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Titanium dioxide mediated solar photocatalytic degradation of thiram in aqueous solution: Kinetics and mineralization

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ABSTRACT

The photocatalyzed degradation conditions of thiram in aqueous titanium dioxide-suspended solution were optimized under sunlight illumination. The effect of various factors, such as photocatalyst loading, initial substrate concentration, temperature, pH, sunlight intensity and illumination time on the photocatalytic degradation of thiram was investigated. The primary photocatalytic decomposition reaction followed a pseudo-first-order kinetic law according to the Langmuir–Hinshelwood model. During the photocatalytic degradation, the first-order rate constant k_{obs} was 0.10 min^{-1}, which was approximately 12 times that observed in direct photolysis. The half-lives ($t_{1/2}$) and the activation energy (E_a) were 6.7 min and 33 kJ mol^{-1}, respectively. Carbon dioxide and sulfate, nitrate and ammonium ions were detected as the end products. The stoichiometric transformation of organic sulfur to sulfate ions was observed at relatively shot illumination time (2 h), whereas the complete mineralization of organic carbon and nitrogen atoms took place at delayed illumination time. Dimethylamine and monomethylamine were identified as the intermediate products. The photocatalytic degradation mechanisms were proposed on the basis of the experimental results with molecular orbital (MO) simulation of frontier electron density. The solar photocatalytic degradation treatment for the wastewater including thiram is simple, easy handling and low cost. Therefore, since the artificial lamp devices, for example Hg-Xe lamp, are particularly expensive in the local and poor areas, the proposed technique seems to become a very powerful method for the treatment of wastewater including thiram in those areas.

1. Introduction

Thiram [thiuram (Japan), tetramethylthiuram disulfide (TMTD, former USSR), bis(dimethyldithiocarbamoyl) disulfide, CAS #137-26-8, Fig. 1] is an alkyldithiocarbamate compounds, which has been widely used as fungicides in agriculture. It is also used as an accelerator and vulcanization agent in the rubber industry and has been in commercial use since 1925. Some reports have been described on the mutagenicity and toxicity of thiram. It has been reported that the plate incorporation assays with *Salmonella typhimurium* TA100 and TA98 demonstrated direct mutagenecity of thiram [1,2]. The oral toxicity of thiram was presented in rodents [3]. In tests on human and rat testicular cells, thiram was found to increase possible carcinogenesis [4]. The U.S. Environmental Protection Agency (USEPA) researchers [5] have reported the reference doses (RfDs) in publicly accessible databases such as the Integrated Risk Information System (IRIS), which contained 0.005 mg kg^{-1} day^{-1} of thiram. Smith [6] has established the risk-based concentration of thiuram in tap water at 0.18 mg L^{-1}. The Ministry of the Environment in Japan released the uniform national effluent standards, which included 0.06 mg L^{-1} of thiram [7]. Until 2004, a regulation of the Ministry of Health, Labour and Welfare in Japan required the level of thiram remaining in tap water to be <0.006 mg L^{-1}. Niitsuma et al. [8] have investigated the degradation of thiram by ozone treatment with or without UV radiation. Ohta et al. [9] have found that thiram was degraded immediately during water purification using sodium hypochlorite, and about 30 mol of sodium hypochlorite reacted with one molecule of thiram. Chew and Harpp [10] have reported that the oxidation of thiram using thionyl chloride or chlorine gas in carbon tetrachloride gave *N*,*N*-dimethylthiocarbamyl chloride and diatomic sulfur. Kodama et al. [11] have studied the degradation pathway of thiram in tap water processed by oxidation with sodium hypochlorite. However, very few works related to the use of semiconductors such as TiO_2 in the degradation of thiram have been reported [12,13], although their purification techniques are simple, easy handing, cheap and environmental-benign. Moreover, the limited information concerning the degradation of thiram with TiO_2

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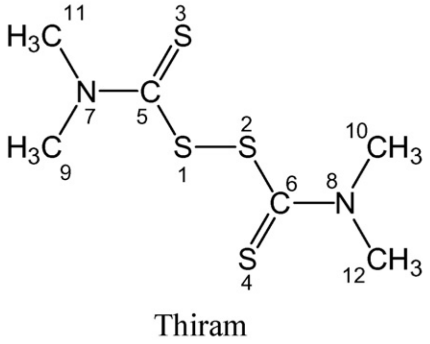

Fig. 1. Chemical structure of thiram.

merely contained the results using the halogen and high-pressure mercury lamp.

Previously, we have investigated the photocatalytic degradation of dibutyl phthalate in aqueous solution under sunlight illumination [14]. In the study, the complete mineralization could not be achieved in the short illumination time (<30 h). In the present work, the solar photocatalytic degradation conditions of thiram in water with TiO_2 were optimized, and the amount of final degradation products was monitored in order to evaluate the complete mineralization of thiram. Furthermore, the photocatalytic degradation pathways were speculated on the base of the evidence of the oxidative intermediate formation.

2. Experimental

Thiram used in this study was purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan (pesticide grade). Thiram aqueous solutions were prepared with ultrapure water, which was purified by an ultrapure water system (Advantec MFS, Inc., Tokyo, Japan) resulting in a resistivity >18 MΩ cm. A 50 mL aqueous solution containing 5 μg mL^{-1} ($\sim$21 μM) thiram was put into a closed columnar Pyrex reaction vessel (100 mL capacity). TiO_2 powder (anatase, purity 99.9%, diameter 230 nm, surface area 8.7 m^2 g^{-1}, Wako Pure Chemical Industries, Ltd.) was added to the solution to produce a given concentration of TiO_2 suspension. The pH of sample solution was adjusted with HCl and NaOH solutions. The temperature was kept constant with a water bath. The detailed typical experimental conditions were shown in Table 1. The TiO_2 suspension containing thiram was allowed to equilibrate for 60 min in the darkness, and then it was irradiated under sunlight illumination. During these treatments, the suspensions were magnetically stirred for the dispersion of TiO_2. In this case, the short ultraviolet radiation ($\lambda < 300$ nm) was filtered out by the vessel wall. The irradiance was measured by a UV radio meter with a sensor of 320–410 nm wavelengths (UVR-400, Iuchi Co., Osaka, Japan). The variations of irradiance for 20 min were less than 10%.

After illumination, TiO_2 was separated through the 0.45 μm Advantec membrane filter. The TiO_2 powders could be almost removed by the filtration. The amount of thiram in the aqueous solution was measured using a high-performance liquid chromatograph. The degradation efficiency of thiram was calculated with the following equation:

$$\text{Degradation efficiency (\%)} = \frac{100 \times (q_0 - q_1 - q_2)}{q_0 - q_1} \qquad (1)$$

where q_0, q_1 and q_2 were the initial amount of thiram, the amount adsorbed onto the catalyst at equilibrium and the residual amount undegraded after the treatment, respectively. The thiram amount adsorbed onto the catalyst was less than 3% of total amount in the solution. The reproducibility of the treatment [relative standard deviation (R.S.D.), for degradation efficiency] was better than R.S.D. 15% for three repeated measurements. The formation of sulfate and nitrate ions was measured by ion chromatography. The evolution of CO_2 was evaluated with a GL Science GC-353B equipped with a methanizer and a flame ionization detector, combined with a Porapack Q using nitrogen carrier gas. The detailed information for the experimental was described in the supplementary data.

Molecular orbital calculations were carried out at the single determinant (Hartree-Fock) level for optimization of the minimum energy obtained at the AM1 level. All semi-empirical calculations were performed in MOPAC Version 6.01 with a CAChe package (Fujitsu Co. Ltd.). An initial position for a possible $^{\bullet}$OH radical attack was estimated from calculations of frontier electron densities of the thiram structure. The mode by which thiram might adsorb onto the TiO_2 surface was estimated from calculated partial charges of thiram [15].

Table 1
Typical experimental conditions

Thiram	5 μg mL^{-1} (50 mL)
TiO_2	0–15 mg (0–300 μg mL^{-1})
Temperature	0–60 °C
pH	2.5–11.4
Light source	Sunlight
Irradiance	0–1.8 mW cm^{-2}
Illumination time	20 min

3. Results and discussion

3.1. UV–vis spectral changes

The temporal absorption spectral changes taking place during the photocatalytic degradation of thiram mediated by TiO_2 particles under sunlight illumination are investigated (supplementary data Fig. S1). Thiram shows a major absorption band at 215 and 276 nm. From the observed absorbance, absorptivity at 215 nm was estimated to be 6.3 cm^2 ng^{-1}. The well-defined absorption bands disappeared after irradiation for 60 min, indicating that thiram had degraded in the presence of TiO_2 particles with sunlight illumination. Therefore, because it was confirmed that TiO_2 was an effective photocatalyst for the decomposition of thiram under sunlight illumination, various factors such as photocatalyst loading, initial substrate concentration, temperature, pH, irradiance and illumination time, were evaluated for the photocatalytic degradation of thiram.

3.2. Effect of photocatalyst loading

In order to optimize the TiO_2 suspension concentration, the effect of photocatalyst loading on the degradation of thiram in aqueous solution was investigated as illustrated in the supplementary data Fig. S2. The degradation efficiency increased with increasing the amounts up to 8 mg, and then the efficiency became nearly flat. When the suspension concentration of TiO_2 increased above the limiting value 8 mg, the number of active sites on the TiO_2 surface may become almost constant because of the decreased light penetration, the increased light scattering and the loss in surface area occasioned by agglomeration (particle–particle interactions) at high solid concentration [16]. Therefore, 8 mg of TiO_2 was selected as the optimal amounts of photocatalyst for the sequential experiment. The TiO_2 amounts corresponded to the suspension concentration of 160 μg mL^{-1}.

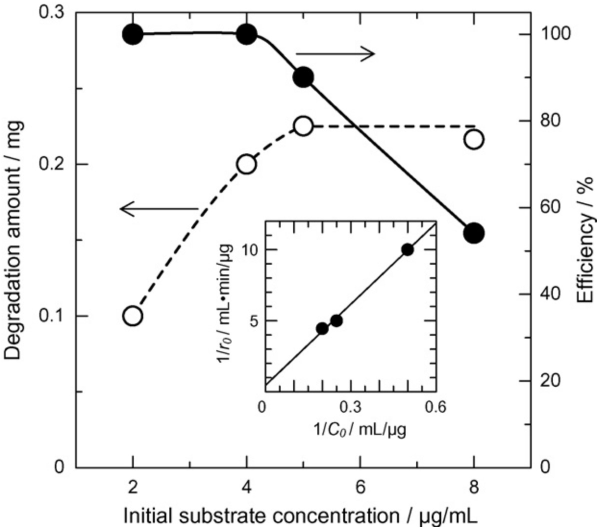

Fig. 2. Effect of initial substrate concentration on the solar photocatalytic degradation of thiram in water using TiO_2. Insert figure: plot of $1/r_0$ versus $1/C_0$. TiO_2: 8 mg (160 μg mL^{-1}); illumination time: 20 min; irradiance: 1.6 mW cm^{-2}; temperature: 30 °C; pH: 6.

3.3. *Effect of initial substrate concentration*

It is very important, from the application point of view, to investigate the dependence of the photocatalytic degradation on the substrate concentration. Therefore, the effect of initial substrate concentration on the photocatalytic decomposition using TiO_2 was investigated, as shown in Fig. 2. With increasing the initial substrate concentration up to 5 μg mL^{-1}, the degradation amounts of thiram increased greatly, although the degradation efficiency decreased. At the initial concentrations exceeding 5 μg mL^{-1}, the degradation amounts of thiram were almost the same. Therefore, 5 μg mL^{-1} of thiram solution was evaluated for the following experiment owing to trade off between the degradation amount and efficiency.

The photocatalytic oxidation kinetics of many organic compounds has often been modeled with the Langmuir–Hinshelwood (L–H) equation, which also covers the adsorption properties of the substrate on the photocatalyst surface. This model was developed by Turchi and Ollis [17] and expressed as Eq. (2):

$$r_0 = -\frac{dC}{dt} = \frac{kKC_0}{1+KC_0} \tag{2}$$

where r_0 is the degradation rate of the reactant, k is the reaction rate constant and K and C_0 are the adsorption equilibrium constant and concentration for the reactant, respectively. The transformation of the L–H equation (Eq. (2)) into its inverse function results in a linear relationship with an intercept of k^{-1} and a slope $(kK)^{-1}$:

$$\frac{1}{r_0} = \frac{1}{k} + \frac{1}{kKC_0} \tag{3}$$

The intercept and the slope can be obtained from a plot of the inverse of r_0 as a function of the reciprocal C_0, as illustrated in the insert figure in Fig. 2. Eq. (3) shows a good fit for the data with a correlation coefficient 0.99. The reaction rate constant and the adsorption coefficient of the reactant from plots are given in Table 2.

3.4. *Effect of temperature*

There is little information on the effect of temperature on the photocatalytic degradation of pollutants in aqueous solution with TiO_2. Therefore, the effect of temperature on the photocatalytic degradation of thiram in water using TiO_2 was investigated in the range of 0–60 °C. The results are shown in Fig. 3. The solution condition at 0 °C was between water and ice water. The degradation efficiency of thiram gradually increased as the temperature increased. In the photocatalytic degradation of imazaquin in an aqueous suspension of titanium dioxide [18], the effect of temperature was studied in the range 20–40 °C, and the rate constants increased with increasing temperature. Ishiki et al. [19] have investigated the photocatalytic degradation of imazethapyr herbicide at TiO_2/H_2O interface. In their works, the temperature effect was studied using a suspension between 20 and 40 °C, and the herbicide was more easily degraded at lower temperatures in the TiO_2 suspension, due to the decrease in the physisorption between the TiO_2 surface and the imazethapyr molecules. By plotting the natural logarithm of the rate constant as a function of reciprocal absolute temperature, a linear behavior was obtained with the correlation coefficient 0.99, as drawn in the insert figure in Fig. 3. The activation energy (E_a) was relatively low and was estimated to become 33 kJ mol^{-1}. It was reported in the TiO_2 photocatalytic degradation of benzene [20], naphthalene [21], imazaquin [18] and Chloramphenicol [22] that the activation energy (E_a) was 3.2, 22, 24.8 and 33 kJ mol^{-1}, respectively. Since the photoactivation process is irrelevant to thermal activation, the activation energy found is only apparent. Consequently, all subsequent illuminations were performed at 30 °C because of the operating cost for the photodegradation system.

Table 2
Reaction rate constant and adsorption equilibrium constant on TiO_2

k		*K*	
μg mL^{-1} min^{-1}	mol L^{-1} s^{-1}	mL $μg^{-1}$	L mol^{-1}
2.1	1.5×10^{-7}	0.025	5900

3.5. *Effect of initial pH*

The amphoteric behavior of most semiconductor oxides affects the surface charge of the photocatalyst. Therefore, the dependence of degradation efficiency for thiram on initial pH was investigated

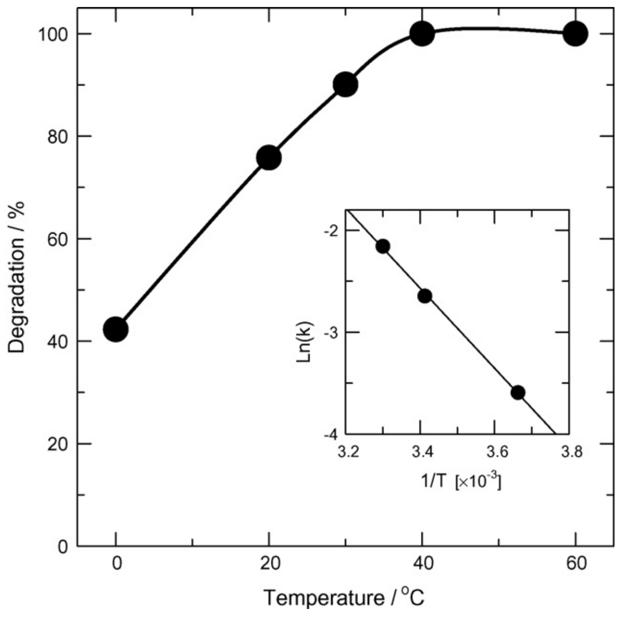

Fig. 3. Effect of temperature on the solar photocatalytic degradation of thiram in water using TiO_2. Insert figure: plot of Ln(k) versus $1/T$. Thiram: 5 μg mL^{-1}; TiO_2: 8 mg (160 μg mL^{-1}); illumination time: 20 min; irradiance: 1.6 mW cm^{-2}; pH: 6.

Table 3
Calculations of partial charge (PC) and frontier electron density (FED) for thiram

Atom	PC	FED	Atom	PC	FED
1S	0.209	0.602	9H-1	0.098	0
2S	0.209	0.602	9H-2	0.098	0
3S	−0.161	0.331	9H-3	0.088	0.001
4S	−0.161	0.331	10H-1	0.098	0
5C	−0.249	0.034	10H-2	0.098	0
6C	−0.249	0.034	10H-3	0.088	0.001
7N	−0.193	0.019	11H-1	0.107	0.001
8N	−0.193	0.019	11H-2	0.107	0.001
9C	−0.098	0.002	11H-3	0.081	0.001
10C	−0.098	0.002	12H-1	0.107	0.001
11C	−0.087	0.007	12H-3	0.107	0.001
12C	−0.087	0.007	12H-3	0.081	0.001

The positions (numbers) of atoms correspond to those illustrated in Fig. 1.

in the pH range 2.5–11.4 (supplementary data Fig. S3). The degradation efficiency increased with increase in pH, and in the pH region of more than 8 the efficiency became flat. When the initial pH was neutral to alkaline, the pH after the degradation of 20 min decreased slightly. The zero point charge (zpc) pH_{zpc} of TiO_2 particles is around 6 [23]. TiO_2 surface is positively charged in acidic media ($pH < 6$) whereas it is negatively charged under alkaline condition ($pH > 6$). The adsorption of thiram onto the TiO_2 surface was estimated from the simulation of molecular partial charges (Table 3). The most negative partial charge atoms in the thiram structure were the two carbon atoms (5C and 6C) in the dimethylthiocarbamoyl group, with the next ones being two nitrogen atoms (7N and 8N). On the other hand, the most positive partial charge atoms were two sulfur atoms (1S and 2S) bonded to the dimethylthiocarbamoyl group. Therefore, we deduce that in alkaline media ($pH > 6$) the positively charged sulfur 1S and 2S atoms are easily adsorbed on the TiO_2 surface through electrostatic interaction, and in acidic condition ($pH < 6$) via the negatively charged carbon 5C and 6C atoms in the dimethylthiocarbamoyl group, because the geometry of thiram molecule is almost plane. On the other hand, at high initial pH, more hydroxide ions (OH^-) in the solution induced the generation of hydroxyl free radicals ($HO^\bullet$), which came from the photooxidation of OH^- by holes forming on the titanium dioxide surface. Since hydroxyl free radical is the dominant oxidizing species in the photocatalytic process, the photocatalytic decay of thiram may be accelerated in the alkaline medium. Similar reaction has been suggested by a number of researchers [16,24–26]. The reason for the results that the degradation efficiency was almost constant in the pH region above 8 may be attributed to the balance between the induced generation of hydroxyl radicals and the electrostatic repulsion of thiram molecular for the photocatalyst surface. Consequently, pH 6 was selected for the optimal experimental conditions, because of the unnecessary of chemical treatment including neutralization process.

3.6. *Effect of irradiance*

The effect of irradiance on the solar photocatalytic destruction of thiram in water with TiO_2 was studied, as shown in the supplementary data Fig. S4. The degradation experiments were performed during different periods of time with various light intensities on sunny and cloudy days. The degradation efficiency increased rapidly with increase in the light intensity up to 0.4 mW cm^{-2}, and above the intensity the efficiency increased gradually. Since the catalyst powders are suspended in a stirred solution, the light intensity will affect the degree of absorption of light by the catalyst surface. Ollis [27] has reviewed the effect of light intensity on the kinetics of photocatalysis and stated that (i) at low light intensities, the rate would increase linearly with increasing light intensity; (ii) at intermediate light intensities, the rate would depend on the square root of the light intensity; and (iii) at high light intensities, the rate is independent of light intensity. Therefore, it was found that the results obtained in this work were very reasonable.

3.7. *Comparison of photocatalytic degradation with direct photolysis*

To compare the photocatalytic degradation with direct photolysis for the purification of thiram solution, the effect of illumination time on the photocatalytic degradation and the direct photolysis was investigated. The results are shown in Fig. 4. The photocatalytic decomposition process proceeded rapidly until 30 min. At 30 min illumination time, the aqueous solution containing thiram showed the complete disappearance of the substrate. The thiram concentration in the treated solution was less than the detection limit of HPLC (<5 ng/mL). On the other hand, the degradation rate with the direct photolysis was slower compared to that obtained in the photocatalytic degradation. These facts may be mainly attributed to the low absorption of the thiram in the λ range above 300 nm. Thus, the photochemical processes are scarcely responsible for the observed fast transformations when the solution was irradiated in the presence of titania.

If the concentration of substrate is very low, i.e. $KC \ll 1$, the L–H equation (Eq. (3)) simplifies to a pseudo-first-order kinetic law (Eq. (4)) where k_{obs} is being the apparent pseudo-first-order rate constant.

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = kKt = k_{obs}t \ \text{ or } C_t = C_0\,\mathrm{e}^{-k_{obs}t} \qquad (4)$$

The primary degradation reaction is estimated to follow a pseudo-first-order kinetic law, according to Eq. (4). In order to confirm the speculation, $-\mathrm{Ln}(C/C_0)$ was plotted as a function of illumination time (the insert figure in Fig. 4). Since the linear plots were observed in the insert figure as expected, the kinetics of thiram in the TiO_2 suspension solution followed the first-order degradation curve which was consistent to the L–H model resulting from the low coverage in the experimental concentration range

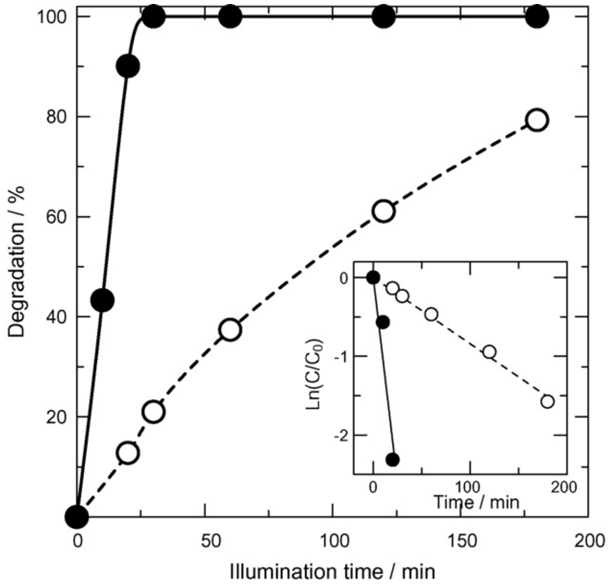

Fig. 4. Effect of illumination time on the solar photocatalytic degradation of thiram in water using TiO_2. Insert figure: plot of $\mathrm{Ln}(C/C_0)$ versus illumination time. Photocatalytic degradation: ●; direct photolysis: ○; thiram: 5 μg mL^{-1}; TiO_2: 8 mg (160 μg mL^{-1}); irradiance: 1.6 mW cm^{-2}; temperature: 30 °C; pH: 6.

Table 4
Photocatalytic degradation kinetic parameters (pseudo-first-order rate constant, correlation coefficient and substrate half-live)

	k_{obs} (min^{-1})	R^2	$t_{1/2}$ (min^{-1})
TiO_2	0.10	0.94	6.7
Photolysis	0.0084	0.99	82

k_{obs}: pseudo-first-order rate constant. R^2: correlation coefficient. $t_{1/2}$: substrate half-live.

(5 μg mL^{-1}). The photocatalytic degradation kinetic parameters such as pseudo-first-order rate constant, correlation coefficient and substrate half-live are shown in Table 4. The pseudo-first-order rate constant in the photocatalytic degradation was about 12 times that observed in direct photolysis.

3.8. Evolution of the mineralization

The following equation is speculated for the total mineralization reaction of thiram in the aqueous solution by photocatalytic degradation with TiO_2 semiconductors, although their stoichiometric coefficients were unbalanced.

$$C_6H_{12}N_2S_4 + OH^- + O_2 \rightarrow CO_2 + NO_3^- + NH_4^+ + SO_4^{2-} + H_2O \quad (5)$$

First, the evolution of sulfate ion the photocatalytic degradation of thiram in water using TiO_2 was investigated. The results are illustrated in Fig. 5a. The conversion yield to sulfate ion increased swiftly until 30 min illumination time, and after 30 min the yield increased steadily. Finally, according to mass balance analysis, it was observed that all sulfur atoms were transferred into sulfate ion after 120 min treatment. Although the evolution of sulfate ion was obtained in the direct photolysis, its rate was slower relative to that obtained in the photocatalytic treatment with TiO_2. Fig. 5b shows the time course for the CO_2 formation in the photocatalytic treatment of thiram in water with TiO_2 under air and helium (without oxygen) atmospheres. Under the air atmosphere, the yield of CO_2 evolution increased with illumination time. Their stoichiometric amounts were reached after 8 h, indicating the disulfuration of thiram is faster compared to the mineralization to CO_2. The CO_2 evolution rate obtained in the helium atmosphere was very smaller compared with that observed in the air atmosphere. These phenomena suggested that oxygen species dissolved in the sample solution play a significant role on the photocatalytic degradation of thiram with TiO_2. Ammonium and nitrate ions could be detected as the nitrogen-containing end products in the photocatalytic degradation of thiram in the aqueous solution using TiO_2, and no formation of nitrite ion was observed owing to its fast oxidation to nitrate ion. The formations of ammonium and nitrate ions as a function of the illumination time are depicted in Fig. 5c. The amounts of ammonium ion increased sharply with the illumination time up to 5 h, and after 5 h the amounts increased gradually. After 10 h of irradiation, the amounts became almost constant. On the contrary, the conversion yield to nitrate ion increased gradually with the time until 20 h. The sum of these two products represents the quantitative recovery of organic nitrogen at the illumination of 20 h. The result that the evolution rate of sulfate ion is faster relative to those of CO_2 and ammonium and nitrate ions supports that breaking of the sulfur–sulfur and sulfur–carbon chemical bonds is the predominant process in the initial stage, in agreement with the data reported in the literature [28].

Taking into account the fact that complete disappearance of the thiram in the irradiated cells occurred after very short illumination time (30 min) in the photocatalytic degradation, whereas the complete mineralization was observed after the 20 h illumination, it could be deduced that transient organic intermediate products

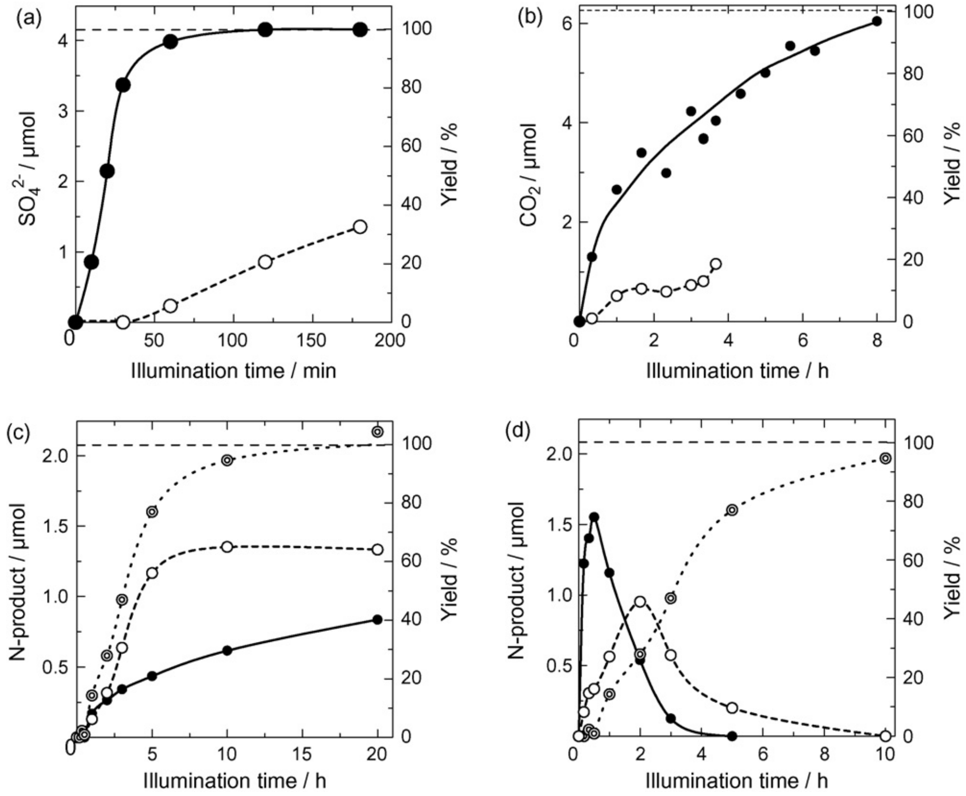

Fig. 5. Evolution of the mineralization during the solar photocatalytic degradation of thiram in water using TiO_2. Thiram: 5 μg mL^{-1}; TiO_2: 8 mg (160 μg mL^{-1}); irradiance: 1.6 mW cm^{-2}; temperature: 30 °C; pH: 6. (a) Photocatalytic degradation; ●, direct photolysis; ○. (b) Air atmosphere; ●, helium atmosphere (without oxygen); ○. (c) NH_4^+; ○, NO_3^-; ●, sum of NH_4^+ and NO_3^-; ◎. (d) $(CH_3)_2NH$; ●, $(CH_3)NH_2$; ○, sum of NH_4^+ and NO_3^-; ◎.

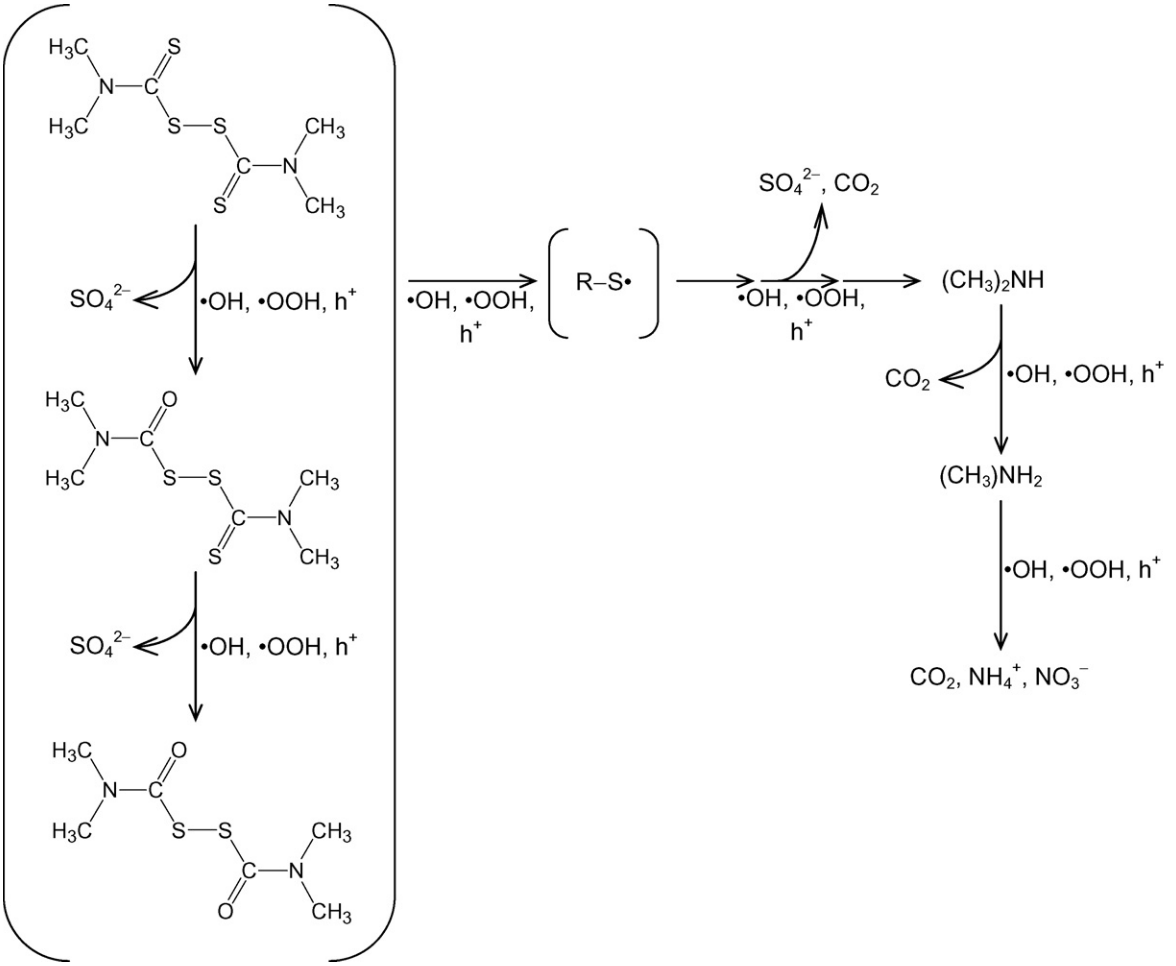

Fig. 6. Proposed photocatalytic degradation pathway of thiram.

are likely to be present in the reaction system after the complete destruction of thiram. As a consequence, the stoichiometric formation of the mineralization was completed in the photocatalytic degradation of thiram in the aqueous TiO_2 suspension, and the stoichiometric transformation of organic carbon and nitrogen into inorganic compounds took place at delayed illumination time, compared with that obtained for organic sulfur.

3.9. Intermediate products and photodegradation mechanism

In order to clarify the photocatalytic degradation mechanism of thiram, the detailed HPLC analysis was performed for the identification of intermediate products. Consequently, dimethylamine and monomethylamine were detected as the intermediate products during the photocatalytic degradation of thiram in water with TiO_2. Fig. 5d shows the time course for the formations of dimethylamine and monomethylamine in the addition of the sum of NO_3^- and NH_4^+. The curve for dimethylamine amounts had a peak at 30 min of illumination time, and the maximum amounts of monomethylamine were observed at 2 h. As the amounts of dimethylamine and monomethylamine decreased, the total amounts of ammonium and nitrate ions increased. Kodama et al. [11] have investigated the degradation pathway of thiram in tap water processed by oxidation with sodium hypochlorite, in which dimethylthiocarbamoyl dimethylcarbamoyl disulfide, bis(dimethylcarbamoyl) disulfide and dimethylamine were reported as intermediate products. According to the MOPAC simulation (see Table 3), two sulfur atoms (1S and 2S) bonded to the dimethylthiocarbamoyl group have the largest frontier electron density, with the next ones being two sulfur atoms (3S and 4S) bonded to carbon. Therefore, these sites would become one of most likely sites of attack by neutral •OH radicals, although the other sites may be attacked by them also.

The photocatalytic degradation of thiram is, apparently, a very complex process whose mechanism is not yet fully clarified. The present experimental data and literature reports [8–13,16–28] suggest the photocatalytic degradation pathway of thiram in water with titanium dioxide, as illustrated in Fig. 6. Most organic molecules undergo photocatalytic degradation when irradiated in the presence of suitable semiconductors. This occurs through a multistep process involving the attack of the substrate by radical species, among which the •OH radical was recognized to be the most powerful oxidant [24–26]. When the radicals or holes primarily attack two sulfur atoms (3S and 4S) bonded to carbon because the atoms have relatively large frontier density, dimethylthiocarbamoyl dimethylcarbamoyl disulfide and bis(dimethylcarbamoyl) disulfide seems to be formed as the intermediate products. Actually, the formation rate of sulfate ion was faster, compared to those of ammonium and nitrate ions and CO_2. Kodama et al. [11] have reported the identification of these intermediates by the analytical system such as NMR, IR and electron impact mass spectrometry. The attack of radicals (or holes) to two sulfur atoms (1S and 2S) with the largest frontier density in thiram and these intermediate products may produce dimethylamine via the intermediate radicals (R–S•).

Dimethylamine is presumably converted to monomethylamine by the further attack of radicals. Lee et al. [29] have investigated the photocatalytic degradation reaction of *N*-nitrosodimethylamine in water using pure and surface-modified TiO_2. In the study, the degradation products of *N*-nitrosodimethylamine were methylamine, dimethylamine, nitrite, nitrate and ammonium. Hence, the transformation of nitrogen atom in monomethylamine to NO_3^- and NH_4^+ may occur since their stoichiometric formations were observed in the present work. The proposed photocatalytic degradation mechanism may be consistent with the results that the stoichiometric transformation of organic carbon and nitrogen into inorganic compounds was observed at delayed illumination time, relative to that obtained for organic sulfur.

4. Conclusion

The optimization of the photocatalytic degradation conditions of thiram in water using titanium dioxide was investigated under sunlight illumination. According to the Langmuir–Hinshelwood model, the primary photocatalytic decomposition reaction followed a pseudo-first-order kinetic law. During the photocatalytic degradation, the first-order rate constant k_{obs} was $0.10\,min^{-1}$, which was approximately 12 times that observed in direct photolysis. The final degradation products were carbon dioxide and sulfate, nitrate and ammonium ions. All sulfur, carbon and nitrogen atoms were transformed into inorganic compounds. Since the artificial lamp device is particularly expensive in the nonexclusive areas, the solar photocatalytic degradation technology developed may be available in those areas.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2008.07.029.

References

[1] A. Hedenstedt, U. Rannug, C. Ramel, C.A. Wachtmeister, Mutagenicity and metabolism studies on 12 thiuram and dithiocarbamate compounds used as accelerators in the Swedish rubber industry, Mutat. Res. 68 (1979) 313–325.

[2] J. Franekic, N. Bratulic, M. Pavlica, D. Papes, Genotoxicity of dithiocarbamates and their metabolites, Mutat. Res. 325 (1994) 65–74.

[3] C.C. Lee, J.Q. Russell, J.L. Minor, Oral toxicity of ferric dimethyl-dithiocarbamate (ferbam) and tetramethylthiuram disulfide (thiram) in rodents, J. Toxicol. Environ. Health 4 (1978) 93–106.

[4] C. Bjorge, G. Brunborg, R. Wiger, J.A. Holme, T. Scholz, E. Dybing, E.J. Soderlund, A comparative study of chemically induced DNA damage in isolated human and rat testicular cells, Reprod. Toxicol. 10 (1996) 509–519.

[5] Integrated Risk Information System (IRIA) Database for Risk Assessment, U.S. Environmental Protection Agency (EPA). http://www.epa.gov/iris/index.html (accessed July 2008).

[6] R.L. Smith, Risk-based concentrations: prioritizing environmental problems using limited data, Toxicology 106 (1996) 243–266.

[7] Uniform National Effluent Standards, Ministry of the Environment in Japan. http://www.env.go.jp/en/water/wq/nes.html (accessed July 2008).

[8] T. Niitsuma, K. Suzuki, E. Hachiya, Y. Takemoto, Degradation of six pesticides by ozone with ultraviolet radiation, Kankyo Kagaku 3 (1993) 350–351.

[9] M. Ohto, A. Yamamoto, A. Matsunaga, N. Takayanagi, T. Kemmei, Y. Saito, E. Mizukami, Chemical change of pesticides used for golf links in chlorinated water, Kankyo Kagaku 3 (1993) 59–64.

[10] W. Chew, D.N. Harpp, Chlorination of tetramethyl thiuram disulfide: a precursor to diatomic sulfur? Sulfur Lett. 16 (1993) 19–24.

[11] S. Kodama, A. Yamamoto, M. Ohto, A. Matsunaga, Major degradation pathway of thiuram in tap water processed by oxidation with sodium hypochlorite, J. Agric. Food Chem. 47 (1999) 2914–2919.

[12] M.M. Haque, M. Muneer, Photocatalysed degradation of a fungicide, thiram in aqueous suspension of titanium dioxide, Indian J. Chem. Technol. 12 (2005) 68–74.

[13] S.R. Thakare, N.S. Bhave, Photocatalytic degradation of thiram (fungicides) under visible light irradiation, E-J. Chem. 2 (2005) 62–69.

[14] S. Kaneco, H. Katsumataa, T. Suzuki, K. Ohta, Titanium dioxide mediated photocatalytic degradation of dibutyl phthalate in aqueous solution—kinetics, mineralization and reaction mechanism, Chem. Eng. J. 125 (2006) 59–66.

[15] F. Kenichi, Y. Teijiro, N. Chikayoshi, S. Haruo, Molecular-orbital theory of orientation in aromatic, heteroaromatic, and other conjugated molecules, J. Chem. Phys. 22 (1954) 1433–1442.

[16] C.C. Wong, W. Chu, The direct photolysis and photocatalytic degradation of alachlor at different TiO_2 and UV sources, Chemosphere 50 (2003) 981–987.

[17] C.S. Turchi, D.F. Ollis, Photocatalytic degradation of organic water contaminants: mechanisms involving hydroxyl radical attack, J. Catal. 122 (1990) 178–192.

[18] J.C. Garcia, K. Takashima, Photocatalytic degradation of imazaquin in an aqueous suspension of titanium dioxide, J. Photochem. Photobiol. A: Chem. 155 (2003) 215–222.

[19] R.R. Ishiki, H.M. Ishiki, K. Takashima, Photocatalytic degradation of imazethapyr herbicide at TiO_2/H_2O interface, Chemosphere 58 (2005) 1461–1469.

[20] J.-F. Wu, C.-H. Hung, C.-S. Yuan, Kinetic modeling of promotion and inhibition of temperature on photocatalytic degradation of benzene vapor, J. Photochem. Photobiol. A: Chem. 170 (2005) 299–306.

[21] A. Lair, C. Ferronato, J.-M. Chovelon, J.-M. Herrmann, Naphthalene degradation in water by heterogeneous photocatalysis: an investigation of the influence of inorganic anions, J. Photochem. Photobiol. A: Chem. 193 (2008) 193–203.

[22] A. Chatzitakis, C. Berberidou, I. Paspaltsis, G. Kyriakou, T. Sklaviadis, I. Poulios, Photocatalytic degradation and drug activity reduction of Chloramphenicol, Water Res. 42 (2008) 193–203.

[23] H.G. Yang, C.Z. Li, H.C. Gu, T.N. Fang, Rheological behavior of titanium dioxide suspensions, J. Colloid Interface Sci. 236 (2001) 96–103.

[24] L. Sánchez, J. Peral, X. Domenéch, Photocatalyzed destruction of aniline in UV-illuminated aqueous TiO_2 suspensions, Electrochim. Acta 42 (1997) 1877–1882.

[25] A.B. Prevot, M. Vincenti, A. Bianciotto, E. Pramauro, Photocatalytic and photolytic transformation of chloramben in aqueous solutions, Appl. Catal. B: Environ. 22 (1999) 149–158.

[26] S. Kaneco, M.A. Rahman, T. Suzuki, H. Katsumata, K. Ohta, Optimization of solar photocatalytic degradation conditions of bisphenol A in water using titanium dioxide, J. Photochem. Photobiol. A: Chem. 163 (2004) 419–424.

[27] D.F. Ollis, Solar-assisted photocatalysis for water purification: issues, data, questions, in: E. Pelizzetti, M. Schiavello (Eds.), Photochemical Conversion and Storage of Solar Energy, Kluwer Academic Publishers, The Netherlands, 1991, pp. 593–622.

[28] V.A. Sakkas, T.A. Albanis, Photocatalyzed degradation of the biocides chlorothalonil and dichlofluanid over aqueous TiO_2 suspensions, Appl. Catal. B: Environ. 46 (2003) 175–188.

[29] J. Lee, W. Choi, J. Yoon, Photocatalytic degradation of *N*-nitrosodimethylamine: mechanism, product distribution, and TiO_2 surface modification, Environ. Sci. Technol. 39 (2005) 6800–6807.