

Photoinduced Oxidation of the Organophosphorus Fungicide Tolclofos-methyl on Clay Minerals

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Photodegradation of the organophosphorus fungicide tolclofos-methyl (I) [*O*-(2,6-dichloro-4-methylphenyl) *O,O*-dimethyl phosphorothioate] on kaolinite and montmorillonite was examined by using a 500-W xenon lamp. Spectroscopic and photodegradation studies showed that photoinduced oxidation of I was the dominant degradation pathway on the clay minerals. The reactions of I with hydroxyl and hydroperoxyl radicals, which were formed by irradiation on the clay minerals in the presence of both molecular oxygen and water, were suggested as the main pathway in forming the oxon derivative of I.

INTRODUCTION

Photodegradation on the soil surface is one of the important factors that determines the environmental fate of pesticides (Miller and Crosby, 1983). Photodegradation studies using sunlight (Mikami et al., 1984; Smith et al., 1978) or artificial light (Allmain and Schmid, 1985; Burkhard and Guth, 1979) have revealed that the organophosphorus pesticides are mainly photodegraded via ester cleavage and/or P=S oxidation. Mikami et al. (1984) have reported that I is photodegraded on intact soils much faster than in water and that the main degradation pathways are P=S oxidation to the corresponding oxon derivative and demethylation of the *O*-methyl group. Spencer et al. (1980), in their studies of the photodegradation of parathion, reported that clay minerals significantly affect the rate of photolysis and the amount of paraoxon formed.

The objectives of the work described in this paper are, first, to determine whether adsorption of I onto clay minerals plays an important role in its photodegradation and, second, to determine whether secondary degradation by active oxygen species could play a role. Thus, the first part of the work is concerned with photodegradation of I adsorbed onto clay minerals under irradiation from a xenon lamp. The second part is concerned with studies on the extent to which active oxygen species such as singlet oxygen (Gohre and Miller, 1983, 1985; Zepp et al., 1981), superoxide anion radical (Draper and Crosby, 1983; Calvert et al., 1954), hydroxyl radical (Draper and Crosby, 1981; Tseng and Chang, 1975), and atomic oxygen (Hauser et al., 1951) are developed under irradiation and participate in the degradation of I.

MATERIALS AND METHODS

Chemicals. Tolclofos-methyl (I), *O*-(2,6-dichloro-4-methylphenyl) *O,O*-dimethyl phosphate (II), *O*-[2,6-dichloro-4-(hydroxymethyl)phenyl] *O,O*-dimethyl phosphorothioate (III), *O*-[2,6-dichloro-4-(hydroxymethyl)phenyl] *O,O*-dimethyl phosphate (IV), 2,6-dichloro-4-methylphenol (V), and 2,6-dichloro-4-(hydroxymethyl)phenol (VI) were synthesized according to methods already reported (Mihara et al., 1981). *O*-(2,6-Dichloro-4-methylphenyl) *O*-methyl *S*-methyl phosphorothioate (VII) was synthesized by treatment of *O*-(2,6-dichloro-4-methylphenyl) *O*-methyl hydrogen phosphorothioate, prepared from I (Mihara et al., 1981), with methyl iodide in acetone. 3,5-

Dichloro-4-hydroxybenzoic acid (VIII) was purchased from Aldrich Chemical Co., Ltd. (Milwaukee). [¹⁴C]-I uniformly labeled in the phenyl ring (149.0 mCi/g, radiochemical purity >99%) was synthesized in our laboratory (Yoshitake et al., 1978). H₂¹⁸O (97 atom %) was purchased from E. Merck (Montreal). For the spectrophotometric assay of a trace amount of hydrogen peroxide, leuco crystal violet (Tokyo Kasei, Tokyo) and horseradish peroxidase (EC 1.11.1.7) (Type IV, 280 units/mg of protein; Sigma, St. Louis) were used. 2,5-Dimethylfuran (DMF) and acetylacetone were purchased from Aldrich. *trans*-Diacetylene was synthesized by the reported method (Armstrong and Robinson, 1934). Pure water of electrical conductivity $5.5 \times 10^{-8} \Omega^{-1}/\text{cm}$ was supplied from a Puric Model R equipped with a G-10 filter (Organo Co., Ltd., Osaka). Kaolinite and montmorillonite clay minerals were purchased from Wako Co., Ltd. (Osaka).

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 a thin film of each clay mineral were obtained with the same spectrophotometer equipped with a 60 i.d. integrating sphere. Each clay mineral (10 g), suspended in pure water, was uniformly spread over a glass plate (20 × 20 cm) and the excess water evaporated at room temperature overnight. I in 1,2-dichloroethane was uniformly applied to a 3 × 3-cm square, the clay film was prepared as above at the rate of 0.12 mg/cm², and the solvent was evaporated at room temperature.

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 5-mL aliquot of 0.5 M 1,2-dichloroethane solution of I was gently stirred with 100 mg of each clay mineral in darkness overnight. The clay mineral was separated by centrifugation (3000 rpm for 10 min) and twice washed with 1,2-dichloroethane to remove excess I. After drying at room temperature overnight, each clay mineral (10 mg) was well mixed with 300 mg of KBr for the preparation of a pellet. 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 production of *trans*-diacetylene, via the reaction of DMF with singlet oxygen, was examined by high-performance liquid chromatography (HPLC). A Hitachi 655A liquid chromatograph equipped with an ODS A-112 reverse-phase column (6 mm i.d. × 15 cm, Sumika Analytical Service Ltd., Osaka) was operated at a flow rate of 1 mL/min, using acetonitrile-water (3:1) as a mobile phase. *trans*-Diacetylene and DMF were detected by a Hi-

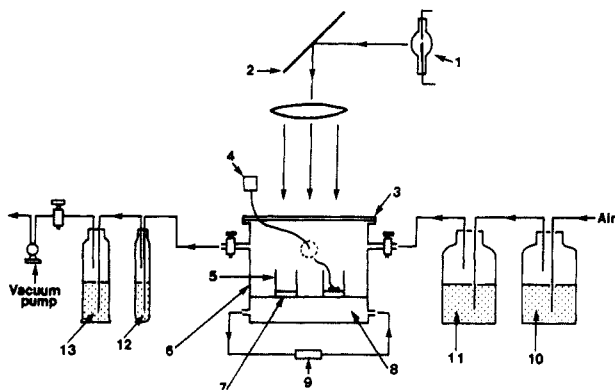


Figure 1. Apparatus used in the photodegradation study. (1) 500-W xenon lamp; (2) UV filter with radiation cutoff of 300 nm and infrared-reflecting coating; (3) quartz glass; (4) thermometer connected to a thermocouple; (5) Pyrex beaker; (6) photoreaction vessel; (7) clay mineral thin film; (8) cooled water; (9) constant temperature bath with a circulator; (10) 10% NaOH; (11) distilled water; (12) ethylene glycol; (13) 0.5 M NaOH.

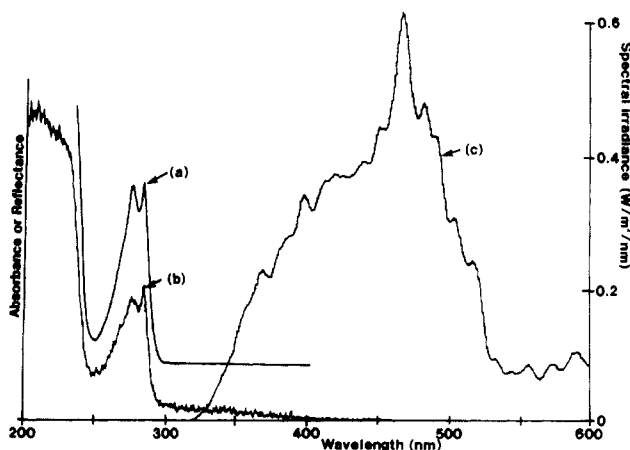


Figure 2. Absorption and reflectance spectra of I and emission spectrum of a 500-W xenon lamp. (a) Absorption spectrum of I in 10% acetonitrile (1.06×10^{-4} M); (b) reflectance spectrum of I adsorbed on kaolinite (0.12 mg/cm²); (c) emission spectrum of a 500-W xenon lamp.

tachi 655A-11 UV monitor at 225 nm (retention times 2.7 and 3.2 min, respectively).

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

Photolysis Studies. The apparatus used is shown diagrammatically in Figure 1. The clay film was prepared from a suspension of 1 g of each clay mineral in 2 mL of pure water in the bottom of a Pyrex glass beaker (3.5 cm i.d. \times 5.0 cm height). After the water had evaporated, the resulting clay film was uniformly treated with [¹⁴C]-I (149 μ Ci, 1 mg) in 1,2-dichloroethane and then continuously irradiated with a 500-W xenon lamp (USIO, Model UIV-5150XE, Tokyo). The emission spectrum of a xenon lamp with a cutoff of 320 nm and a maximum of 468 nm was obtained by a Licor Model LI-1800 photometer (Figure 2). Air, free of CO₂ 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 ¹⁴C. The first contained ethylene glycol (100 mL) and the second 0.5 M NaOH (400 mL). The temperature at the clay surface was maintained at 25 ± 1 °C by a continuous flow of cooled water below the beakers. The temperature was monitored by attaching to the clay surface a Chino C060-K thermo-

couple connected to a Chino CD700 thermometer. The dark control experiment was conducted in the same way except that the photoreaction vessel was covered with aluminum foil.

At an appropriate interval, samples of the clay were scraped from the beaker in the photoreaction vessel and extracted with 30 mL of ethyl acetate 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 used for TLC analysis after being concentrated in a rotating evaporator. I and its degradation products were separated on TLC (60F₂₅₄, 20 \times 20 cm, 0.25 mm layer thickness, E. Merck) with a solvent system of toluene–acetic acid (7:1), and the autoradiogram was prepared. The amount of each product was quantified by radioassay of the ¹⁴C gel region scraped from the TLC plate. Chemical identification was by cochromatography of the extracts with the authentic standards. The unextractable ¹⁴C bound to the clay residue was radioassayed by a sample oxidizer and LSC.

For the determination of volatile activity, the gas-washing bottles were sampled periodically. A 2.0-mL aliquot of ethylene glycol was radioassayed in duplicate, the remaining glycol was extracted twice with 100 mL of ethyl acetate, and the extract was analyzed by TLC. A 2.0-mL aliquot of sodium hydroxide was also radioassayed. In this case, a further aliquot (10 mL) of the remaining solution was treated with 20 mL of 1 M BaCl₂ to precipitate Ba¹⁴CO₃, which was separated by centrifugation. A 2.0-mL aliquot of the supernatant was radioassayed in duplicate to quantify ¹⁴CO₂. The liquid in the two traps was replaced at each sampling time.

Separate experiments were conducted to examine the extent of indirect photolysis. The clay film treated with [¹⁴C]-I was irradiated under N₂ (>99.99%) for 14 days to examine the effect of molecular oxygen. The dried clay film, prepared by heating at 120 °C for 2 h, was treated with [¹⁴C]-I and irradiated in the same way under dry air to examine the effect of water. A further study on the photodegradation of [¹⁴C]-I on kaolinite prepared by using H₂¹⁸O (0.5 mL/g of clay) was conducted under air for 7 days to examine the incorporation of ¹⁸O into II. The ratio of incorporation was estimated by MS analysis.

Assay of Active Oxygen Species. The generation of hydrogen peroxide on the irradiated clays was examined as follows. Pure water (5 mL) was added to the clay film after irradiation, and a 1.0-mL aliquot of the supernatant obtained by centrifugation at 3000 rpm for 10 min was assayed spectrophotometrically in duplicate according to the method reported by Mottla et al. (1970). Hydrogen peroxide was quantified by using a standard response curve.

The generation of singlet oxygen on the clay film was also examined according to the method reported by Gohre and Miller (1983). Kaolinite (1 g) was added to the pear-shaped Pyrex flask (20 mL) sealed up with a rubber septum, followed by an injection of DMF (5 μ L). After irradiation for an appropriate period, methanol (6 mL) was added to quench the reaction and *trans*-diacetylene in the methanol extract was quantified by HPLC, using a standard response curve.

RESULTS

Spectroscopy. The reflectance spectra of I adsorbed onto kaolinite and montmorillonite showed maxima at 275 and 283 nm, as shown in Figure 2. The UV absorption spectrum of I in 10% aqueous acetonitrile exhibited weak absorption at 275 (474.2 M⁻¹ cm⁻¹) and 282 nm (484.6 M⁻¹ cm⁻¹) due to the $n \rightarrow \pi^*$ transition of the phenyl ring. There was no significant difference in the spectral patterns between the reflectance and absorption spectra of I. The IR spectra of I dispersed in KBr, kaolinite and KBr, and montmorillonite and KBr are shown in Figure 3. The strong absorption at 1400–930 cm⁻¹ was derived from the clays themselves. Although each absorption, especially peak(s) deriving from the P=S moiety observed at about 600–650 cm⁻¹ (Hooge and Christen, 1958), could not be assigned, the shift caused by the clays was within 1 cm⁻¹ in every case. On the basis of these spectra, it is likely

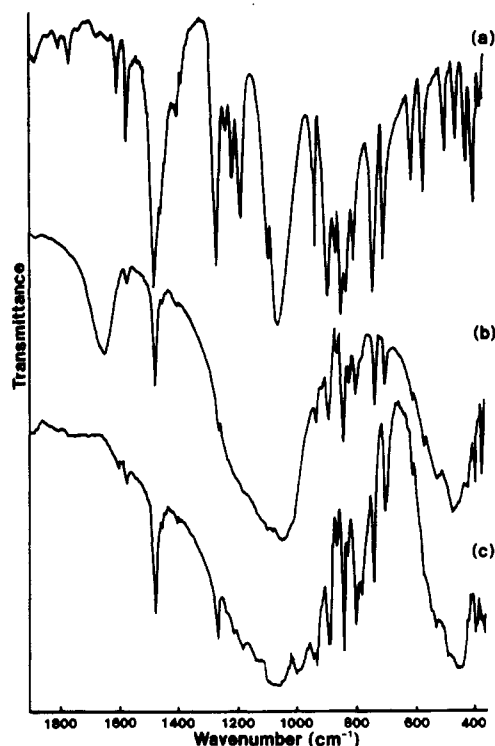


Figure 3. IR spectra of I. (a) KBr; (b) montmorillonite; (c) kaolinite.

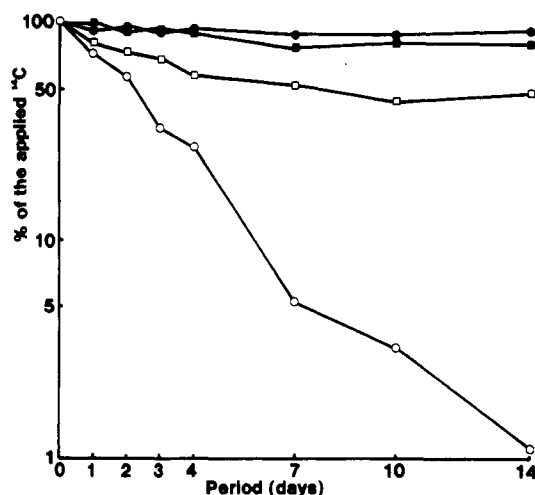


Figure 4. Decline curves of I. (○) Light, kaolinite; (●) dark, kaolinite; (□) light, montmorillonite; (■) dark, montmorillonite.

that the characteristic interactions of I with both of the clays are insignificant.

Photolysis Studies. The decline curves of I are shown in Figure 4. Its degradation on the clay surface was significantly accelerated; the half-lives on kaolinite were estimated to be 2.1 days under irradiation compared with 115.2 days in the dark. In the case of montmorillonite, two reactions were involved under irradiation. The half-life of I in the slower reaction was 61.3 days on the basis of the data at 7–14 days, which was fairly close to the half-life observed on montmorillonite in the dark of 54.1 days. The half-life of I in the faster reaction was calculated on the basis of the data at 0–4 days to be 1.5 days by subtracting the contribution from the slower reaction. This value was close to that observed for kaolinite under irradiation. According to Yaron (1978) montmorillonite adsorbs more organophosphorus pesticides into the interlayer space of the silicates than does kaolinite. It is

therefore likely that the faster of the two reactions is due to photodegradation on the clay surfaces and the slower one due to a reaction in the interlayer space, which is largely independent of irradiation.

The amounts of I and its degradation products formed under irradiation on the two clays are summarized in Table I. Under the influence of irradiation, the extractable ^{14}C gradually decreased, and after 14 days, 45.2% or 65.7% of the activity originally applied was extracted from kaolinite or montmorillonite, respectively. The bound and the volatile activity correspondingly increased. On the kaolinite, bound activity was 35.1% of that applied and on the montmorillonite 13.1%. Corresponding figures for the volatile activity were 17.5% and 16.6%. The major components of the volatile ^{14}C were I and $^{14}\text{CO}_2$ with a trace of V. Since the amounts of bound ^{14}C and volatile ^{14}C in dark conditions were much smaller than those observed under irradiation, it may be inferred that most of the bound and volatile ^{14}C is derived from the photoproducts, but not from the microbial degradation. The irradiation causes the gradual mineralization of I. It is likely that the photoproducts derived from the phenol moiety of I react with the active oxygen species followed by the degradation via the quinone intermediate finally to carbon dioxide (Crosby and Tutass, 1966; Choudhry, 1984).

The main photoproduct in the extracts was II, formed via oxidation of the P=S moiety of I, amounting to 9.9% and 42.8% at 10 days on montmorillonite and kaolinite, respectively. Only a trace amount of II (0.4–2.8% at 14 days) was detected in the dark control, which indicated that irradiation greatly enhanced the formation of II. Although I and II were the only compounds detected under dark conditions, other photoproducts were identified on both clays after irradiation. III and IV formed via oxidation of the arylmethyl group and/or the P=S moiety and VIII formed via rearrangement of the *O*-methyl group to the sulfur atom of I were detected but amounted to less than 2.8% of the applied ^{14}C . V–VII, formed via cleavage of the P-OAr bond followed by the successive oxidation of the arylmethyl group, were also detected but at less than 4.5% of the activity originally applied.

Indirect Photolysis. The effects of molecular oxygen and water on the photodegradation of I are summarized in Table II. The removal of water from montmorillonite and kaolinite retarded the photodegradation of I. The half-lives of I on the dried clays were estimated to be 101.1 and 8.0 days for montmorillonite and kaolinite, respectively. The amount of II slightly decreased on the dry clays, as shown in Figure 5. The retarded photodegradation of I was also observed on kaolinite under N_2 (half-life = 4.1 days). Since molecular oxygen and water are not considered to be completely removed from the clays under the conditions tested, the results obtained here are only qualitative. Furthermore, the EI-MS spectrum of II formed on kaolinite in the presence of H_2^{18}O showed that the ratio of the peak intensities at m/e 284, 286, and 288 was 100:135.1:60.2. This indicates that about 40% of the P=O oxygen is derived from ^{18}O .

These results strongly suggest that both molecular oxygen and water participate in the photoinduced oxidation of the P=S moiety of I.

Formation of Active Oxygen Species. The irradiation of the clays by themselves caused the formation of hydrogen peroxide (Table III). The amount formed gradually increased with irradiation, reaching a maximum of 9.2 ppb after 8 h of irradiation on kaolinite. Hydrogen

Table I. Amounts of I and Its Degradation Products on the Clay Films

	% of the applied ^{14}C									
	montmorillonite					kaolinite				
	light			dark		light			dark	
	3 days	7 days	14 days	7 days	14 days	3 days	7 days	14 days	7 days	14 days
volatile $^{14}\text{C}^a$	4.0	9.3	16.6	5.0	8.0	4.3	9.9	17.5	1.1	2.5
EG trap ^b	0.9	3.7	6.4	2.4	5.4	1.4	3.4	6.0	0.4	1.8
I	0.9	3.5	6.1	2.3	4.8	1.0	2.8	5.1	0.4	1.5
V	<0.1	0.1	0.1	<0.1	<0.1	0.4	0.4	0.5	<0.1	<0.1
others	<0.1	0.1	0.2	0.1	0.6	<0.1	0.2	0.4	<0.1	0.3
alkali trap	3.1	5.6	10.2	2.6	2.6	2.9	6.5	11.5	0.7	0.7
CO ₂	2.1	4.6	9.2	1.9	1.9	1.8	3.5	8.1	0.7	0.7
others	1.0	1.0	1.0	0.7	0.7	1.1	3.0	3.4	<0.1	<0.1
extractable ^{14}C	88.3	74.9	65.7	89.3	84.7	75.5	62.7	45.2	90.1	93.0
I	68.8	52.1	47.6	87.8	80.6	32.8	5.3	1.1	88.8	91.6
II	9.5	9.7	8.1	0.8	2.8	34.1	41.9	36.5	0.4	0.4
III	2.8	1.5	1.3	- ^c	-	1.1	<0.1	<0.1	-	-
IV	<0.1	<0.1	<0.1	-	-	0.5	<0.1	<0.1	-	-
VIII	1.2	1.4	2.5	-	-	0.8	1.3	1.2	-	-
V	1.6	1.2	1.1	-	-	2.2	0.8	<0.1	-	-
VI	1.7	1.2	0.9	-	-	1.9	4.5	2.9	-	-
VII	0.8	<0.1	<0.1	-	-	0.9	3.3	1.4	-	-
others	1.9	7.8	4.2	0.6	1.3	1.1	5.5	2.1	0.9	1.0
bound ^{14}C	4.1	7.8	13.1	0.6	1.4	14.2	21.0	35.1	1.5	3.1
total ^{14}C	96.4	92.0	95.4	94.9	94.1	94.0	93.6	97.8	92.7	98.6

^a Volatile ^{14}C = EG trap + alkali trap. ^b EG, ethylene glycol. ^c Not detected.

Table II. Amounts of I and Its Degradation Products under the Light Conditions in the Absence of Molecular Oxygen or Water

	% of the applied ^{14}C								
	dry under air						under N ₂		
	montmorillonite exposed for			kaolinite exposed for					
	3 days	7 days	14 days	3 days	7 days	14 days	3 days	7 days	14 days
extractable ^{14}C	101.8	100.6	100.6	91.5	84.0	73.7	87.6	68.6	49.2
I	97.9	93.5	91.1	73.7	52.2	31.2	75.3	24.7	8.5
II	0.9	3.4	6.6	15.4	33.8	34.6	7.0	31.5	30.7
VIII	- ^a	-	-	-	0.4	-	0.7	2.8	-
V	2.4	2.0	-	-	1.9	-	0.9	1.0	-
VI	-	-	-	-	0.5	1.9	0.4	3.0	1.3
VII	-	-	-	-	1.0	3.1	0.3	1.4	4.8
others	0.6	1.7	2.9	2.4	5.8	2.9	3.0	4.2	3.9
bound ^{14}C	0.3	1.0	2.0	3.3	5.5	6.6	5.1	14.1	37.4
total ^{14}C	102.1	101.6	102.6	94.9	89.5	80.3	92.6	82.7	86.6

^a Not detected.

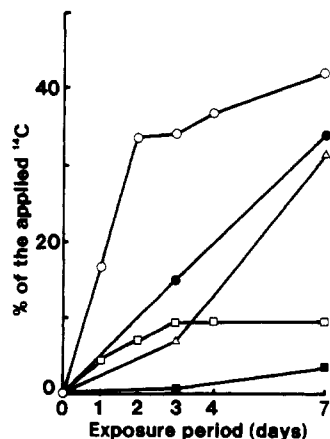


Figure 5. Amount of II formed by irradiation in the various conditions. (○) Kaolinite under air; (●) dried kaolinite under air; (△) montmorillonite under N₂; (□) dried montmorillonite under air.

peroxide was also detected on montmorillonite, but to a lesser extent.

In contrast, *trans*-diacetylene could not be detected after continuous irradiation for 1 day under air, which

Table III. Amounts of Hydrogen Peroxide Produced via the Irradiation of Clays

irradiation period, h	[H ₂ O ₂], ^a ppb	
	montmorillonite	kaolinite
0	ND ^b	ND
1	ND	1.7
2	ND	5.3
4	0.9	8.8
8	1.4	9.2
24	1.4	4.6

^a Calculated on the clay weight basis. ^b Not detected.

showed that the photoinduced formation of singlet oxygen is unlikely on the clay surfaces tested.

DISCUSSION

It is well-known that the rate of photolysis of a chemical is greatly influenced by the extent of spectral overlap between its absorption spectrum and the emission spectrum of the light source with which it is being irradiated (Leifer, 1988). Where the overlap is small, photodegradation is usually slow. However, adsorption onto a clay substrate can sometimes increase spectral overlap

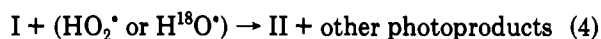
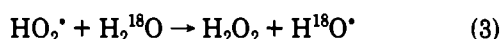
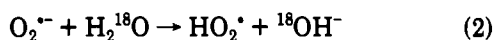
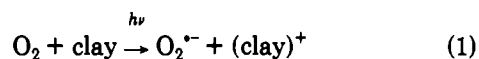
in the visible range by causing a shift in the absorption spectrum of the chemical to a longer wavelength (Weis et al., 1968), and this in turn can accelerate the rate of photolysis under a given light source. This was demonstrated, for example, by Gab et al. (1975) in the case of DDT and poly(chlorobenzene)s when adsorbed onto silica gel. However, such a spectral shift was not observed in the reflectance spectrum when I was adsorbed onto clays, and its spectral overlap with the emission spectrum of the xenon lamp remained negligible. Consequently, direct photolysis is unlikely to be the mechanism for the photodegradation of I that has been observed under irradiation in the visible range.

Another possible mechanism might have been a change in the vibrational modes of I when adsorbed onto clays. For example, a shift in the IR spectrum has been reported for various organophosphorus pesticides following adsorption on clays (Sanchez-Camazano and Sanchez-Martin, 1983, 1987), in particular the band deriving from the P=S moiety (Sanchez-Martin and Sanchez-Camazano, 1984). But this did not occur in the case of I adsorbed onto either kaolinite or montmorillonite; as shown in Figure 3, the IR spectra are little changed by adsorption onto clays. Therefore, this mechanism also would appear to be ruled out.

A third possibility is surface-catalyzed hydrolysis on kaolinite reported to occur for various organophosphorus pesticides by Mingelgrin et al. (1979), but this is also unlikely because the likely hydrolysis products, i.e., V-VII, only occurred under irradiation; none was detected in the dark controls.

It would appear, therefore, that the primary mechanism is indirect photolysis brought about by oxidation. This would appear to be caused by the formation of active oxygen species as a result of the irradiation of oxygen or water associated with the clays.

The first observation supporting this possibility is the detection of hydrogen peroxide on the irradiated clays. The active oxygen species needed for its formation could well participate in the oxidation of I. Since the rates at which I is photolyzed and II is formed were both decreased by the removal of molecular oxygen or water, it is probable that both oxygen and water are needed for the formation of the active oxygen species. The incorporation of ^{18}O into II also shows the involvement of water. The active oxygen species are probably singlet oxygen ($^1\text{O}_2$), superoxide anion radical ($\text{O}_2^{\cdot-}$), hydroperoxyl radical (HO_2^{\cdot}), hydroxyl radical ($\cdot\text{OH}$), and atomic oxygen. The following reactions are suggested.



Since photoinduced electron transfer from aluminosilicates to adsorbed molecular oxygen has been reported (Che and Tench, 1983), a mechanism similar to that described in eq 1 can be assumed. Meanwhile, the photoinduced formation of $^1\text{O}_2$ on the surfaces of soils, silica gels, and non-transition-metal oxides has been clarified by using efficient $^1\text{O}_2$ trapping reagents such as tetramethylethylene and 2,5-dimethylfuran (DMF) (Gohre and Miller, 1983, 1985). It is also known that *trans*-diacetylene is the final product by the reaction of DMF with $^1\text{O}_2$.

After irradiation of the kaolinite treated with DMF, *trans*-diacetylene was not detected by HPLC analysis, which indicated that an alternative mechanism, electron transfer from clays to $^1\text{O}_2$, is ruled out. Supposing that $\text{O}_2^{\cdot-}$ is formed on the clays by irradiation, the successive reactions of $\text{O}_2^{\cdot-}$ with water (Mill, 1980) cause the formation of $\cdot\text{OH}$ and HO_2^{\cdot} as described in eqs 2 and 3. The radical reactions of I with these species would lead to the formation of II (eq 4) as the same reaction of the hydroxyl radical with *O,O,O*-trimethyl phosphorothioate (Atkinson et al., 1989). This means that (1) light is required for oxidation, (2) hydrogen peroxide is formed by irradiation, (3) both molecular oxygen and water are required for oxidation, and (4) the oxygen atom in the P=O moiety in II is partly (ca. 40%) derived from ^{18}O of H_2^{18}O . Supposing that the reaction rates of $\cdot\text{OH}$ and $\cdot\text{HO}_2$ with I are almost equal, the ratio of the ^{18}O incorporation seems to show that the reaction of $\cdot\text{HO}_2$ with I is slightly more favorable than that with H_2O .

Meanwhile, Spencer et al. (1980) have suggested that the photooxidation of parathion to paraoxon on dried clays is due to the reaction with ozone present in air. Since ozone photolysis in the presence of water produces two hydroxyl radicals (Peyton and Glaze, 1987), the oxidation of I via reaction with $\cdot\text{OH}$ formed from ozone might be an alternative mechanism. However, the ozone level would have been very low under the conditions tested, since irradiation from a xenon lamp ($\lambda > 320 \text{ nm}$) scarcely produced any ozone at all from molecular oxygen (Volman, 1963). Furthermore, as reported by Spencer et al. (1980), there was no significant difference in the amount of paraoxon produced in either light or dark conditions unless ozone was introduced artificially. It is unlikely, therefore, that the photodegradation of I proceeds via oxidation by ozone.

It is possibly significant that a smaller amount of II was produced by the irradiation of I when it was adsorbed onto montmorillonite than when adsorbed onto kaolinite. While this may have been due to its greater adsorption by montmorillonite compared with adsorption by kaolinite, it is also possible that it is due to a lower level of radical production in the case of montmorillonite. This may be inferred from the lower production of hydrogen peroxide observed from the irradiation of montmorillonite compared with that observed from kaolinite.

In the photodegradation of I on the surface of intact soils, the main photodegradation pathway other than P=S oxidation is demethylation (Mikami et al., 1984), yet in these studies there was no evidence of demethylation. In this case, demethylation is highest on soils of high organic matter, and it would appear that demethylation brought about by irradiation of I on intact soils would seem to be a consequence of the involvement of humic substances in the soil. Since it has been shown that singlet oxygen can be formed by the irradiation of humic substances (Zepp et al., 1981), the reaction of I with singlet oxygen might cause the demethylation. On the other hand, the formation of II was less on intact soils (Mikami et al., 1984) than that reported in this study. The oxidation of the P=S moiety by singlet oxygen is unlikely as shown by Katagi (1989) in the studies with fenitrothion. On the basis of the mechanisms proposed, the electron transfer from the clay minerals to molecular oxygen in the ground state is necessary for the formation of the radicals to cause the P=S oxidation. Therefore, it is considered that the partial coverage of the clay minerals with the humic substances in the intact soils inhibits efficient electron transfer from the clay minerals, which retards the formation of II.

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