

Photodegradation of Esfenvalerate in Clay Suspensions

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Photodegradation of the pyrethroid insecticide esfenvalerate (I) [(2*S*, α *S*)- α -cyano-3-phenoxybenzyl 2-(4-chlorophenyl)-3-methylbutyrate] was examined in clay suspensions (kaolinite and montmorillonite) with a xenon lamp ($\lambda > 290$ nm). The suspended clays slightly accelerated the photolysis rate with a significant epimerization at the benzyl carbon of I to form the (2*S*, α *R*)-isomer (II). Most of the epimerization was a dark reaction of I caused by the suspended clays, as shown by indirect photolysis at $\lambda > 320$ nm and the dark control. Hydroxyl radical was generated by exposure of the suspended clays to UV light and participated in the formation of the desphenyl derivative of I.

INTRODUCTION

Synthetic pyrethroids are highly toxic to aquatic organisms (Leahey, 1985), and buffer zones are commonly used when they are sprayed from the ground or air. When pyrethroids drift or accidentally contaminate an aquatic environment, photolysis would be one of the most important degradation routes, so photochemistry of pyrethroids in distilled water, aqueous buffers, or natural waters has been studied (Miyamoto, 1981; Leahey, 1985). Since pyrethroids are scarcely soluble in water (<0.1 ppm) and have an extremely high soil sorption coefficient ($>5 \times 10^3$) (Wauchope et al., 1992), photochemistry on the surface of various particles where pyrethroids are adsorbed would determine their environmental fates in natural waters.

Natural waters contain a wide range of dissolved and particulate materials that are rich in organic components (Sigleo and Means, 1990), including humic substances with a variety of molecular weights, and colloidal inorganic material. Photosensitization via energy transfer and/or photoinduced degradation of pesticides is known to occur in the presence of humic substances (Choudhry, 1982). Inorganic materials may reduce a photolysis rate by quenching excited states of organic molecules or by shielding them from incident light, while they may accelerate the degradation via photocatalytic processes (Zafiriou et al., 1984; Langford and Carey, 1987). It has been reported in the photolysis studies of methoxychlor (Oliver et al., 1979), 3,4-dichloroaniline, and butyrophe none derivatives (Miller and Zepp, 1979a) that the suspended sediments simply shield a chemical from an incident light. In contrast, DDE becomes more photo-reactive by adsorption to sediments (Miller and Zepp, 1979a). Some suspended clays are known to enhance the photolysis rate of a chemical via efficient light scattering (Miller and Zepp, 1979b). Although the photocatalytic role of montmorillonite and kaolinite has been examined under UV irradiation, the generation of hydroxyl radical has not been observed (Oliver et al., 1979). The conflicting observations are likely to stem from the complex constitution of these natural materials, and therefore, it becomes difficult to systematically understand their effects on the photodegradation of a chemical.

Although photolysis studies of pyrethroids in natural waters are scarce, Takahashi et al. (1985a,b) have examined the aqueous photolysis of cypermethrin and fenprothrin in the presence of humic acids and have observed their photosensitization. However, the effects of colloidal inorganic materials on the photolysis of pyrethroids have not been examined. In this work, the photodegradation profile of the synthetic pyrethroid esfenvalerate [(2*S*, α *S*)- α -cyano-3-phenoxybenzyl 2-(4-chlorophenyl)-3-methylbutyrate (I)], which showed the highest insecticidal activity among the four isomers of fenvalerate, was examined in clay suspensions to determine its effects on photolysis. Suspensions of Fe₂O₃, FeO(OH), and TiO₂ were also examined because they are major transition metal oxides in soils (Shirozu, 1988) and act as semiconductors (Langford and Carey, 1987; Leland and Bard, 1987). Throughout these experiments, it was examined whether epimerization proceeded in the presence of these inorganic materials.

MATERIALS AND METHODS

Chemicals. Esfenvalerate (I) and its related compounds (II-VIII and XI) as shown in Figure 1 were synthesized by the methods already reported [Katagi, 1991, and references therein]. IX, X, and metal oxides [Fe₂O₃, FeO(OH), TiO₂] were purchased from Aldrich Co., Ltd. (Milwaukee). 2-Nitroso-5-[*N*-propyl-*N*-(sulfopropyl)amino]phenol (nitroso-PSAP) and ascorbic acid used for colorimetry of iron ions, and thiobarbituric acid, deoxyribose, and mannitol for the detection of hydroxyl radical, were purchased from Wako Pure Chemicals (Osaka). For the spectrophotometric assay of a trace amount of hydrogen peroxide, leuco crystal violet (Tokyo Kasei, Tokyo) and horseradish peroxidase (EC 1.11.1.7) (type IV, 280 units/mg of protein; Sigma, St. Louis) were used. Pure water with an electrical conductivity of $5.5 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$ supplied from a Puric Model R (Organo Co., Ltd., Osaka) was used to prepare phosphate buffer. [¹⁴C]-I uniformly labeled in the phenoxyphenyl ring (81.2 mCi/g; radiochemical and optical purities, $>99\%$) was synthesized in our laboratory (Kanamaru et al., 1980). Kaolinite (K5, acid-washed American standard) from Fisher Scientific (New Jersey), montmorillonite K10 (MK10), and montmorillonite KSF (MKSF) from Aldrich Co., Ltd. (Milwaukee), were purchased and used without any treatment. The transition metal contents (Fe, Mn, Zn, and Ti) of each clay were determined by ICP emission spectrometry at Sumika Chemical Analysis Ltd. (Osaka): kaolinite: Fe, 0.5%; Mn, 0.007%; Zn, 0.003%; Ti, 0.03%; MK10: Fe, 1.4%; Mn, 0.008%; Zn, 0.01%; Ti, 0.2%; MKSF: Fe, 3.5%; Mn, 0.03%; Zn, 0.009%; Ti, 0.2%.

Spectroscopy. A Hitachi U-3210 spectrophotometer was used to measure the ultraviolet (UV) absorption spectrum of I in 10% aqueous acetonitrile and for the spectrophotometric quantitation of H₂O₂ or iron ions, with a quartz cuvette (1-cm path length).

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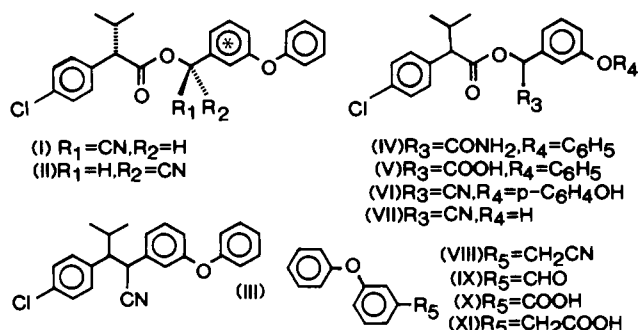


Figure 1. Chemical structures of I and its related compounds. (*) Radiolabeled position.

The absorption spectrum of the suspension of each clay was obtained with the same spectrophotometer equipped with a 60-mm i.d. integrating sphere.

Thin-Layer Chromatography (TLC). Two-dimensional (2D) TLC (silica gel 60F₂₅₄, 20 × 20 cm, 0.25-mm layer thickness, E. Merck) chromatography with the solvent systems, benzene saturated with formic acid–diethyl ether (10:3) and hexane–toluene–acetic acid (3:15:2), was done to separate and quantify photoproducts derived from I, as previously reported (Mikami et al., 1980). The resolved radioactive spots were detected by autoradiography with the developed TLC plates held under X-ray SB film (Eastman Kodak Co.) at 4 °C for 1 week. The radioactivity in the resolved spot was quantified with a Packard 460CD liquid scintillation spectrometer (LSC), using 10 mL of Packard emulsifier–scintillator 299. The chemical identity of each photoproduct was confirmed by cochromatography with unlabeled standard chemicals.

High-Performance Liquid Chromatography (HPLC). A Hitachi L-6200 liquid chromatograph was operated at a flow rate of 1.0 mL min⁻¹, using the Sumipax ODS A-212 column (5 μm, 6-mm i.d. × 15 cm; Sumika Analytical Service Ltd., Osaka). The composition of the mobile phase was changed stepwise as follows: 0–5 min, isocratic, % A (acetonitrile)–% B (methanol)–% C (0.1% trifluoroacetic acid), 50:10:40; 5–25 min, linear, % A–% C, 80:20 at 25 min; 25–40 min, isocratic; 40–45 min, linear, % A–% B–% C, 50:10:40 at 45 min; 45–50 min, isocratic. Amounts of I and its photoproducts were quantified, using a Radiomatic Flo-one/beta A-120 radiodetector. At the same time, the UV absorbance at 250 nm was monitored with a Hitachi L-4000 variable-wavelength UV monitor. The detection limit was about 0.1% of the radioactivity injected. The typical retention times of I and its related compounds are as follows: I and II, 44.2 min; III, 39.8 and 41.5 min; IV, 30.3 and 30.8 min; V, 34.9 min; VI, 32.4 min; VII, 25.6 min; VIII, 13.2 min; IX, 14.5 min; X, 9.1 min; XI, 8.3 min. Each ¹⁴C peak was identified by comparing its retention time with those of authentic chemicals. The epimerization of I during photolysis was also examined by normal-phase HPLC with the Sumipax OA-2000 chiral column (4-mm i.d. × 25 cm, Sumika Analytical Service Ltd., Osaka). Hexane–1,2-dichloroethane–2-propanol (500:30:1) at a flow rate of 1 mL min⁻¹ was the mobile phase. Retention times of I and its isomers were 21.2 min (I), 17.6 min (II), 18.8 min (2*R*,*α*S), and 22.6 min (2*R*,*α*R). In every analysis, an aliquot of the eluant was radioassayed, and >95% recovery of ¹⁴C injected was confirmed.

Adsorption Studies. Since the adsorption of I to clay was considered to influence its photolysis kinetics as previously reported for DDE (Zepp and Schlotzhauer, 1981), the extent of adsorption to each clay used was examined prior to the photolysis experiments. The supernatant (top 10 cm) of the suspended clay in the phosphate buffer (0.01 M, pH 7), allowed to settle for 24 h (particle size <2 μm), was used to prepare the clay suspension of I. The concentration of each clay was gravimetrically estimated to be 255, 462, and 64 mg L⁻¹ for kaolinite, MK10, and MKSF, respectively. Acetonitrile (5% v/v) was used as a cosolvent to prepare the clay suspensions of I at a concentration of 25 ppb. After the addition of [¹⁴C]-I in 5 mL of acetonitrile to clay suspensions (95 mL), a 1.0-mL aliquot was taken in duplicate at appropriate intervals for radioassay to determine the ¹⁴C concentration in the suspension. The 10-mL aliquot was separately taken and centrifuged at 16000g for 1 h. The radioactivity in a 1.0-mL aliquot of the supernatant was quantified, and the

radioactivity adsorbed to each clay was estimated by subtracting this value from the ¹⁴C concentration.

Analysis of Iron Ions. The elemental analysis by ICP showed that the clays used in this study contained 0.5–3.5% iron, part of which was considered to be dissolved in the suspension as Fe²⁺ or Fe³⁺. It has been reported that Fe³⁺ greatly promotes photodegradation of triazine herbicides via reaction of hydroxyl radical (Larson et al., 1991). Therefore, the concentrations of iron ions in the clay suspensions were spectrophotometrically examined at 756 nm ($\epsilon = 4.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) by using nitroso-PSAP according to the reported method (Yoshida et al., 1988). A supernatant free from clay particles was first prepared by centrifugation at 16000g and used for a determination of [Fe²⁺]. Fe³⁺ in the supernatant was reduced to Fe²⁺ with excess ascorbic acid to determine the total concentration of iron ions. [Fe³⁺] was then calculated by subtracting [Fe²⁺] from the total concentration of iron. It was considered that some of the iron ions were adsorbed on the clay surface and/or present as species not reactive with nitroso-PSAP. Therefore, the supernatant derived from the clay suspension acidified at pH 1 was similarly analyzed.

Photolysis Studies. The phosphate buffer or clay suspension of [¹⁴C]-I at 25 ppb (100 mL) was similarly prepared as in the adsorption study and photolyzed after vigorous stirring for 4 h in darkness. The solution in the 100-mL quartz cell stoppered with a rubber septum was continuously irradiated with a 500-W xenon lamp (USIO, Model UIV-5150XEQ, Tokyo). The temperature of the solution was kept at 25 ± 1 °C by immersing the cell in a thermostated bath. The emission spectrum of a xenon lamp through a Pyrex glass (2-mm thickness) was measured at the inner surface of the cell by an Ushio USR-20B photometer and was found to show a cutoff of 290 nm and a maximum of 464 nm (44.34 μW cm⁻² nm⁻¹). Light with a cutoff of 320 nm obtained from Ushio Model 5150XE was used to examine the photocatalytic activity of clays and metal oxides. The metal oxide suspension was prepared by adding 0.1% (w/v) TiO₂, Fe₂O₃, or FeO(OH) to the phosphate buffer. The dark control experiment was conducted in a similar manner except that the cell was covered with aluminum foil. At appropriate intervals, a 1.0-mL aliquot was taken in duplicate for radioassay and a 95-mL aliquot was separately extracted three times with 60 mL of ethyl acetate after adding 10 mL of 0.1 M HCl. A 2.0-mL aliquot of the combined extracts was radioassayed in duplicate, and the remaining portion was used for 2D-TLC and HPLC analyses after being concentrated in a rotating evaporator. Since I and III (also VI and VII) could not be clearly separated on 2D-TLC, their relative ratio was calculated by using radio-HPLC. The ¹⁴C spot containing I and its isomers was purified by 2D-TLC and analyzed by HPLC with the chiral column to quantify each isomer. The unextractable ¹⁴C was radioassayed by taking a 2.0-mL aliquot of the aqueous layer for LSC. When a low recovery of ¹⁴C was observed, a separate experiment to trap volatiles was conducted by using ethylene glycol (100 mL) and 0.5 M NaOH (200 mL) as a trapping medium, as reported previously (Katagi, 1991). All experiments were done in duplicate.

The generation of hydroxyl radical during UV irradiation ($\lambda > 320 \text{ nm}$) of the clay suspensions was first examined according to the method reported by Gutteridge (1981). Deoxyribose and thiobarbituric acid were used to form the chromogen via reaction with hydroxyl radical, and its formation was monitored at 532 nm. Second, since the formation of H₂O₂ was considered to confirm the presence of hydroxyl radical, its production during photolysis of the clay suspensions was examined with leuco crystal violet and horseradish peroxidase as previously reported (Katagi, 1990).

RESULTS

Spectroscopy. The absorption spectrum of I in 10% aqueous acetonitrile showed a maximum at 277 nm ($\epsilon = 2.63 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) due to the $\pi \rightarrow \pi^*$ transition of the phenyl ring with an $n \rightarrow \pi^*$ character and had a measurable tail above the base line at wavelengths up to 310 nm. Therefore, direct photolysis of I was unlikely when the xenon lamp ($\lambda > 320 \text{ nm}$) was used as a light source. The weak absorption was observed at 290–400 nm for the suspended kaolinite and MK10, and the absorbance at

Table I. Amount of Iron Ions Dissolved in Clay Suspensions

clay suspension	concn ^a (μM)			
	pH 7		pH 1	
	Fe ³⁺	Fe ²⁺	Fe ³⁺	Fe ²⁺
kaolinite	1.6	<0.1	2.9	<0.1
MK10	1.3	<0.1	4.3	<0.1
MKSF	1.1	<0.1	53.4	<0.1

^a Iron ions in the supernatant of each clay suspension centrifuged were quantified.

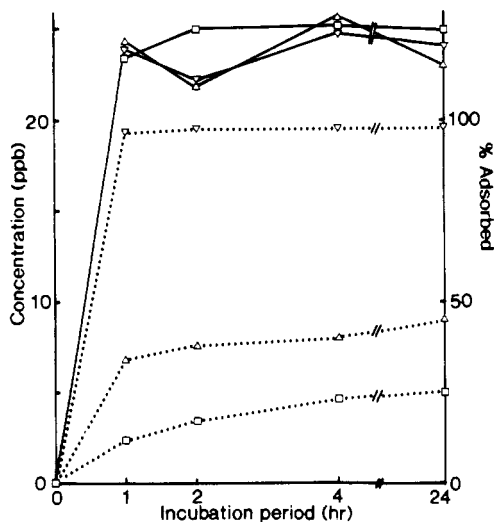


Figure 2. Adsorption of I to clays. Concentration of I (in ppb): (□—□) kaolinite; (△—△) MK10; (▽—▽) MKSF. Percentage of I adsorbed: (□—□) kaolinite; (△—△) MK10; (▽—▽) MKSF.

300 nm (A_{300}) was 0.022 and 0.065, respectively. The larger absorption with a maximum at 300 nm was observed for the suspended MKSF ($A_{300} = 0.274$). Spectrophotometric quantitation by using nitroso-PSAP showed that iron ion was mainly present as Fe³⁺ in the clay suspensions (Table I). The acidification of the suspension to pH 1 increased the amount of Fe³⁺ available to form a complex with nitroso-PSAP. It was considered that these iron ions were adsorbed to the clays or existed as a form other than Fe(H_2O)₆³⁺.

Adsorption Studies. The concentration of ¹⁴C rapidly reached an almost constant value within 4 h in every clay suspension (Figure 2). The extent of adsorption of I and the equilibration time were likely to depend on the clay used. The equilibration was slow (>4 h) for kaolinite and MK10, where about 25% and 45% of I applied were adsorbed after 24 h, respectively. In contrast, a rapid equilibrium was reached within an hour for MKSF and about 98% of I was adsorbed, which might be due to the large surface area of MKSF (220–270 m² g⁻¹).

Photolysis Studies. (a) *Clay Suspensions at $\lambda > 290$ nm.* By exposure to UV light, I was immediately photodegraded in both phosphate buffer at pH 7 and clay suspensions. The decline curves of I are shown in Figure 3. Photodegradation of I in the buffer obeyed first-order kinetics, and the half-life was estimated by the least-squares approximation method to be 1.0 day. When the spectral differences in the emission between the xenon lamp and natural sunlight (August) and the difference of the exposure periods were taken into account, about a 3-fold photolysis rate of I was expected under the xenon lamp on the basis of the method proposed by Miller and Zepp (1983). Since the half-life of fenvalerate under natural sunlight in summer has been reported to be about 4 days (Mikami et al., 1980), the value obtained here is reasonable.

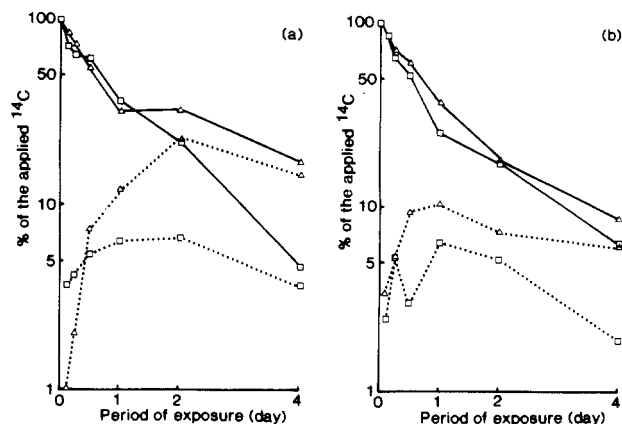


Figure 3. Decline and epimerization of I via photolysis at $\lambda > 290$ nm in the buffer and clay suspensions. (a) (□—□) I, (▽—▽) II in phosphate buffer at pH 7; (△—△) I, (▽—▽) II in the kaolinite suspension. (b) (□—□) I, (▽—▽) II in the MK10 suspension; (△—△) I, (▽—▽) II in the MKSF suspension.

In the case of the clay suspensions, a break at 1–2 days was detected in the decline curves, showing that two reactions at least were involved in the photodegradation. Based on the amounts of I up to 1 day, the initial half-lives were estimated to be 0.6 day (kaolinite), 0.5 day (MK10), and 0.7 day (MKSF). The presence of clay was likely to accelerate the photodegradation of I slightly. In every case, the epimerization at the α -cyanobenzyl carbon caused the formation of II [(2*S*, α *R*)-isomer], which showed a maximum amount at 1–2 days (Figure 3), but the amount of II gradually decreased afterward. The other isomers derived from an epimerization in the acid moiety, (2*R*, α *S*) and (2*R*, α *R*), were not detected by HPLC using the chiral column. II amounted to less than 6.7% and 6.5% of the applied ¹⁴C in the phosphate buffer and the MK10 suspension, respectively, while the epimerization proceeded to a greater extent in the kaolinite and MKSF suspensions, with the maximum amounts of II being 23.2% and 10.2%, respectively. In darkness, neither degradation nor epimerization of I proceeded significantly in the phosphate buffer within 2 weeks, and the half-life of I was estimated to be 256 days. In contrast, the presence of the clays caused a marked epimerization (Figure 4). After incubation at 25 ± 1 °C for 2 weeks, the reaction was likely to reach an equilibrium where the relative ratios of I to II were 53:47 (kaolinite), 64:36 (MK10), and 61:39 (MKSF).

The amounts of I and its degradation products formed under the irradiation are summarized in Table II. In every case, the recovered radioactivity was more than 92% of the applied ¹⁴C. The amount of ¹⁴CO₂ generated by irradiation was estimated in the separate experiments to be 3.1–6.4% at 4 days. Therefore, the lower ¹⁴C recovery under light conditions was due to the loss of untrapped ¹⁴CO₂. One of the main photodegradation pathways was decarboxylation to form III (28.6–39.4% at 4 days) as previously reported (Mikami et al., 1980) and supported by the detection of VIII and XI (0.7–2.2% and 2.0–5.6% at 4 days, respectively) in the extracts of the clay suspensions. The other main pathway was ester cleavage followed by oxidation to form X (13.5–18.3% at 4 days). As an intermediate, IX was detected with an amount of 1.0–4.0%. The hydration of the cyano group to amide IV followed by its hydrolysis to carboxylic acid V, hydroxylation at the 4'-position of 3-phenoxybenzyl moiety (VI), and ether cleavage to form VII were also observed, but they were the minor pathways under the conditions tested. In darkness, hydrolysis was the only degradation pathway other than epimerization.

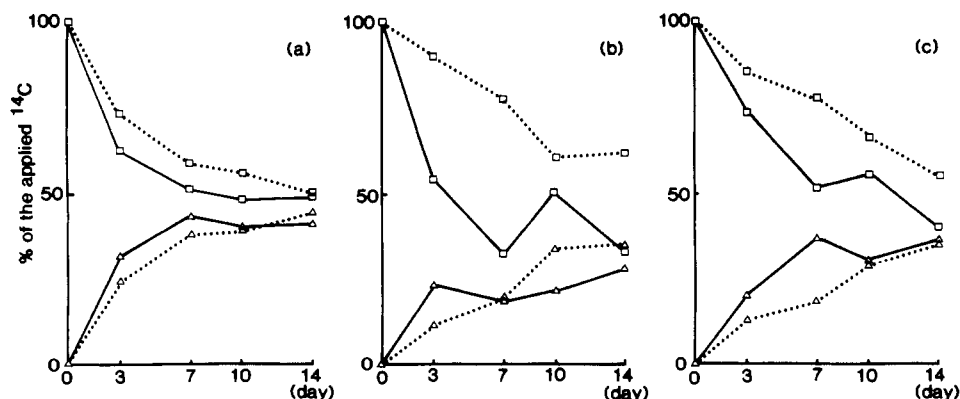


Figure 4. Epimerization of I via photolysis at $\lambda > 320$ nm and in darkness in the clay suspensions. (a) kaolinite; (b) MK10; (c) MKSF. (\square — \square) I, (Δ — Δ) II via photolysis at $\lambda > 320$ nm; (\square — \square) I, (Δ — Δ) II in darkness.

Table II. Amounts of I and Its Degradation Products^a

	% of the applied ¹⁴ C ^b											
	pH 7			kaolinite			MK10			MKSF		
	A	B	C	A	B	C	A	B	C	A	B	C
extractable ¹⁴ C	91.5	98.5	96.8	92.2	97.5	96.5	89.2	85.9	99.6	91.5	95.1	98.3
I	4.7	95.6	94.1	17.3	49.2	50.1	6.3	32.9	62.0	8.7	39.7	55.0
II	3.7	1.2	1.1	14.6	41.5	44.6	1.9	28.1	34.3	6.3	36.4	35.3
III	39.4	—	—	28.6	<0.1	—	39.2	—	—	36.9	—	—
IV	0.8	—	—	0.5	0.4	0.4	0.1	0.8	0.3	0.3	0.6	0.4
V	<0.1	—	—	<0.1	<0.1	<0.1	0.7	0.4	<0.1	0.5	0.2	<0.1
VI	—	—	—	<0.1	<0.1	<0.1	<0.1	0.6	<0.1	<0.1	0.3	<0.1
VII	0.8	—	—	0.6	0.2	<0.1	1.2	5.6	<0.1	1.1	2.2	1.4
VIII	2.0	—	—	0.7	—	—	0.8	—	—	2.2	—	—
IX	2.1	0.5	0.7	1.0	1.3	0.3	3.7	<0.1	<0.1	4.0	<0.1	<0.1
X	18.3	0.9	0.2	17.9	2.3	0.5	16.6	11.8	2.4	13.5	13.5	4.9
XI	5.4	—	—	2.0	—	—	5.5	—	—	5.6	—	—
others	14.3	0.3	0.7	9.0	5.5	0.6	13.2	5.7	0.6	12.4	2.2	1.3
aqueous ¹⁴ C	0.7	0.4	0.5	2.9	0.5	0.4	4.0	9.4	0.8	2.9	1.8	0.6
total ¹⁴ C	92.2	98.9	97.2	95.1	98.0	96.9	93.2	95.3	100.4	94.4	96.9	98.9
<i>T</i> _{1/2} ^c	1.0	260.3	256.1	0.6	95.2	178.9	0.5	22.6	170.2	0.7	37.5	104.6

^a Key: A, irradiated with 500-W xenon lamp ($\lambda > 290$ nm) at 25 ± 1 °C for 4 days; B, irradiated with 500-W xenon lamp ($\lambda > 320$ nm) at 25 ± 1 °C for 14 days; C, incubated in darkness at 25 ± 1 °C for 14 days; —, not detected. ^b Averaged values between duplicate experiments. ^c Half-life of I in days. The total amount of I and II was used for estimation under the conditions B and C of the clay suspensions.

(b) *Clay Suspensions at $\lambda > 320$ nm.* Since the light was absorbed only by the clays, the direct photolysis of I was most unlikely. In the phosphate buffer, no significant difference from the dark control was observed. The lack of involvement of direct photolysis was confirmed by the absence of III, VIII, and XI, which were the typical photoproducts (Table II). After 2-week irradiation, epimerization at the benzyl carbon was likely to reach an equilibrium (Figure 3) where the relative ratios of I to II were 54:46 (kaolinite), 54:46 (MK10), and 52:48 (MKSF). These values were similar to those obtained for the incubation of I in darkness, indicating that the epimerization was mainly a dark reaction. When the total amounts of I and II were used in estimating the half-lives of the epimers, it was found that the irradiation clearly enhanced their degradation (Table II). This difference first stemmed from the enhanced ester cleavage of I under irradiation. The amounts of IX and X slightly increased in the kaolinite suspension, but more formation of X was observed in MK10 and MKSF. Second, more formation of VII in the clay suspensions seemed to result in the enhanced degradation of I. During the 2-week photolysis, it amounted to 0.1–3.3%, 4.3–12.4%, and 0.2–2.2% in the kaolinite, MK10, and MKSF suspensions, respectively. A trace amount of VI (<1%) was also detected in every case.

In the spectrophotometric monitoring of hydroxyl radical using thiobarbituric acid, the absorbance at 532 nm was about 0.09 for the MKSF suspensions after a 2-h irradiation ($\lambda > 320$ nm). Furthermore, the spectropho-

metric assay using leuco crystal violet and horseradish peroxidase showed that 0.5 μ M (kaolinite) or 1.8–2.0 μ M (MK10 and MKSF) of H₂O₂ was constantly present in the clay suspensions for 7 days and that no formation of H₂O₂ was found in darkness. These results strongly suggested that the clays generated hydroxyl radical by absorbing light ($\lambda > 320$ nm).

(c) *Metal Oxides.* An almost constant ¹⁴C concentration was reached by stirring the suspension for an hour. On exposure to the UV light ($\lambda > 320$ nm), Fe₂O₃ did not accelerate either epimerization or ester cleavage of I, while FeO(OH) greatly facilitated the epimerization (Table III). The relative ratios of I to II at 4 h were 61:39 and 65:35 under the light and dark conditions, respectively, and these values were close to those obtained for the clay suspensions incubated in darkness for 1–2 weeks. The main degradates other than II were IV, IX, and X, each of which amounted to less than 1.4% of the applied ¹⁴C. In contrast, faster photodegradation of I was observed in the TiO₂ suspension, with the formation of VII as a main degradate. The amount of VII reached a maximum at 30 min (5.4%) and gradually decreased thereafter. The ¹⁴C recovery was low (75.8% at 4 h), which was mainly due to a loss of ¹⁴CO₂. In separate experiments, 18.7–20.5% and 1.2–2.5% of radiocarbons were recovered as ¹⁴CO₂ and other volatile ¹⁴C, respectively. Insignificant degradation was observed in darkness. Meanwhile, the degradation was completely retarded by adding a 100-fold molar equivalent of mannitol to I, a quencher of hydroxyl radical (Halliwell and

Table III. Photodegradation of I in the Presence of Metal Oxides^a

	% of the applied ¹⁴ C ^b					
	Fe ₂ O ₃		FeO(OH)		TiO ₂	
	L	D	L	D	L	D
extractable ¹⁴ C	96.1	99.5	97.0	98.3	72.1	99.2
I	91.5	89.4	56.8	62.1	52.4	98.3
II	2.4	6.2	36.9	33.0		
III	- ^c	-	-	-	-	-
IV	1.0	0.5	1.4	1.1	<0.1	<0.1
V	<0.1	-	<0.1	-	0.3	-
VI	-	-	-	-	0.3	-
VII	-	-	-	-	3.9	-
IX	<0.1	<0.1	0.6	0.5	0.6	0.1
X	0.7	1.2	0.7	0.5	0.5	0.2
others	0.5	2.2	0.6	1.1	14.1	0.6
aqueous ¹⁴ C	0.3	0.8	0.3	0.5	3.7	0.4
total ¹⁴ C	96.4	100.3	97.3	98.8	75.8	99.6

^a Key: L, I (25 ppb) in the metal oxide suspension (1 mg mL⁻¹) irradiated with a xenon lamp ($\lambda > 320$ nm) for 4 h; D, without irradiation. ^b Averaged values between the duplicate experiments. ^c Not detected.

Gutteridge, 1981), to the TiO₂ suspension. Therefore, it was concluded that hydroxyl radical participated in the reaction.

DISCUSSION

Photochemistry both on the clay surface and in the bulk water phase is considered to determine the fate of a chemical in the suspended clays. Since Zepp and Schlotzhauer (1981) have suggested that two adsorption sites for DDE were present in the sediments and afforded the different photoreactivities, the role of the clay in the photodegradation of I was considered to be complex. The presence of the suspended clays caused deviations from first-order kinetics in the photodegradation of I at $\lambda > 290$ nm, and two reactions at least were involved (Figure 3). The initial rates of photolysis in every clay suspension were larger than that in the phosphate buffer, which implied a participation of the suspended clay in the faster reaction. Light scattering due to clay particles has been reported to accelerate the photolysis of butyrophene derivatives (Miller and Zepp, 1979b). In this study, about 25% and 45% of I were adsorbed to kaolinite and MK10, respectively, while I was almost completely adsorbed to MKSF. Therefore, the faster reaction at $\lambda > 290$ nm might be attributed to the photodegradation of I in the bulk water and/or on the clay surface, which was enhanced by light scattering. Incidentally, the greater I was adsorbed to the clay, the smaller the deviation from the first-order kinetics became (Figures 2 and 3). These results suggested that the slower reaction was not controlled by the amount of adsorption but by the clay species. The amounts of I adsorbed into the lamellar structures of clays where the light was attenuated would be different among the clay species, which was considered to result in the different extents of the deviation.

Epimerization in the alcohol moiety of the synthetic pyrethroids has been reported in a few studies. Ruzo et al. (1977) have shown in the photodegradation of delta-methrin in methanol that the epimerization at the benzyl carbon proceeds by both photochemical and ground-state reactions. It has been suggested that the exchange of an α -proton at the benzyl carbon with the solvent results in the epimerization (Perschke and Hussain, 1992). This type of epimerization in methanol has been monitored by ¹H-NMR for the (*RR*,*SS*) enantiomeric pair of fenvalerate, and the ratio of (*RR*,*SS*) to (*RS*,*SR*) at equilibrium has been found to be 1:1.11 (Hill, 1981). Since the epimer-

ization of I in the phosphate buffer at pH 7 was insignificant in darkness (Table II), it was evident that the suspended clays caused the epimerization. Kaolinite and montmorillonites are clay minerals composed of Si-O tetrahedral and Al-O octahedral sheets arranged in different ways (Shirozu, 1988). It was considered that hydroxyl groups at the edges of these sheets acted as a nucleophile and facilitated the abstraction of the α -proton when I was adsorbed onto these surfaces. The ratio of I to II in the suspended clays was (1.1-1.2):1, which was close to that reported for the enantiomeric pairs (Hill, 1981). The slight difference in the ratio might be due to the specific interaction of I and II with the clay surfaces. Meanwhile, it has been reported that the epimerization scarcely proceeds on the clay thin layer (Katagi, 1991). The surface acidity of clay minerals is known to markedly increase at a low water content (Theng, 1982). This is the case for the clay thin layer prepared, and the high acidity was considered to retard the proton exchange leading to the epimerization, as previously reported (Perschke and Hussain, 1992). In the case of the suspended iron oxides, FeO(OH) caused significant epimerization, but Fe₂O₃ only to a small extent. The three types of oxygen species, -O-, -OH, or -OH₂⁺, were considered for the metal oxide surfaces. It is expected that the hydroxide and hydroxyl groups would facilitate the epimerization, while retardation would occur in the protonated form. The reactions FeOH₂⁺ → FeOH + H⁺ (pK_{a1}) and FeOH → FeO⁻ + H⁺ (pK_{a2}) have been examined, and the pK_{a1} and pK_{a2} values are 4.2 and 10.5 for FeO(OH) and 6.7 and 10.3 for Fe₂O₃, respectively (James and Parks, 1982). Since the reactions in this study were conducted at pH 7, the dominant species on the FeO(OH) surface was FeOH, but almost half of the hydroxyl groups on Fe₂O₃ were in the protonated form. This difference was considered to result in the lesser epimerization of I in the Fe₂O₃ suspension. These iron oxides (goethite and hematite) are common minerals, and the clays tested contained iron at 0.5-3.5%. Therefore, the epimerization observed in the suspended clays might be partly due to these iron oxides in the clays.

Absorption spectra of the suspended kaolinite and montmorillonite have a peak at about 240 nm assigned to charge transfer in the oxo-Fe³⁺ octahedral with a shoulder up to about 350 nm (Karickhoff and Bailey, 1973). Therefore, the absorption maximum at 300 nm observed for the suspended MKSF was not due to the structural iron in the clay. It was shown that a significant amount of Fe³⁺ reactive with nitroso-PSAP only after acidification was present in the MKSF suspension. On the basis of the solution chemistry of Fe³⁺ (Knight and Sylva, 1975), this absorption was assigned to Fe(H₂O)₅(OH)²⁺. It has been reported that Fe²⁺ and hydroxyl radical are formed by UV irradiation of this iron species (Faust and Hoigne, 1990). Therefore, this photoreactive iron species was considered to be one of the hydroxyl radical sources in the photolysis of I in the suspended clays. The other source was the irradiated clay surfaces as previously reported by Katagi (1990). The clays used in this study contained TiO₂ at a level of 0.03-0.2%, and this oxide might generate hydroxyl radical photocatalytically as previously reported (Langford and Carey, 1987). Since VII was most likely to be formed via reaction of I with hydroxyl radical (Katagi, 1991, 1992a,b) and this was supported by the photodegradation of I in the suspended TiO₂, its formation implied the existence of hydroxyl radical. The photoinduced decarboxylation to give III was so efficient in the photolysis at the wavelengths of greater than 290 nm that the differences in the formation of VII were not clearly observed among the phosphate buffer and the clay suspensions. In contrast, the results of indirect photolysis

when I was exposed at wavelengths of $\lambda > 320$ nm demonstrated that the formation of VII was enhanced in the clay suspensions, indicating the formation of hydroxyl radical. Formation of the largest amount of hydroxyl radical was expected for the MKSF suspension since the absorbance due to $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ was largest among the clays tested. Almost the same amount of H_2O_2 was detected for both MK10 and MKSF, implying that this photoreactive iron species was unlikely to dominantly produce hydroxyl radical. Although the similar contents of TiO_2 in both clays could explain almost the equal photoproduction of hydroxyl radical, it could not explain the result that a lesser amount of VII in MKSF was observed than in MK10. On the basis of these considerations, it was suggested that the clay surface played a significant role in the photoproduction of hydroxyl radical and that the different ways of adsorption of I to each clay might control photoreactions on the surfaces. The absence of VII indicated that both iron oxides did not act as a photocatalyst generating hydroxyl radical.

Meanwhile, the irradiation of the montmorillonite suspensions at $\lambda > 320$ nm caused more formation of X than in darkness, showing that part of ester cleavage at $\lambda > 290$ nm was likely to be due to an indirect photolysis of I. It has been reported that the irradiation at $\lambda > 320$ nm enhances the ester cleavage of I on the kaolinite thin layer but not on montmorillonite (Katagi, 1991). The addition of water might alter the reactivity of clay surfaces under irradiation, which resulted in the different degrees of the ester cleavage.

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