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Reaction of Organic Phosphate Esters with Chlorine in Aqueous Solution

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Recently, organic chlorides which are produced during chlorination in drinkingwater supply treatment or wastewater treatment are becoming a world-wide problem. Some chlorination products have been identified(Bellar et al. 1974; Ishikawa et al. 1986; Pereira et al. 1973; Rook 1974; Sakurai and Sawamura 1983; Sayato et al. 1982) and their toxicity have been also confirmed(Kada and Ishidate 1981), but it is aspected that there would be much of other toxic products. Therefore it is necessary to examine the chlorination of organic pollutants and chemicals which exist in natural waters or wastewaters.

Organic phosphate esters(OPEs) are widely used as plasticizers, industrial hydraulic fluids, and lubricant additives and several kinds of OPEs have been detected in environmental waters, sediments(Ishikawa et al. 1985b), industrial wastewaters, and domestic wastewaters(Ishikawa et al. 1985a). Then we are interested in the behaviors of OPEs, a kind of chemicals, during chlorination in water treatments. We studied on the reactions of 7 OPEs, which had ever been detected, with chlorine in aqueous solution.

MATERIALS AND METHODS

Seven OPEs were purchased from Tokyo Chemical Co. Japan. Tributyl phosphate(TBP), Tris(2-chloroethyl) phosphate (TCEP), trioctyl phosphate(TOP) and tricresyl phosphate (TCP) were purified by distillation under reduced pressure. Tris(chloropropyl) phosphate(TCPP) and Tris(dichloropropyl) phosphate(CRP) were used without further purification. Triphenyl phosphate(TPP) was purified by zone refining. The purity of these OPEs was checked by gas chromatography(GC) and gas chromatograph /mass spectrometry(GC/MS). The TCP was a

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mixture of isomers. Aqueous solution of OPEs was prepared, dissolving OPEs in purified water by vigorously shaking for 1 hr. Standard solutions were prepared in acetone. The water was purified using a Yamato, Model WA-715, auto-still equipped with filter, distiller and ion exchanger.

GC analyses were conducted on a Nihon Denshi, Model JGC-20K, GC equipped with a flame photometric detector (FPD) having a 526 nm filter and with nitrogen as the carrier gas at a flow rate of 20 ml/min. The 2 m x 2 mm glass column was packed with 2% OV-17 + 2% PZ-179 on Uniport HPS, 60-80 mesh. The column temperature was programmed from 200 to 300 °C at 10 °C/min for quantitation and varied from 210 to 300°C depending on the OPE for the identification of chlorination products. The injector and the detector temperatures were 300 °C.

GC/MS analyses were performed on a Nihon Denshi, Model JGC-20KP/JMS-01SG-2, GC/MS. The carrier gas was helium at a flow rate of 20 ml/min. The other GC conditions were the same as above described. The ionizing energy was 75 eV.

Chlorine was prepared from calcium hypochlorate and hydochloric acid, and dissolved in purified water. The chlorine concentration was determined iodometrically (Japan Society of Sewerage 1974).

The mixed solution of OPEs(each OPE 0.1 mg/l) and chlorine(3-1000 mg/l) which had been adjusted at each pH with hydrochloric acid or sodium hydroxide was stirred in a 500 ml of stoppered flask in the dark at 20 °C. Forty milliters of the sample was withdrawn periodically, dechlorinated with sodium sulfite and adjusted at pH 5 with hydrochloric acid or sodium hydroxide. The remaining OPEs were extracted with two 10 ml portions of dichloromethane from the solution. The extracts were combined, dried over anhydrous sodium sulfate, concentrated until almost dry, filled up to 1 ml with acetone and then analyzed by GC or GC/MS. The blank test was performed in the same way without a addition of chlorine.

RESULTS AND DISCUSSION

Figure 1 shows the decreasing ratio of OPE vs. pH at 100 mg/l of chlorine concentration after 24 hr. TOP, TPP and TCP decreased in all pH ranges, especially under strongly acidic and strongly alkaline conditions. Under alkaline conditions, OPE degradation involves a hydrolysis with sodium hydroxide, which was confirmed by the blank test(Figure 2). But the reactions of TOP,

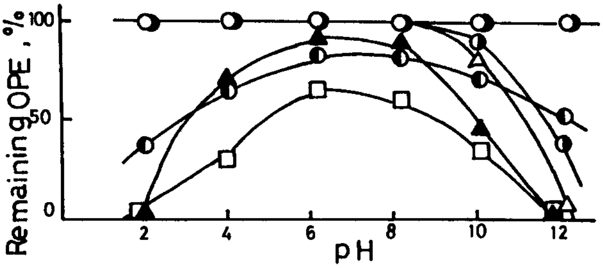

Figure 1. Effect of pH on the chlorination. Chlorine 100 mg/l, reaction time 24 hr, each OPE 0.1 mg/l, -○- TBP, -●- TCPP, -◑- TCEP, -◐- TOP, -△- CRP, -▲- TPP, -□- TCP.

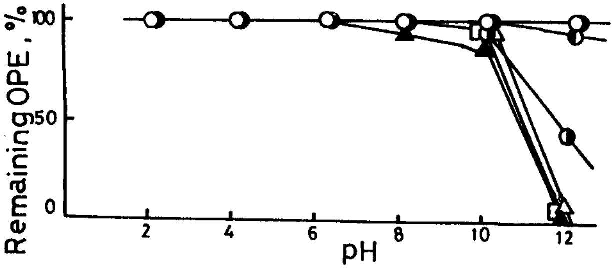

Figure 2. Degradation of OPEs with HCl or NaOH. Reaction time 24 hr, each OPE 0.1 mg/l, -○- TBP, -●- TCPP, -◑- TCEP, -◐- TOP, -△- CRP, -▲- TPP, -□- TCP.

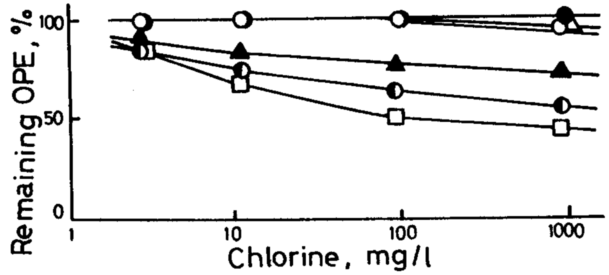

Figure 3. Relationship between OPE decrease and chlorine concentration at pH 7. Reaction time 24 hr, each OPE 0.1 mg/l, -○- TBP, -●- TCPP, -◑- TCEP, -◐- TOP, -△- CRP, -▲- TPP, -□- TCP.

TPP and TCP with chlorine were also proceeded in alkaline media because the decreasing ratio of TOP at pH 12 was about 10 times as that of sodium hydroxide hydrolysis at the same pH and because some chlorinated compounds were produced in all pH ranges as later described. The equibirum equation of chlorine in water is shown in equation 1. Almost of chlorine is existed in the form of HOCl at a pH below 6(Isomura 1971). The

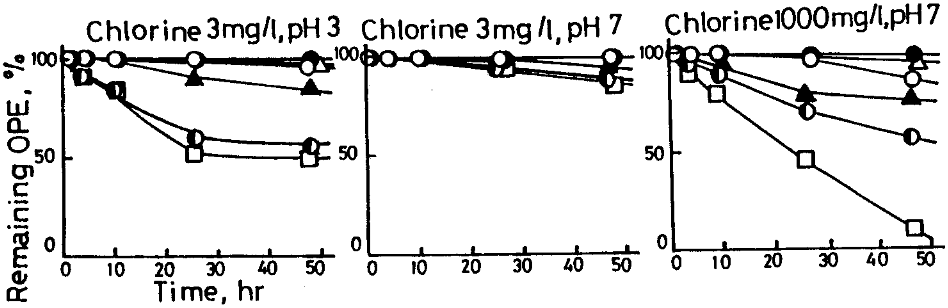

Figure 4. Degradation of OPEs at 3 mg/l and 1000 mg/l of chlorine concentration. Each OPE 0.1 mg/l, −○− TBP, −●− TCPP, −◑− TCEP, −◐− TOP, −△− CRP, −▲− TPP, −□− TCP.

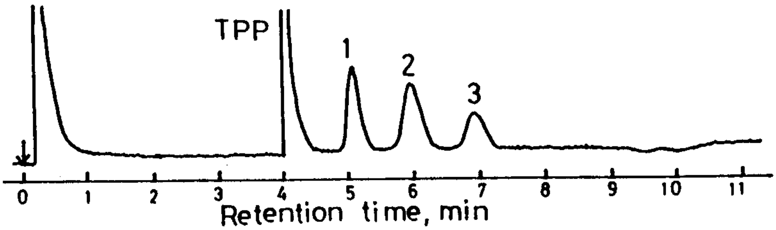

Figure 5. FPD−GC chromatogram of chlorination products of TPP at pH 3. Chlorine 100 mg/l, reaction time 24 hr, TPP 0.1 mg/l, column 2% OV−17 + 2% PZ−179 on Uniport HPS, column temperature 300°C.

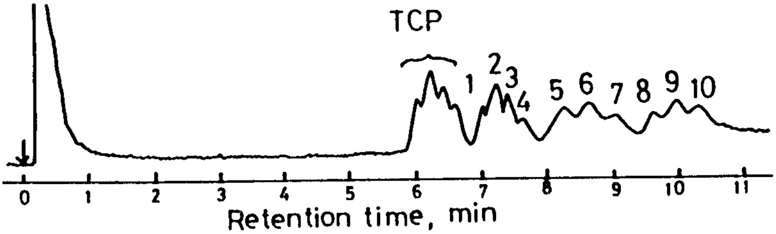

Figure 6. FPD−GC chromatogram of chlorination products of TCP at pH 3. Chlorine 100 mg/l, reaction time 24 hr, TCP 0.1 mg/l, column 2% OV−17 + 2% PZ−179 on Uniport HPS, column temperature 300°C.

decreasing ratios of TOP, TPP and TCP were higher in acidic media because of its strong oxidizing ability. The decreases of TCEP and CRP in alkaline media were mostly caused by sodium hydroxide hydrolysis. TBP and TCPP were stable in all pH ranges.

$$Cl_2 + 2H_2O \rightleftarrows HOCl + H_3O^+ + Cl^- \rightleftarrows OCl^- + H^+ + Cl^- \cdots\cdots(1)$$

The relationship between OPE decrease and chlorine concentration at pH 7 was shown in Figure 3. Even at lower chlorine concentration(3 mg/l) which is a concentration level used in usual disinfection, TOP, TPP and TCP decreased in the ratios of 5, 3 and 5%

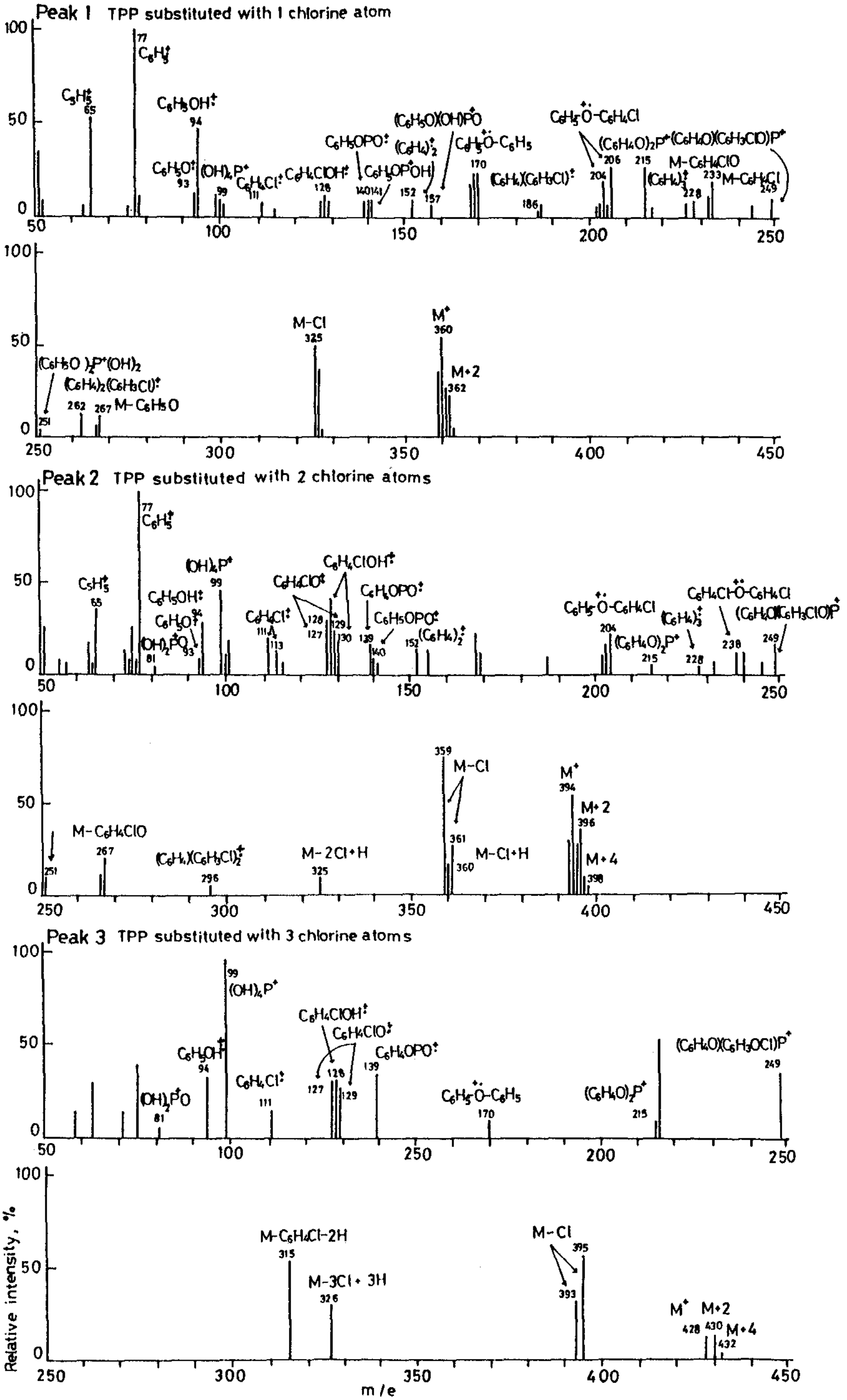

Figure 7. Mass spectra of peaks 1-3 in Figure 5.

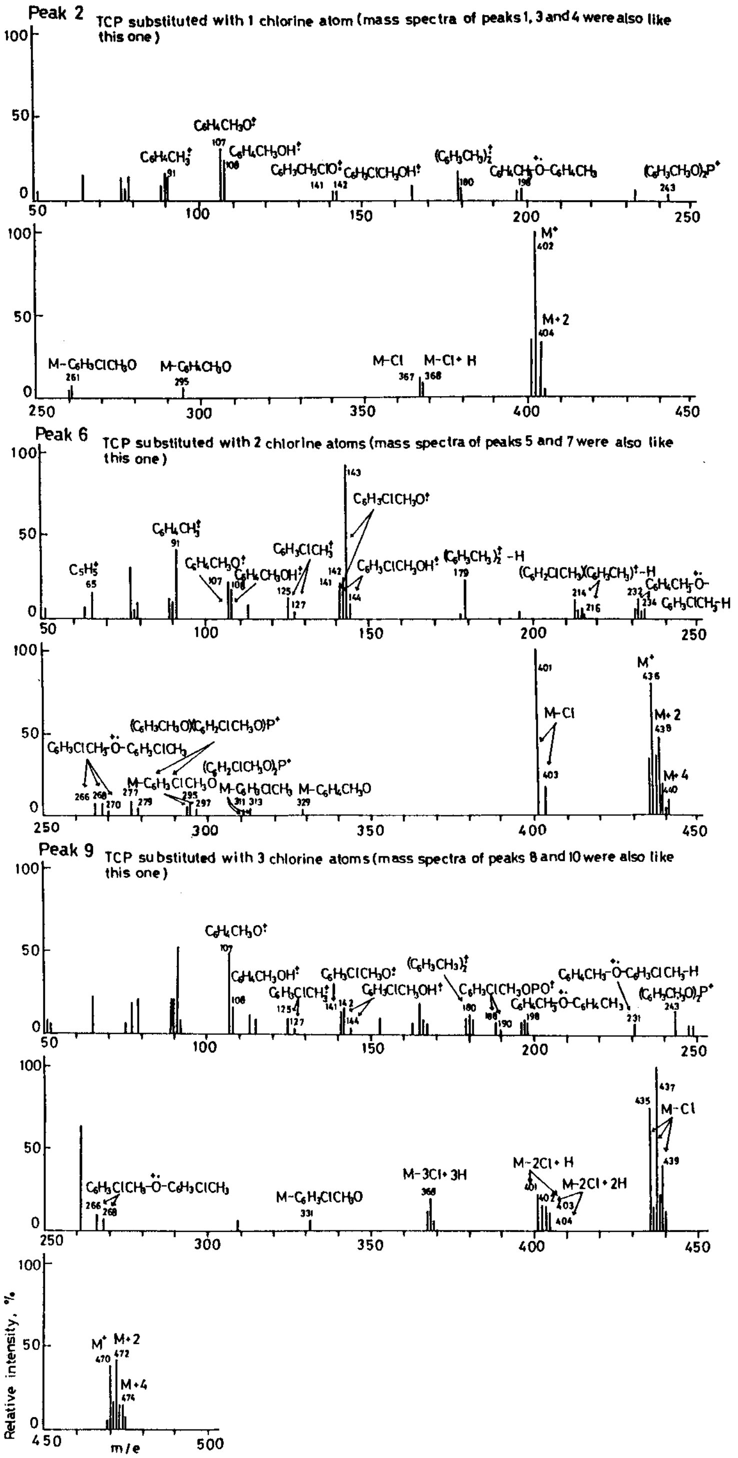

Figure 8. Mass spectra of peaks 1-10 in Figure 6.

vafter 24 hr, respectively.

Figure 4 shows the periodical decrease of OPE under the conditions: chlorine 3 mg/l, pH 3 and 7; chlorine 1000 mg/l, pH 7. At 3 mg/l of chlorine concentration, 50% of TOP, 20% of TPP, and 55% of TCP at pH 3 and 10% of TOP, 5% of TPP, and 15% of TCP at pH 7 decreased after 48 hr. At 1000 mg/l of chlorine concentration and at pH 7, 10% of TBP, 5% of CRP, 35% of TOP, 25% of TPP and 80% of TCP decreased for 48 hr.

In the cases of TPP and TCP, new peaks were observed on each FPD-GC chromatogram after the chlorination(Figures 5 and 6). These peaks were identified by GC/MS. Considering these mass spectra, peaks 1-3 in Figure 5 and peaks 1-10 in Figure 6 would be those of chlorinated TPP and TCP, respectively, which benzene rings were substituted with 1-3 of chlorine atoms. These mass spectra and the estimation of each fragment ion(Budzikiewicz et al. 1973) were shown in Figures 7 and 8. These peaks were higher in acidic region than in the other regions.

REFERENCES

Bellar TA, Lichtenberg JJ, Kroner RC (1974) The occurrence of organohalides in chlorinated drinking waters. J Amer Water Works Assoc 66: 703-706

Budzikiewicz H, Djerassi C, Williams DH (1973) Mass spectrometry of organic compounds. Maruzen, Tokyo

Ishikawa S, Fujino H, Yasuda K, Shigemori N (1986) Products at the reaction of amino acids in aqueous solution with chlorine. Japan J Water Pollut Res 9: 786-792

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

Isomura Y (1971) Chlorination. In: the Editorial Committee of Handbook of Water and Wastewater(ed) Handbook of Water and Wastewater. Maruzen, Tokyo, p 301

Japanese Society of Sewerage (1974) Testing Methods for Sewerage. Maruzen, Tokyo, p 167

Kada T, Ishidate M (1981) Environmental mutagens data book 1. Scientist Inc, Tokyo

Pereira WE, Hoyano Y, Summons RE, Bacon VA, Duffield AM (1973) The reaction of aqueous hypochlorous acids with α-amino acids and dipeptides. Biochemica et Biophysica Acta 313: 170-180

Rook JJ (1974) Formation of haloforms during chlorination of natural waters. Water Treat Exam 23: 234-243

Sakurai E, Sawamura R (1983) The reaction of hypochlorite with glycine(II): the mechanisms of the formation of chloroglycines and their decomposition. Eisei Kagaku 29: 368-375

Sayato Y, Nakamoto K, Matsui S (1982) Studies on mechanism of volatile chlorinated organic compound formation(III): mechanism of formation of chloroform and chloropicrin by chlorination of humic acid. Japan J Water Pollut Res 5: 127-134

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