
H17	0.198	0.006
H18	0.191	0.005

both compounds was almost the same after irradiation of 8 h. Only formic acid was detected as a carboxylic acid intermediate in the photooxidation process.



Fig. 3. Photomineralization of N, N'-bis(ethoxycarbonyl)hydrazide. (The experimental conditions are the same as in Fig. 1.)

Table 4

Frontier electron densities and point charge calculations of the hydrazo diethylester using the MOPAC system in the CAChe package

O ®	O	
® H ₃ C−H ₂ C−O ® ①	H-NH-C 2 &	-сн ₂ -сн ₃

Atom	Point charge	Frontier electron density
N1	-0.218	0.290
N2	-0.219	0.290
C3	0.735	0.356
C4	0.736	0.351
C5	0.104	0.003
C6	-0.103	0.001
C7	0.103	0.003
C8	-0.103	0.001
O9	-0.629	0.305
O10	-0.389	0.043
011	-0.628	0.304
O12	-0.389	0.043
H13	0.229	0.004
H14	0.229	0.003
H15	0.075	0.001
H16	0.073	0.001
H17	0.042	0.000
H18	0.042	0.000
H19	0.035	0.001
H20	0.075	0.001
H21	0.073	0.001
H22	0.045	0.000
H23	0.042	0.000
H24	0.035	0.001

The mineralization yield for N, N'-bis(ethoxycarbonyl)hydrazide in a TiO₂ dispersion is depicted in Fig. 3. The conversion yield to N₂ gas was 70% after illumination for 8 h and the apparent first-order rate constant was $k = 3.6 \times 10^{-3}$ min⁻¹. A high frontier electron density, and the most negative point charge in N, N'-bis(ethoxycarbonyl)hydrazide were at O9 and O11 as listed in Table 4. The formation of NH₄⁺ and NO₃⁻ ions was scarcely observed as shown in Fig. 3. The photodecomposition of the $-CH_2CH_3$ moiety was expected and evidenced to generate both acetic acid and formic acid, and finally to evolve CO₂ gas (see Table 1).

In the photodegradation of malonyldihydrazide, N_2 gas was rapidly evolved upon illumination for less than 2 h, but CO₂ generation from the photooxidation of carbon atoms in the substrate was observed to increase gradually as shown in Fig. 4(a). The two oxygen atoms have a large negative point charge, and the C2, C3, O4, O5, N6 and N8 atoms possess a high frontier electron density (see Table 5), resulting in easy attack by •OH radicals. In contrast to oxalyldihydrazide, C1 had a very



Fig. 4. (a) Photomineralization of malonyldihydrazide. (b) Formation of intermediates of formic acid and amalonic acid in the photooxidation of malonyldihydrazide. (The experimental conditions are the same as in Fig. 1.)

low frontier electron density (0.059). The adsorption of malonyldihydrazide on the TiO₂ surface proceeds via the two oxygen atoms. N₂ was evolved rapidly since the C–N bond is photocleaved more easily than the C–C bond. The formation of carboxylic acid intermediates in the photooxidation of malonydihydrazide was also determined as shown in Fig. 4(b). Malonyldihydrazide was photooxidized to generate formic acid and malonic acid, and finally to evolve CO₂. The concentration of malonic acid increased with increasing irradiation time to reach a maximum at about 2 h of irradiation, and then decreased

Table 5

Frontier electron densities and point charge calculations of the malono carbodihydrazide using the MOPAC system in the CAChe package

	H ₂ N—NH Ø©	NH-NH ₂ ® 9
Atom	Point charge	Frontier electron density
C1	-0.212	0.059
C2	0.269	0.291
C3	0.269	0.289
O4	-0.358	0.224
O5	-0.358	0.224
N6	-0.316	0.256
N7	-0.185	0.141
N8	-0.316	0.248
N9	-0.184	0.135
H10	0.147	0.008
H11	0.146	0.008
H12	0.255	0.020
H13	0.142	0.013
H14	0.151	0.027
H15	0.255	0.020
H16	0.142	0.014
H17	0.152	0.024



Fig. 5. Photomineralization of *N*-malonyl-bis[(*N'*-ethoxycarbonyl)hydrazide]. (The experimental conditions are the same as in Fig. 1.)

with further irradiation. Formic acid was also produced in the photodegradation process. The amount of formic acid formed was more than that of malonic acid, but was also decomposed at longer irradiation times. The photomineralization yields and the frontier electron density simulation for *N*-malonyl-bis[(*N'*-ethoxycarbonyl)hydrazide] are depicted in Fig. 5 and Table 6.

The four carbonyl oxygen atoms have the most negative point charges in the structure, and the frontier

Table 6

Frontier electron densities and point charge calculations of the malono dicarbodihydrazide diethylester using the MOPAC system in the CAChe package

	₿ (¹) (¹)	
	C-NH-NH	NH-NH-C®
H ₃ C—H ₂ C		
Atom	Point charge	Frontier electron density
C1	-0.209	0.067
C2	0.257	0 194
C3	0.256	0 194
04	-0.275	0.162
05	-0.276	0.163
N6	-0.251	0.181
N7	-0.150	0.169
N8	-0.248	0.178
N9	-0.155	0.169
C10	0.321	0.084
C11	0.317	0.083
C12	-0.004	0.014
C13	-0.221	0.004
C14	-0.003	0.016
C15	-0.221	0.004
O16	-0.266	0.034
O17	-0.265	0.032
O18	-0.375	0.072
O19	-0.375	0.070
H20	0.137	0.018
H21	0.150	0.016
H22	0.231	0.019
H23	0.232	0.011
H24	0.229	0.019
H25	0.233	0.012
H26	0.097	0.002
H27	0.096	0.002
H28	0.093	0.001
H29	0.090	0.001
H30	0.091	0.002
H31	0.098	0.002
H32	0.094	0.003
H33	0.090	0.001
H34	0.092	0.001
H35	0.091	0.002
H20	0.137	0.018
H21	0.150	0.016
H22	0.231	0.019

electron densities of the C2 and C3 atoms of the carbonyl groups are larger than those of all the other atoms. The initial photooxidation reaction proceeds easily from the cleavage of either the C3–N8 or the C2–N6 bond in *N*-malonyl-bis[(N'-ethoxycarbonyl)hydrazide].

The formation of N_2 gas in the photodegradation of this compound was lower than that of malonyldihydrazide within 4 h irradiation owing to the generation of some complicated intermediates. As listed in Table 1, the intermediates of formic acid, acetic acid and malonic acid were also generated in the photooxidation process prior to CO₂ evolution.

4. Conclusion

The nitrogen atoms in the hydrazine derivatives investigated were photocatalytically converted predominantly to N₂ gas with a mineralization yield of more than 70% and partially to NH_4^+ ions with less than 10% mineralization yield. The formation of NO₃⁻ ions was scarcely observed in the photooxidation of any substrates used. The carbon atoms in the substrates were photomineralized into CO₂ via intermediates of various carboxylic acids. Owing to the higher point charges of oxygen atoms in the carbonyl groups, adsorption of the substrates onto the TiO₂ surface takes place via the carbonyl groups and the initial photooxidation proceeds to cleavage of the bond between the carbonyl carbon and the neighboring atoms by attack of ·OH and/or ·OOH radicals. The methylene moiety between the two carbonyl groups in malonyldihydrazide and N-malonylbis[(N'-ethoxycarbonyl)hydrazide] has a lower frontier electron density and the generation of CO₂ gas from the methylene carbon was very slow, since the attack of •OH radicals is difficult.

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References

Hidaka, H., Nohara, K., Zhao, J., Pelizzetti, E., Serpone, N., Guillard, C., Pichat, P., 1996. J. Adv. Oxid. Technol. 1, 27.

Hidaka, H., Takashima, K., Nohara, K., Zhao, J., Pelizzetti, E., Serpone, N., 1994. New J. Chem. 18, 541.

- Low, G.K.C., McEvoy, S.R., Matthews, R., 1989. Chemosphere 19, 1611.
- Low, G.K.C., McEvoy, S.R., Matthews, R., 1991. Environ. Sci. Technol. 25, 460.
- Nohara, K., Hidaka, H., Pelizzetti, E., Serpone, N., 1996. Catal. Lett. 36, 115.
- Nohara, K., Hidaka, H., Pelizzetti, E., Serpone, N., 1997. J. Photochem. Photobiol. A: Chem. 102, 265.
- Pellizzetti, E., Maurino, V., Minero, C., Zerbinati, O., Borgarello, E., 1989. Chemosphere 18, 1437.
- Pelizzetti, E., Minero, C., Carlin, V., Vincenti, M., Dolci, M., 1992. Chemosphere 24, 891.
- Pelizzetti, E., Minero, C., Piccinini, P., Vincenti, M., 1993. Coord. Chem. Rev. 125, 183.
- Waki, K., Wang, L., Nohara, K., Hidaka, H., 1995. J. Mol. Catal. 95, 53.