Photodegradation of the Pyrethroid Insecticide Esfenvalerate on Soil, Clay Minerals, and Humic Acid Surfaces

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Photodegradation of the pyrethroid insecticide esfenvalerate (I) [(2S,αS)-α-cyano-3-phenoxybenzyl 2-(4-chlorophenyl)-3-methylbutyrate] on the thin films of intact soil, clay minerals, and humic acid was examined by using a xenon lamp (λ > 300 nm). Photodegradation studies and reactions with oxidants showed that hydration of the cyano group and ether cleavage in the alcohol moiety were dominant reactions on the surfaces tested. It was strongly suggested that the hydrogen peroxide photochemically produced participated in the hydration reaction and that the ether cleavage proceeded via reaction with hydroxyl radical but not via photonucleophilic substitution by water molecule.

INTRODUCTION

Sunlight irradiation significantly accelerates the degradation of synthetic pyrethroids, and photodegradation on the soil surface is one of the important factors that determines the environmental fate of synthetic pyrethroids (Miyamoto, 1981; Leahey, 1985). Synthetic pyrethroids possessing the α-cyano-3-phenoxybenzyl moiety such as fenvalerate (Mikami et al., 1980), cypermethrin (Takahashi et al., 1985a), and fenpropathrin (Takahashi et al., 1985b) predominantly undergo the photoinduced hydration of the cyano group to form the carbamoyl derivative in a greater extent than that detected in the soil metabolism (Ohkawa et al., 1978; Roberts and Standen, 1977; Sakata et al., 1986). The extent of its formation is dependent on the soil characteristics. It has been also reported that ether cleavage is a characteristic degradation pathway in the soil (Ohkawa et al., 1978; Sakata et al., 1986) enhanced by sunlight irradiation (Takahashi et al., 1985). Since the previous photolysis studies have been done by using the intact soils under the conditions in which neither the temperature at the soil surface nor the humidity of the soil is controlled, the factor determining the significance of these degradation pathways cannot be specified.

The objects of the work described in this paper are first to examine the degradation profiles of synthetic pyrethroids in a solid phase under controlled conditions and second to determine whether secondary degradation by active oxygen species could play a role. For this purpose, (2S,αS)-α-cyano-3-phenoxybenzyl 2-(4-chlorophenyl)-3-methylbutyrate (esfenvalerate, I), showing the highest insecticidal activity among the four isomers of fenvalerate (Aketa et al., 1978), was used. Thus, the first part of the work is concerned with photodegradation of I adsorbed onto the intact soil, clay minerals, and humic acid under irradiation with a xenon lamp. The second part is concerned with the chemical reactions of I with oxidants to explain the photodegradation mechanisms of I, especially hydration of the cyano group and ether cleavage.

MATERIALS AND METHODS

Chemicals. Esfenvalerate (I), 2-(3-phenoxyphenyl)-3-(4-chlorophenyl)-4-methylpentanenitrile (II), α-carbamoyl-3-phenoxybenzyl 2-(4-chlorophenyl)-3-methylbutyrate (III), 3-phenoxybenzyl cyanide (IV), 3-phenoxyphenylacetic acid (V), and α-cyano-3-(4-hydroxyphenoxy)benzyl 2-(4-chlorophenyl)-3-methylbutyrate (VI) were synthesized according to previously reported methods, (Aketa et al., 1978; Ohkawa et al., 1978; Holmstead et al., 1978).

α-Cyano-3-hydroxybenzyl 2-(4-chlorophenyl)-3-methylbutyrate (VII) was synthesized in the following way. The hydroxyl group of m-hydroxybenzaldehyde was protected, using tert-butyl dimethyl silyl chloride (Corey and Venkateswarlu, 1972). The corresponding cyanohydrin, prepared from the aldehyde and potassium cyanide, was treated with 2-(4-chlorophenyl)-3-methylbutyric acid chloride to form the silylated derivative of VII. The silyl group was removed by using tetrabutylammonium fluoride in dry tetrahydrofuran. α-Cyano-3-cyanobenzyl 2-(4-chlorophenyl)-3-methylbutyrate (VIII) was synthesized by reacting the corresponding acid chloride with the cyanohydrin prepared from 3-cyanobenzaldehyde. 3-Phenoxybenzaldehyde (IX), 3-phenoxybenzoic acid (X), and the other organic materials were purchased from Aldrich Chemical Co. (Milwaukee). [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). $H_2^{18}O$ (97 atom %) was purchased from E. Merck (Montreal). Pure water of electrical conductivity $5.5 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$ was supplied from a Puric Model R apparatus equipped with a G-10 filter (Organo Co., Ltd., Osaka). Kaolinite and montmorillonite clay minerals and humic acid were purchased from Wako Co., Ltd. (Osaka). The transition-metal contents (Fe, Mn, Zn, and Ti) of each clay were determined by ICP emission spectrometry at Sumika Chemical Analysis Ltd. (Osaka): montmorillonite, Fe, 0.3-1.2%; Mn, 0.02-0.06%; Zn, <0.01%; Ti, 0.3-1.0%: kaolinite, Fe, 0.02-0.08%; Mn, <0.01%; Zn, <0.01%; Ti, 0.04-0.2%. The Noichi upland soil (sandy clay loam) was passed through a 1-mm sieve prior to use. Its characteristics were as follows: sand, silt, clay, and organic matter contents of 72.5%, 8.1%, 19.4%, and 1.4%, respectively; cation-exchange capacity of 8.8 mequiv/100 g of dry soil; pH (H_2O) 5.7; one-third bar moisture, 32.8 mL/100 g of dry soil; clay mineral, kaolinite, and montmorillonite.

Spectroscopy. The ultraviolet (UV) absorption spectrum of I in 10% aqueous acetonitrile was determined with a Hitachi U-3210 spectrophotometer using a quartz cuvette (1 cm path length). Reflectance spectra of I adsorbed on clay minerals were obtained with the same spectrophotometer equipped with a 60 mm i.d. integrating sphere. The clay films of I were prepared at the rate of 0.14 mg cm^{-2} in a manner similar to that reported previously (Katagi, 1990). The infrared (IR) spectra of I in KBr and clay pellets were obtained with a Nicolet ZDX Fourier transform spectrometer according to the method reported by Rockley and Rockley (1987). The difference spectrum of I adsorbed on each clay mineral was measured by subtracting the contribution from each clay. The phosphorescence spectrum of I at 77K was obtained in acetonitrile with a Hitachi 650-60 spectrophotometer. The spectrum was calibrated with Rhodamine B as a standard. Mass spectra were measured in electron ionization (EI) mode at 70 eV with a Hitachi M-80 mass spectrometer equipped with a Hitachi M-003 data processing unit.

The isomerization of I during the experiment was examined by high-performance liquid chromatography (HPLC). A Hitachi L-6000 liquid chromatograph equipped with a Sumipax OA-2000 chiral column (4 mm i.d. × 25 cm, Sumika Analytical Service Ltd., Osaka) was operated at a flow rate of 1 mL/min, using hexane–1,2-dichloroethane–2-propanol (500:30:1) as a mobile phase. I and its isomers were detected by a Hitachi 655A-11 UV monitor at 250 nm and a Radiomatic Flo-one β A-120 radiodetector with the following retention times: I, 21.2 min; [2S,αR], 17.6 min; [2R,αS], 18.8 min; [2R,αR], 22.6 min.

Radioassay. The radioactivity of ^{14}C was quantified with a Packard 460CD liquid scintillation spectrometer (LSC), using 10 mL of Packard 299 emulsifier–scintillator. The radioactivity bound to the soil, clay, and humic acid was quantified by combusting an aliquot (100–200 mg) with a Packard 306 sample oxidizer prior to the LSC measurement. The recovery of ^{14}C in a sample oxidizer was >95% when 13 mL of Packard Permafluor V and 9 mL of Carbosorb were used.

Photolysis Studies. The thin film (ca. 2-mm thickness) was prepared from a suspension of 2 g each of soil, clay mineral, or humic acid in 2 mL of pure water in the bottom of a Pyrex glass beaker (3.5 cm i.d. × 5.0 cm height). After the water had evaporated, the resulting film was uniformly treated with [^{14}C]-I (1.68 μCi) in 1,2-dichloroethane at a rate of 10 ppm and then continuously irradiated with a 500-W xenon lamp (USIO Model UIV-5150XE, Tokyo), using the apparatus reported previously (Katagi, 1990). The emission spectrum of a xenon lamp with a cutoff of 300 nm and a maximum of 468 nm (69.59 μW cm^{-2} nm^{-1}) was obtained by an Ushio USR-20B photometer. Air, free of CO$_2$ and saturated with water vapor, was passed continuously over the irradiated samples at a flow rate of 100 mL/min. It was then passed through two gas-washing bottles to trap volatile ^{14}C. The first contained ethylene glycol (100 mL) and the second 0.5 M NaOH (400 mL). The temperature at the surface of each film was maintained at 25 ± 1 °C in a manner similar to that reported previously (Katagi, 1990). The dark control experiment was conducted in the same way except that the photoreaction vessel was covered with aluminum foil.

At an appropriate interval, each film was scraped from the beaker in the photoreaction vessel and extracted with 25 mL of methanol–distilled water (5:1) followed by centrifugation at 3000 rpm for 10 min. After decantation, the extraction was repeated twice. A 0.5-mL aliquot of the combined supernatant liquid was radioassayed in duplicate, and the remaining portion was used for TLC analysis after being concentrated in a rotating evaporator. I and its degradation products were first separated on TLC (silica gel 60F$_{254}$, 20 × 20 cm, 0.25 mm layer thickness, Merck) with benzene saturated with formic acid–diethyl ether (10:3, eluent system A) (Ohkawa et al., 1978). I, II, IV, and IX were separated more efficiently in the six-time development with hexane–diethyl ether (20:1, eluent system B), as previously reported (Mikami et al., 1980). Since VI and VII could not be separated on TLC in the two eluent systems above, these degradation products separated in the eluent system A were again subject to TLC analysis using hexane–acetone (4:1, eluent system C) instead. The R_f values of VI and VII in the four-time development with this eluent system were 0.18 and 0.24, respectively. I and each product were detected by preparing autoradiograms, and their amounts were quantified by radioassay of the ^{14}C-labeled gel region scraped from the TLC plate. Chemical identification was achieved by cochromatography of the extracts with the authentic standards. [^{14}C]-I was purified from the extracts on TLC and subjected to the HPLC analysis to examine whether the isomerization occurred during the study. The unextractable ^{14}C bound to the residue was radioassayed by a sample oxidizer and LSC. For the determination of volatile activity, the gas-washing bottles were sampled periodically in a manner similar to that reported previously (Katagi, 1990). The liquid in the two traps was replaced at each sampling time.

The photoinduced cleavage of the ether linkage in the alcohol moiety of I was separately examined on kaolinite. Nonlabeled I (1 mg/g of clay) together with [^{14}C]-I (1.68 μCi) was uniformly applied to 2 g of kaolinite prepared by using (1) H$_2$^{18}O (0.5 mL/g of clay) and (2) the aqueous solution of potassium cyanide (0.1 mmol/g of clay). After 14 days of exposure to UV light, the
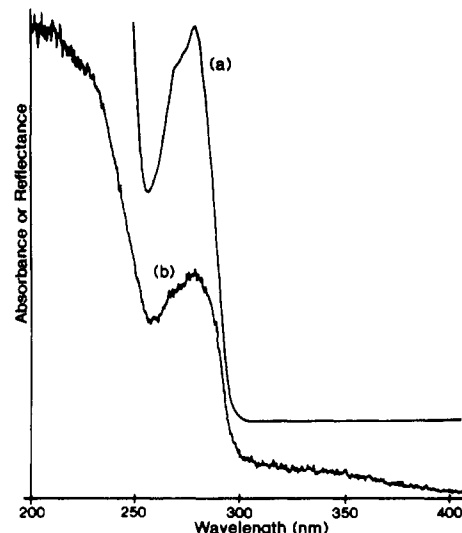

Figure 1. Absorption and reflectance spectra of I: (a) absorption spectrum of I in 10% acetonitrile (1.12 × 10^{-4} M); (b) reflectance spectrum of I adsorbed on kaolinite (0.14 mg/cm^2).

incorporation of ^{18}O into VII and the formation of VIII (R_f 0.30 in eluent system C) were examined by MS and TLC analysis.

Reaction of I with Active Oxygen Species. Active oxygen species such as hydrogen peroxide and hydroxyl radical, formed on clay and soil surfaces under irradiation, are considered to participate in the degradation of some pesticides (Katagi, 1990). To examine this possibility, the following experiments were conducted. [^{14}C]-I (2.34 μM) in 20 mL of 0.1 M phosphate buffer (pH 9)–acetone (1:1) was treated with hydrogen peroxide (4.34 mM) in darkness at 25 ± 1 °C (experiment A). The control study without hydrogen peroxide was carried out to examine the hydrolytic stability of I (experiment B). The buffer catalysis was also examined by using distilled water instead of the phosphate buffer (experiment C). The effect of kaolinite on the reaction of I with hydrogen peroxide was studied in acetone–distilled water (1:1) (experiment D). The radical oxidation of I was studied by using Fenton's reagent. Ferrous sulfate heptahydrate granule (120 μM) was added to a rapidly stirred 1% aqueous acetonitrile solution (500 mL) of [^{14}C]-I (80 ppb) at 25 °C after the addition of hydrogen peroxide (60 μM) and allowed to react for 30 min (experiment E). The oxidation was twice repeated after fresh addition of oxidant, followed by more ferrous sulfate. The reaction mixture (5 mL) was extracted with ethyl acetate (10 mL × 3) followed by TLC analysis in experiments A–C and E. In the case of experiment D, the clay residue was extracted three times with 20 mL of methanol-distilled water (5:1) after decantation of the supernatant. All experiments were conducted in duplicate.

RESULTS

Spectroscopy. The reflectance spectra of I adsorbed on kaolinite and montmorillonite showed maxima at ca. 276 nm and had a measurable tail above the baseline at wavelengths between 300 and 400 nm (Figure 1). The weak reflectance above 300 nm was considered to be due to the clay minerals because of their similar reflectance in this spectral region. The UV absorption spectrum of I in 10% aqueous acetonitrile exhibited weak absorption at 277 nm due to the π → π* transition of the phenyl ring with a n → π* character. There was no significant difference in the spectral patterns between the reflectance and absorption spectra of I. The phosphorescence spectrum showed emission maxima at 425 nm, indicating that the energy level of excited triplet states of I relative to the ground singlet state is 67.2 kcal/mol.

The IR difference spectra of I dispersed in KBr, kaolinite plus KBr, and montmorillonite plus KBr are shown in Figure 2. The strong absorption at 1400–1000 cm^{-1} was
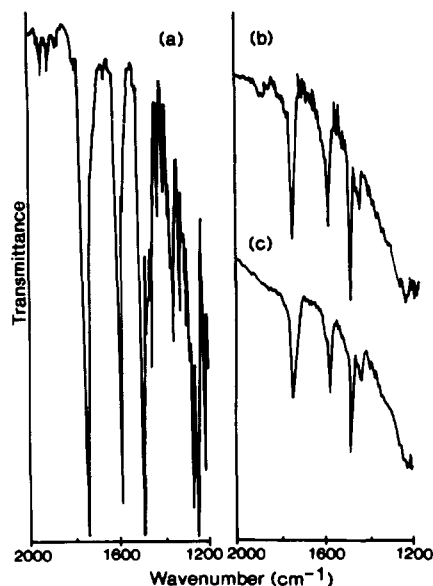
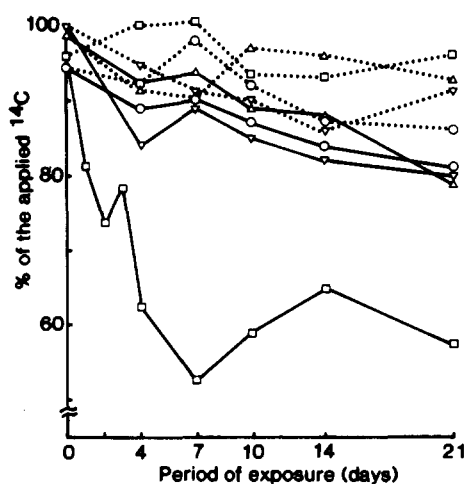**Figure 2.** IR spectra of I: (a) KBr; (b) kaolinite; (c) montmorillonite.

Figure 3. Decline curves of I: (O—O) light, Noichi soil; (O···O) dark, Noichi soil; (□—□) light, kaolinite; (□···□) dark, kaolinite; (△—△) light, montmorillonite; (△···△) dark, montmorillonite; (▽—▽) light, humic acid; (▽···▽) dark, humic acid.

Table I. Half-Life of I

thin film	half-life,[a] days	
	light	dark
Noichi upland soil	100.0	138.2
kaolinite	7.8[b]	391.2
montmorillonite	68.3	553.4
humic acid	80.6	150.8

[a] Half-life was calculated on the basis of data at 0–21 days. [b] (0–4 days).

derived from the clay minerals themselves. The IR absorption due to the C=O moiety of I observed at 1737.4 cm^{-1} in KBr was shifted to higher values when I was adsorbed on kaolinite (1753.6 cm^{-1}) and montmorillonite (1750.8 cm^{-1}). Smaller shifts (ca. 2 cm^{-1}) were also detected for the C=C stretching of the phenyl ring (1586.1 and 1488.9 cm^{-1} in KBr) but to an extremely smaller extent.

Photolysis Studies. The decline curves of I are shown in Figure 3. Its degradation on the clay surfaces was accelerated by irradiation, as listed in Table I. The half-life on montmorillonite was estimated to be 68.3 days under irradiation as compared with 553.4 days in the dark. In the case of kaolinite, I rapidly decreased with the half-life

of 7.8 days but stayed approximately constant after 10 days. The acceleration was also observed on the surfaces of the Noichi upland soil and humic acid but to a smaller extent.

The amounts of I and its degradation products formed under irradiation on the four surfaces tested are summarized in Table II. More radiocarbons were bound to humic acid than to clays and soil. There was a slight increase of bound ^{14}C to all surfaces under the influence of irradiation. The volatile activity gradually increased with time under irradiation in every surface tested. The major component of the volatile ^{14}C was ^{14}CO$_2$, and an insignificant amount of volatiles (<0.1%) was detected in the ethylene glycol trap. Since the amounts of bound ^{14}C and ^{14}CO$_2$ in dark conditions were smaller than those observed under irradiation on clays and soil, it may be inferred that most of the bound and volatile ^{14}C is derived from the photoproducts, not from the microbial degradation.

I did not undergo any isomerization on every surface during the study, as evidenced by HPLC cochromatography with the nonlabeled I. The major photoproduct in the extracts from the Noichi soil was III formed via hydration of the cyano group attached to the benzyl carbon, amounting to 4.3% at 21 days. On kaolinite, VII and X were detected as major photoproducts and amounted to 4.3% and 8.8% at 10 days, respectively. It is considered that VII is formed via cleavage of the ether bond in the alcohol moiety of I. X was also detected on the humic acid and considered to be formed via oxidation of IX, which originated from the unstable α-cyano-3-phenoxybenzyl alcohol formed via hydrolysis of I. In contrast, V was a major photoproduct on montmorillonite. Although the amide derivative of IV was not detected in this study, V was considered to be formed via hydrolysis of the metastable amide derivative. The smaller or trace amounts of these products detected in darkness indicated that irradiation greatly enhanced their formation. II and IV were only detected under irradiation, but at a trace amount (0.1–2.0%). It is known that I predominantly undergoes homolytic cleavage of the ester moiety via a radical mechanism to form II and IV in a solution phase (Holmstead, 1978; Mikami et al., 1985). Their minority may be, at least in part, due to the light attenuation in the thin films tested. Since the degradation products originated from the alcohol moiety of I (IX and X) were mainly detected, it was considered that hydrolysis followed by oxidation was the main degradation pathway under the dark conditions.

The extract from the kaolinite containing potassium cyanide after 14 days of irradiation was subjected to two-dimensional TLC cochromatography with VIII (first direction with eluent system A and second with C). Neither VII nor VIII was detected, indicating that the photonucleophilic substitution of I by cyanide ion does not proceed on kaolinite. Since the EI-MS spectrum of VII formed on kaolinite in the presence of H$_2$^{18}O after 14 days of irradiation did not exhibit the parent peak (m/e = 343) clearly, the ratio of the peak intensities at m/e = 132 and 134 corresponding to the α-cyano-3-hydroxybenzyl fragment was used to estimate the incorporation of ^{18}O in VII. The ratio of the peak intensities at m/e = 132 and 134 was approximately 55:45, which indicated that about half of the hydroxyl oxygen in VII was derived from ^{18}O.

Chemical Oxidation of I. The amounts of I and degradation products via chemical oxidation are listed in Table III. As shown in Figure 4, I rapidly degraded with the half-life of 17.9 days to III and IX in the phosphate buffer (pH 9) when hydrogen peroxide existed (experiment

Table II. Amounts of I and Its Degradation Products

	\% of the applied ^{14}C											
	Noichi upland soil			kaolinite			montmorillonite			humic acid		
	L^d		D^d	L		D	L		D	L		D
	10 days	21 days	21 days	10 days	21 days	21 days	10 days	21 days	21 days	10 days	21 days	21 days
volatile ^{14}C^a	1.8	3.6	1.1	4.7	8.3	0.3	1.2	4.7	0.2	0.9	2.5	0.1
EG trap^b	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
alkali trap	1.8	3.6	1.1	4.7	8.3	0.3	1.2	4.7	0.2	0.9	2.5	0.1
CO$_2$	1.6	3.1	1.0	4.5	7.8	0.3	1.0	4.4	0.2	0.9	2.5	0.1
others	0.2	0.5	0.1	0.2	0.5	<0.1	0.2	0.3	<0.1	<0.1	<0.1	<0.1
extractable ^{14}C	91.6	90.0	92.1	85.6	77.2	96.8	93.4	85.4	94.9	88.1	84.9	94.9
I	87.0	81.2	86.3	60.8	57.7	95.9	88.8	78.7	92.6	85.1	80.1	91.4
II	1.3	2.0	–^{c}	1.9	1.3	–	0.8	1.1	–	0.4	1.4	–
III	1.5	4.3	0.1	1.5	1.1	<0.1	0.4	0.7	0.5	0.2	0.2	–
VII	0.2	0.7	–	4.3	3.0	–	0.6	0.9	–	0.2	0.4	–
IV	0.1	0.4	–	0.9	0.9	–	0.7	0.9	–	0.3	0.4	–
V	<0.1	<0.1	–	<0.1	2.4	–	1.2	2.0	–	0.4	<0.1	–
IX	0.1	0.1	0.4	0.8	0.1	0.3	0.2	0.2	0.3	<0.1	<0.1	0.5
X	1.0	0.8	4.4	8.8	4.4	<0.1	<0.1	<0.1	1.1	1.0	1.5	0.8
others	0.4	0.5	0.9	6.6	6.3	0.6	0.7	0.9	0.4	0.5	0.9	2.2
bound ^{14}C	4.6	5.5	2.9	3.1	6.4	0.6	0.4	2.0	0.3	10.1	10.8	8.8
total ^{14}C	98.0	99.1	96.1	93.4	91.9	97.7	95.0	92.1	95.4	99.1	98.2	103.8

^{a} Volatile ^{14}C = EG trap + alkali trap. ^{b} EG, ethylene glycol. ^{c} –, not detected. ^{d} L, D, light and dark conditions, respectively.

Table III. Chemical Oxidation of I

	\% of the applied ^{14}C^a				
compd	A	B	C	D	E
I	58.4	98.4	97.0	51.6	93.6
III	23.6	–^{b}	1.0	30.5	–
VII	–	–	–	–	1.9
IX	13.7	–	0.8	9.8	0.8
X	1.6	0.4	0.5	2.8	–
others	2.7	1.2	0.7	5.3	3.7
$T_{1/2}{}^c$	17.9	1572	360.3	14.8	–

^{a} Averaged values between the duplicate experiments. Key: A, I (2.34 μM) in 0.1 M phosphate buffer (pH 7.0)–acetone (1:1) with 4.34 mM H_2O_2 at 14 days; B, (A) without H_2O_2; C, (A) using distilled water instead of buffer; D, (C) in the presence of kaolinite; E, I (80 ppb) in 1\% aqueous acetonitrile with Fenton's reagent. ^{b} Not detected. ^{c} Half-life of I (in days) estimated on the basis of data at 0–14 days.
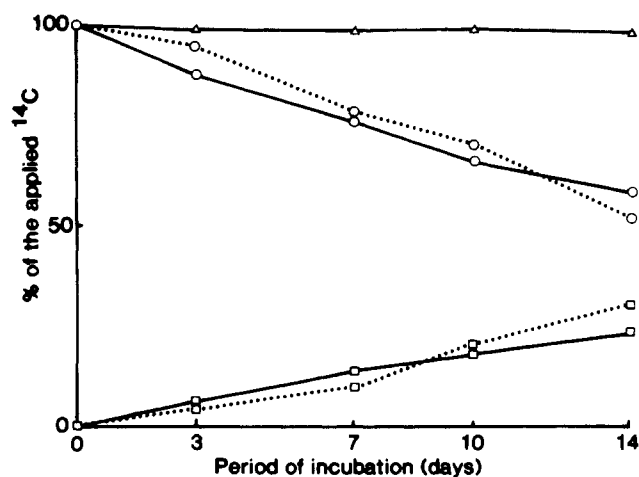

Figure 4. Amount of I and III formed via chemical oxidation: (O–O) I in experiment A; (Δ–Δ) I in experiment C; (O⋯O) I in experiment D; (□–□) III in experiment A; (□⋯□) III in experiment D.

A). Since I scarcely degraded under the conditions of experiments B and C, it was concluded that hydrogen peroxide participates in the hydration of the cyano group of I under the basic conditions. The concomitant formation of IX is likely to be due to the nucleophilic attack of OOH⁻ at the carbonyl carbon of I followed by the elimination of the cyano group of the resultant cyanohydrin. In experiment D, the degradation of I with the concomitant formation of III was similar to that in experiment A (Figure 4), and the half-life of I was estimated to be 14.8 days. These results indicate that kaolinite can act as a base catalyst. The oxidation of I with Fenton's reagent caused the formation of VII and IX, but the hydroxylated derivative of I such as VI was not detected in the TLC analysis.

DISCUSSION

It is unlikely that the direct photolysis dominantly participates in the degradation of I under the conditions tested. The spectral shift of absorption was not caused by adsorption of I on kaolinite (Figure 1), where the degradation of I was greatly accelerated by irradiation. In this case, the spectral overlap between the reflectance spectrum of I and the emission spectrum of a xenon lamp ($\lambda > 300$ nm) was very small. Furthermore, the insignificant contribution of direct photolysis is evidenced by the smaller amount of II formed on the surfaces tested, as compared with that reported in the aqueous photolysis (Mikami et al., 1980). The formation of III and VII also shows the presence of degradation pathways other than direct photolysis. Meanwhile, shorter half-lives of I have been reported previously (Mikami et al., 1980) than those obtained in this study except on kaolinite. These results could not be simply compared due to the different conditions. However, the direct photolysis seems to be important in the environment, since natural sunlight affords more irradiance than the xenon lamp used at the wavelengths of 290–320 nm where the absorption of light by I is observed.

The IR spectra of I on the clay surfaces showed the upper shift of the C=O vibration. It has been reported for a carbamate insecticide that the wavenumber of the C=O vibration decreases with its adsorption on clay minerals due to the dipole–dipole interactions with countercations (Mortland and Meggitt, 1966). Therefore, the observed shift for I may be originated from other interactions which cause the conformational change around the ester linkage. However, this possible conformational change is not considered to affect the extent of the surface-catalyzed hydrolysis of I, since the amounts of IX and X
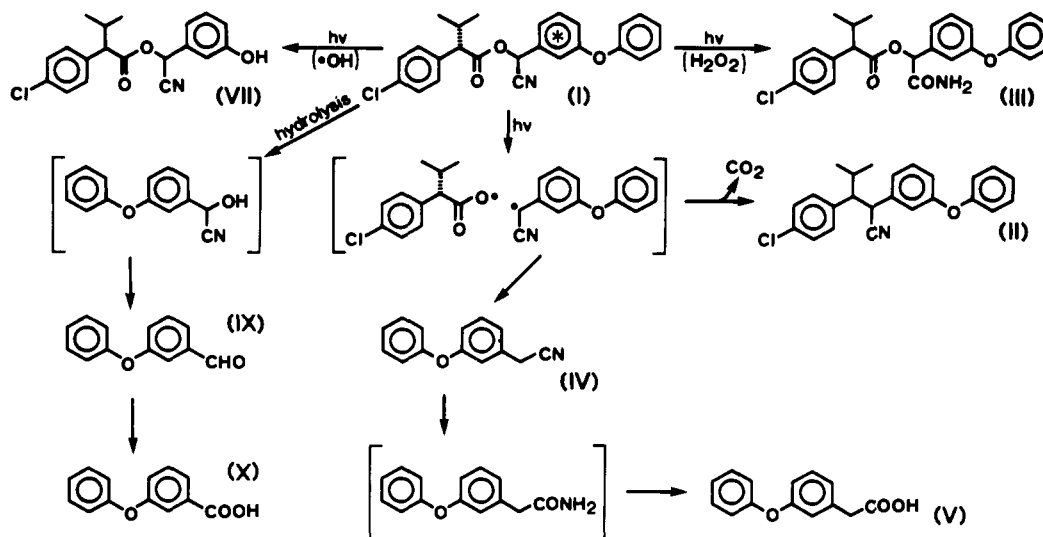
Figure 5. Photodegradation pathways of I: (*) ^{14}C-labeled position.

are smaller than those detected on the intact soil and humic acid (Table II).

Zepp et al. (1985) have reported that the excited triplet state of humic substances can transfer its energy to a chemical adsorbed but that its excited singlet state plays an insignificant role due to its extremely short lifetime. Since the triplet energy of many humic substances has been reported to be about 250 kJ/mol (ca. 60 kcal/mol) (Zepp et al., 1985) and that of I is estimated to be 67.2 kcal/mol by phosphorescence spectrum, the photosensitized degradation of I by humic substances via electronic energy-transfer mechanism is unlikely to be the major degradation pathway. Therefore, the accelerated degradation of I observed on the Noichi upland soil and humic acid surfaces seems to be mainly due to the photoinduced processes.

One of the photoinduced degradations is the hydration of the cyano group to form III, which has been also reported in the aerobic soil metabolism (Ohkawa et al., 1978), but its mechanism is not specified. The enzymatic hydration of the cyano group (Briggs and Dawson, 1970; Mahadevan and Thimann, 1964) is a possible mechanism, but both a trace formation of III even in the Noichi upland soil in darkness and the enhancement of its formation by irradiation exclude this possibility in photodegradation. The other mechanism is the catalyzed hydration of I by clay minerals in the presence of hydrogen peroxide. The photogeneration of hydrogen peroxide has been shown on the surface of clay minerals (Katagi, 1990) and in the aqueous dispersion of humic acid (Takahashi, 1988). Furthermore, the efficient hydration of I by hydrogen peroxide to form III was observed when the base or kaolinite clay was present (Table III). The base-catalyzed conversion of nitriles to amides has been suggested to involve the nucleophilic attack of the peroxy anion on the cyano carbon (Wiberg, 1953), and the various metal oxides are known as a catalyst (Sugiyama et al., 1986). Therefore, it is strongly suggested that the photoinduced hydration of the cyano group proceeds via (1) photochemical generation of hydrogen peroxide on the surfaces, (2) proton abstraction from hydrogen peroxide by clay minerals or humic substances to form the peroxy anion, and (3) nucleophilic attack of peroxy anion on the cyano carbon of I.

The other photoinduced degradation pathway is the cleavage of the ether bond in the 3-phenoxybenzyl moiety. By analogy with the solution photochemistry of the diphe-

nyl ether herbicides (Nakagawa and Crosby, 1974; Ruzo et al., 1980), the photonucleophilic substitution by water to form VII was considered. It was expected that VII or VIII would be produced when the photolysis of I on kaolinite was conducted in the presence of cyanide ion which was a stronger nucleophile than water (Heijer et al., 1977). However, neither of the products was detected in this study. Since it was theoretically estimated that the unpaired electrons in the triplet state of I were predominantly distributed at the phenoxyphenyl ring and 20–24% of them were located at the 3-position [Katagi, unpublished observations. (The semiempirical AM1 molecular orbital calculations including the configuration interactions (MOPAC package, QCPE Program No. 523) were conducted for the fully optimized molecular geometry of I in the triplet state.)], the complete incorporation of water into VII was expected if the photonucleophilic reaction would occur. On the kaolinite surface where the formation of VII was predominant, EI-MS showed that about half of the ^{18}O was incorporated into VII from $H_2^{18}O$. On the basis of these results, VII was unlikely to be formed via photonucleophilic substitution.

Meanwhile, the photogeneration of hydroxyl radical where about half of the oxygen is derived from water has been suggested on the clay surfaces (Katagi, 1990). It is known that the oxides of titanium and other transition metals act as a photocatalyst in generating a hydroxyl radical (Fujihira et al., 1981). The clay minerals used contained Ti, Fe, Zn, and Mn metals and showed absorption at wavelengths of 300–400 nm (Figure 1), corresponding to the band gap energies of various semiconductors. Therefore, it may be inferred that these metal oxides act as a photocatalyst. Since VII was formed via reaction of I with Fenton's reagent, the reaction with the hydroxyl radical produced on the clay surfaces by irradiation was a feasible pathway, which could well elucidate the experimental results. Similar mechanisms would be possible on soils and humic acid, since the formation of the hydroxyl radical photosensitized by humic substances was confirmed by electron spin resonance study (Takahashi et al., 1988).

On the basis of these considerations, the photodegradation pathways of I on the surfaces tested are proposed in Figure 5. Indirect photolysis, i.e., reactions with the photogenerated active oxygen species, was likely to play an important role in the photodegradation of I on these surfaces.

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