Comparative Photodegradation Study of Fenthion and Disulfoton under Irradiation of Different Light Sources in Liquid- and Solid-Phases

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To assess the photodegradation extent of the organophosphorus pesticides, fenthion and disulfoton in the environment, degradation rates of their chemicals under irradiation by visible light and each region of the ultraviolet (UV) sources, UVA (320–400 nm radiation), UVB (280–320 nm radiation) and UVC (250–260 nm radiation) in liquid- and solid-phases were determined and their photolysis products identified. Although visible light did not cause photodegradation of either fenthion or disulfoton even after the maximal irradiation of 8 hr in both phases, all the ranges of UV sources resulted in the photolysis of both pesticides, despite the solid-phase. The photolysis rates of fenthion under UVB and UVC irradiation in both phases were higher than that under UVA irradiation and also exceeded all of the degradation rates of disulfoton. This confirms that fenthion is more readily degraded than disulfoton in the UVB range. Fenthion sulfoxide and disulfoton sulfoxide were identified as oxidative photolysis products whose photolysis rates were considerably slower than parent compounds, and the oxidation reaction of both pesticides in the liquid-phase was superior to those on the solid-phase, indicating that dissolved oxygen in water is an important factor affecting the photolysis. These results suggest that fenthion in the environment is more rapidly degraded by UVB irradiation in natural sunlight than disulfoton, and sulfoxides of both pesticides remain stable as a photolysis product in the environment.

Key words —— fenthion, disulfoton, photodegradation, oxidation, ultraviolet irradiation

INTRODUCTION

Residual pesticides are known to be decomposed by various natural conditions in the environment: by hydrolysis in water,[1,2] photodegradation,[3–7] metabolism in plants[8,9] and animals,[10,11] and bacteriological degradation in soil.[12,13] The degraded products of the pesticides then have the potential to be ingested by humans with agricultural products. Some of these are often more toxic than the parent pesticides. Indeed, the environmental metabolites of parathion and dieldrin, paraoxon[14] and photodieldrin[15] show high toxic effect in animals compared with their parent chemicals. Therefore, the evaluation of toxicity of these decomposed products is important from the viewpoint of human health. Photodegradation is one of the most important fac-

tors involved in decomposition of pesticides in the environment.[16] We previously reported that fenthion and disulfoton were the most sensitive to photolysis among 79 pesticides including organophosphorus, organonitrogen, organochlorine and pyrethroid by exposure to UVA.[17] Fenthion sulfoxide and disulfoton sulfoxide have been recognized to be photolytic products of fenthion and disulfoton under the irradiation of natural sunlight.[18,19] Elucidation of the photodegradation of these products is lacking but is important in relation to their persistence in the environment.

The individual photolysis reactions of fenthion and disulfoton have been studied,[20–23] although little is known of their comparative decomposition under the conditions of light source, exposure time of light and reaction phase. Most of the photolysis studies have used natural sunlight, so that it is unclear what wavelength range of light actually contributes to the photolytic reaction. We therefore compared the photolysis of fenthion and disulfoton in the liquid- and

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solid-phases with different sources of visible light and ultraviolet (UV) to estimate the extent of their photodegradation.

MATERIALS AND METHODS

Reagents —— Fenthion (> 98.0% purity), fenthion sulfoxide (> 99.0% purity) and fenthion sulfone (> 99.0% purity) were provided from Wako Pure Chemical Industries. Disulfoton, disulfoton sulfoxide (10 ng/ml in cyclohexane) and disulfoton sulfone (10 ng/ml in cyclohexane) were from Hayashi Pure Chemical Industries. The cyclohexane as a dissolved solvent of disulfoton sulfoxide and disulfoton sulfone was removed under a gentle stream of nitrogen. Standard solutions of fenthion (5 μg/ml), fenthion sulfoxide (5 μg/ml), fenthion sulfone (5 μg/ml), disulfoton (10 μg/ml), disulfoton sulfoxide (10 μg/ml) and disulfoton sulfone (10 μg/ml) were prepared with methanol (HPLC grade) and distilled water.

Photolysis Study ——

Photolysis: Four different artificial sources of light were used for the photolysis study. Visible light was derived from a fluorescent bulb (Toshiba, Japan, FL20SN-SDL•NU) which had an ultraviolet ray-absorbing filter and wavelengths between 380 and 750 nm; fluorescent lights UVA (FL20S-BLB), UVB (FL-20SE) and UVC (GL20) were also used and had wavelengths from 320 to 400 nm (maximum emission at 352 nm), from 280 to 320 nm (max at 315 nm), and from 250 to 260 nm (max at 254 nm), respectively. One ml of an aqueous solution of fenthion, fenthion sulfoxide, disulfoton or disulfoton sulfoxide was added to a quartz cell (1 × 1 × 4.5 cm) for the aqueous photodegradation experiment. For the solid photodegradation experiment, a methanol solution containing each pesticide was added to a quartz dish (8 × 2 × high 1 cm) and the methanol was then removed under a gentle stream of nitrogen. These samples were exposed to visible light, UVA, UVB or UVC for a period of 1 min to 8 hr at room temperature, adjusting their light intensity on the sample surface to the same level (1.0 mW/cm²) at a distance of 9 cm, 17 cm and 23 cm by varying the distance from each of the UVA, UVB and UVC light sources with a UVX digital radiometer and a UVX-36, UVX-31 or UVX-25 sensor (UVP, Inc., U.S.). After irradiation, methanol was added to the aqueous solution up to two ml volume, and the solid sample was dissolved and filled with

methanol to the same volume. A photolytical experiment was carried out in a dark place, and a control experiment was conducted keeping samples under the same conditions as the irradiated samples.

Analysis: Identification and quantitative analysis of the starting materials and their photoproducts in the liquid- and solid samples was done using a Shimadzu high performance liquid chromatograph (HPLC) equipped with an UV-100 variable-wavelength UV-VIS detector, a photodiode array detector and a Rheodyne injector (50 μl loop) and a high performance liquid chromatograph mass spectrometer (LC-MS). The HPLC column was fitted with a 4.6 × 150 mm i.d. STR ODS-II(Shinwa Chemical Industries, Ltd., Japan). The mobile phase was a mixture of acetonitrile and water (60 : 40 v/v) isocratically delivered by pump at a flow rate of 1.0 ml/min at 40°C. Based on the UV absorption spectra of fenthion and disulfoton, a wavelength of 200 nm was chosen for the simultaneous determination of authentic standards and samples. The LC-MS system consisted of a Shimadzu LCMS-QP8000 liquid chromatograph-mass spectrometer. LC separations were performed with a 2.00 mm × 150 mm i.d. Wakosil-II 3C18R5 column. The flow rate was 0.2 ml/min with an oven temperature of 40°C and an injection volume of 10 μl. Solvent A was water and solvent B was acetonitrile. The gradient elution conditions were initially A (100), programming to 100% B over 15 min, holding 100% B for 10 min (25 min total analysis time). Column equilibration was accomplished by using the initial condition for 5 min prior to the next injection. The other operational parameters of the LC-MS systems used for the condition were as follows: the analytical mode of ionization was electrospray ionization (ESI, negative), drying gas (N$_2$) flow was 4.5 l/min, probe voltage was +20 V, deflector voltage was –20 V, curved desolvation line (CDL) voltage –4.5 kV, CDL temperature was 230°C and detector gain was 1.6 kV.

RESULTS AND DISCUSSION

Effects of UV Irradiation on Photolysis of Fenthion and Disulfoton in the Liquid- and Solid-Phases

As shown in Fig. 1, a course of comparative light-irradiation tests of fenthion and disulfoton in the liquid- and the solid-phases under the irradiation of visible light resulted in no photodegradation even for 8 hr; however, both underwent degradation
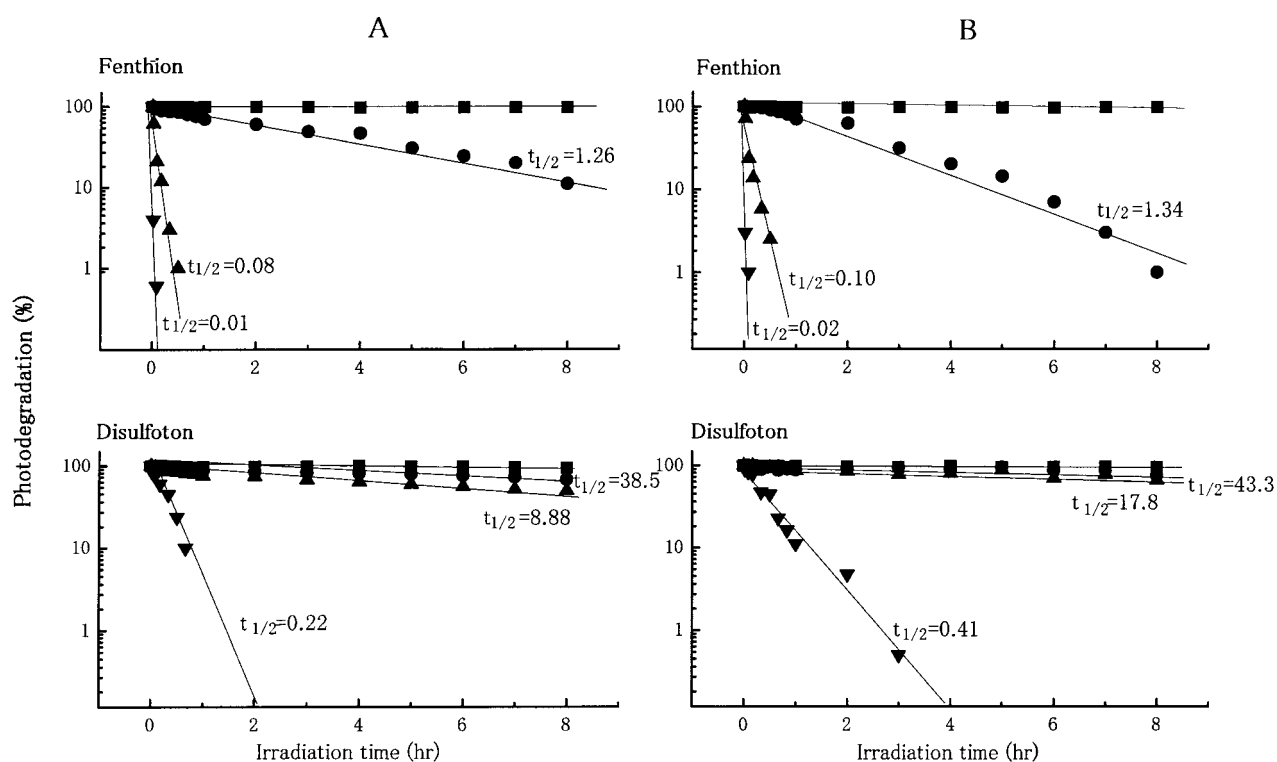
Fig. 1. Photodegradation of Fenthion and Disulfoton by Visible- and Ultraviolet-Light in Liquid- (A) and Solid-Phases (B)

The initial concentrations of fenthion and disulfoton in the liquid-phase reaction were 5 and 10 μg/ml, respectively; the initial doses on the solid-phase reaction were 5 and 10 μg. Half-life values ($t_{1/2}$) of their degradation were calculated from the amount of parent materials remaining after exposure to UV irradiation for 8 hr or for the time until the initial amount decreased by 1%. ■ Visible light, ● UVA, ▲ UVB, ▼ UVC

under all ranges of UV-irradiation in the two phases. As no photodegradation of either pesticide in the dark was observed in the liquid- or solid-phase, their degradation is attributed to the UV-irradiation. Degradation kinetic data revealed high correlation to irradiation time (the correlation coefficient ranged between r = –0.802 to –0.989), indicating first-order kinetics. Photodegradation half-life value ($t_{1/2}$) was estimated from the parent pesticides remaining following exposure to UV irradiation for 8 hr or for the time until the initial amount decreased by 1%.

Elimination kinetics of both pesticides under UVC-irradiation showed the shortest $t_{1/2}$ values among all ranges of UV-irradiation, and photolysis in the liquid-phase was more readily degraded than those on the solid-phase, showing shorter $t_{1/2}$ value of the former. This indicates that water is an important factor for the photolysis under UV-irradiation.

The $t_{1/2}$ value of disulfoton, however, was larger than that of fenthion in either phase (Fig. 1), indicating that fenthion is probably degraded much more easily than disulfoton. According to the Grotthus–Drapper law,[24] photolysis is generally triggered by the absorption of light by the chemical compound. Although disulfoton has no UVB absorption,

fenthion has the absorption within the range from 280 to 320 nm that belongs to the UVB wavelength because it possesses an aromatic ring (data not shown). This suggests that the UVB absorption of fenthion may be responsible for the greater extent of photodegradation, that UV wavelength and reaction phase are the most important factors affecting photolysis of these two pesticides, and that UVB and UVC cause their photolysis.

Photolysis Products of Fenthion and Disulfoton

Identification of the mechanism of the photolytic reaction of fenthion and disulfoton was made using HPLC and LC-MS measurement of the degradation products of both compounds under irradiation of UVA, UVB and UVC. As shown in Fig. 2, sulfoxide (–S=O) compounds of the parent pesticides were detected as the photolytic products with UVB irradiation. The sulfoxides were identified by LC-MS with negative ionization mode. The fragment ions of fenthion sulfoxide and disulfoton sulfoxide were monitored at m/z 295 and m/z 291, respectively, and no fragment ion derived from another product was recognized. Other unknown products (Peaks I and II) were also detected in a mixture of UVB-exposed
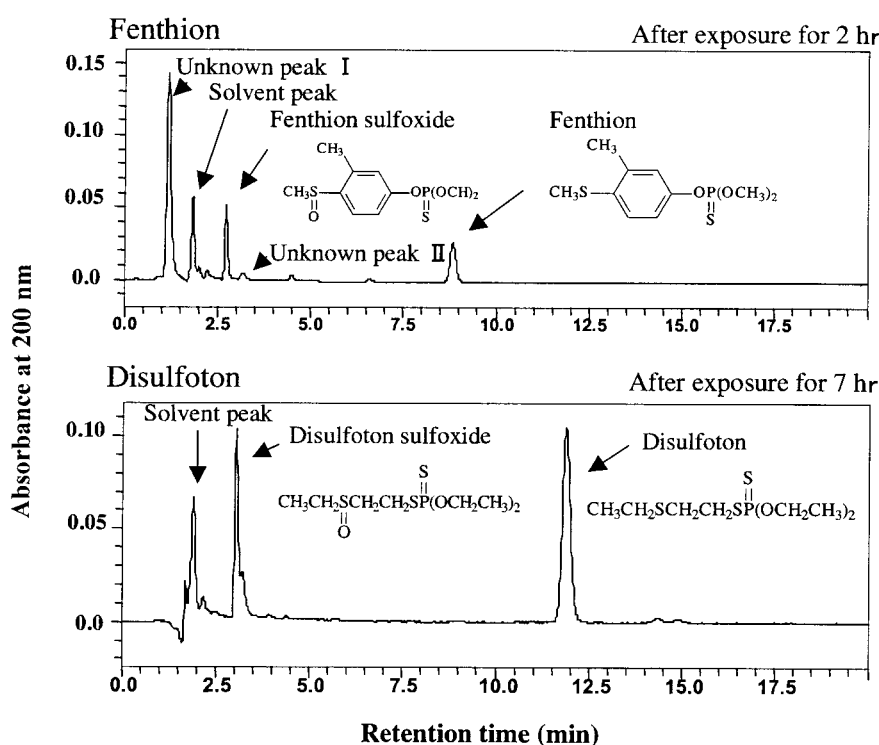
Fig. 2. HPLC Chromatogram of Photolytic Products of Fenthion and Disulfoton under Irradiation of UVB in the Liquid-Phase
    The initial concentrations of fenthion and disulfoton in the liquid-phase reaction were 10 and 5 μg/ml, respectively. Column, STR ODS-II 150 mm in length $\times$ 4.6 mm ; mobile phase, acetonitrile-water (60 : 40) at 1 ml/min; detection wavelength, 200 nm; injection volume, 20 μl.

fenthion and are relatively polar compounds because of their short retention times. Similar photolysis products were also observed with irradiation of the UVA and UVC in the liquid- and solid-phases (data not shown). As shown in Fig. 3, the amounts of the sulfoxide derivatives formed by UVA-, UVB- and UVC-irradiation of the pesticides gradually increased with irradiation time. After 8 hr of UVB-irradiation, the yields of fenthion sulfoxide and disulfoton sulfoxide both corresponded to approximately 40% of the amount of the parent pesticide. The oxygenation reaction was predominant in the liquid-phase, compared to that on the solid-phase, suggesting that dissolved oxygen in water plays an important role in the photochemical reaction of fenthion and disulfoton.

    The major metabolism reaction of these pesticides in rats,[25] pigs[26] and insects[27] is the oxygenation of sulfur atom to sulfoxide and a further step to sulfone (O=S=O) by cytochrome P450. Fenthion sulfone was also determined in plants.[28,29] However, as shown in Table 1, the $t_{1/2}$ values of fenthion sulfoxide and disulfoton sulfoxide in the liquid phase were much larger than the parent compounds and sulfone was not produced by direct photolysis. Oae

and Tamgai[30] reported that oxidative reaction from sulfide to its sulfoxide and sulfone proceeds by nucleophilic attack, for instance, by hydrogen peroxide, singlet oxygen, nitrogen oxides or ozone, and the reactive ability of such attack on the sulfur atom of sulfides possessing two unshared electron pairs is higher than that of sulfoxide. Therefore, weak intermolecular reaction of the nucleophilic attack on the sulfur atom of sulfoxide is apparently responsible for the slow oxygenation rate of this group to the sulfone group. These results suggest that the oxygenated pathway to sulfone from sulfoxide compounds is rarely by direct photolysis reaction, and is probably produced via metabolic processes in animals, insects and plants.

    It has been reported that there is little UVC radiation in the solar light spectrum reaching the Earth's surface.[31,32] This means that UVB wavelengths of sunlight contribute to photodegradation of both pesticides in the natural environment. Since the oxidative reaction was accelerated in the liquid-phase, these two pesticides are thought to be more readily decomposed in an aquatic environment such as paddy than on a dried soil surface or agricultural leaves, and their stable sulfoxide metabolites may
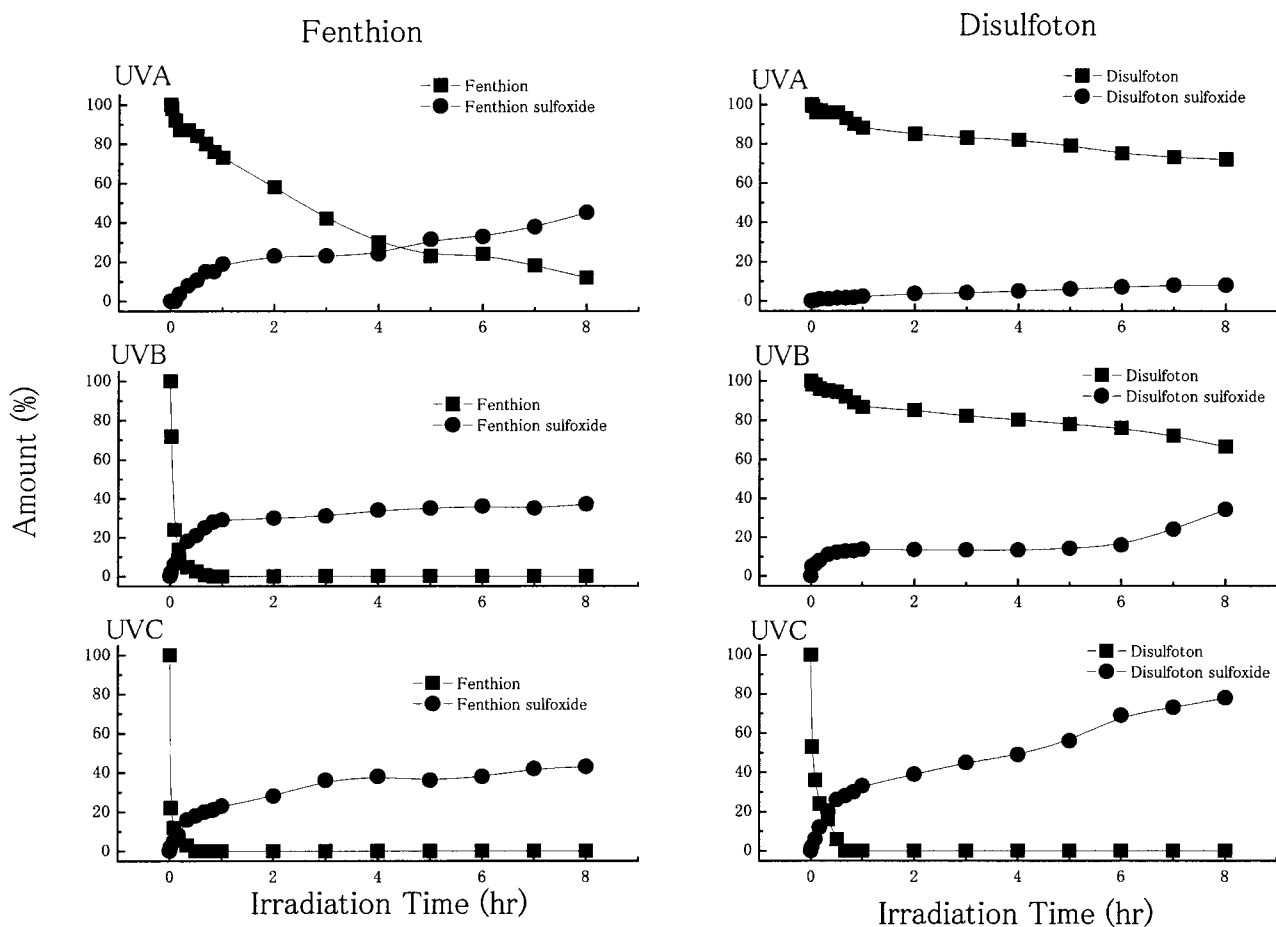
Fenthion

Disulfoton

Irradiation Time (hr)

Irradiation Time (hr)

Fig. 3. Photodegradation of Fenthion, Disulfoton and their Product Formation under Irradiation of UVA, UVB and UVC in the Liquid-Phase Reaction

The initial concentration of fenthion and disulfoton was 5 and 10 μg/ml, respectively. Amount (%) indicates the photodegradation percentage for the starting materials and the production percentage of their sulfoxides.

Table 1. The Half-Life Values of Fenthion, Disulfoton and Their Sulfoxide Compounds under Irradiation of UV Sources in the Liquid-Phase

Starting material	Half-life value ($t_{1/2}$)		
	UVA	UVB	UVC
Fenthion	1.26	0.08	0.01
Fenthion sulfoxide	> 24	11.2	0.39
Disulfoton	38.5	8.88	0.22
Disulfoton sulfoxide	> 24	> 24	2.31

Fenthion, disulfoton and their sulfoxide compounds were exposed to UV for 8 hr in the liquid-phase. The initial concentrations of fenthion, fenthion sulfoxide, disulfoton and disulfoton sulfoxide in the liquid-phase reaction were 5, 5, 10 and 10 μg/ml, respectively. Photodegradation half-life value ($t_{1/2}$) was calculated from the amount of the starting materials remaining after exposure to UV irradiation for 8 hr or for the time until the initial amount decreased by 1%.

continue to exist under such a condition.

In conclusion, these findings clearly indicate that although an UV wavelength of light is capable of causing the photolysis of fenthion and disulfoton, UVB is primary responsible for the photodegradation in the environment, and that fenthion is more readily degraded than disulfoton. The sulfoxide compounds are thought to remain stable as photolysis products in the environment. Further studies on identification of unknown photolysis products and determination of the photolytic mechanism of fenthion are under way.

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