Photodegradation of 3-Phenoxybenzoic Acid in Water and on Solid Surfaces

Toshiyuki Katagi

Environmental Health Science Laboratory, Sumitomo Chemical Company, Ltd., 4-2-1 Takatsukasa, Takarazuka, Hyogo 665, Japan

3-Phenoxybenzoic acid (I) was irradiated with a xenon lamp ($\lambda > 290$ nm) in buffered aqueous solutions and on the surfaces of Noichi upland soil, kaolinite clay, and silica gel. Hydroxylation at both phenyl rings and ether cleavage were the main photodegradation pathways, and I was finally mineralized to carbon dioxide. Chemical oxidation and ^{18}O isotopic dilution studies showed that the participation of a hydroxyl radical was of importance in photodegradation of I and that the ether cleavage proceeded via reaction with a hydroxyl radical but via neither photonucleophilic substitution by water molecule nor degradation of 2'-hydroxylated derivative of I.

INTRODUCTION

Synthetic pyrethroids possessing an α-cyano-3-phenoxybenzyl moiety are some of the most potent insecticides, and their environmental fates have been extensively examined (Leahey, 1985). Since the ester linkage is mostly cleaved to form the corresponding acid and cyanohydrin, which successively degrades to I via hydrolysis and oxidation, their further degradation becomes dominant rather than that of the pyrethroids by themselves. For the alcohol moiety of these synthetic pyrethroids, the hydroxylation of aromatic rings and ether bond cleavage have been reported under various conditions. In the soil metabolism of cypermethrin (Sakata et al., 1986), fenpropathrin (Roberts and Standen, 1977), and fenvalerate (Ohkawa et al., 1978), 2'-hydroxy and 4'-hydroxy derivatives of I and/or 3-hydroxybenzoic acid were detected as metabolites. Some soil microorganisms are known to metabolize pyrethroids via cleavage of an ester linkage followed by oxidation and hydroxylation (Maloney et al., 1988). I and its hydroxylated derivatives have been identified mainly as their conjugated forms in plant and rat metabolism studies (Leahey, 1985). Besides these biological processes, photodegradation of I is considered to be one of the important factors in its environmental fate. Both in the aqueous phase and on soil surfaces, the photoproducts formed via ether bond cleavage of I have been detected with a trace amount from permethrin (Holmstead et al., 1978), cypermethrin (Takahashi et al., 1985a) and fenpropathrin (Takahashi et al., 1985b).

In contrast to that of the pyrethroids by themselves, the degradation of I has been scarcely studied. Recently, 3-hydroxybenzoic acid has been shown to be a main degradate in chicken metabolism (Akhtar, 1990) and microbial degradation (Topp and Akhtar, 1990) of I. Although the photochemistry of 3-phenoxybenzyl alcohol (Huang and Wan, 1991) and 2- and 4-phenoxybenzoic acids (Yang et al., 1972) has been examined, no photochemical information on I is available. Meanwhile, diphenyl ether is known to photodegrade via Claisen rearrangement in organic solvents (Hageman et al., 1970; Ogata et al., 1970), and the photonucleophilic substitution has been reported for diphenyl ether herbicides (Nakagawa and Crosby, 1974; Ruzo et al., 1980) in aqueous solutions. These mechanisms may be applicable to the photodegradation of I in the environment. To examine the importance of photodegradation of I in the environment, the photolysis profile of I was first studied in the aqueous phase by using a

xenon arc lamp ($\lambda > 290$ nm). The effects of the parameters pH, hydrogen peroxide, and humic acids were also examined. Since I was a main metabolite in the soil metabolism of synthetic pyrethroids, its photodegradation on an intact soil was also studied. To estimate the participation of active oxygen species on solid surfaces (Katagi, 1990, 1991), kaolinite clay and silica gel were used as media.

MATERIALS AND METHODS

Chemicals. The hydroxylated derivatives of I (II–VII in Figure 5) were prepared according to the reported methods (Unai and Casida, 1977). The chemical structure of each compound was confirmed by ^1H NMR, IR, and MS spectroscopies. The chemical purity of each compound was >99%, as determined by HPLC analysis. I, 3-phenoxyphenol (XII), 3-cyanobenzoic acid, ferrous perchlorate hexahydrate, the sodium salt of humic acid from Aldrich Chemical Co. Ltd. (Milwaukee), and 3-hydroxy-(VIII), 3,4-dihydroxy- (IX), 2,5-dihydroxy- (X), and 3,5-dihydroxybenzoic acids (XI) from Wako Pure Chemical Industries, Ltd. (Osaka) were used without further purification. [^{14}C]-I uniformly labeled at the phenyl ring (317 mCi/g, >99%) in the benzoic acid moiety from Amersham was purified by a thin-layer chromatography prior to use. $H_2^{18}O$ (97 atom %) was purchased from E. Merck (Montreal). (Trimethylsilyl)diazomethane (TM-SCHN₂) in 10% hexane from Tokyo Kasei (Tokyo) was used for methylation of VIII. Pure water with an electrical conductivity of 5.5×10^{-8} Ω^{-1} cm^{-1} supplied from a Puric Model-R (Organo Co., Ltd.) equipped with a G-10 filter (Organo) was used to prepare buffer solutions. PIC-A (tetrabutylammonium phosphate) used in a mobile phase of HPLC was purchased from Waters Co., Ltd. (Milford, MA). Kaolinite clay (K5, acid-washed American standard) from Fisher Scientific (Fair Lawn, NJ) and silica gel (Keieselgel 60, no. 7734) from E. Merck were used. The characteristics of the Noichi upland (sandy clay loam) soil were the same as reported previously (Katagi, 1991).

Spectroscopy. The ultraviolet (UV) absorption spectra of I in 1% aqueous acetonitrile (1.07×10^{-5} M) were measured at pH 2 and 7 with a Hitachi U-3210 spectrophotometer. Reflectance spectra of I (0.14 mg cm^{-2}) on solid surfaces were obtained with the same spectrophotometer equipped with a 60 i.d. integrating sphere in a manner similar to that reported previously (Katagi, 1990). 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.

Thin-Layer Chromatography (TLC). Precoated silica gel 60F₂₅₄ chromatoplates (20 × 20 cm, 0.25-mm layer thickness, E. Merck) were used for an analytical purpose. The TLC R_f values of each compound in the two solvent systems are listed in Table I. The resolved radioactive spots were detected by autoradiography with the developed TLC plates held under X-ray SB film

Table I.   TLC R_f Values and HPLC Retention Times of I and Its Degradates

| compd | R_f value[a] | | RT,[b] | compd | R_f value[a] | | RT,[b] |
	A	B	min		A	B	min
I	0.49	0.38	30.5	VII	0.54	0.32	38.2
II	0.33	0.27	21.6	VIII	0.25	0.14	3.5
III	0.31	0.19	19.0	IX	0.11	0.02	3.8
IV	0.29	0.19	16.2	X	0.21	0.04	5.8
V	0.39	0.32	14.2	XI	0.09	0.00	4.0
VI	0.31	0.18	25.3	XII	0.56	0.33	44.4

[a] Solvent system: A, benzene saturated with formic acid–diethyl ether (10:3); B, toluene–acetic acid (7:1). [b] Typical retention times in HPLC.

Table II.   HPLC Mobile Phase Conditions

step	time, min	A,[a] %	B,[a] %	C,[a] %	step	time, min	A,[a] %	B,[a] %	C,[a] %
0	0	25	0	75	4	25	40	10	50
1	5	25	0	75	5	35	40	10	50
2	10	30	5	65	6	40	25	0	75
3	20	30	5	65	7	45	25	0	75

[a] Component of a mobile phase: A, acetonitrile; B, methanol; C, distilled water containing 5×10^{-3} M PIC-A.
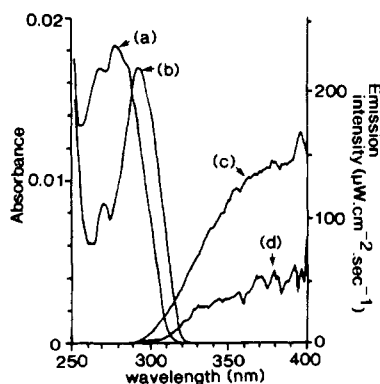

Figure 1. Absorption spectra of I at pH 7 (a) and pH 2 (b) (1.07 $\times 10^{-5}$ M) and emission spectra of xenon lamp (c) and natural sunlight (d).

(Eastman Kodak Co.) at 4 °C for a week, and each of them was quantified with a Packard Model 460CD Tri-carb scintillation spectrometer (LSC). The unlabeled standard chemicals were detected by ultraviolet light fluorescence quenching.

High-Performance Liquid Chromatography (HPLC). A Hitachi L-6200 liquid chromatograph was operated at a flow rate of 1.0 mL/min, using the Sumipax ODS A-112 (5 μm, 6 mm i.d. $\times$ 15 cm; Sumika Analytical Service Ltd., Osaka) column. The composition of a mobile phase was changed stepwise as described in Table II. The amounts of I and its photoproducts were quantified, using a Radiomatic Flo-one/β A-120 radiodetector (time constant, 6.0 s; chart speed, 5 mm/min). At the same time, the UV absorbance at 240 nm was monitored by using a Hitachi L-4000 variable-wavelength UV monitor. The detection limit of radioactivity was ca. 0.1% of the applied ^{14}C. The retention times of I and its related compounds are listed in Table I. The identity of each compound was confirmed by comparing retention times.

Photolysis Studies. *a. Aqueous Photolysis.* A 50-mL aliquot of the 1% aqueous acetonitrile solution of [^{14}C]-I (0.3 ppm) in a quartz vessel was irradiated with a 500-W xenon arc lamp (UXL-500D; Ushio, Tokyo; λ = 290–800 nm) through a Pyrex glass filter at 25 $\bullet$ 1 °C. The emission spectrum of a xenon lamp measured with a USR-20B photometer (Ushio) is shown in Figure 1. Photolysis was conducted under air at pH 7 (0.067 M phosphate buffer), and the effect of hydrogen peroxide (100 μM) or humic acid (1 ppm) was examined according to the methods reported previously (Draper and Crosby, 1984; Takahashi et al., 1988). The pK_a value of I has been reported to be 3.95 at 20 °C (Dippy, 1939), indicating a pH dependency of the absorption spectrum of I. Therefore, the photolysis profile was also examined at pH
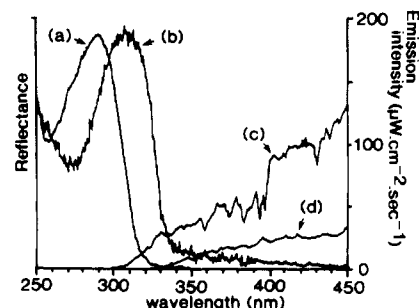

Figure 2. Reflectance spectra of I adsorbed on silica gel (a) and kaolinite (b) at a rate of 0.14 mg cm^{-2} and emission spectra of xenon lamp (c) and natural sunlight (d).
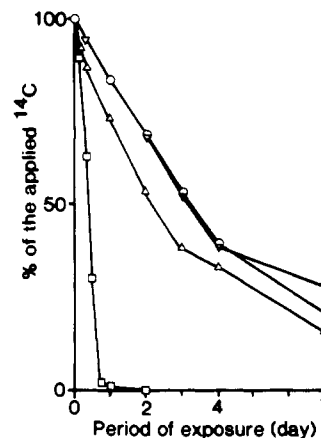

Figure 3. Photodegradation of I (0.3 ppm) in aqueous phases. ($\square$) pH 2; ($\bigcirc$) pH 7; ($\triangle$) pH 7 with H$_2$O$_2$ (100 μM); ($\triangledown$) pH 7 with humic acids (1 ppm).

2 (0.067 M HCl plus CH$_3$COONa). At appropriate intervals, a 0.1-mL aliquot was taken in duplicate to determine the concentration of ^{14}C by LSC, and another 10-mL aliquot was extracted three times with 20 mL of ethyl acetate. The reaction mixture at pH 7 was acidified to pH 2 with 0.1 M HCl prior to extraction. After the radioactivities in organic and aqueous fractions were measured with LSC, the extracts were analyzed by both two-dimensional (2D) TLC with solvent systems A and B and HPLC. The unextractable ^{14}C in >10% yield was analyzed by TLC with solvent system C (butanol–acetic acid–distilled water 6:1:1) after lyophilization. When the recovery of ^{14}C was lower than 95% of the applied dose, the similar experiments were separately conducted to collect volatile ^{14}C, and it was analyzed by the reported methods (Katagi, 1990). Radioactive compounds collected in ethylene glycol (100 mL) and 0.5 M NaOH (400 mL) were analyzed by LSC. ^{14}CO$_2$ dissolved in the reaction mixture at pH 7 was purged into traps with nitrogen gas after acidification with concentrated H$_2$SO$_4$.

The mechanism of an ether cleavage of I to form VIII was separately examined at pH 2 and 7. Since II was suggested to be a precursor of VIII (Gaughan et al., 1977), its stability under the acidic conditions was first monitored. The buffer solutions of nonlabeled II (0.6 ppm) at pH 2 and 7 were incubated at 25 $\pm$ 1 °C, and a 2-mL aliquot was periodically analyzed by HPLC. Its photostability was also examined at pH 2 by exposure to UV light in a manner similar to that taken in aqueous photolysis of I. The photonucleophilic substitution at the ether linkage could be considered as another mechanism as reported for diphenyl ether herbicides (Nakagawa and Crosby, 1974; Ruzo et al., 1980). The possibility of this mechanism in photolysis of I was also examined. The buffered aqueous solution of I at pH 2 and 7 was similarly irradiated in the presence of potassium cyanide (10 mM). The formation of VIII and/or 3-cyanobenzoic acid was examined by 2D-TLC and HPLC after irradiation. Furthermore, the ^{18}O isotopic dilution study was conveniently conducted at pH 2, where VIII was obtained in greater than 10% yield to examine which C–O bond of an ether moiety was cleaved via photolysis of I. The nonlabeled I (1 mg) and [^{14}C]-I (2 μCi) in

Table III. Amounts of I and Its Photoproducts in Aqueous Phases

| | % of the applied ¹⁴Cᵃ | | | | | | | |
| | A | | B | | C | | D | |
	3 days	7 days	3 days	7 days	3 days	7 days	0.5 day	2 days
ext ¹⁴Cᵇ	82.3	64.3	68.3	53.1	80.1	68.0	62.8	15.2
I	52.7	20.7	38.5	15.5	52.0	28.2	30.5	0.1
II	1.4	0.1	1.1	0.7	1.5	3.2	–ᵈ	–
III	1.2	1.0	–	1.0	–	–	–	–
IV	2.6	–	1.9	1.4	2.6	5.9	0.8	1.2
V	1.1	4.4	1.7	0.7	0.3	1.3	–	0.2
VI	0.7	–	–	–	–	–	–	–
VII	0.5	–	1.6	0.7	0.7	0.6	–	–
VIII	1.9	–	1.9	2.0	1.3	2.0	11.3	2.1
IX	3.9	–	2.1	3.5	2.7	3.6	2.8	0.8
XI	2.9	–	2.4	–	–	–	–	–
XII	1.0	0.7	0.3	0.1	0.7	1.0	–	–
others	12.4	25.0	16.8	27.5	18.3	22.2	21.1	10.8
aq ¹⁴Cᶜ	12.0	22.0	16.9	22.3	12.0	15.4	23.6	17.6
VIII	–	–	–	–	–	–	6.3	0.4
IX	–	–	0.5	0.7	1.1	0.4	–	–
X	0.8	2.0	1.2	1.7	0.7	0.7	1.1	0.9
XI	1.1	0.9	2.0	1.6	–	–	–	–
others	7.1	19.1	13.2	18.0	10.2	14.3	16.2	16.3
rec ¹⁴Cᵉ	94.4	86.3	85.2	75.4	92.0	83.5	84.9	32.8
¹⁴CO₂ᶠ	5.7	11.3	13.7	20.1	4.6	12.2	15.3	70.1

ᵃ Key: A, no additive at pH 7; B, 100 μM of H_2O_2 at pH 7; C, 1 ppm of humic acid at pH 7; D, no additive at pH 2. ᵇ Extractable ¹⁴C with ethyl acetate. ᶜ Aq ¹⁴C, unextractable radioactivity. ᵈ Not detected. ᵉ Rec ¹⁴C = ext ¹⁴C + aq ¹⁴C. ᶠ Quantified in separate studies. Radioactivity recovered from ethylene glycol trap amounted to <0.1% of the applied ¹⁴C.

1 mL of acetonitrile were added to 4 mL of pH 2 buffer containing 2 mL of $H_2^{18}O$ (97 atom %). The mixture was irradiated for 7 days, followed by extraction with ethyl acetate. The concentrated extract was dissolved in 2 mL of methanol–benzene (1:9) and reacted with an excess amount of $TMSCHN_2$ (Hashimoto et al., 1981) at room temperature for 2 h. Methyl 3-methoxybenzoate formed was separated by TLC with a solvent system of chloroform–ethyl acetate (6:1) (R_f = 0.62) and was analyzed by MS to quantify ¹⁸O incorporated into VIII.

b. Photolysis on Solid Surfaces. The thin film (ca. 1-mm layer thickness) was prepared from a suspension of 1 g of Noichi soil, kaolinite clay, or silica gel in 2 mL of pure water in the bottom of a Petri dish (6.2 cm²). After water had evaporated, the resulting film was uniformly treated with [¹⁴C]-I (1 μCi) in acetonitrile at a rate of 3.15 ppm by using a microsyringe and then continuously irradiated in duplicate with a 500-W xenon lamp (λ > 300 nm; Ushio, Model UIV-5150XE) at 25 ± 1 °C, using the apparatus reported (Katagi, 1990). The emission spectrum of a xenon lamp is shown in Figure 2. Each film was three times extracted with 20 mL of methanol–distilled water (5:1) in a manner similar to that previously reported (Katagi, 1991). For further extraction, 20 mL of methanol–0.1 M HCl (5:1) was used when the bound ¹⁴C amounted to >10% of the initial dose. The radioactivity in each fraction was assayed, and the extracts were separately subjected to 2D-TLC and HPLC. The bound ¹⁴C in each medium was quantified by radioassay after its aliquot was combusted with a sample oxidizer. Volatile ¹⁴C was separately quantified in a manner similar to that taken in aqueous photolysis.

Reaction of I with Active Oxygen Species. Active oxygen species such as hydroxyl radical and singlet oxygen are considered to participate in the photodegradation of pesticides (Katagi, 1989). Therefore, the radical oxidation of I was first studied, using Fenton's reagent (Kurata et al., 1988). [¹⁴C]-I (2.9 μM) and $HClO_4$ (2.9 mM) in 5 mL of 90% aqueous acetonitrile were mixed with ferrous perchlorate hexahydrate (260 μM) and hydrogen peroxide (530 μM) at 25 °C and allowed to react for 30 min under air or nitrogen atmosphere. Second, [¹⁴C]-I (1.44 μM) in 10 mL of methanol was reacted with NaClO (100 μM) and hydrogen peroxide (100 μM) at 10 °C for 1 h to examine whether singlet oxygen reacted with I (Katagi, 1989). All experiments were conducted in duplicate. The reaction mixture was concentrated after dryness with anhydrous $MgSO_4$ and subject to 2D-TLC and HPLC.

RESULTS

Photolysis in the Aqueous Phase. I was rapidly degraded under light conditions as shown in Figure 3, while in darkness 99.6–100.4% of the applied ¹⁴C was recovered as I unchanged throughout the experiments. The half-lives at pH 7 were estimated to be 3.0 (no additive), 2.6 (+H_2O_2), and 3.6 days (+humic acids), and therefore significant effect of additives on photolysis was not observed. Photolysis of I was greatly enhanced at pH 2 with the half-life of 4.3 h. Since the absorption maxima of I were 292 (ϵ = 1574 M^{-1} cm⁻¹) and 279 nm (ϵ = 1704 M^{-1} cm⁻¹) at pH 2 and 7, respectively (Figure 1), this red shift at pH 2 caused more light to be available for photodegradation of I, which might at least in part result in the acceleration of the photolysis. The extractable ¹⁴C decreased to 53.1–68.0% of the initial dose after 7 days of irradiation at pH 7, while 15.2% was only extracted even after 2 days at pH 2 (Table III). The radioactivity located in the origin of TLC and the unextractable ¹⁴C increased with irradiation. Each of them was found to consist of more than eight polar degradates by TLC analysis with solvent system C; none of the unidentified degradates amounted to >5% of the applied ¹⁴C. The recovered ¹⁴C decreased with irradiation, but the separate study to quantify volatile ¹⁴C clearly showed that this decrease was mostly due to the loss of CO_2 untrapped.

The various hydroxylated derivatives (II–VII) of I were detected in extracts with insignificant effect of additives on the product distribution, as listed in Table III (experiments A–C). The 2′-, 4′-, 4, and 6 positions of the phenyl rings were likely to be hydroxylated to a slightly larger extent as compared with the other positions. VIII was a main photoproduct at pH 2, amounting to 17.6% of the applied ¹⁴C in total after 0.5 day but immediately decreased thereafter. Although the pyrethroid derivatives hydroxylated in the phenyl rings have not been detected, the several photoproducts formed via ether bond cleavage of I and its alcohol derivatives have been detected in the photodegradation study of permethrin (Holmstead et al., 1978). XII was detected at pH 7 as a minor product (<1%). The dihydroxybenzoic acids (IX–XI) were detected in both

the extractable and aqueous fractions but gradually degraded to more polar degradates with irradiation, as evidenced in TLC analysis. Photoproducts formed via ether cleavage followed by Claisen rearrangement were considered to have polarities similar to those of the hydroxylated derivatives of I (II–VII). 2D-TLC analysis showed that such degradates amounted to less than 1% if present, and therefore such a rearrangement was likely to be a minor pathway.

During incubation at 25 °C for 3 days, it was clarified by HPLC that II was stable at pH 2 and 7 in the dark, while it completely degraded at pH 2 by exposure to UV light for 4 h without formation of VIII. Therefore, II was not a precursor of VIII, in contrast to the previous observation (Gaughan et al., 1977). MS analysis of methyl 3-methoxybenzoate, derivatized from VIII formed in the presence of $H_2^{18}O$, showed the following peak patterns; m/z 166 (9.5), 168 (100.0), 170 (88.0), and 172 (16.7). Since the nonlabeled methyl 3-methoxybenzoate exhibited the parent peak at m/z 166, MS data showed that a series of the ^{18}O-labeled (0–3 × ^{18}O) derivatives were formed. Supposing that the $^{16}O-^{18}O$ exchange at the carboxyl group with $H_2^{18}O$ was so rapid and the photoreaction of I with $H_2^{18}O$ occurred at the 3 position, the theoretical pattern of the peak intensity at m/z 166–172 should be 1:3:3:1, since ^{18}O atom % of water was about 50% under the conditions tested. Although the difference between the observed and theoretical data made the precise estimation of the extent of ^{18}O incorporation impossible, the photoreaction at the 3 position of I would be likely. Meanwhile, in the presence of an excess amount of a cyanide ion at pH 2 and 7, both HPLC and 2D-TLC analysis showed that neither VIII nor 3-cyanobenzoic acid was formed after irradiation for 1 week. Since the cyanide ion is more nucleophilic than water, these acids should be detected if the photonucleophilic substitution at the ether linkage (C_3 or $C_{1'}$ position) of I mainly takes place. Therefore, this mechanism was unlikely for the formation of VIII.

Photolysis on Solid Surfaces. Insignificant spectral difference between reflectance of I on silica gel surface and its absorption at pH 2 (Figures 1 and 2) was observed. In contrast, I on kaolinite surface showed a reflectance maximum at 305 nm (Figure 2). The reflectance spectrum of I on Noichi soil could not be measured since an appropriate thin film for measurement failed to be prepared. On exposure to UV light, I degraded with half-lives of 47.4 (Noichi soil), 28.6 (kaolinite clay), and 16.8 days (silica gel), while insignificant degradation of I was observed in the dark (half-life > 1 year), as shown in Figure 4.

The product distribution after 14 days of exposure is summarized in Table IV. Most of the radiocarbons extracted were derived from I unchanged, and VIII was a main photoproduct (1.8–5.4%) formed via ether cleavage of I. Similar bond cleavage has been recently reported for esfenvalerate by Katagi (1991). As minor photoproducts, XII and the hydroxylated derivatives of I (II–VII) were detected in trace amounts (<1.6%). The three dihydroxybenzoic acid isomers (IX, X, and XI) in a total amount of <3.6% indicated that the further degradation of VIII or V–VII proceeded on the surface tested. Since the bound ^{14}C derived from the dark control samples amounted to <1% of the initial dose, those from the exposed Noichi soil (8.6%) and kaolinite clay (5.1%) were considered to stem from photoproducts. Except for the Noichi soil, the recovered ^{14}C was less than 90% of the initial dose. However, the separate study to trap the volatile ^{14}C has revealed that almost all of the volatiles were due to CO_2
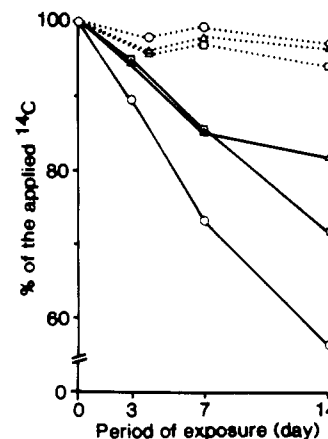

Figure 4. Photodegradation of I (3.15 ppm) on solid surfaces. (△) Noichi soil; (□) kaolinite; (○) silica gel; (—) light conditions; (- - -) dark conditions.

Table IV. Amounts of I and Its Photoproducts after 14 Days of Exposure on Noichi Soil, Kaolinite, and Silica Gel

	% of the applied ^{14}C					
	Noichi soil		kaolinite		silica gel	
compd	ext 1[a]	ext 2[b]	ext 1	ext 2	ext 1	ext 2
ext ^{14}C	67.8	22.5	79.7	5.8	70.0	6.4
I	62.6	19.1	69.3	2.4	56.0	0.6
II	–[c]	0.1	–	–	–	–
III	–	0.1	–	–	–	–
IV	–	0.1	–	–	0.5	–
V	0.2	0.1	0.5	0.1	–	–
VI	0.3	–	0.8	–	–	–
VII	0.2	0.2	0.5	–	–	–
VIII	1.7	0.6	1.6	0.2	5.4	–
IX	–	–	2.5	0.2	1.7	–
X	–	–	–	0.7	–	–
XI	–	0.1	–	0.2	–	–
XII	1.3	0.3	0.7	0.1	0.5	–
others	1.5	1.8	3.8	1.9	5.9	5.8
bound ^{14}C		8.6		5.1		0.4
rec ^{14}C[d]		98.9		90.6[e]		76.8[e]

[a] Extractable ^{14}C with CH_3OH-H_2O (5:1). [b] Extractable ^{14}C with $CH_3OH-0.1$ M HCl (5:1). [c] Not detected. [d] Rec ^{14}C = ext ^{14}C + bound ^{14}C. [e] In a separate study, $^{14}CO_2$ amounted to 7.2% (kaolinite) and 19.0% (silica gel) of the applied ^{14}C after 14 days of exposure. In either case, the radioactivity recovered from ethylene glycol trap amounted to <0.1% of the applied ^{14}C.

(7.2 and 19.0% for kaolinite and silica gel, respectively, after 14 days). By taking into account the amount of $^{14}CO_2$ generated, a good material balance was ascertained for both cases. On the basis of these results, I was considered to photodegrade to its various hydroxylated derivatives and finally be mineralized to CO_2.

Reaction of I with Active Oxygen Species. After a 30-min reaction with Fenton's reagent under N_2, I decreased to 62.9% of the applied ^{14}C. The main degradates were VII (3.9%) and VIII (9.4%), and the other hydroxylated derivatives (II–V) were detected in a trace amount (<1.5%). Although the degradation of I was slightly retarded under air (81.3% after 30 min), similar product distribution was observed. In the absence of hydrogen peroxide or ferrous ion, insignificant degradation was exhibited by 2D-TLC analysis. These results clearly showed that the ether bond of I was cleaved via reaction with a hydroxyl radical along with hydroxylation at both phenyl rings. In the case of the reaction of I with singlet oxygen, 2D-TLC analysis of the extract showed that >99% of the applied ^{14}C was recovered as I. Therefore, singlet oxygen was unlikely to react with I under the conditions tested if formed.

Photodegradation of 3-Phenoxybenzoic Acid

J. Agric. Food Chem., Vol. 40, No. 7, 1992 **1273**

DISCUSSION

The reaction rate in a direct photoprocess is in proportion to the summation of the product of the light intensity used and the chemical absorptivity of each wavelength, assuming that a quantum yield is constant (Miller and Zepp, 1983). If the quantum yield in the direct photolysis of I is independent of pH tested, the ratio of the half-life at pH 2 to that at pH 7 was estimated to be 0.37 by using the absorption spectra at both pHs and the emission spectrum of a xenon lamp. However, the observed ratio was 0.06, indicating that the photoreactivity of I was enhanced at pH 2. By analogy with the solution photochemistry of diphenyl ether herbicides (Nakagawa and Crosby, 1974; Ruzo et al., 1980), the photonucleophilic substitution by water to form VIII could be considered as one of the mechanisms. When a strong nucleophile such as the cyanide ion is present, it has been demonstrated in aqueous photolysis of these herbicides that the benzonitrile derivatives are formed via nucleophilic attack at the ether linkage. Supposing that such a reaction predominates the photodegradation of I, a faster photolysis rate should be observed at pH 7 than at pH 2 since the hydroxide ion is more nucleophilic than water. However, I was faster photodegraded at pH 2 with a greater amount of VIII formed. Furthermore, even in the presence of an excess amount of the cyanide ion, no kind of benzoic acid was formed in the photolysis of I at pH 2 and 7. On the basis of these results, the photonucleophilic substitution mechanism was unlikely for the formation of VIII from I.

The homolytic cleavage of an ether bond followed by Claisen rearrangement has been reported for the photodegradation of diphenyl ethers ($\lambda > 250$ nm) (Ogata, 1970). However, such a reaction was considered to proceed to a lesser extent by irradiation with a longer wavelength ($\lambda > 290$ nm) as used in this study. No detection of benzoic acid in photolysis by 2D-TLC and HPLC seemed to exclude the homolytic cleavage of the C_3–O bond. Furthermore, the MS spectral pattern of ^{18}O-labeled methyl 3-methoxybenzoate was likely to deny the possibility of the C_1–O bond cleavage. As demonstrated in the chemical oxidation study, the hydroxylated derivatives (II–VII) and VIII were formed via reaction of I with a hydroxyl radical. The similarity of a product distribution between photodegradation and chemical oxidation studies together with the results of the ^{18}O isotopic dilution experiment strongly suggested that VIII was formed via radical reaction at 3 position of the phenyl ring of I, as reported for esfenvalerate (Katagi, 1991). A similar mechanism has been suggested for the reaction of aryl ethers with benzoxyl radicals (Nowada et al., 1976). Since methoxybenzoic acid derivatives have been reported to undergo acid-catalyzed ipso substitution by a hydroxyl radical via protonation of the ether oxygen (O'Neill et al., 1977), the accelerated photodegradation of I at pH 2 may be due to the similar acid catalysis.

Photodegradation of I was slightly accelerated in the presence of hydrogen peroxide, which also showed the importance of indirect photolysis by a hydroxyl radical, as reported previously for some pesticides (Draper and Crosby, 1984). In contrast, the photodegradation of I was slightly retarded in the presence of humic acids. Although humic acids are known to accelerate photolysis of pesticides by acting as a photosensitizer and/or by generating active oxygen species, neither reaction was likely to proceed. Since the optical density (1 cm path length) of the humic acid solution was 0.027–0.029 at wavelengths of 290–300 nm under the conditions tested, 3–4% of the light was
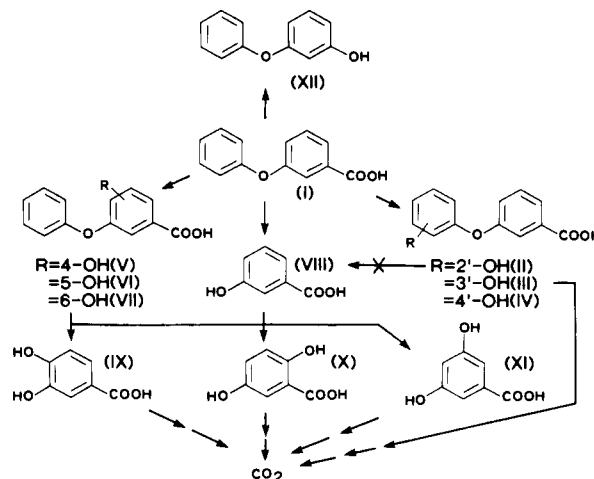

Figure 5. Photodegradation pathways of I.

considered to be absorbed by humic acids (Miller and Zepp, 1983). It was likely that this filter effect, at least in part, caused the slight retardation of the photodegradation.

Further oxidation of VIII was observed in every case. IX was a major degradate, which was in accordance with the observation in the chemical oxidation of VIII with Ti^{3+}/H_2O_2 (Günther et al., 1971). The successive oxidation of dihydroxybenzoic acids (IX–XI) would cause the degradation of a phenyl ring to form the various polar products, as observed in TLC autoradiograms of the unextractable ^{14}C. The increase of CO_2 generated with irradiation was considered to be due to the mineralization of these polar metabolites, as reported for photooxidation of benzoic acid (Ogata et al., 1980). Meanwhile, the mechanism to explain the formation of XII was not clarified. Although the ipso attack of a hydroxyl radical at the α-carbon to the carboxyl group of I might be considered, such a reaction has not been reported for hydroxybenzoic acids (Günther et al., 1971). On the basis of these results, the photodegradation pathways of I in water are proposed in Figure 5. Indirect photolysis, i.e., reaction with the photogenerated hydroxyl radical, was likely to play an important role.

The similarity between absorption at pH 2 and reflectance spectra showed that I was adsorbed on silica gel in an undissociated form. It has been reported for polychlorinated aromatics and DDT that an adsorption onto silica gel causes their absorption spectrum to become broader with a spectral shift to a longer wavelength (Gäb et al., 1975). Therefore, I was considered to be simply adsorbed via a carboxyl group without a significant interaction of their phenyl rings with a silica gel surface. In contrast, a significant red shift (ca. 13 nm) of reflectance spectrum was observed on kaolinite, along with its shoulder up to a wavelength of ca. 500 nm. Kaolinite is known to have a lamellar structure of aluminosilicates and well adsorbs a chemical between these lamella (Goring and Hamaker, 1972). The interaction of phenyl rings of I with these lamella was likely to cause the change of the reflectance spectrum observed. Meanwhile, the red shift of a spectrum would result in the faster photodegradation of I, supposing that direct photolysis was predominant on the surfaces tested. Under the conditions tested, photodegradation of I was fastest on silica gel, where the spectral overlap between the reflectance spectrum of I and the emission spectrum of a xenon lamp ($\lambda > 300$ nm, Figure 2) was insignificant. These results also suggested that indirect photolysis would play a great role on the solid surfaces tested.

The main photodegradation pathway on the solid surfaces was an ether cleavage, as shown in Figure 5. A similar reaction has been recently reported for esfenvalerate (Katagi, 1991) adsorbed on kaolinite and an intact soil where a hydroxyl radical participates in the indirect photolysis. A hydroxyl radical was considered to be generated via excitation of humic substances in an intact soil, while the oxides of transition metals would participate in its production in the case of kaolinite. The kaolinite clay showed a reflection up to a wavelength of 500 nm, which was probably due to TiO_2 and other oxides detected (Katagi, 1991). In kaolinite clays most titanium is considered to exist as an anatase (TiO_2) (Dolcater et al., 1970), which can generate a hydroxyl radical by irradiation. Meanwhile, a hydroxyl radical has been also detected by ESR on exposure of silica gel to UV light (Tseng and Chang, 1975). Therefore, the ether bond cleavage via radical reaction was likely to proceed on every surface tested in a way similar to that observed in aqueous photolysis, and the successive oxidation of VIII would result in the formation of CO_2.

LITERATURE CITED

Akhtar, M. H. Fate of 3-Phenoxybenzaldehyde: Diphenyl Ether Cleavage, a Major Metabolic Route in Chicken. *J. Agric. Food Chem.* **1990**, *38*, 1417.

Dippy, J. F. J. The Dissociation Constants of Monocarboxylic Acids; Their Measurement and Their Significance in Theoretical Organic Chemistry. *Chem. Rev.* **1939**, *25*, 15.

Dolcater, D. L.; Syers, J. K.; Jacobson, M. L. Titanium as Free Oxide and Substituted Forms in Kaolinites and Other Soil Minerals. *Clays Clay Miner.* **1970**, *18*, 71.

Draper, W. M.; Crosby, D. G. Solar Photooxidation of Pesticides in Dilute Hydrogen Peroxide. *J. Agric. Food Chem.* **1984**, *32*, 231.

Gäb, S.; Nitz, S.; Parlar, H.; Korte, F. Photomineralization of Certain Aromatic Xenobiotica. *Chemosphere* **1975**, *4*, 251.

Gaughan, L. C.; Unai, T.; Casida, J. E. Permethrin Metabolism in Rats. *J. Agric. Food Chem.* **1977**, *25*, 9.

Goring, C. A. I., Hamaker, J. W., Eds. *Organic Chemicals in the Soil Environment*; Dekker: New York, 1972.

Günther, K.; Filby, W. G.; Eiben, K. Hydroxylation of Substituted Phenols: An ESR-Study in the Ti^{3+}/H_2O_2-System. *Tetrahedron Lett.* **1971**, 251.

Hageman, H. J.; Louwerse, H. L.; Mijs, W. J. The Photoreactions of Some Diaryl Ethers. *Tetrahedron* **1970**, *26*, 2045.

Hashimoto, N.; Aoyama, T.; Shioiri, T. New Methods and Reagents in Organic Synthesis 14. A Simple Efficient Preparation of Methyl Esters with Trimethylsilyldiazomethane (TMSCHN$_2$) and its Application to Gas Chromatographic Analysis of Fatty Acids. *Chem. Pharm. Bull.* **1981**, *29*, 1475.

Holmstead, R. L.; Casida, J. E.; Ruzo, L. O.; Fullmer, D. G. Pyrethroid Photodecomposition. *J. Agric. Food Chem.* **1978**, *26*, 590.

Huang, C.-G.; Wan, P. Photochemistry of Phenoxybenzyl Alcohols in Aqueous Solution: Photosolvolysis vs. Photorearrangement to 6*H*-Dibenzo[*b,d*]pyrans. *J. Org. Chem.* **1991**, *56*, 4864.

Katagi, T. Molecular Orbital Approaches to the Photolysis of Organophosphorus Insecticide Fenitrothion. *J. Agric. Food Chem.* **1989**, *37*, 1124.

Katagi, T. Photoinduced Oxidation of the Organophosphorus Fungicide Tolclofos-Methyl on Clay Minerals. *J. Agric. Food Chem.* **1990**, *38*, 1595.

Katagi, T. Photodegradation of the Pyrethroid Insecticide Esfenvalerate on Soil, Clay Minerals, and Humic Acid Surfaces. *J. Agric. Food Chem.* **1991**, *39*, 1351.

Kurata, T.; Watanabe, Y.; Katoh, M.; Sawaki, Y. Mechanism of Aromatic Hydroxylation in the Fenton and Related Reactions. One-Electron Oxidation and the NIH Shift. *J. Am. Chem. Soc.* **1988**, *110*, 7472.

Leahey, J. P. Metabolism and Environmental Degradation. In *The Pyrethroid Insecticides*; Leahey, J. P., Ed.; Taylor and Francis: London, 1985; p 263.

Maloney, S. E.; Maule, A.; Smith, A. R. Microbial Transformation of the Pyrethroid Insecticides: Permethrin, Deltamethrin, Fastac, Fenvalerate and Fluvalinate. *Appl. Environ. Microbiol.* **1988**, *54*, 2874.

Miller, S. C.; Zepp, R. G. Extrapolating Photolysis Rates from the Laboratory to the Environment. *Residue Rev.* **1983**, *85*, 89.

Nakagawa, M.; Crosby, D. G. Photonucleophilic Reactions of Nitrofen. *J. Agric. Food Chem.* **1974**, *22*, 930.

Nowada, K.; Sakuragi, H.; Tokumaru, K.; Yoshida, M. Homolytic Aromatic *ipso*-Substitution in Aryl Ethers by Benzoxyl Radicals. *Chem. Lett.* **1976**, 1243.

Ogata, Y.; Takagi, K.; Ishino, I. Photochemical Rearrangement of Diaryl Ethers. *Tetrahedron* **1970**, *26*, 2703.

Ohkawa, H.; Nambu, K.; Inui, H.; Miyamoto, J. Metabolic Fate of Fenvalerate (Sumicidin^R) in Soil and by Soil Microorganisms. *J. Pestic. Sci.* **1978**, *3*, 129.

O'Neill, P.; Schulte-Frohlinde, D.; Steenken, S. Formation of Radical Cations and Zwitterions versus Demethoxylation in the Reaction of OH with a Series of Methoxylated Benzenes and Benzoic Acids. *Faraday Discuss. Chem. Soc.* **1977**, *63*, 141.

Roberts, T. R.; Standen, M. E. Degradation of the Pyrethroid Insecticide WL 41706, (±)-α-Cyano-3-phenoxybenzyl 2,2,3,3-Tetramethylcyclopropanecarboxylate, in Soils. *Pestic. Sci.* **1977**, *8*, 600.

Ruzo, L. O.; Lee, J. K.; Zabik, M. J. Solution-Phase Photodecomposition of Several Substituted Diphenyl Ether Herbicides. *J. Agric. Food Chem.* **1980**, *28*, 1289.

Sakata, S.; Mikami, N.; Matsuda, T.; Miyamoto, J. Degradation and Leaching Behavior of the Pyrethroid Insecticide Cypermethrin in Soils. *J. Pestic. Sci.* **1986**, *11*, 71.

Takahashi, N.; Mikami, N.; Matsuda, T.; Miyamoto, J. Photodegradation of the Pyrethroid Insecticide Cypermethrin in Water and on Soil Surface. *J. Pestic. Sci.* **1985a**, *10*, 629.

Takahashi, N.; Mikami, N.; Yamada, H.; Miyamoto, J. Photodegradation of the Pyrethroid Insecticide Fenpropathrin in Water, on Soil and on Plant Foliage. *Pestic. Sci.* **1985b**, *16*, 119.

Takahashi, N.; Ito, M.; Mikami, N.; Matsuda, T.; Miyamoto, J. Identification of Reactive Oxygen Species Generated by Irradiation of Aqueous Humic Acid Solution. *J. Pestic. Sci.* **1988**, *13*, 429.

Topp, E.; Akhtar, M. H. Mineralization of 3-Phenoxybenzoate by a two-membered bacterial co-culture. *Can. J. Microbiol.* **1990**, *36*, 495.

Tseng, S.-S.; Chang, S. Photochemical Synthesis of Simple Organic Free Radicals on Simulated Planetary Surfaces—An ESR Study. *Origin Life* **1975**, *6*, 61.

Unai, T.; Casida, J. E. Synthesis of Isomeric 3-(2,2-Dichlorovinyl)-2-hydroxymethyl-2-methylcyclopropanecarboxylic Acids and Other Permethrin Metabolites. *J. Agric. Food Chem.* **1977**, *25*, 979.

Yang, N.-C. C.; Kumler, P.; Yang, S. S. Photorearrangement of *o*-Phenoxybenzoic Acid to Phenyl Salicylate and Related Reactions. *J. Org. Chem.* **1972**, *37*, 4022.