Formation of polybrominated and polychlorinated alkylphenoxyalkylphenols (PXAPAPs) during aqueous chlorination of 4-alkylphenol solutions in the presence of bromide ion.

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Introduction

Alkylphenols were used widely as industrial materials in the world and these compounds have been concerned typical pollutant in aqueous environment. Alkylphenol polyethoxylates (APEs) are also widely used as surfactant in detergents, pesticides, paints, cosmetics, and so on. Biodegradation of APEs in wastewater treatment plants and formation of alkylphenols during biodegradation processes were reported in the previous study[1]. Therefore, these alkylphenols have been detected in river water and sediment [2-4].

On the other hand, chlorination is used in the water treatment process for pre-oxidation treatment and final disinfection. Formations of chlorinated substances having mutagenicity or other toxicological potentials were reported [5,6]. Since some kinds of river water or underground water contained bromide ion relative high concentration[7] and bromide ion was contaminant of commercially sodium hypochlorite used for disinfection of drinking water[8], formation of brominated substances during chlorination process were also reported in the several investigations[9-11]. It was considered that brominated substances might be more toxic than chlorinated substances[12]. Therefore, formation and fate of brominated by-products during chlorination was investigated[13].

Formations of polychlorinated phenoxyphenols (PCPPs) and alkylphenoxyalkylphenols (PCAPAPs) during aqueous chlorination of phenol and alkylphenol solution were reported in our previous studies[14-16]. PCPPs and PCAPAPs have been concerned as one of the toxic pollutants because these compounds have a mutagenicity and bioaccumulation potential[17, 18]. In addition, their 2-hydroxy isomers called "predioxin" have been shown to undergo both thermal and photochemical ring closure to form polychlorinated dibenzo-*p*-dioxins[19, 20]. We already reported that formations of polychlorinated and polybrominated methylphenoxymethylphenol during aqueous chlorination of methylphenol solution with bromide ion[21]. In this paper, some findings about formation of PXAPAPs during chlorination of 4-alkylphenol solutions with bromide ion were reported.

Materials and methods

4-Alkylphenols (methyl, ethyl, propyl, butyl) were obtained from Tokyo Chemical Industry Co., Ltd. Methanol and n-hexane were of pesticide residue grade and were obtained from Wako Pure Chemical Industries, Ltd. Standard stock solutions were prepared in methanol. Sodium hypochlorite was obtained from Kanto Chemical Co., Inc., and it was diluted with distilled water. The hypochlorite concentration was determined by iodometric titration. One hundred milliliter of aqueous 4-alkylphenol solutions (0.5 mmol l^{-1}) were prepared with various pH (6, 7, 8, 9) using potassium dihydrogenphosphate / sodium tetraborate buffer solution. These solutions also contained the various concentrations of bromide ion prepared from potassium bromide. The 4-alkylphenol buffer solution was treated with 5 equivalent of hypochlorous acid and 0, 0.1, 0.5, 1.0, 5.0, 10 equivalent of bromide ion per mol of compound in a separately funnel at 20℃ for 1 hour with moderately shaking. After reaction, residual active chlorine and bromine were removed by addition of 0.5 mol l^{-1} sodium sulfite. The reacted solution was then acidified to pH 2 with 6 mol l^{-1} hydrogen chloride solution before extraction with 20 ml of n-hexane. This extraction procedure was conducted twice and the organic phases were combined and filtered through anhydrous sodium sulfate. The filtrate was concentrated to 2 ml with a rotary evaporator and a gentle flow of nitrogen gas. PXAPAPs in the

sample were quantified by gas chromatography (GC) and flame ionization detector (FID), and the sample was diluted to one fifteenth for qualify analysis of PXAPAPs by GC mass spectrometry (MS), according to the method described in the previous study[14, 16, 21]. Analytical conditions of GC-FID and GC-MS were shown in table 1.

Table 1. Analytical conditions of GC-FID and GC-MS.

GC-FID (Shimadzu 14B)	GC-MS (Varian CP-3800 Saturn 2200)
Column: ZB-5 (30m x 0.25mm I.D. x 0.25μm Phenomenex)	Column: VF-5ms (30m x 0.25mm I.D. x 0.25μm Varian Factor four)
Oven temp. 80℃(5min hold)→10℃/1min→ 280℃(15min hold)	Oven temp. 80℃(5min hold)→10℃/1min→280℃ (15min hold)
Carrier gas: Helium constant pressure	Carrier gas: Helium constant flow (1ml/min)
Injecter & Detecter temp. 280℃	Injecter temp. 280℃

Results and discussion

In the previous studies[9, 10], it was demonstrated that chlorination of water containing bromide ion produced brominated compounds by the following reactions:

$Br^- + HOCl \rightarrow BrO^- + H^+ + Cl^-$ (1)

Precursor compound + HOBr → brominated compounds (2)

Therefore, formation of bromine-substituted alkylphenoxyalkylphenol (APAPs) was easily expected to occur during chlorination of 4-alkylphenol solutions containing bromide ion. In actually, productions of PXAPAPs were confirmed each 4-alkylphenol solutions treated with chlorine under various pH and bromide concentrations. Number of substituted chlorine and bromine atoms ranged one to four. Relative large amounts of polyhalogented methylphenoxymethylphenol in the hexane extract were detected in weak alkaline solution comparing with weak acidic conditions. This tendency was similar to the previous study[21] and it was also observed in the hexane extracts obtained from other 4-alkylphenol solutions treated with chlorine in this study.

Formations of bromine-substituted APAPs were observed treatment with 0.1 equivalent of bromide ion per mol of 4-alkylphenols. Number of bromine atom substituted increased as the amount of co-existence bromide ion, and many kinds of PXAPAPs formed treatment with one equivalent of bromide ion per mol of 4-alkylphenols. When the amounts of co-existence bromide ion increased more than one equivalent of bromide ion per mol of 4-alkylphenols, number of bromine atom substituted APAPs increased whereas those of chlorine-substituted APAPs decreased.

Formations of polybrominated and polychlorinated 2-phenoxyphenols (predioxin) were observed on GC-MS total ion chromatogram during aqueous chlorination of methylphenol with bromide ion similar to our previous study[21]. In other previous study[16], polychlorinated 2-phenoxyphenols were detected in 4-ethylphenol solutions after treatment with chlorine. In this study, we found that polybrominated and polychlorinated 2-phenoxyphenols formed by chlorination of 4-ethylphenol solutions with bromide ion. GC retention times and mass spectra of PXAPAPs including predioxins at pH 7 and one equivalent bromide ion per mol of 4-ethylphenol, were described in Table 2. The mass spectra of the compound corresponding to peak 1 gave the molecular ion (M^+) at m/z 242 (no halogen atom) and several fragment ions, suggesting this

compound to be ethylphenoxyethylphenol[16]. The compounds corresponding to the peak 3, 5, 8 and 11 gave the characteristic fragment ion at m/z 174 (two chlorine atoms) in indicative of a 2-phenoxyphenol (predioxin), since the hydrogen transfer rearrangement from the hydroxy group to the nearest aromatic ring is typical fragmentation of an ortho hydroxy ether[22] The compounds corresponding to the peak 10 and 12 also gave the characteristic fragment ion at m/z 218 (one chorine and one bromine atom) in indicative of predioxin. PXAPAPs of peak 10 and 11 gave the same molecular ion (M^+) at m/z 388 (two chlorine atoms and one bromine atom) and these predioxins might be isomer. The chemical structures of these two predioxins were estimated from mass fragmentation pattern and these were shown in Fig.1. As the result of GC-MS analysis, six kinds of polybrominated and chlorinated predioxins in hexane extracts were observed and numbers of substituted halogen atoms in these predioxins were two or three (Table 2).

Table 2. GC retention times and mass spectral data for PXAPAPs formed during reactions of 4-ethylphenol with chlorine in water containing one equivalent of bromide ion per mol of 4-ethylphenol at pH 7 and 20℃ for 1hour.

Peak No.	R.T.	Number of Cl and Br atoms		Mass flagmentation (m/z, EI-MS)
		Cl	Br	
1	19.290			242 213(-C_2H_5) 185(-C_2H_5-CO)
2	20.901	1		276 247(-C_2H_5) 219(-C_2H_5-CO)
3	21.080	2		310 295(-CH_3) 240(-2Cl) 174* 139*
4	21.703		1	320 291(-C_2H_5) 263(-C_2H_5-CO) 235(-C_2H_5-2CO)
5	21.788	1	1	354 339(-CH_3) 313(-CH_3-CO) 240(-ClBr) 174* 139*
6	22.031		1	320 291(-C_2H_5) 212(-C_2H_5-Br)
7	22.493		2	398 383(-CH_3) 240(-2Br) 225(-2Br-CH_3)
8	23.000	3		344 329(-CH_3) 309(-Cl) 274(-2Cl) 174* 139*
9	23.420	1	1	354 325(-C_2H_5) 246(-C_2H_5-Br)
10	23.680	2	1	388 373(-CH_3) 331(-C_2H_5) 309(-Br) 274(-ClBr) 259(-CH_3-ClBr) 218* 139*
11	23.779	2	1	388 373(-CH_3) 309(-Br) 274(-ClBr) 174* 139*
12	24.455	1	2	432 417(-CH_3) 318(-ClBr) 274(-2Br) 218* 139*
13	25.121		3	476 397(-Br) 318(-2Br) 303(-2Br-CH_3)

*The asterisk indicates the characteristic flagment ion of 2-ethylphenoxyphenol (predioxin).

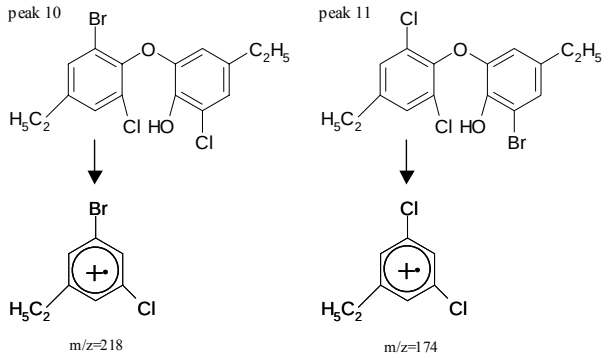

Fig. 1 Estimated structures of monobromodichloroethylphenoxyethylphenol isomers and the characteristic ions.

On the other hand, formations of predioxin during chlorination of 4-propyl and 4-butyl phenol solutions with bromide ion were not observed. However, these solutions included many kinds of unknown compounds might be due to alkyl chain breakage during chlorination. Therefore, it was necessary that the careful examination of mass fragment pattern about these unknown compounds to confirm whether formations of predioxins were occurred or not.

Although predioxins have been most concerned among PXPPs and PXAPAPs, the structure of other PXPPs and PXAPAPs are similar to polybrominated diphenyl ethers (PBDEs) used as flame retardants and its metabolite hydroxylated PBDEs. Because these flame retardants and metabolites might distract thyroid hormone action[23], further study is necessary to clarify the structure and formation mechanism of PXAPAPs during aqueous chlorination of alkylphenol solutions with bromide ion.

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