

Comparative Study on the Quantum Yields of Direct Photolysis of Organophosphorus Pesticides in Aqueous Solution

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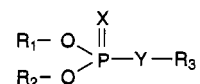
The quantum yields for direct photolysis of 16 organophosphorus pesticides and their phenolic products in aqueous solutions were determined at 254 and 313 nm. Highly significant correlation between the quantum yields at 254 nm and those at 313 nm was obtained ($r = 0.89$, $n = 14$). There also exists a highly significant correlation between the quantum yields of the organophosphorus pesticides and those of their phenolic products ($r = 0.92$, $n = 15$). The pesticides tend to have quantum yields similar to those of their phenolic products. The relationship between the quantum yields and the molecular structure was also investigated. On the basis of the quantum yields, the UV spectra of the compounds, and the solar radiance intensity on the Earth's surface, the relative rate constants for direct photodegradation of the organophosphorus pesticides and their corresponding phenolic products was estimated. The phenolic compounds have much higher rate constants than their parent compounds due to their stronger absorption of solar radiance.

Keywords: Photolysis; organophosphorus pesticides; quantum yields; comparative study

The photodecomposition of pesticides and other man-made pollutants in the aquatic environment occurs in both direct and indirect photochemical processes (Draper and Crosby, 1984). Direct photolysis involves direct absorption of light by the pollutant followed by chemical reactions, while indirect photolysis may be initiated via light absorption by natural substances. Sunlight-induced direct photolysis plays an important role in the degradation of some pollutants in the aquatic environment (Mikami et al., 1985). In addition to the environmental conditions, such as the solar spectral radiance at the water surface and the transmission of sunlight in the water body, the rate of direct photolysis of pollutants in the aquatic environment depends on two factors related to the pollutants: the rate of light absorption and the quantum yield for direct photolysis (Zepp, 1978; Zepp and Cline, 1977). The quantum yield for direct photolysis (hereafter referred to as quantum yield) of the pollutants is a very useful parameter for assessing the relative importance of direct photolysis under a given set of environmental conditions where other competing processes such as biodegradation and hydrolysis occur. A successful model has been developed for predicting the direct photolysis rate of pesticides and other pollutants in the aquatic environment according to their light absorption rate and the quantum yield (Zepp and Cline, 1977).

One important class of pesticides is the organophosphate esters. An indication of the prevalence of organophosphorus pesticide use is the fact that in 1988 more than a third of the total world insecticide market was accounted for by this popular class (Racke, 1992). These pesticides may enter a water body through drift during application, rainfall elution, and accidental or deliberate release. Many studies on the photolysis of organophosphorus pesticides in aqueous solutions have been reported. However, most of these studies are concerned with the identification of the photoproducts and the investigation of the reaction mechanisms (Katagi, 1989, 1993; Walia et al., 1989; Mansour et al., 1983; Durand et al., 1992, 1994), and relatively few studies deal with the quantum yield of direct photolysis (Mikami et al., 1985; Dilling et al., 1984).

Most organophosphorus pesticides have the structure



in which R_1 and R_2 are generally methyl or ethyl groups, X and Y are sulfur or oxygen atoms, and in many cases R_3 is a substituted phenyl or pyridinyl group. It is usually the π -conjugated structure in R_3 that is responsible for the absorption of UV light in the solar radiance with wavelength greater than 295 nm. In the present study, the quantum yields of 16 organophosphate esters were determined. As shown in Figure 1, most selected compounds are diethyl or dimethyl thiophosphates with R_3 as a substituted aromatic group. One of the aims of the present study is to investigate the effects of the variation in molecular structure on the photodegradation quantum yields of these compounds.

In the aquatic environment, thermal hydrolysis is a very important pathway for the degradation of many organophosphorus pesticides (Racke, 1992). The selected compounds will produce phenolic products through both thermal hydrolysis and photohydrolysis. Although thermal hydrolysis can considerably shorten the persistence of many organophosphorus pesticides, it has no such effects on the persistence of the phenolic products, which may also contribute to environmental pollution. In this regard, the degradation of the phenolic products may depend on other pathways, such as photolysis and biodegradation, to a greater extent than does the degradation of the parent compounds. Although there have been some studies on the persistence of organophosphorus pesticides in the aquatic environment (Wang et al., 1989; Wang and Hoffman, 1991; Macalady and Wolfe, 1983), very few such studies have been made on the corresponding phenolic products (Dilling et al., 1984). In the present study, the quantum yields of some phenolic products were determined so as to shed light on the importance of the photodegradation of these products.

Ideally, the quantum yields should be determined at a wavelength that is within the UV spectrum of the

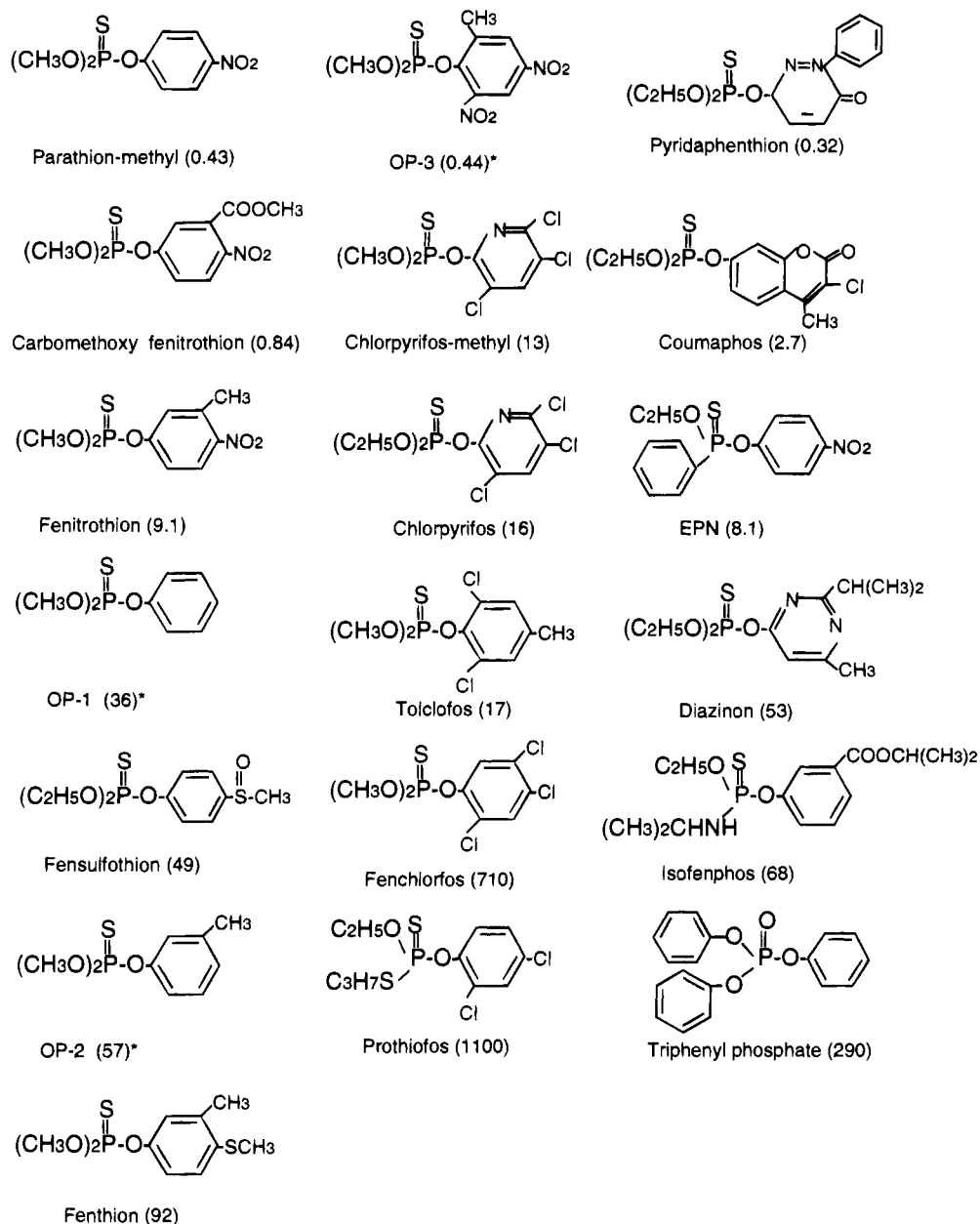


Figure 1. Structural formulas of the organophosphorus pesticides selected and their photodegradation quantum yields at 254 nm in aqueous solutions (the number in parentheses divided by 1000). (*) The quantum yield was calculated according to the quantum yield of the phenolic product.

solar radiance (295–360 nm), and thus the 313-nm radiation obtained from using a medium-pressure mercury lamp is an obvious choice. However, the molar absorptivities of many organophosphorus pesticides at 313 nm are too low for practical quantum yield determination. In contrast, at 254 nm the absorptivities of many organophosphorus pesticides are sufficiently high for quantum yield determination and the radiation can be readily obtained by using a low-pressure mercury lamp. In the present study, a comparison between the quantum yield at 313 nm and that at 254 nm was made to examine the effect of the excitation wavelength and determine whether there is any empirical correlation between the quantum yield at 254 nm and that at 313 nm.

MATERIALS AND METHODS

Chemicals. The structural formulas of the organophosphate esters studied are shown in Figure 1. The compounds were purchased from ChemService, Inc. (West Chester, PA)

with purities greater than 97%. They were dissolved in methanol at 1 mg mL⁻¹ as stock solutions. Except for the phenolic products of parathion-methyl, fenitrothion, diazinon, and chlorpyrifos, which were of reagent grade, the phenolic compounds for other organophosphorus pesticides were obtained by hydrolyzing the corresponding organophosphate esters in alkaline solutions. A pesticide dissolved in methanol (1 mg mL⁻¹; 1 mL) was mixed with 0.5 N NaOH solution (1 mL). The mixture was heated at 70 °C for 5 h and then neutralized with 1 N HCl solution. The validity of the method for preparing the phenolic compounds based on the knowledge that, in the alkaline hydrolysis of the organophosphate esters like the class selected here, the phenolic products will predominate (Eto, 1974; Fest and Schmidt, 1982; Katagi, 1993; Mikami et al., 1985). This was verified by product analysis using reversed-phase liquid chromatography, UV–visible spectrophotometry, and authentic compounds in representative cases. Usually the hydrolyzed solution, after dilution with water, was used directly for the determination of the photodegradation quantum yield of the phenolic compound. No attempt was made to separate any *O,O*-dialkylthiophosphoric acid, since it did not absorb light of wavelength above 250 nm

and was not likely to cause any interference. For the convenience of reference, all of the phenolic products are referred to as the hydrolyzed products of their parent compounds, even though they were either prepared by hydrolyzing the parent compounds or purchased as reagent phenolic compounds.

Photolysis. The quantum yields were determined at 254- and 313-nm wavelength. For the quantum yield at 313 nm, a 200-W Hanovia medium-pressure mercury lamp with a light-focusing lens system was used for the photolysis. The monochromatic light was obtained using an interference filter which gave maximum transmittance at 313 nm. The light intensity was measured using potassium ferrioxalate as a chemical actinometer. The pesticide stock solution was diluted with deionized and distilled water with a pH at 5.6 or with water plus 20% methanol to 10–20 mg L⁻¹. The diluted solution was bubbled with air at ca. 200 mL min⁻¹ for 10 min. The diluted solution in a quartz cell with 1-cm path length was irradiated for 1–10 h until ca. 5–10% of the pesticide had been photolyzed. The light absorbance of the solution was measured prior to the photolysis using a UV-vis spectrophotometer (Shimadzu UV-160). The quantum yield was calculated from the rate of light absorption and the rate of disappearance of the pesticide (Calvert and Pitts, 1967).

For the determination of the quantum yields at 254 nm, a Rayonet photochemical reactor installed with four RPR 2537 A low-pressure mercury lamps was used. The photochemical reactor had a merry-go-round sample rack and a fan for cooling. The pesticide solution (1.5–3 mg L⁻¹) in a quartz tube with a 1-cm diameter was irradiated until more than 75% of the pesticide had been degraded. The degradation curve was obtained by plotting the log concentration against the irradiation time. Fenitrothion was used as the reference. Its quantum yield for irradiation at 254 nm was determined in the same way as that described for the 313-nm irradiation. The degradation quantum yield of a pesticide was calculated by the equation

$$\phi = (\text{slope})_P / (\text{slope})_R \times \epsilon_R \phi_R / \epsilon_P \quad (1)$$

where (slope)_P and (slope)_R are the gradients of the plots of log concentration vs exposure time for the pesticide and the reference compound, respectively, ϵ_R and ϵ_P are molar extinction coefficients of the reference compound and the pesticide, and ϕ_R is the quantum yield for reaction of the reference compound. The details of this method have been given by Zepp (1978).

Before each irradiation, an aliquot of the prepared solution was taken as control sample and stored in the dark at room temperature. No concentration change was observed with all of the pesticides in the control during the period of irradiation experiment (less than 10 h).

Analysis of the Pesticides and the Phenolic Products. The analysis was conducted on a Perkin-Elmer binary-pump liquid chromatograph equipped with a UV detector set at 215 or 254 nm and an LC-ABZ column (25 cm × 4.6 mm i.d.; Supelco, Inc.). The latter is a silica-based column embedded with amino groups and is suitable for analysis of acidic, basic, and neutral compounds. The mobile phase was a mixture of acetonitrile and phosphate buffer with pH at 2.6 (60/40 v/v). The buffer solution was prepared by dissolving diammonium hydrogen phosphate (0.65 g) in distilled water (1 L) followed by adding phosphoric acid solution (2 M) to adjust the pH.

RESULTS AND DISCUSSION

Table 1 lists the degradation quantum yields of 16 organophosphate esters and 14 of the corresponding phenolic compounds. The quantum yields were determined by two wavelengths and in two solvents. For the quantum yield at 313 nm, the determination was duplicated. For the quantum yield at 254 nm, at least three points were obtained to draw the log plot, and the correlation coefficient between the log of concentration and the exposure time was above 0.98.

For most of the compounds listed, this is the first time that their degradation quantum efficiencies have been

Table 1. Photodegradation Quantum Yields of the Selected Organophosphorus Pesticides and the Corresponding Phenolic Products

compound	ϵ			$\phi \times 10^3$		
	254 nm ^a	254 nm ^b	313 nm	254 nm ^a	254 nm ^b	313 nm
parathion-methyl	4580	5770	3756	0.43	1.1	0.17
carbomethoxyfenitrothion	5020			0.84		
fenitrothion	4660	4750	2717	9.1	3.4	3.1
fensulfothion	1736	2663		49	110	
fenthion	10260	10600		92	35	
chlorpyrifos-methyl	610		110	13		40
chlorpyrifos	650	770	330	16	17	52
tolclofos	774			17		
fenchlorfos	635	132		710	340	
prothiofos	121	293		1100	660	
pyridaphenthion	1870		3890	0.32		0.10
coumaphos	2400	2686		2.7	2.4	
EPN	4360	7636	3150	8.1	12.0	7.0
diazinon	3890	3270	90	82	53	12
isofenphos	1260	850		68	21	
triphenyl phosphate	644	714		290	94	
phenol	980			21		
3-cresol	302	341		57	81	
2-nitrophenol	4310	3980		2.0	1.7	
3-nitrophenol	3410	3858		0.19	0.23	
hyd-parathion-methyl	4140	2600	11000	0.53	2.0	0.09
4,6-dinitro- <i>o</i> -cresol	6831	9095		0.48	0.91	
hyd-fenitrothion ^c	2290		6470	1.8		2.3
hyd-fensulfothion	4933			19		
hyd-chlorpyrifos	4305		6475	38		58
hyd-tolclofos	820			14		
hyd-fenchlorfos	5250			110		
hyd-prothiofos	1062			200		
hyd-pyridaphenthion	3060			2.4		
hyd-diazinon	5060		110	40		5.4
hyd-isofenphos				7.1		

^a In aqueous solution. ^b In pure methanol. ^c Hyd, hydrolyzed.

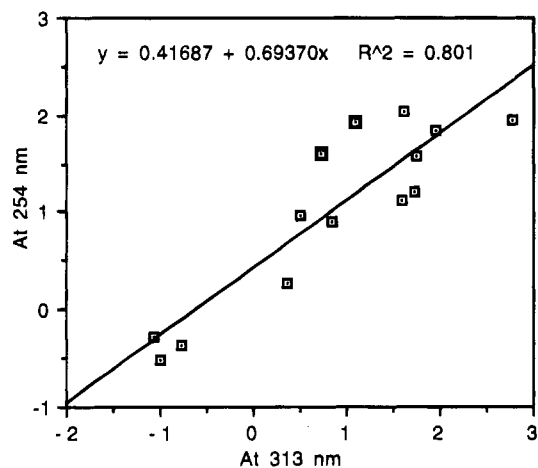


Figure 2. Relationship between log of quantum yields ($\times 10^{-3}$) of the compounds at 313 nm and that at 254 nm.

reported. The values vary over a wide range of approximately 4 orders of magnitude, reflecting a great variation in reactivity. Few studies of the quantum yields of organophosphorus pesticides in aqueous medium have been reported in the literature (Mikami et al., 1985; Dilling et al., 1984), and direct comparison cannot be made due to differences in experimental conditions.

Effect of the Wavelength on the Quantum Yields.

Table 1 shows that the quantum yields for most pesticides and the phenolic products at 254 nm are higher than those at 313 nm. The exceptions are chlorpyrifos, chlorpyrifos-methyl, and their phenolic product, whose quantum yields at 254 nm are lower than at 313 nm. Figure 2 shows the relationship between the quantum yields at 254 nm and those at 313 nm in aqueous solutions. As shown in Figure 2, the

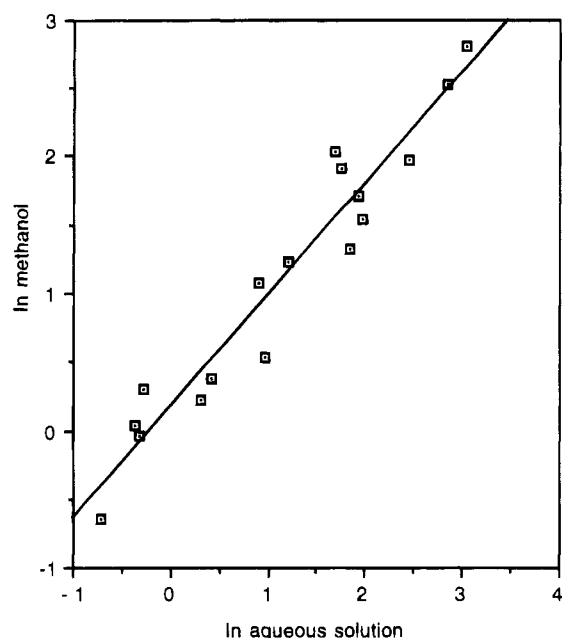


Figure 3. Relationship between log of quantum yields ($\times 10^{-3}$) at 254 nm in aqueous solution and that in methanol.

slope of the line is not 1, suggesting that the effects of irradiation wavelength on the quantum yields of different compounds are not the same. The regression analysis gave a correlation coefficient of 0.89 based on the results of 14 compounds (pesticides and some phenolic products) for which the yields have been determined at both wavelengths, indicating a very significant linear correlation between the quantum yield at 254 nm and the quantum yield at 313 nm. This relationship suggests that it is possible to estimate the quantum yields at 313 nm from the results obtained at 254 nm. The results of comparison study among different organophosphorus pesticides conducted at 254 nm should thus serve as a useful guide to the photochemical behavior of the pesticides in the wavelength range within the solar spectrum on the Earth's surface.

Quantum Yields in Aqueous Solution and in Methanol. The degradation quantum yields in aqueous solution and in methanol are correlated in Figure 3 for those compounds for which the measurements have been made in both solvents. The regression analysis gave a correlation coefficient of 0.96. The data in Table 1 indicate that most of the organophosphate esters have equal or higher quantum yields in aqueous solution than in methanol, while the phenolic compounds have higher quantum yields in methanol. This could be due to the facts that the solvolysis of the organophosphate esters in aqueous solution is more important than in methanol and that solvolysis is not an important pathway in the photodegradation of the phenolic compounds.

Quantum Yields of the Phenolic Products. Figure 4 shows the relationship between the organophosphorus pesticides and the corresponding phenolic products. The data obtained at both 254 and 313 nm are included. The regression analysis indicated a very significant correlation between the quantum yield of the organophosphorus pesticides and that of the phenolic products ($r = 0.912$, $n = 15$). Table 1 also shows that the phenolic products tend to have quantum yields similar to those of their parent compounds. These results suggest that the quantum yields of the organophosphorus pesticides selected depend to a great extent on the nature of the phenyl groups.

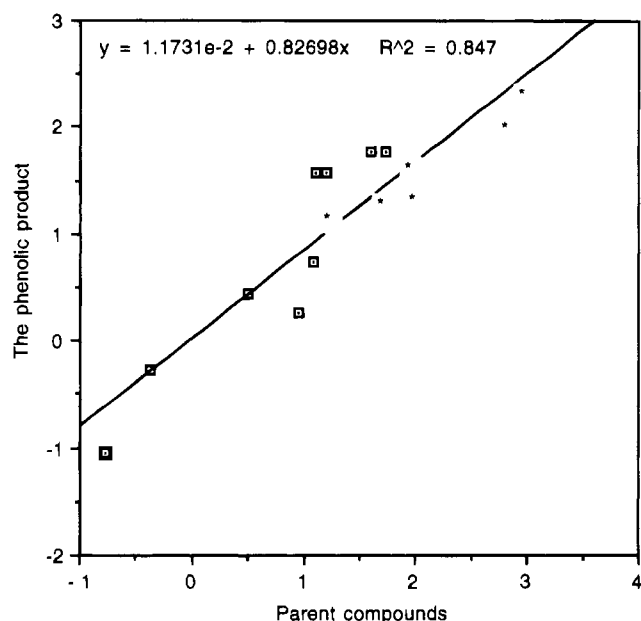


Figure 4. Relationship between the quantum yields ($\times 10^{-3}$) of the organophosphorus pesticides and that of their phenolic products. (\square) The phenolic product was of reagent grade. (*) The phenolic product was obtained by hydrolysis of the parent compound.

Table 2. Quantum Yields of Some Phenolic Products at Different pH (254 nm)

compound	ϵ_{254}		$\phi_{254} \times 10^3$	
	pH 3.4	pH 7.8	pH 3.4	pH 7.8
phenol	752	893	38	21
4-nitrophenol	2600	6300	0.30	0.17
hyd-fenitrothion	2120	3970	5.9	2.4

Phenolic compounds can exist in acidic and basic forms according to the pH of the medium, and the two forms may have different quantum yields. To study the effect of pH on the quantum yields of the phenolic products, the distilled water was replaced with phosphate buffers with pH at 3.4 and 7.8, and the quantum yields of three phenolic compounds were determined at 254 nm. The results are given in Table 2. The phenolic products have higher quantum yields at lower pH. The percentages of the acidic form in the total phenolic compound calculated from the pK_a are 100 and 99.4 for phenol at pH 3.4 and 7.8. For 4-nitrophenol, the values are 100 and 18.6, respectively. From pH 3.4 to 7.8, the ratio of the two forms of phenol changed very little, while the quantum yield decreased by half. Therefore, the difference of the quantum yield caused by pH is not likely to be due to the two different forms of phenols. However, the difference in quantum yield caused by the pH change is normally less than 100%, much smaller than the difference in the quantum yield among different compounds. Therefore, in the study of the photostability of the phenolic compounds under environmental conditions (pH varies between 5 and 8), the effect of pH on the quantum yield is relatively small.

Relationship between Quantum Yield and Molecular Structure. In Figure 1, the organophosphorus pesticides in each column are arranged in the order of their quantum yields at 254 nm in aqueous solution. The quantum yields of phenol, *m*-cresol, and 4,6-dinitro-*o*-cresol were used to calculate the quantum yields of the corresponding dimethyl thiophosphates using the equation in Figure 4. The results given in Figure 1 suggest that the organophosphorus pesticides with strongly electron-withdrawing groups (e.g., C=O and

Table 3. Estimated Relative Rate Constants (*k*) for Direct Photolysis of the Organophosphorus Pesticides and the Phenolic Products in Water at 0° Latitude in Midsummer

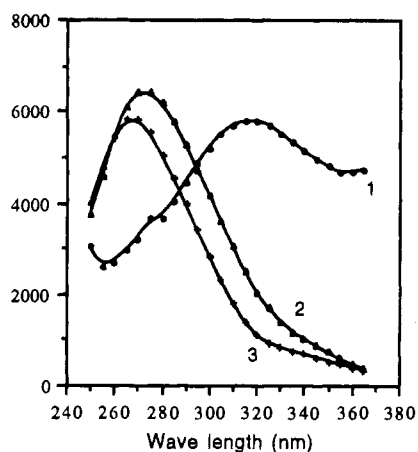
compound	quantum yield × 10 ³	$\sum(I_{\lambda}\epsilon_{\lambda})^a \times 10^{-18}$ (quanta mol ⁻¹ s ⁻¹)	<i>k</i>
tolclofos	17	0	0
prothiofos	1100	0	0
pyridaphenthion	0.32	72.8	1
phenol	21	0.54	1
parathion-methyl	0.43	67.4	1
fensulfothion	49	0.88	2
hyd-fensulfothion	19	2.4	2
chlorpyrifos	16	6.3	3
hyd-diazinon	40	2.8	4
hyd-prothiofos	200	0.56	4
diazinon	85	2.0	6
fenthion	92	2.7	9
EPN	8.1	40.2	11
hyd-tolclofos	14	21.9	11
hyd-parathion-methyl	0.53	679.3	12
fenitrothion	9.1	45.6	14
coumaphos	2.7	165.9	15
hyd-fenitrothion	1.8	302.5	19
triphenyl phosphate	290	3.4	34
hyd-fenchlorfos	110	12.7	48
fenchlorfos	710	2.1	51
hyd-chlorpyrifos	38	94.6	124
isofenphos	68	87.3	205

^a Calculated from 295 to 365 nm.

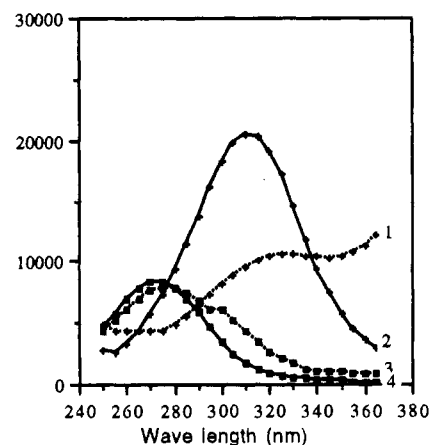
NO₂) attached to the aromatic ring tend to have lower quantum yields, while the compounds with alkyl or chloro groups attached to the aromatic ring tend to have

higher quantum yields. A comparison between chlorpyrifos and fenchlorfos indicates that replacing a carbon with a nitrogen in the aromatic ring lowers the quantum yield considerably. It is known that the effect exerted by a nitrogen atom in an aromatic ring on the π -electron density distribution is similar to that of a nitro group attached to the aromatic ring.

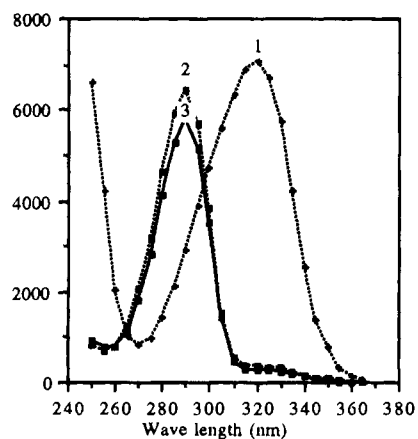
The small groups attached to the aromatic ring may have two types of effects on the quantum yields: such a group may supply a photosensitive position for photoreactions to occur, or it may alter the density distribution of the π -electrons on the aromatic ring. The relatively low quantum yields of pyridaphenthion, parathion-methyl, and carbomethoxyfenitrothion could be due to the second effect caused by their electron-withdrawing groups. The relatively high quantum yields of fenthion, fenchlorfos, and prothiofos could be due to the first effect caused by the methylthio or chloro groups. As shown in Figure 1, fenitrothion and parathion-methyl have very similar structures but their quantum yields differ by 20 times. It has been reported that the oxidation of the methyl group attached to the aromatic ring is the predominant photoreaction both in water and in methanol (Mikami et al., 1985; Katagi, 1989; Durand et al., 1992, 1994). This effect of the methyl group in fenitrothion is apparently an important factor contributing to the higher quantum yield of fenitrothion. In the case of isofenphos, the relatively large quantum yield may also be attributed to the effects



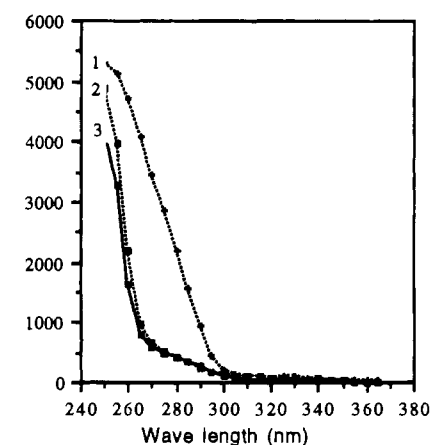
1, hydrolyzed fenitrothion in water; 2, fenitrothion in methanol; 3, fenitrothion in water.



1, p-nitrophenol in water; 2, p-nitrophenol in methanol; 3, parathion-m in water; 4, parathion-m in methanol.



1, hydrolyzed chlorpyrifos in water; 2, chlorpyrifos in water; 3, chlorpyrifos in methanol.



1, hydrolyzed diazinon in water; 2, diazinon in water; 3, diazinon in methanol.

Figure 5. UV spectra of some organophosphorus pesticides and their corresponding phenolic products.

of its phosphoramidate group, although direct evidence is not available.

Prediction on the Photostability of the Organophosphorus Pesticides and Their Phenolic Products. Under natural conditions, the relative pseudo-first-order rate constant (k) for the photodegradation of a compound in water can be approximately estimated by comparing the term $\phi \sum(I_{\lambda}\epsilon_{\lambda})$ of the compound with that of a reference. ϕ is the quantum yield for the photodegradation, which is assumed to be relatively independent of the light wavelength within the range studied, I_{λ} is the sunlight intensity at wavelength λ , and ϵ_{λ} is the molar extinction coefficient at wavelength λ .

The solar radiation intensity at the Earth's surface at different wavelengths and seasons is available from Benner's (1972) report. The sunlight intensity at 0° latitude in the summer was used to calculate the relative rate constants of the pesticides and their phenolic products in Singapore (1° N latitude) using methyl parathion as the reference. The results, given in Table 3, show that many compounds with high quantum yields do not have high relative rate constants because their absorption of sunlight is weak. These compounds normally do not contain suitable chromophores for absorption at wavelengths longer than 295 nm. In contrast, since the phenolic products tend to absorb more sunlight than their parent compounds, the hydrolyzed products have much higher rate constants as compared to the corresponding parent compounds, despite the fact that the quantum yields of a parent compound and its phenolic product may be similar. Figure 5 gives the spectra of some pesticides and their phenolic products. It shows the absorption peaks of the phenolic products caused by $\pi-\pi^*$ transition are at longer wavelength than their parent compounds. This red shift can partly be attributed to the ionization of the phenolic compounds, resulting in a more extended conjugated system in the phenolate anions. The pH of natural water may vary between 5 and 8. Phenolic compounds with their pK_a values falling in this range (such as nitrophenols) can have very different ϵ_{λ} values with slight variation in the pH of the medium, due to the drastic change in the ratio of the two forms of the phenolic compounds. It is thus expected that the photostability of such phenolic compounds should be very sensitive to pH change under natural conditions.

The estimated photolysis rates given in Table 3 are for direct photolysis only. Under natural conditions, other processes such as indirect photolysis catalyzed by natural sensitizers, thermal hydrolysis, and biodegradation are also involved in the degradation of these pesticides. The importance of each process depends on the properties of the pesticides and the media (e.g., pH and populations of the microorganisms) (Freed et al., 1979). Thus, for fenitrothion, whose estimated photolysis rate is 14 times that methyl parathion, the dissipation under sunlight is 30 times faster than in the dark (Mikami et al., 1985), whereas malathion and monocrotophos, two organophosphorus pesticides without large conjugated systems, are degraded mainly through thermal hydrolysis (Wang and Hoffman, 1991; Lee et al., 1990).

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