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Photochemical Behavior of Organic Phosphate Esters in Aqueous Solutions Irradiated with a Mercury Lamp

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Pollution by toxic chemicals that are resistant to biological degradation and have a potential for accumulation in biological organisms is becoming a world-wide problem. Organic phosphate esters(OPEs) are widely used as plasticizers, industrial hydraulic fluids, and lubricant additives. Various OPEs have been detected in environmental samples (Tachikawa et al. 1975; Office of Health Studies 1977; Ishikawa et al. 1985c) and in industrial and domestic wastewaters (Ishikawa et al. 1985a).

Ultraviolet(UV) irradiation is known as a effective treatment for persistent chemicals in natural water or wastewater (Crosby and Hamadmad 1971; Tissot et al. 1984). Therefore, in order to develop a means of removal of OPEs in water, some fundamental experiments with UV irradiation were performed with a mercury lamp, and photochemical behaviors and photodecomposition products were examined for 7 OPEs, namely tributyl phosphate(TBP), tris(chloropropyl) phosphate (TCPP), tris(2-chloroethyl) phosphate(TCEP), trioctyl phosphate(TOP), tris(dichloropropyl) phosphate(CRP), triphenyl phosphate(TPP), and tricresyl phosphate(TCP).

MATERIALS AND METHODS

The reactor used in these experiments was a Taika Kogyo Model HLV-A equipped with a 15 W low-pressure mercury lamp. The gas chromatograph(GC) was a Nihon Denshi Model JGC-20K equipped with a flame ionization detector and a flame photometric detector having a 526-nm filter. The GC conditions were as follows: 2 mm i.d. x 2 m glass column packed with 2% OV-17 + 2% PZ-179 coated on 60-80 mesh

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Uniport HPS; inlet temperature, 300 °C; column temperature, 100-300 °C and 200-300 °C(10 °C/min); carrier gas, 20 mL/min of nitrogen gas; detector temperature, 300 °C. GC-mass spectrometer(GC-MS) was a Nihon Denshi Model JMS-DX 303. The operational conditions had the same column and column temperature was programmed from 100 to 280 °C at 10 °C/min. Inlet temperature was 290 °C. The helium flow rate was 10 mL/min. Ionizing energy was 70 eV. Total organic carbon (TOC) and inorganic carbon(IC) were measured with a Beckman Model 915A TOC analyzer.

Seven OPEs were obtained from Tokyo Chemical Co. TBP, TCEP, TOP, and TCP were purified by distillation under reduced pressure. TCPP and CRP were used without further purification. TPP was purified by zone refining. The purity of these OPEs was checked by GC. TCPP, CRP, and TCP were mixtures of isomers. All solvents were reagents with a purity that was suitable for pesticide residue analysis. Purified water was prepared using a Yamato Model WA-715 auto-still equipped with filter, distiller, and ion exchanger.

Each amount of OPE was placed in a 200-mL flask and 100 mL of purified water was added. Then, the OPE was dissolved or dispersed by ultrasonication for 1 h. The solution was placed in the reactor, and 1900 mL of purified water was added to the solution while it was being stirred with a magnetic stirrer. After 30 min of stirring, 200 mL of the solution was taken as a reference solution and the remaining solution was adjusted to a desired pH with HCl or NaOH. The UV lamp was switched on. A 100-mL subsample of the irradiated solution was periodically withdrawn during irradiation. Each subsample withdrawn was stored in the dark at 5 °C after adjusting the solution to pH 3 with HCl. UV intensity was checked by using an UVP Model UVX radiometer having 254, 297, and 365 nm sensors. These values on the surface in the center of lamp were 6.640-6.800, 0.140-0.143, and 0.153-0.158 mW/cm^2, respectively.

TOC, IC, and pH were measured by the methods of Japanese Industrial Standard (Japan Industrial Standards Committee 1986). Phosphoric acid, Cl$^-$ ion, and phenols were measured by the Ascorbic Acid Method (American Public Health Association et al. 1975), the Mohr Method (Environmental Health Bureau 1978a), and the 4-Aminoantipyrine Method (Environmental Health Bureau 1978b), respectively.

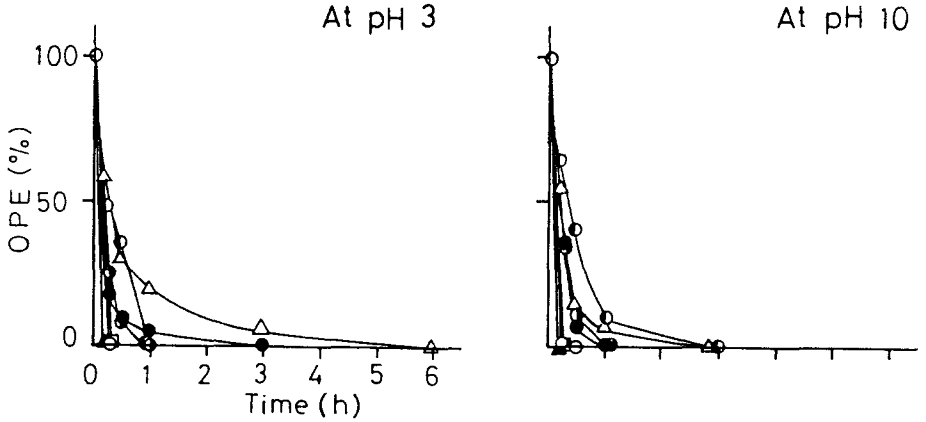

Figure 1 Degradation of OPEs at pH 3 and 10. Each OPE concentration is 0.1 mg/L, ○ TBP, ● TCPP, ◑ TCEP, ◐ TOP, △ CRP, ▲ TPP, □ TCP.

A 50-mL portion of each subsample withdrawn during the study was saturated with NaCl. The OPE was extracted with two 10-mL portions of dichloromethane. The extracts were combined. The combined extract was dried over anhydrous Na_2SO_4, concentrated until almost dry, reconstituted to 2 mL with acetone, and analyzed by GC.

One gram of K_2CO_3 was added to the second 50-mL portion of the subsample, and 1 mL of acetic anhydride was added to the solution and thoroughly mixed at room temperature. After a few minutes, the acetylated compounds and other compounds were extracted with 5 mL of hexane, and the hexane layer was analyzed by GC or GC-MS (Krijgsman and Kamp 1977).

RESULTS AND DISCUSSION

Figure 1 shows the disappearance curves of each OPE at the concentration of 0.1 mg/L at pH 3 and 10. The concentration of each OPE decreased exponentially with time, and the rate of OPE disappearance was represented by a first-order

$$-d[OPE]/dt = k\ [OPE]$$

process. The values of the pseudo-first-order rate constant k of TBP, TCPP, TCEP, TOP, CRP, TPP, and TCP determined from the plot of data points(in $[OPE]/[OPE]_0$ vs. time) were >15, 2.3, 5.1, 3.0, 0.73, >40, and >20 h^{-1} at pH 3 and >10, 4.5, 4.1, 1.5, 1.6, >40, and >15 h^{-1} at pH 10, respectively. Aryl phosphates, TPP and TCP, which had large molar extinction coefficients in the range of 230-280 nm due to the benzene ring were more degradable than the other OPEs.

All OPEs, especially chloroalkyl phosphates, became more degradable at pH 3 and 10 than without pH adjustment. The degradation of TCEP, CRP, TPP, and TCP at pH 10 may involve the hydrolysis with NaOH (Ishikawa et al. 1985b).

Although the substrate disappearance was relatively fast, it is necessary to clarify the degradation process, particularly with regard to toxic-substance formation. Therefore, the UV irradiation of OPEs at high concentration (3×10^{-4} mole/L) was performed without pH adjustment or at initial pH 12, and the photodecomposition products were identified.

Phosphoric acid, Cl^- ion, and phenols were produced, and the pH value decreased with the decrease in the OPE concentration. The changes of each item are shown in Figure 3. At a high OPE concentration of 3×10^{-4} mole/L, the degradation of OPE was delayed. The times of 80% OPE disappearance were <3 h for TBP, TCEP, CRP, TPP, and TCP and <4 h for TCPP. TOP was hardly degraded. At pH 12, the disappearance rate of OPE, except for TOP, was equal or faster than without pH adjustment.

The rate of PO_4^{3-} ion production by photohydrolysis was

Table 1. Changes of each item after 6 h of irradiation.

	OPE						
Item	TBP	TCPP	TCEP	TOP	CRP	TPP	TCP
Without pH adjustment							
Reacted OPE(%)	100	94	100	50	100	100	100
pH	3.7	3.0	2.8	5.6	2.9	3.4	3.6
PO_4^{3-}(%)*	14	26	64	4	27	60	66
Cl^-(%)*	-	58	68	-	59	-	-
Phenols(%)*	-	-	-	-	-	0	0
At initial pH 12							
Reacted OPE(%)	98	97	100	31	100	100	100
PO_4^{3-}(%)	22	18	35	2	12	60	74
Cl^-(%)	-	77	60	-	64	-	-
Phenols(%)	-	-	-	-	-	9	1

* Ratio of number of PO_4^{3-} ion, Cl^- ion, and phenols produced for initial number of P atom, Cl atom, and benzene ring, respectively.

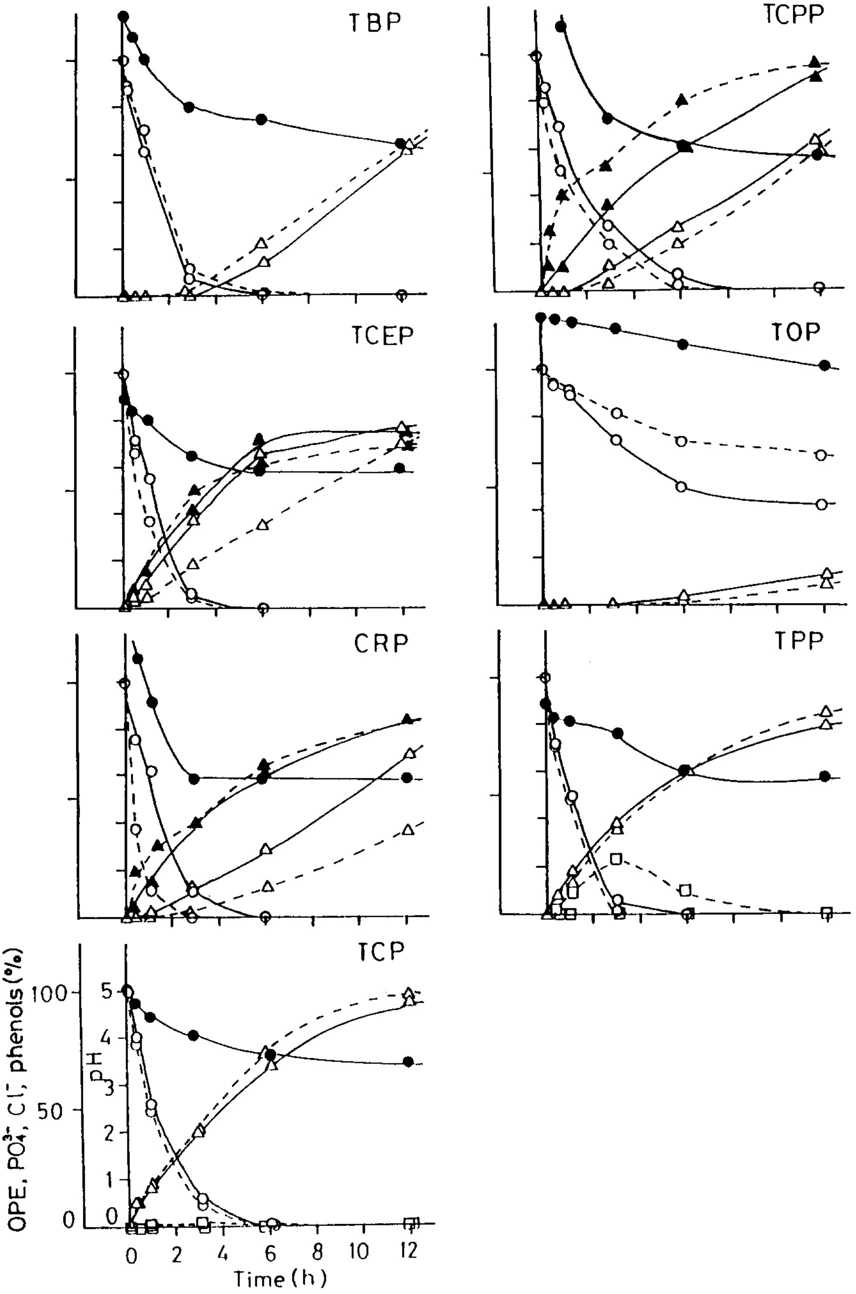

Figure 2 Changes of each item during UV irradiation with a low-pressure mercury lamp. Each OPE concentration is 3 x 10^{-4} mole/L, ○ OPE, ● pH, △ PO_4^{3-}, ▲ Cl^-, □ phenols, — without pH adjustment, ---- at initial pH 12.

different among chloroalkyl and aryl phosphates in spite of the same disappearance rate of each OPE. For chloroalkyl phosphates, the amount of PO_4^{3-} ion produced under alkaline condition was also less than under acidic condition. This would be caused by the difference of stability of each intermediate for photohydrolysis in both conditions. The formation of PO_4^{3-} ion and Cl^- ion led to the decrease of pH value.

About 23% and 2% of phenols(as phenol) were produced after 3-h irradiation for TPP and TCP, respectively, under alkaline condition. The produced phenols were decomposed by further irradiation. Though same amount of PO_4^{3-} ion was produced by photohydrolysis under acidic condition as well as alkaline condition, little amount of phenols was detected during the irradiation. Then, the reaction of benzene ring would have been faster than the production of phenols under acidic condition. These phenols were identified by GC-MS after acetylation. As the TOC value was not changed and IC was not detected during the irradiation in all experiments, all OPEs were not converted into CO_2 or other volatile low-molecular-weight carbon compounds. Colors of the 6-h irradiated solutions of TPP and TCP became yellowish under acidic and alkaline conditions. A grayish black deposit and a yellow deposit were also produced under acidic condition, for TPP and TCP, respectively. Table 1 shows changes of each item after 6-h irradiation.

REFERENCES

American Public Health Association, American Water Works Association, Water Pollution Control Federation(1975) Phosphate. In: Standard Methods(14th). American Public Health Association, Washington, p 481-482

Grosby DG, Hamadmad N(1971) The photoreduction of pentachlorobenzene. J Agr Food Chem, 19:1171-1174

Environmental Health Bureau(1978a) Chlorine ion. In: Testing Methods for Water Supply. Japanese Society of Water Supply, Tokyo, p 334-338

Environmental Health Bureau(1978b) Phenols. In: Testing Methods for Water Supply. Japanese Society of Water Supply, Tokyo, p 449-454

Ishikawa S, Shigezumi K, Yasuda K, Shigemori N(1985a) Determination of organic phosphate esters in factory effluent and domestic effluent. Japan J Water Pollut Res, 8: 529-535

Ishikawa S, Shigezumi K, Yasuda K, Shigemori N(1985b)

Behaviors of organic phosphate esters in several water treatment processes. Japan J Water Pollut Res, 12: 799-807

Ishikawa S, Taketomi M, Shinohara R(1985c) Determination of trialkyl and triaryl phosphates in environmental samples. Water Res, 19: 119-125

Japan Industrial Standards Committee(1986) Testing methods for industrial wastewater. In: Japanese Industrial Standard(K0102). Japanese Standards Association, Tokyo

Krijgsman W, Kamp CGVD(1977) Determination of chlorophenols by capillary gas chromatography. J Chromatog, 131: 412-416

Office of Health Studies(1977) Chemicals in the environment In: The Report of Environmental Survey of Chemicals in 1976. Environmental Agency, Tokyo

Tachikawa R, Wakimoto T, Okada K(1975) Water pollution by organic phosphate ester plasticizers and flame retardants. In: JSWPR Symposium Series(No. 9). Japan Society on Water Pollut Res, Tokyo, p 7-12

Tissot A, Boule P, Lemaire J(1984) Photochemistry and environment(7): the photohydrolysis of chlorobenzene. Chemosphere, 13: 381-389

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