Photochemistry of Organophosphorus Herbicide Butamifos

Toshiyuki Katagi

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

The photochemistry of the organophosphorus herbicide butamifos (I) [Cremart, O-ethyl O-5-methyl-2-nitrophenyl sec-butylphosphoramidothioate] was studied in various aqueous media by using a 500 W xenon arc lamp ($\lambda > 290$ nm). Butamifos underwent photoinduced intramolecular oxygen transfer from the nitro group to the P=S moiety, resulting in the formation of the nitroso–oxon derivative. Through the successive reduction of the nitroso group to hydroxylamino and amino groups as well as oxidation to the nitro group, the nitroso–oxon derivative was finally photodegraded to various polar compounds, as evidenced by LC–MS analysis.

INTRODUCTION

Butamifos (I) [Cremart, O-ethyl O-5-methyl-2-nitrophenyl sec-butylphosphoramidothioate] is an organophosphorus pre-emergence herbicide developed by Sumitomo Chemical Co., Ltd., and controls a broad spectrum of weeds (Ueda, 1975). Its metabolism in rats and plants has been studied from the standpoint of environmental safety (Mihara et al., 1976). I undergoes cleavage of the P–O aryl linkage followed by conjugation of the phenol liberated with glucose and glucoronic acid. Although a hydrolytic profile is not available, I is considered to be resistant to hydrolysis under environmental conditions on the basis of previous studies of phosphoramidothioates and phosphoramidates (Sanborn and Fukuto, 1972; Hamer and Tack, 1974; Fahmy et al., 1972). Therefore, photodegradation in water would determine its persistence in an aquatic environment. Although the photochemistry of phosphoramidothioates has not been extensively studied, photooxidation of the P=S moiety on silica gel surface has been previously reported for the isopropyl derivative of I (S-2571) (Mikami et al., 1977) and ester cleavage is a main pathway in the aqueous photolysis of the structural analogue of I (Yuxin and Qinsun, 1988).

This paper first deals with photolysis of I at pH 5, 7, and 9 together with its hydrolytic stability, since the photoinduced hydrolysis has been previously reported for nitrophenyl phosphate monoesters (Cornelisse and Havinga, 1975). The various nitroaromatics are reduced via photoexcited hydrogen abstraction by a nitro group, and the corresponding anilines are formed through nitroso and hydroxylamino derivatives (Hurley and Testa, 1966, 1968). Azo and azoxy compounds are obtained as final photoproducts (Jarosiewicz and Szychlinski, 1982), and their distribution is dependent on either the medium used or molecular oxygen. Therefore, the photolysis in diethyl ether, deuterium oxide, or $H_2{}^{18}O$ was secondly examined as well as that under argon. The photolysis of I in river water or aqueous acetone was also conducted to estimate the importance of photosensitization, which is one of the important factors accelerating the degradation of nitroaromatics in natural water (Simmons and Zepp, 1986). By conducting the photolysis of the 4-nitro derivative of I (IV), the role of a nitro group at the 2-position of the phenyl ring was studied.

MATERIALS AND METHODS

Chemicals. O-Ethyl O-5-methyl-2-nitrophenyl sec-butylphosphoramidothioate (I), its oxon derivative (II), and O-ethyl O-2-amino-5-methylphenyl sec-butylphosphoramidate (III) were

prepared according to the reported methods (Kohsaka et al., 1987; Mihara et al., 1976). The structural isomers of I and II with a nitro group substituted at the 4-position of the phenyl ring (IV and V, respectively) were similarly synthesized. The chemical structure of each authentic standard was confirmed by ^1H NMR, IR, and MS spectroscopies. The chemical purity of each compound was >99%, as determined by HPLC analysis. The corresponding phenols, 5-methyl-2-nitrophenol (VI) and 3-methyl-4-nitrophenol (VII), were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification.

Photoproducts derived from I was prepared as follows. A 200-mL acetonitrile solution of I (100 mg) was added to 800 mL of 0.01 M phosphate buffer (pH 7), and the mixture was continuously irradiated with a 500-W xenon lamp ($\lambda > 300$ nm; Ushio, Model UIV-5150XE, Tokyo) for a week. The reaction mixture was extracted three times with 500 mL of ethyl acetate, and photoproducts in the condensed extract were separated and purified by TLC with solvent system A.

[^{14}C]-I and [^{14}C]-IV uniformly labeled at the phenyl ring (99%; 89.7 and 91.0 mCi/g, respectively) were prepared in our laboratory (Yoshitake et al., 1977) and purified by TLC prior to use. D_2O (>99.75 atom %) and $H_2{}^{18}O$ (97 atom %) were purchased from E. Merck (Montreal). Pure water with an electrical conductivity of $5.5 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$ supplied from a Puric Model-R (Organo Co., Ltd.) was used to prepare buffer solutions. The river water (pH 7.6) was collected at the middle courses of the Muko River (Hyogo Prefecture, Japan) and used after sterilization by passing through a 0.45-μm membrane filter (Labo Disc-50CP, Toyo).

Spectroscopy. The ultraviolet (UV) absorption spectra of I and its related compounds were measured with a Hitachi U-3210 spectrophotometer. NMR spectra were measured in CDCl₃ with a Hitachi 90H FT-NMR spectrometer, using tetramethylsilane (TMS) as an internal standard ($\delta = 0.0$ ppm). IR spectra were obtained by using a Nicolet ZDX FT-IR spectrometer.

High-Performance Liquid Chromatography (HPLC). A Hitachi L-6200 liquid chromatograph was operated at a flow rate of 1.0 mL/min, using a Sumipax ODS A-212 (5 μm, 6 mm i.d. × 15 cm; Sumika Analytical Service Ltd., Osaka) column. The composition of the mobile phase was changed stepwise as described in Table I. The amounts of I (or IV) and its photoproducts were quantified, using a Radiomatic Flo-one/beta A-120 radiodetector (time constant, 6.0 s), where a detection limit of radioactivity was ca. 0.1% of the ^{14}C applied to the HPLC. At the same time, the UV trace at 250 nm was monitored by using a Hitachi L-4000 variable-wavelength UV monitor. Typical retention times are as follows: 52.5 (I), 45.0 (II), 23.5 (III), 53.6 (IV), 46.0 (V), 35.5 (VI), and 27.5 min (VII). In every analysis, a 2.0-mL aliquot of eluant was duplicately radioassayed to estimate the recovery of ^{14}C throughout HPLC analysis.

Thin-Layer Chromatography (TLC). Polar photoproducts with a retention time of shorter than 10 min were fractionated by HPLC. A methanol aliquot of the lyophilized fraction was analyzed by using precoated silica gel 60F₂₅₄ chromatoplates (20

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Table I. HPLC Mobile Phase Used for the Separation of I and Its Photoproducts

time, min	% A[a]	% B[a]	% C[a]	curve
0	20	0	80	isocratic
5	20	0	80	linear
20	50	0	50	linear
30	10	40	50	linear
35	10	70	20	linear
40	80	0	20	isocratic
55	80	0	20	linear
60	20	0	80	isocratic
70	20	0	80	

[a] Component of mobile phase. A, acetonitrile: B, methanol: C, 0.1% H_3PO_4. Flow rate was 1.0 mL/min throughout analysis.

× 20 cm, 0.25-mm layer thickness, E. Merck). The following two solvent systems were used for development: A, toluene–ethyl formate–formic acid (5:7:1); B, ethanol–H_2O–28% NH_4OH (9:1:2). 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 a week, and each of them was quantified with a Packard Model 1600 TR liquid scintillation spectrometer (LSC).

Liquid Chromatography–Mass Spectrometry (LC–MS). LC–MS spectra of I, IV, and their degradates in reaction mixtures were measured by using a Hitachi M-1000 LC–MS equipped with an atmospheric pressure chemical ionization (APCI; Sakairi and Kambara, 1988) interface. The drift voltages in the positive ion (PI) and negative ion (NI) modes were 35 and −35 V, respectively, and the aperture temperature was 260 °C. The mobile phase was similar to that in Table I, but 0.1% H_3PO_4 was replaced with 0.01 M ammonium acetate–HCl (pH 2.6), which afforded the similar elution pattern. LC–MS analysis was conducted at an exaggerated concentration of I or IV. A 20-mL aliquot of acetonitrile solution containing nonlabeled I or IV (5 mg) was mixed well with 30 mL of 0.01 M phosphate buffer (pH 7), resulting in 100 ppm of aqueous solution. At appropriate intervals under irradiation with a xenon lamp, a 50-μL aliquot was subjected to LC–MS analysis. The characterization of each peak detected at 250 nm was separately conducted by cochromatography with an appropriate photoreaction mixture derived from [^{14}C]-I or -IV.

Hydrolysis Study. To examine the hydrolytic stability of I, hydrolysis at pH 5, 7, and 9 was conducted by using the following buffers; 0.01 M acetic acid–sodium acetate (pH 5.0), 0.01 M Na_2HPO_4–KH_2PO_4 (pH 7.0), and 0.01 M H_3BO_3 + KCl–NaOH (pH 9.0). The buffer solution was sterilized by autoclaving at 120 °C and 1.5 psi for an hour before use. The concentration of I was adjusted to 1.0 ppm below the water solubility of I (5.1 ppm at 20 °C). The buffered aqueous solution at each pH was duplicately prepared by adding a 1.0-mL aliquot of acetonitrile solution of [^{14}C]-I (9 μCi) to each buffer (100 mL) in a heat-sterilized Erlenmeyer flask under continuous stirring. The flasks were kept in a Sanyo Model SHR-200M incubator at 25 ± 1 °C in darkness for 42 days. At each sampling time, a 0.5-mL aliquot of each solution was taken in duplicate to determine the concentration of ^{14}C with LSC. A 1.0-mL aliquot of the water sample separately taken was well mixed with a 0.2-mL aliquot of the acetonitrile–distilled water (1:1) solution containing nonlabeled I and its related compounds, and the mixture was directly analyzed by HPLC.

Photolysis Studies. A 50-mL aliqout of the 1% aqueous acetonitrile solution of [^{14}C]-I or -IV (1 ppm) in a quartz bottle stoppered with a rubber septum was duplicately irradiated with a 500-W xenon arc lamp (UXL-500D; Ushio, Tokyo) for 1.5 h through a Pyrex glass filter at 28 ± 1 °C. The emission spectrum showed a cutoff at 290 nm, as measured with a USR-20B photometer (Ushio). At appropriate intervals, the reaction mixture was analyzed by HPLC and LSC in a manner similar to that taken in hydrolysis. The pH profile of photolysis was first examined at pH 5, 7, and 9 under air by using the same buffers in hydrolysis. In the case of pH 7, I was continuously irradiated for 12 h to determine the degradation profile in detail. The photolysis of I in Muko River water (pH 7.6) was conducted to examine a sensitization effect on the rate and route of photolysis.

Since acetone is a good photosensitizer (Ross and Crosby, 1975), the phosphate buffer (pH 7) including 2% acetone was also used as a medium. The solvent effect in the photolysis of I was examined under air by using diethyl ether dried over sodium metal. D_2O and H_2O were used to examine an isotopic effect on a photolysis rate. The participation of water in the photolysis was further examined as follows. A 2.5-mL aliquot of $H_2^{18}O$–acetonitrile (3:2) solution of nonlabeled I (0.5 mg) in a quartz cuvette (1-cm path length) was irradiated with a xenon lamp for 3 h, and a 50-μL aliquot of the reaction mixture was subjected to LC–MS to estimate the incorporation of ^{18}O into I and its photoproducts. The effect of molecular oxygen was studied by conducting the photolysis at pH 7 in the presence and absence of acetone under argon (>99.99%). Prior to irradiation, the reaction mixture was bubbled with argon for 15 min in darkness, and the photolysis was conducted under a moderate stream of argon.

Sunlight photodegradation of I was similarly conducted at pH 7 to estimate its rate in the environment. The quartz bottle was placed in a greenhouse (latitude 38° N) maintained at 25 ± 1 °C and was exposed to sunlight for 8 h/day in February 1992. The sunlight intensity was continuously monitored by using an actinograph Model S-180 (Ishikawa, Tokyo), which showed that the accumulated sunlight intensity on a clear day was about half of that from a xenon lamp.

RESULTS

Hydrolysis of I. Insignificant hydrolysis of I was observed at pH 5 and 7 under the test conditions, and half-lives ($T_{1/2}$) of I were estimated to be 2.7 × 10³ and 1.5 × 10³ days, respectively. The hydrolysis was accelerated at pH 9 with the half-life of 3.2 × 10² days, which was close to that of O-methyl O-4-nitrophenyl cyclohexylphosphoramidothioate (Gerrard and Hamer, 1967). Its alkaline hydrolysis rate in 60% aqueous dioxane at 29 °C has been reported to be 0.275 M^{-1} min^{-1}, and thus $T_{1/2}$ at pH 9 is estimated to be 1.8 × 10² days. The only hydrolysis product detected was the corresponding phenol VI (Figure 5), which amounted to 3.0% (pH 5), 3.6% (pH 7), and 10.4% (pH 9) after 42 days. These results indicated that cleavage of the P–O-aryl linkage predominated in the base-catalyzed hydrolysis of I.

Photolysis of I. *a. Identification of Photoproducts.* I–III were detected by HPLC in the photolysate derived from nonlabeled I (100 ppm) at pH 7. Their chemical identities were first confirmed by comparison of their retention times with those of authentic standards and further by LC–MS spectra where a M + H peak (PI) and a M–H or M + Cl peak (NI) were observed (Table III). One unknown photoproduct (VIII) whose retention time was 46 min had a molecular weight of 300 and was considered to be a phosphoramidate derivative of I from its MS fragment pattern (Table III). In the IR spectrum of VIII, which was photochemically prepared and purified by TLC (R_f = 0.58 in solvent system A, >99% by HPLC), the absorptions at 1526 and 1352 cm^{-1} due to the nitro group of I disappeared and that at 1503 cm^{-1} was detected instead. The UV–vis spectrum of VIII in acetonitrile (5.49 × 10⁻⁵ M) exhibited absorption maxima at 228 (4.81 × 10³ M^{-1} cm^{-1}), 292.4 (6.37 × 10³ M^{-1} cm^{-1}), 319 (7.93 × 10³ M^{-1} cm^{-1}), and 760 nm (34.9 M^{-1} cm^{-1}). These spectroscopic profiles were characteristic to aromatic nitroso compounds (Nakamoto and Rundle, 1956). Each proton in the ^{1}H NMR spectrum of VIII in $CDCl_3$ was assigned as follows: 0.76 (t, 3 H, J = 6Hz, OCH_2CH_3), 1.03 (dd, 3H, J = 4 Hz, CH_3CH), 1.30 (t, 3 H, J = 6Hz, CH_3CH_2CH), 2.35 (s, 3 H, aryl CH_3), 2.80 (m, 1 H, CHN*H*), 3.1–3.5 (m, 1 H, C*H*NH), 4.0–4.4 (2 H, m, OCH_2CH_3), 6.23 (d, J = 8 Hz, 1 H, aryl 3-H), 6.85 (d, J = 8 Hz, 1 H, aryl 4-H), 7.63 (s, 1 H, aryl 6-H). On the basis of the ^{1}H NMR spectra of various aromatic nitroso compounds (Sundberg, 1967), the upfield

Table II. Half-Life and Amounts of Degradates in the Photodegradation of I

medium/atmosphere	light	$T_{1/2}$, min	% of applied $^{14}C^a$					
			I	II	III	VI	VIII	IX
pH 5, air	Xe[b]	17.2	27.7	1.9	7.4	1.7	55.4	<0.1
pH 7, air[c]	Xe	14.9	24.0	0.8	8.2	2.0	58.8	0.5
pH 7, Ar[d]	Xe	18.2	24.8	1.4	12.3	1.4	53.6	2.1
pH 7, air	sun[e]	21.6	38.2	1.5	4.2	2.6	51.8	<0.1
pH 9, air	Xe	16.7	27.4	<0.1	31.2	2.1	17.6	10.6
2% acetone,[f] air	Xe	17.5	22.2	49.7	1.8	1.3	8.8	<0.1
2% acetone,[g] Ar	Xe	2.9	<0.1	<0.1	4.7	<0.1	<0.1	<0.1
river water,[h] air	Xe	15.4	24.9	2.7	18.3	1.9	39.4	4.2
Et₂O, air	Xe	13.7	22.8	11.0	6.7	<0.1	7.7	<0.1

[a] After exposure for 30 min. [b] 500-W xenon arc lamp (λ > 290 nm). [c] $T_{1/2}$ values in H_2O and D_2O were 15.2 and 12.7 min, respectively, under the same test conditions. [d] Argon (>99.99%). [e] Natural sunlight. [f] Aqueous acetone in 0.01 M phosphate buffer (pH 7). [g] Amounts of degradates after 15 min. [h] Taken at Muko River in Hyogo Prefecture, Japan, pH 7.6.

Table III. LC–MS (APCI Interface) of I and Its Related Compounds

compd	mode	m/e (rel intensity, assignment)[c]
I	PI[a]	333 (19, M + H), 260 (45, M − C₄H₉NH), 198 (26, M − Ar + 2 H), 180 (100, M − ArO)
	NI[b]	331 (100, M − H)
II	PI	317 (100, M + H), 287 (42, M − C₂H₅), 244 (19, M − C₄H₉NH)
	NI	315 (100, M − H), 180 (11, M − Ar), 135 (19, Ar − H)
III	PI	287 (100, M + H), 214 (3, M − C₄H₉NH)
	NI	321 (23, M + Cl), 257 (100, M − C₂H₅)
IV	PI	333 (100, M + H), 277 (42, M − C₄H₉ + 2 H)
	NI	367 (10, M + Cl), 331 (100, M − H), 303 (16, M − C₂H₅), 152 (94, ArO)
V	PI	317 (100, M + H), 301 (13, M − CH₃)
	NI	315 (100, M − H)
VIII	PI	342 (35, M + CH₃CN + H), 301 (29, M + H), 287 (100, III + H), 228 (52, M − C₄H₉NH), 182 (16, M − Ar + 2 H), 138 (ArOH + H)
	NI	299 (23, M − H), 180 (100, M − Ar)
IX	PI	303 (13, M + H), 287 (III + H)
	NI	337 (100, M + Cl), 274 (13, M − C₂H₄), 230 (29, M − C₄H₉NH), 198 (65, M − ArO + Cl), 180 (48, M − Ar)
X	PI	363 (13, M + H), 317 (M − CO₂H)
	NI	397 (10, M + Cl), 361 (100, M − H), 333 (42, M − C₂H₅), 317 (77, M − CO₂H), 182 (8, ArO), 138 (13, ArO − CO₂H)

[a] Positive ion mode. [b] Negative ion mode. [c] Ar, aromatic moiety of each phosphate or phosphorothioate ester.

shift of the aromatic proton at the 3-position was explained by the presence of a nitroso group. These results indicated that VIII was O-ethyl O-(5-methyl-2-nitrosophenyl) sec-butylphosphoramidate (Figure 5). Another unknown photoproduct (IX) was detected at a retention time of 20 min. IX separated by HPLC was unstable and completely degraded to many components during TLC development. LC–MS showed that its molecular weight was 302, and IX was degraded to III during measurement in the PI mode (Table III). Through analysis of MS patterns in both ion modes and analogy with the photochemistry of nitrobenzene (Hurley and Testa, 1966), IX was concluded to most likely be the hydroxylamino derivative of VIII (Figure 5).

b. Photolysis Profiles. I was rapidly photodegraded with a half-life of less than 20 min at any pH tested, and no significant pH dependency of its rate was observed (Table II). The product distribution at pH 7 was similar to that at pH 5. As shown in Figure 1, the primary photoproduct was VIII, which amounted to 61.7–65.7% of the applied ^{14}C after 1 h. III was formed in concomitant decrease of VIII and exhibited a maximun value (15.0–17.0%) at 1.5 h but decreased thereafter. The other degradates were II and IX, amounting to less than 5% up to 1.5 h. At pH 9, the amount of VIII decreased to about one-third of those at pH 5 and 7 and III became a major photoproduct instead (37.3% at 45 min), as shown in Figure 2. Although II was detected at a trace amount, the formation of IX was greatly enhanced at pH 9 (10.6% at 30 min). The photoinduced ester cleavage of I was not a major pathway at any pH tested since the amount of VI was less than 3% throughout the study. The two polar products whose retention times were 2.6 and 5.0 min
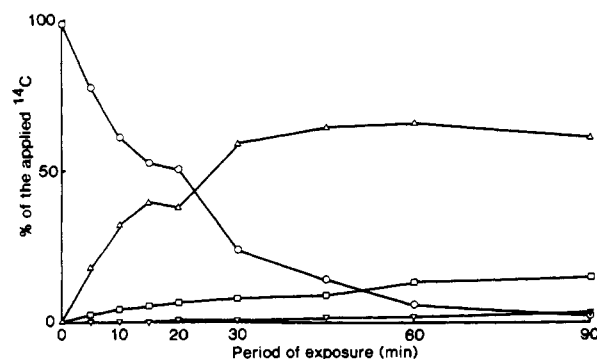

Figure 1. Photolysis of I at pH 7 under air by irradiation with a xenon lamp. (O) I; (□) III; (△) VIII; (▽) IX.

appeared with irradiation, and each of them at pH 7 amounted to 6.6–6.9% after 12 h. However, TLC analysis with solvent system B showed that each fraction consisted of several components, none of which exceeded 2.5% of the applied ^{14}C. The photodegradation profile at pH 7 under sunlight was almost the same as under artificial light, but its rate slightly decreased ($T_{1/2}$ = 21.6 min). This difference originated mainly from the weaker intensity of sunlight compared to that of the xenon lamp used. HPLC analysis showed that the degradates mainly detected after 21 days of exposure were III (7.9%) and IX (6.3%) with trace amounts of II (0.9%) and VIII (2.1%). The total amount of polar photoproducts with retention times of less than 10 min was 21.4% at 21 days, but each of the photoproducts fractionated by HPLC was dem-
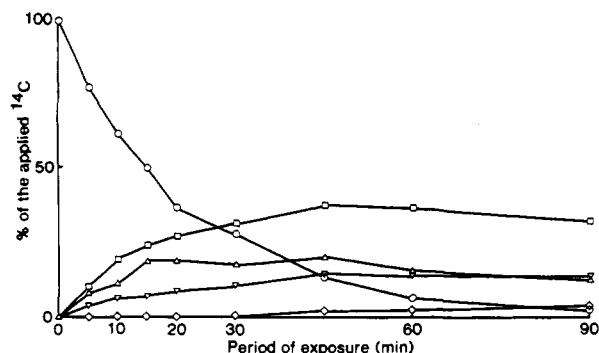
Figure 2. Photolysis of I at pH 9 under air by irradiation with a xenon lamp. (O) I; (◊) II; (□) III; (△) VIII; (▽) IX.
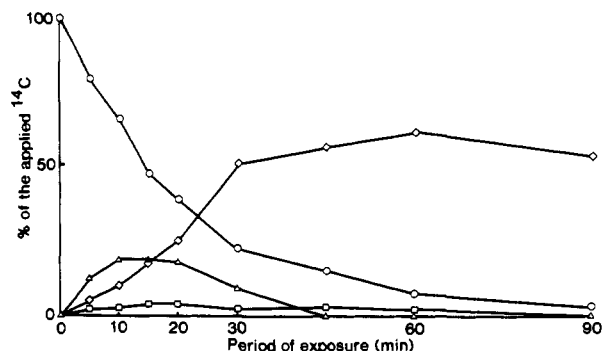

Figure 3. Photolysis of I at pH 7 in the presence of 2% acetone under air by irradiation with a xenon lamp. (O) I; (◊) II; (□) III; (△) VIII.

onstrated to consist of several components of less than 5% of the applied ^{14}C by TLC analysis with solvent system B.

Photosensitization was not observed either in Muko River water or 2% aqueous acetone under air, since the half-lives of I (15.4 and 17.5 min, respectively) were similar to that at pH 7 (14.9 min). In Muko River water, the amounts of III and VIII showed medium values between those at pH 7 and 9. Since the pH of Muko River water was 7.6, the product distribution was likely to depend on pH tested. In contrast, the presence of acetone caused a significant change in the product distribution (Figure 3). II was the main photoproduct, amounting to 60.4% at 1 h. Although VIII seemed to be primarily formed from I (18.3% at 10 min), it was immediately degraded and disappeared after 45 min. III was detected in a trace amount (<3.5%), and IX was below the detection limit, if formed. A slight retardation of photolysis of I was observed at pH 7 ($T_{1/2}$ = 18.2 min) under argon atmosphere, showing that molecular oxygen was unlikely to act as a triplet quencher. The amount of III was 1.2–1.5 times as under air, which was due to the absence of autoxidation. Meanwhile, photolysis under argon was greatly enhanced in the presence of 2% acetone ($T_{1/2}$ = 2.9 min). III was the only photoproduct with a yield greater than 5% (7.4% at 10 min), and more than 20 unidentified products, each of which amounted to less than 5%, were detected by HPLC.

The photolysis profile of I in distilled water was almost the same as at pH 7, indicating no buffer effect. When $H_2{}^{18}O$ was used instead for photolysis at an exaggerated concentration, a similar HPLC elution pattern was obtained for the aliquot taken after a 3-h exposure to the xenon lamp. LC–MS of the fractions corresponding to I, II, and VIII exhibited M + H peaks at m/e 333, 317, and 301 in the PI mode, and no (M + 2) + H peak due to the incorporation of ^{18}O was observed. Meanwhile, photolysis

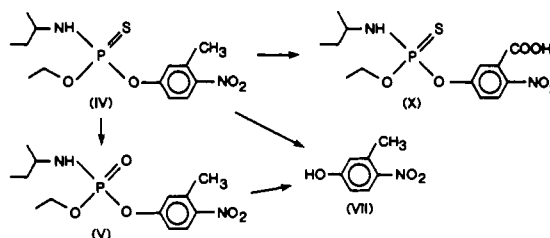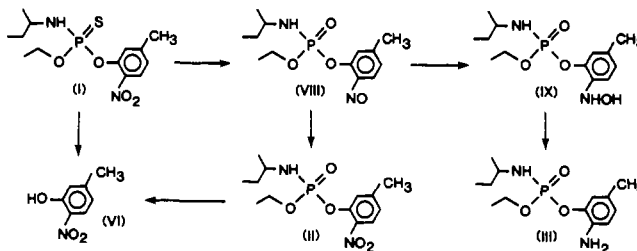**Figure 4.** Photodegradation pathways of IV in water.

Figure 5. Photodegradation pathways of I in water.

in D_2O was slightly enhanced ($T_{1/2}$ = 12.7 min). If hydrogen abstraction from water by the nitro group of I in the excited states is a rate-determining step in the photolysis, the opposite isotope effect should be observed. The photolysis in $H_2{}^{18}O$ as well as in D_2O strongly suggested that a water molecule was not directly involved in the photoreactions of I. Meanwhile, the $T_{1/2}$ value did not significantly change in dry diethyl ether as compared with that at pH 7 under air (Table II). The major photoproducts were II, III, and VIII, amounting to 24.6%, 4.6%, and 12.3% at 1 h, respectively. Several nonpolar photoproducts whose retention times were longer than that of I were detected together with many unidentified photoproducts, but none of them exceeded 5% of the applied ^{14}C.

In every experiment, the concentration of ^{14}C was kept constant (1.0 ppm) throughout the experiment, and good recovery of ^{14}C (>95%) was demonstrated in HPLC analysis. Although no trap to collect volatiles generated via photolysis was utilized, these results indicated that the formation of volatiles was minimal under the conditions tested.
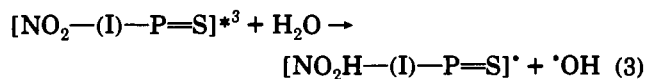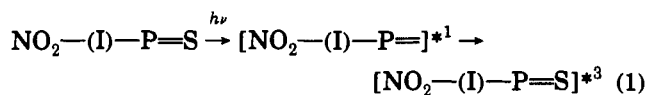
Photolysis of IV. IV was photodegraded more slowly than I under air. The half-life at pH 7 was 2.3 h, and the main unknown photoproduct (X) was detected at a retention time of 48 min. X exhibited a maximum value (32.4%) at 4 h. As with an increase of X, the recovered ^{14}C gradually decreased to 84.8% of the applied ^{14}C at 8 h. The molecular weight of X was estimated to be 362 by LC–MS and the M – 45 peak was detected in both ion modes (Table III). From analysis of the MS fragment pattern, X was estimated to be a carboxyl derivative of IV formed via oxidation of the aryl methyl group (Figure 4). As the other photoproducts, V and VII were identified by HPLC cochromatography with authentic standards, and the chemical identity of V was further confirmed by LC–MS (Table III). Both amounted to less than 3% of the applied ^{14}C throughout the experiment, and none of the unidentified products exceeded 5% of the applied ^{14}C.

DISCUSSION

The absorption spectrum of I in 1% aqueous acetonitrile showed a maximum at 275 nm (5.52×10^3 M^{-1} cm^{-1}) at any pH tested. The shoulder of an absorption up to about 400 nm accounted for the rapid photodegradation of I in water under the various test conditions. Greater overlap of absorption spectrum with emission spectrum of the xenon lamp was observed for IV (λ_{max} = 279 nm, ϵ = 1.04 × 10^4

M^{-1} cm^{-1}), and faster photolysis than that of I was expected. However, its half-life was much longer than that of I. The main photodegradation pathway of IV was oxidation of the aryl methyl group to form X (Figure 4), and it was considered to proceed via Norrish-type II reaction by analogy with the photolysis of fenitrothion (Katagi, 1989). The nitro group of I is in the para position to the aryl methyl group, and therefore similar intramolecular hydrogen abstraction is unlikely to proceed. I underwent intramolecular redox reaction with reduction of the nitro group and oxidation of the P=S moiety. Although each reaction is known for nitrofen (Draper and Casida, 1983; Ruzp et al., 1980) and fenitrothion (Mikami et al., 1985), this type of an efficient redox reaction has not been reported in the photochemistry of pesticides. A similar reaction has been reported for vapor-phase photolysis of nitrobenzene (Hastings and Matsen, 1948) and sunlight photodegradation of o-nitrophenylarsonous acid (Karrer, 1914).

It was considered that the excited triplet state participated in the photolysis of I (eq 1)by analogy with

$$NO_2-(I)-P=S \xrightarrow{h\nu} [NO_2-(I)-P=]^{*1} \rightarrow$$
$$[NO_2-(I)-P=S]^{*3} \quad (1)$$

$$[NO_2-(I)-P=S]^{*3} \rightarrow NO-(I)-P=O + S \quad (2)$$

$$[NO_2-(I)-P=S]^{*3} + H_2O \rightarrow$$
$$[NO_2H-(I)-P=S]^{\cdot} + {}^{\cdot}OH \quad (3)$$

nitrobenzene (Hurley and Testa, 1968). After formation of the excited triplet state, two mechanisms were proposed. The first mechanism was oxygen atom transfer from the nitro group to the P=S moiety to directly form VIII (eq 2). The other possible pathways were initiated by hydrogen abstraction from the water molecule by the photoexcited nitro group, which caused the formation of a hydroxyl radical and the NO$_2$H radical of I (eq 3). Since a hydroxyl radical has been reported to oxidize the P=S moiety of trimethyl phosphorothioate to its oxon derivative (Atkinson et al., 1989), a similar reaction may be considered for I. If this hydrogen abstraction mechanism predominates the photolysis, the retardation of its rate in D$_2$O as compared with that in H$_2$O should be observed as well as the incorporation of ^{18}O into VIII when the photolysis is conducted in H$_2$^{18}O. However, neither was observed in this study. Furthermore, the stepwise formation of VIII, reduction of the nitro group followed by radical oxidation of the P=S moiety, may be considered. According to the photochemistry of nitrobenzene (Hurley and Testa, 1966), however, IX should be primarily formed, which could not explain the efficient formation of VIII and the low yield of IX. Therefore, the intramolecular redox reaction in eq 2 was the most likely mechanism. Meanwhile, the IR absorptions due to the nitro group of I (ν_{sym}, 1352 cm^{-1}; ν_{asym}, 1526 cm^{-1} showed higher wavenumbers than those of IV (ν_{sym}, 1345 cm^{-1}; ν_{asym}, 1521 cm^{-1}), and the intensity of UV absorption of I at 275–280 nm was about half of that of IV. These results imply that the nitro group of I is under a steric constraint (Rao, 1969) from the O—P=S moiety. The proximity between the two moieties is likely to facilitate the intramolecular oxygen transfer.

Supposing that the secondary photoproducts were derived from VIII, the concentration of VIII at time t can be estimated by using eq 4. Here, k_1 and k_2 are the pseudo-first-order rate constants for photolysis of I and VIII,

$$[VIII]_t = C[\exp(-k_2 t) - \exp(-k_1 t)]/(k_1-k_2) \quad (4)$$

respectively, and C is a constant. To determine the k_1 and k_2 values, the nonlinear curve fitting of data to eq 4 was conducted using the MULTI(RUNGE) program (Yamaoka and Nakagawa, 1983). The k_2 values in the photolysis with the xenon lamp at pH 5, 7, and 9 were estimated to be (7.36 ± 0.13) × 10^{-3}, (2.89 ± 0.24) × 10^{-3}, and (1.78 ± 0.24) × 10^{-2} min^{-1}, respectively. The half-lives are calculated to be 1.6 h (pH 5), 4.6 h (pH 7), and 39 min (pH 9), indicating that VIII is unlikely to be persistent in an aquatic environment. By analogy with the photochemistry of nitrosobenzene, VIII is considered to be successively photoreduced to III via IX (Pak and Testa, 1972; Fahmy et al., 1988). It is known that nitrosobenzene is liable to react with a hydroxide (Russel et al., 1967). Furthermore, N-hydroxyaniline is unstable under acidic conditions and easily degraded to polar compounds via Bamberger rearrangement (March, 1977). These degradation profiles of aromatic nitroso and hydroxyamino compounds explained the pH dependency of the k_2 value and why less of VIII and more of IX was formed at pH 9 than at pH 5 or 7.

II was formed at a trace amount in the aqueous photolysis of I unless acetone was present. There was no pH dependency of its formation, and the yield of II increased in dry ether where hydrogen abstraction by VIII was minimal, showing that oxidation of VIII by molecular oxygen was predominant as reported for nitrosobenzene (Go and Waddell, 1983). The presence of acetone under air greatly accelerated oxidation of VIII. It has been strongly suggested that Norrish-type I homolysis of acetone followed by reaction with molecular oxygen causes the formation of peracetic acid (Ross and Crosby, 1975). Oxidation of nitrosoaromatics with the peracid is known to proceed quantitatively to form the corresponding nitro compounds (Ibne-Rasa et al., 1963). Therefore, acetone is likely to act as a radical source to generate the peracid which oxidizes VIII to II. Under the argon atmosphere, it was considered that methyl and acetyl radicals formed via photolysis of acetone reacted with I and VIII to form the various minor unidentified compounds.

Azo and azoxy compounds are known to be photochemically formed from nitrobenzene and its related compounds via the corresponding amino derivatives (Fahmy et al., 1988; Hurley and Testa, 1966; Jarosiewicz and Szychlinski, 1982; Shamma et al., 1965). However, these compounds derived from VI were unlikely in the photodegradation of I. The cleavage of the P–O-aryl linkage was not accelerated with irradiation, and a trace amount of VI was detected in every case studied. Furthermore, the amino derivative of VI prepared by reduction with zinc powder in dilute HCl (retention time, 3.2 min) was utilized in HPLC analysis of photolysates, but the corresponding ^{14}C peak was not detected. In the aqueous photolysis, the two polar unknown fractions with retention times of 2.6 and 5.0 min increased with irradiation. Although each of them was a mixture of several components as demonstrated by TLC analysis, they were separately subjected to LC–MS in the NI mode. Since no peak with a m/e value of greater than 300 was not detected, azo and azoxy derivatives from reaction between VIII and IX were unlikely to be involved in these fractions. It was considered that these polar photoproducts were, at least in part, mixtures of the oxidized derivative of VIII and IX and/or those of several phenols rearranged from IX (Fahmy et al., 1988).

On the basis of these considerations, the photodegradation pathways of I in water are proposed in Figure 5.

Although I is hydrolytically stable at any pH tested, the photolysis of I and its photoproducts is so rapid that they are unlikely to persist in an aquatic environment.

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