PERGAMON

Chemosphere 46 (2002) 1215–1223

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

Chlorination of bisphenol A in aqueous media: formation of chlorinated bisphenol A congeners and degradation to chlorinated phenolic compounds

Takashi Yamamoto *, Akio Yasuhara

Regional Environment Division, National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki 305-0053, Japan

Received 11 December 2000; received in revised form 31 August 2001; accepted 18 September 2001

Abstract

The chlorination of bisphenol A (BPA) in aqueous media was investigated in order to describe the degradation profile of this compound and the formation of chlorinated products. Aqueous solutions of BPA (approx. 1 mg/l) were chlorinated by sodium hypochlorite solution at room temperature and under weakly alkaline conditions. Chlorinated compounds were extracted with dichloromethane and determined by gas chromatography/mass spectrometry (GC/MS). BPA was consumed completely within 5 min of chlorination, when the initial chlorine concentration was 10.24 mg/l (molar ratio to BPA, 58.7). On the other hand, when the initial chlorine concentration was 1.03 mg/l (molar ratio, 6.56), 9.3% of BPA still remained after 60 min chlorination. Five chlorinated BPA congeners, 2-chlorobisphenol A (MCBPA), 2, 6-dichlorobisphenol A (2, 6-D_2CBPA), 2, 2′-dichlorobisphenol A (2, 2′-D_2CBPA), 2, 2′,6-trichlorobisphenol A (T_3CBPA) and 2, 2′, 6, 6′-tetrachlorobisphenol A (T_4CBPA) were formed in the earlier stages of chlorination. Several chlorinated phenolic compounds, 2, 4, 6-trichlorophenol (T_3CP), 2, 6-dichloro-1, 4-benzoquinone (D_2CBQ), 2, 6-dichloro-1, 4-hydroquinone (D_2CHQ), $C_9H_{10}Cl_2O_2$, $C_9H_8Cl_2O$ and $C_{10}H_{12}Cl_2O_2$, were also formed by further chlorination.

Keywords: Bisphenol A; Chlorination; Chlorinated bisphenol A congeners

1. Introduction

Bisphenol A (BPA) is used in the manufacture of polycarbonate and epoxy resins. It is also used as stabilizer or antioxidant for many types of plastics such as polyvinyl chloride (PVC) (Ash and Ash, 1995). Annual production of this compound in Japan was about 250,000 tons in 1996 (Ministry of International Trade and Industry of Japan, 1997). Since the recent recognition that BPA possesses weak estrogenic properties (Krishnan et al., 1993), many studies have been done to estimate human exposure and environmental concentrations of the compound. BPA migrates at ppb levels from polycarbonate products (Krishnan et al., 1993) or the epoxy coating on cans (Brotons et al., 1995) to water during thermal processes. BPA also migrates from PVC hoses to water at room temperature and at neutral pH (Yamamoto and Yasuhara, 2000). Concentrations of BPA of 4.0–1730 μg/l were found in water after exposure to PVC hoses for 24 h. Moreover, water that had only passed through a PVC hose was contaminated with BPA at ppb levels. These plastic-to-water migrations are thought to be a significant source of human exposure. BPA that has migrated from plastics to tap water may react with residual chlorine in the tap water that had been added as a disinfectant. As far as the environmental occurrence of BPA is concerned, hazardous waste landfill

* Corresponding author. Tel.: +81-298-50-2547; fax: +81-298-50-2570.

E-mail address: tyama@nies.go.jp (T. Yamamoto).

0045-6535/02/$ - see front matter
PII: S0045-6535(01)00198-9

site leachates (Yasuhara et al., 1997, 1999; Yamada et al., 1999; Yamamoto et al., 2000) or sewage treatment plant effluents (Lee and Peart, 2000) are thought to be significant sources. Several landfill leachates were found to be contaminated by BPA at ppm levels and effluents from these landfills were still contaminated at ppb levels. Some of these landfill sites and sewage treatment plants have chlorinating disinfection facilities and landfill leachates or sewage effluents are chlorinated before being discharged. Although human exposure to, and environmental contamination with, BPA are closely related to chlorination processes, the chlorination reactions of BPA in aqueous media are not well described. Therefore, we carried out experiments on the chlorination of BPA in aqueous media to investigate the products of BPA chlorination and their degradation profiles.

2. Experimental

2.1. Materials and reagents

BPA was purchased from Wako Pure Chemicals (Japan). 2, 4, 6-Trichlorophenol (T_3CP), 2, 2′, 6, 6′-tetrachlorobisphenol A (T_4CBPA) were of technical grade and from Tokyo Chemicals (Japan). BPA-d_{16} was of environmental analytical grade (Wako). Dichloromethane, acetone, sodium chloride, and anhydrous sodium sulfate were of pesticide analysis grade (Wako). Hydrochloric acid and sodium thiosulfate were of reagent grade (Wako). Sodium hypochlorite solution (5% available chlorine) was purchased from Kanto Chemicals (Japan). Purified water used in experiments was made by a MilliQ water purification system (Waters, US). The BPA spike solution was prepared by dissolving 50 mg of BPA in 50 ml of acetone. The surrogate compound solution was prepared by dissolution of BPA-d_{16} in acetone. For preparing stock solutions for calibration, 50 mg each of BPA, T_4CBPA and T_3CP were dissolved in 50 ml of acetone. A series of calibration solutions (0.001–10 ng/μl for each compound) was prepared by dilution of the stock solution with acetone followed by spiking of the surrogate solution. Sodium hypochlorite solution was diluted with purified water before being used and available chlorine was determined by iodometric titration.

2.2. Chlorination procedure of BPA

The acetone solution of BPA (500 μl) was placed in a glass bottle which was then heated to evaporate the

Table 1
Levels of BPA and chlorination products from various chlorination conditions

Initial Cl[a] (mg/l)	Reaction time (min)	Residual Cl (mg/l)	Residual Cl (μmol/l)	BPA (μmol/l)	T_4CBPA (μmol/l)	T_3CP (μmol/l)	2-M[b] (μmol/l)	2, 6-D_2[b] (μmol/l)	2, 2′-D_2[b] (μmol/l)	2, 2′, 6-T_3[b] (μmol/l)
1.03 (29.2)	0	–		4.45	N.D.[c]	N.D.	N.D.	N.D.	N.D.	N.D.
	5	0.61	17.2	2.97	0.01	0.005	0.94	0.19	0.22	0.10
	15	0.43	12.1	1.26	0.11	0.008	0.98	0.39	0.31	0.36
	30	0.31	8.74	1.28	0.20	0.014	1.02	0.44	0.33	0.70
	60	0.13	3.77	0.41	0.31	0.021	0.56	0.27	0.18	0.62
2.07 (58.3)	0	–		4.45	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	5	1.18	33.3	0.62	0.25	0.008	0.83	0.41	0.65	0.53
	15	0.80	22.6	0.070	1.38	0.015	0.16	0.12	1.02	1.16
	30	0.58	16.4	0.009	1.70	0.024	0.03	0.02	0.61	0.82
	60	0.22	6.21	N.D.	0.74	0.062	N.D.	N.D.	0.08	0.07
5.12 (144)	0	–		4.91	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	5	2.93	82.7	0.064	0.98	0.014	0.17	0.11	0.39	0.54
	15	2.60	73.3	0.005	1.67	0.039	0.06	0.07	0.05	0.13
	30	2.04	57.5	N.D.	1.04	0.11	0.03	0.04	0.06	0.10
	60	1.61	45.5	N.D.	0.60	0.093	0.02	0.02	0.02	0.04
10.24 (289)	0	–		4.91	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	5	7.90	223	N.D.	0.73	0.022	N.D.	N.D.	0.04	0.13
	15	7.38	208	N.D.	0.70	0.029	N.D.	N.D.	N.D.	0.02
	30	7.23	204	N.D.	0.47	0.037	N.D.	N.D.	N.D.	N.D.
	60	5.99	169	N.D.	0.25	0.040	N.D.	N.D.	N.D.	N.D.

BPA = bisphenol A; T_4CBPA = 2, 2′, 6, 6′-tetrachlorobisphenol A; T_3CP = 2, 4, 6-trichlorophenol; 2-M = 2-chlorobisphenol A; 2, 6-D_2 = 2, 6-dichlorobisphenol A; 2, 2′-D_2 = 2, 2′-dichlorobisphenol A; 2, 2′, 6-T_3 = 2, 2′, 6-trichlorobisphenol A.

[a] Molar concentrations (μmol/l) are shown in parentheses.

[b] These congeners are tentatively determined using calibration curves for BPA and T_4CBPA.

[c] N.D.: non detectable; detection limits were 0.002 μmol/l for BPA, 0.005 μmol/l for T_4CBPA, 0.002 μmol/l for T_3CP.

solvent. The bottle was then charged with 500 ml of purified water and allowed to stand for some time to dissolve the BPA (1 μg of BPA per ml water). A predetermined amount of sodium hypochlorite solution was then added to the aqueous BPA solution. Initial concentrations of available chlorine and BPA and the reaction times are listed in Table 1. The reaction temperatures and pHs of the solutions were not especially adjusted, but they ranged from 20 to 25 °C and from 8 to 9, respectively. For the duration of the reaction, the bottle was placed in the dark. After predetermined reaction time, a portion of the chlorinated sample was taken for residual chlorine determination (iodometric titration which was quenched by addition of 0.1 mol/l sodium thiosulfate solution).

2.3. Analysis of BPA and chlorination products

Chlorinated samples (400 ml) were transferred to a separatory funnel. 8 g of sodium chloride were added and completely dissolved. They were then fortified with the surrogate compound solution (1 μg of BPA-d_{16}), and acidified with 1 mol/l of hydrochloric acid. The sample was extracted twice with 50 ml of dichloromethane by shaking for 5 min. The combined extracts were dried over with anhydrous sodium sulfate, evaporated to approx. 5 ml with a rotary evaporator, transferred to a test tube and concentrated to 1 ml under a flow of nitrogen. Each concentrated extract was analyzed by gas chromatography/mass spectrometry (GC/MS) {model 5890II plus (Hewlett Packard, US) GC equipped with a splitless injector (260 °C) and a PTE-5 capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness, Supelco, US)}. Injection volume was 1 μl. Helium was used as the carrier gas with a flow rate of 1 ml/min. The initial column temperature was 60 °C and was raised to 280 °C at a rate of 10 °C/min and then held for 2 min. For quantitative analysis, a model 5972MSD mass spectrometer (Hewlett Packard, US) was operated in selected ion monitoring (SIM) mode. Ionization was by electron ionization (70 eV). The ionization chamber temperature was maintained at 180 °C. Mass numbers of monitored ions were *m/z* 213 for BPA, 351 for T_4CBPA, 196 for T_3CP and 224 for BPA-d_{16}. Dwell time was 50 ms for each channel. For qualitative analysis, the mass spectrometer was operated in scan mode and the scan range was from *m/z* 25 to 500. Scan rate was 1.4 scan/s.

3. Results and discussion

3.1. Degradation of BPA under several different chlorination conditions

Chlorination experiments were carried out with various initial concentrations of available chlorine and for different reaction times. The levels of BPA, T_4CBPA and T_3CP are listed in Table 1. Other chlorination products were not determined because of the lack of standard samples. BPA reacted rapidly in highly chlorinated water. When the initial chlorine concentration was 10.24 mg/l (289 μmol/l, molar ratio to BPA 58.7), BPA disappeared completely within 5 min. When the initial chlorine concentration was 5.12 mg/l (144 μmol/l, molar ratio 29.3), only 1.3% of BPA remained after 5 min and it was not detected after more than 30 min chlorination. In the case of an initial chlorine concentration of 1.03 mg/l (29.2 μmol/l, molar ratio to BPA 6.56), 9.3% of BPA still remained after a reaction time of 60 min. As for the concentrations of the typical chlorination product T_4CBPA that was formed; the dependence on reaction time was quite different at low and high chlorine levels. When the initial chlorine concentration was 10.24 mg/l, the amount T_4CBPA formed decreased with reaction time. On the other hand, when the initial chlorine concentration was 1.03 mg/l, T_4CBPA steadily increased with reaction time. When the initial chlorine concentration was 2.07 and 5.12 mg/l, the T_4CBPA concentration was maximized at 30 and 15 min, respectively. These results suggest that when the initial chlorine concentration is not enough for the amount of BPA, chlorine will be consumed by the formation of chlorinated BPA congeners and chlorination will stop there. When the initial chlorine concentration was 1.03 mg/l, consumption of chlorine in a reaction time of 5 min was 0.42 mg/l (11.9 μmol/l, molar ratio 2.67). Since the molar ratio of consumed chlorine to the initial amount of BPA was below 4, only a small quantity of T_4CBPA was formed. On the other hand, chlorine consumption in a reaction time of 5 min was 2.34 mg/l (66.0 μmol/l, molar ratio 13.5), when the initial chlorine concentration was 10.24 mg/l. In this case, when the molar ratio was larger than 4, further chlorination occurred with decomposition of T_4CBPA. The yields of T_3CP were very small (less than 1% of the initial BPA) through the all experimental conditions. There are two possible reason to explain these results; (i) the reaction path for formation of T_3CP is minor compared with the other degradation

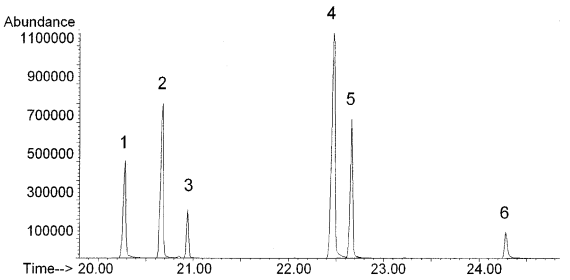

Fig. 1. Total ion chromatogram of chlorinated BPA congeners (initial chlorine concentration 5.12 mg/l, reaction time 5 min).

pathways for T_4CBPA, or (ii) the degradation rate of T_3CP is faster than that of its formation. We cannot on these data decide between these explanations.

3.2. Formation of chlorinated BPA congeners

Several compounds were formed in the earlier stages of the chlorination reaction. The total ion chromatogram of an extract of the chlorinated sample is presented in Fig. 1. Mass spectra of these peaks are shown in Fig. 2. Peak #1 in Fig. 1 may be interpreted as BPA by comparing of its mass spectrum with one of authentic material; peak #6 may be interpreted as T_4CBPA by its chromatographic retention time. Mass spectra of peaks #2 to #5 are very similar to that of BPA The mass numbers of the molecular ions (M^+) of peaks #2 to #5 are 262, 296, 296, 330, respectively. Considering these stepwise increases in mass number and the isomer pattern of M^+, these peaks may be interpreted as chlorinated BPA congeners. Since the chlorination of phenol in aqueous media usually starts at the ortho- or para-position (Burttschell et al., 1959; Onodera et al., 1984), peak #2 may be interpreted as ortho-chlorinated isomer, 2-chlorobisphenol A (MCBPA). In the case of dichlorobisphenol A (D_2CBPA), two isomers, 2, 2′-D_2CBPA and 2, 6-D_2CBPA may be present. These two isomers can be distinguished by specific fragment ions that depend on their structure. The mass spectrum of BPA has a fragment ion at *m*/*z* 119. This fragment ion is assigned to $C_8H_7O^+$ (4-hydroxystyrene radical) formed by

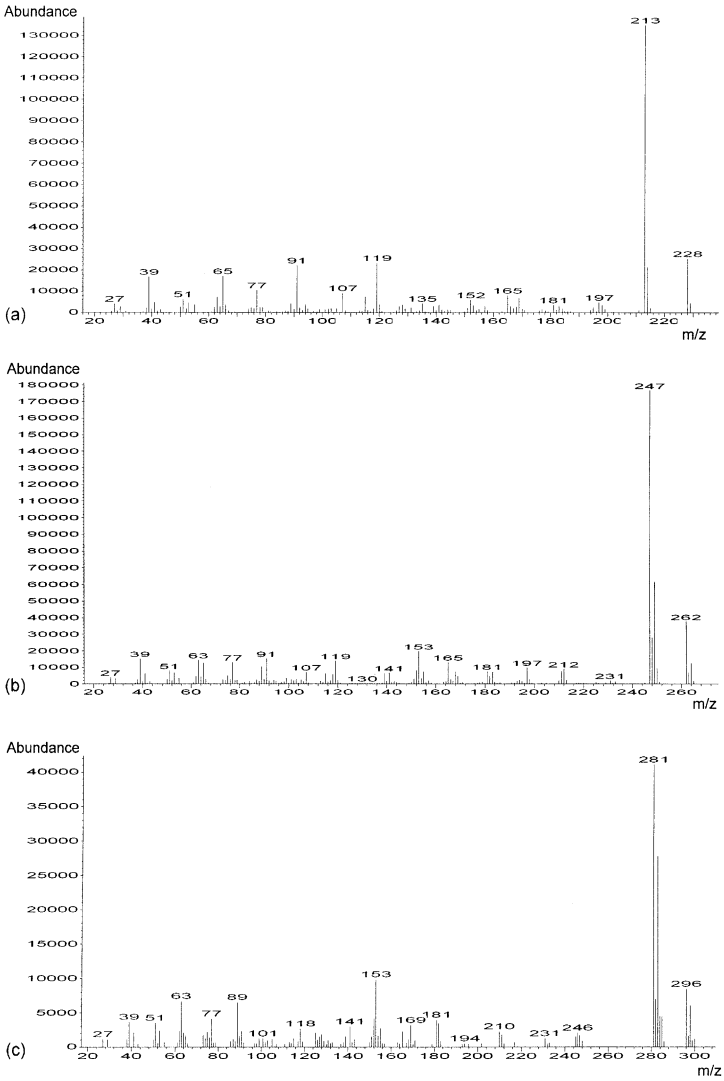

Fig. 2. Mass spectra of chlorinated BPA congeners. (a) BPA (peak #1 in Fig. 1), (b) 2-MCBPA (peak #2), (c) 2, 2′-D_2CBPA (peak #3), (d) 2, 6-D_2CBPA (peak #4), (e) 2, 2′, 6-T_3CBPA (peak #5), (f) 2, 2′, 6, 6′-T_4CBPA (peak #6).

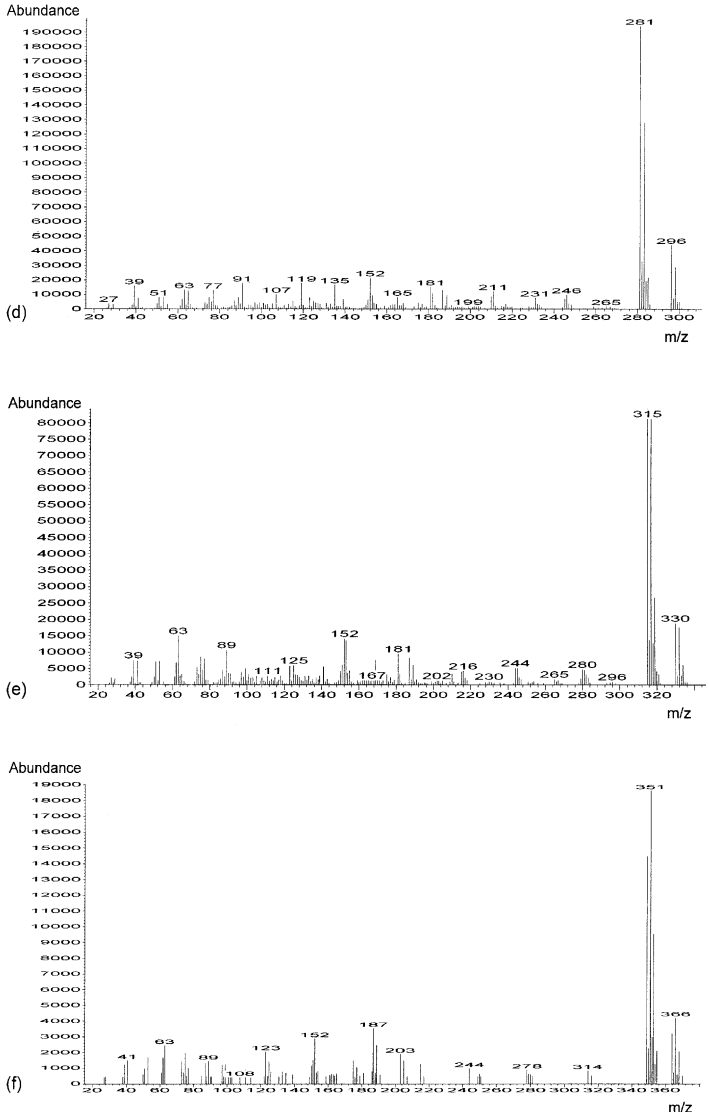

Fig. 2 (*continued*)

cleavage of the isopropylidene chain. The mass spectrum of MCBPA has significant fragment ions at *m*/*z* 119 and 153. The fragment ion *m*/*z* 153 is assigned to $C_8H_6ClO^+$ (3-chloro-4-hydroxystyrene radical). The mass spectrum of T_4CBPA does not have these fragment ions but has another fragment ion at *m*/*z* 187 which can be assigned to $C_8H_5Cl_2O^+$ (3,5-dichloro-4-hydroxystyrene radical). So, the mass spectrum of 2,2′-D_2CBPA should have a fragment ion at *m*/*z* 153 and lack those at *m*/*z* 119 and 187, since each aromatic ring bears one chlorine atom. On the other hand, the mass spectrum of 2,6-D_2CBPA should have fragment ions at *m*/*z* 119 and 187 and lack that at *m*/*z* 153, since one only of its aromatic rings has two chlorine atoms. Therefore, peak #3 may be interpreted as 2,2′-D_2CBPA, since the mass spectrum of peak #3 has a fragment ion at *m*/*z* 153 and no fragment ions at *m*/*z* 119 or 187. Peak #4 also may be interpreted as 2,6-D_2CBPA because of the lack of a fragment ion at *m*/*z* 153 in its mass spectrum. Peak #5 may be interpreted as 2,2′,6-trichlorobisphenol A (T_3CBPA) by a similar interpretation.

The levels of chlorinated BPA congeners which are tentatively determined using calibration curves of BPA and T_4CBPA, are listed in Table 1. When initial chlorine concentration was 1.03 or 2.07 mg/l and reaction time was within 30 min, the sums of the yields of BPA and chlorinated BPA congeners were over 70% of initial BPA. Therefore, if initial chlorine concentration is

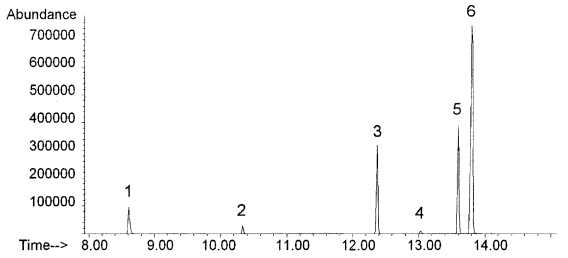

Fig. 3. Total ion chromatogram of cleavage products (initial chlorine concentration 10.24 mg/l, reaction time 5 min).

relatively low to BPA concentration, chlorine will be nearly consumed by formation chlorinated BPA congeners and further chlorination will be stopped.

What environmental impact are these chlorinated BPA congeners likely to give? One of the most interesting and significant properties of these compounds is estrogenicity. Does the estrogenicity of chlorinated BPA congeners increase when compared with the original BPA? Unfortunately, there are no reports about the estrogenicity of chlorinated BPA. Only brominated BPA, $2,2',6,6'$-Tetrabromobisphenol A (T_4BBPA), has been examined for its estrogenic properties. Körner et al.

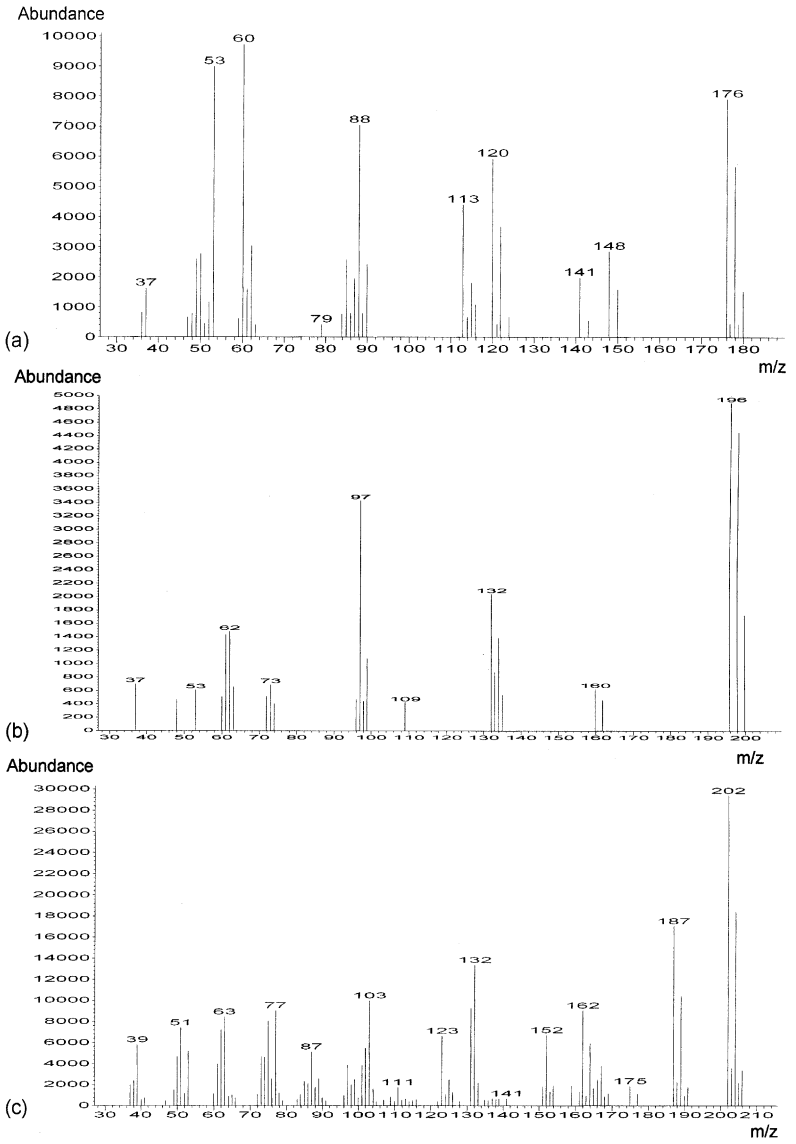

Fig. 4. Mass spectra of cleavage compounds. (a) D_2CBQ (peak #1 in Fig. 3), (b) T_3CP (peak #2), (c) $C_9H_8Cl_2O$ (peak #3), (d) D_2CHQ (peak #4), (e) $C_{10}H_{12}Cl_2O_2$ (peak #5), (f) $C_9H_{10}Cl_2O_2$ (peak #6).

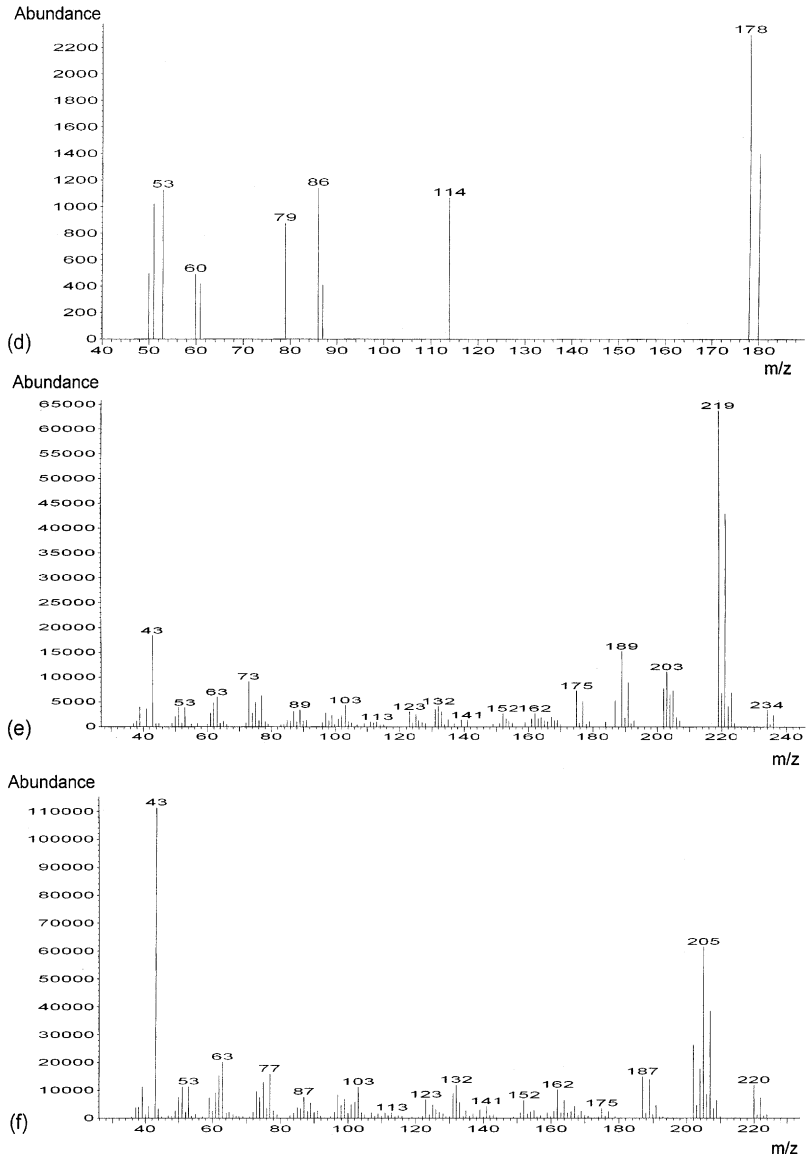

Fig. 4 (*continued*)

(1998) estimated that the estrogenicity of T_4BBPA was 5×10^{-6} times that of 17β-estradiol and about one tenth the estrogenicity of BPA (5×10^{-5}) by E-screen assay. From this result, it can be assumed that halogenation of BPA somewhat weakens its estrogenic properties. As for the acute toxicity of chlorinated BPA, the oral LD_{50} values for T_4CBPA for rats and mice are 7432 and 5050 mg/kg, respectively (National Institute for Occupational Safety and Health, 1987). Although these values are lower than those for BPA (3250 and 2500 mg/kg), there is no reason to disregard these chlorinated BPA congeners since their degree of chlorination may increase with environmental and biological accumulation, as has been observed for other organochlorine compounds.

3.3. Cleavage products of chlorinated BPA congeners

Chlorinated phenolic compounds were formed during the chlorination through the degradation of chlorinated BPA congeners. A typical total ion chromatogram of an extract of a chlorinated sample is shown in Fig. 3. 2, 6-Dichloro-1,4-benzoquinone (D_2CBQ, peak #1), T_3CP (peak #2), 2, 6-dichloro-1, 4-hydroquinone (D_2CHQ, peak #4) are identified by comparing their

mass spectra (Fig. 4(a),(b) and (d)) and retention times with those of authentic standards. Peak intensities of T_3CP, D_2CBQ and D_2CHQ were lower than one of the other products. The mass spectrum of peak #3 is shown in Fig. 4(c). The ion recorded at *m*/*z* 202 may be taken to be M^+. The isomeric pattern of this molecular ion suggest that the molecule from which it is derived has two chlorine atoms. A fragment ion at *m*/*z* 187 is generated by loss of CH_3 and a fragment ion at *m*/*z* 162 may be formed by loss of C_3H_4 from M^+. Since this fragmentation pattern resembles the fragmentation pattern of α-methylstyrene (The National Institute of Standards and Technology, 2000a), the formula of this compound is taken to be $C_9H_8Cl_2O$ (2-(3,5-dichloro-4-hydroxyphenyl)-prop-1-ene). The mass spectrum of peak #5 is presented in Fig. 4(e). The molecular ion is at *m*/*z* 234. A fragment ion appearing at *m*/*z* 219 may be generated by loss of CH_3. The isomeric pattern of this fragment ion indicates that this compound has two chlorine atoms. Since the fragment ion at *m*/*z* 203 is likely to have been formed by loss of CH_3O, this compound may be assumed to possess a methoxy group. The presumed formula of this compound is $C_{10}H_{12}Cl_2O_2$ (2-(3,5-dichloro-4-hydroxyphenyl)-2-methoxypropane). The mass spectrum of peak #6 is shown in Fig. 4(f). The molecular ion appears at *m*/*z* 220. The fragment ion at *m*/*z* 205 may be generated by loss of CH_3. The fragment ion at *m*/*z* 202 is assumed to have been generated by dehydration, and the fragment ion *m*/*z* 162 may be formed by release of C_2H_3O from $(M–CH_3)^+$. This fragment pattern resembles that of 2-phenylpropan-2-ol (National Institute of Standards and Technology, 2000b). Therefore, the presumed formula of this compound is $C_9H_{10}Cl_2O_2$ (2-(3,5-dichloro-4-hydroxyphenyl)-propan-2-ol). Non- or mono-chlorinated phenolic compounds were not found among the all experimental conditions. This result may suggest that T_4CBPA is the only congener cleaved to form chlorinated phenolic products since cleavage of lower chlorinated BPA congeners give non- or mono-chlorinated phenolic compounds. We also could not find cleavage products when the initial chlorine concentration was 1.03 mg/l. This result also suggests that the rate of cleavage of the isopropylidene chain may be much slower than the rate of chlorination of the aromatic ring. Therefore, formation reaction of chlorinated BPA congeners (Cl = 1–4) preceded the cleavage reaction of the isopropylidene chain.

The probable reaction scheme is presented in Fig. 5. BPA is chlorinated stepwise to form mono to tetra-chlorinated congeners. The isopropylidene chain of T_4CBPA was attacked by hypochlorite ion, and then cleaved to form T_3CP and $C_9H_{10}Cl_2O_2$. $C_9H_8Cl_2O$ was formed by dehydration of $C_9H_{10}Cl_2O_2$. $C_{10}H_{12}Cl_2O_2$ was formed by methylation of $C_9H_{10}Cl_2O_2$. We cannot say at this time what drives these dehydration and methylation reactions. D_2CBQ will be formed from

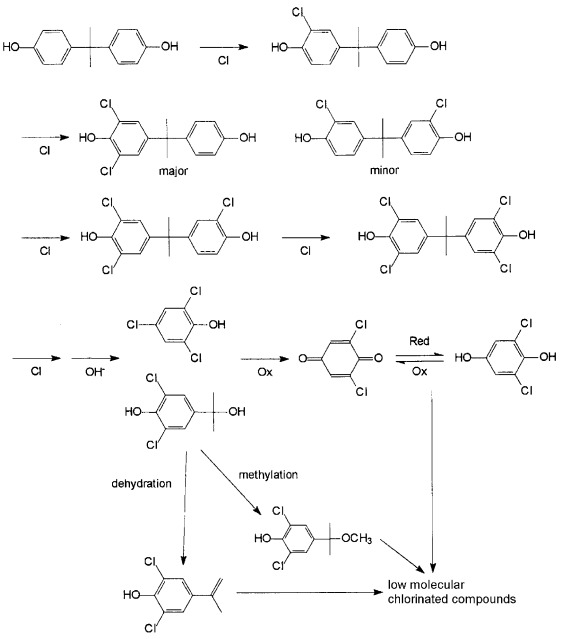

Fig. 5. Presumed chlorination reaction scheme of BPA.

oxidation of T_3CP. D_2CHQ may be present as a result of the redox equilibrium with D_2CBQ. The sums of the yields of these chlorinated phenolic compounds, which were estimated from their peak areas recorded by GC/MS measurements (in scan mode and not quantitative), were not exceeded 10% of initial BPA. Therefore, this scheme may be not stoichiometric and other compounds may exist, which are not detectable by our analytical procedure (solvent extraction – GC/MS determination). For one thing, highly polar compounds and volatile compounds formed from these chlorinated phenolic compounds by further chlorination.

References

Ash, M., Ash, I., 1995. Handbook of Plastic and Rubber Additives. Gower, Hampshire, UK.

Brotons, J.A., Olea-Serrano, M.F., Villalobos, M., Pedraza, V., Olea, N., 1995. Xenoestrogens released from lacquer coatings in food cans. Environ. Health Perspect. 103, 608–612.

Burttschell, R.H., Rosen, A.A., Middleton, F.M., Ettinger, M.B., 1959. Chlorine derivatives of phenol causing taste and odor. J. AWWA 51, 205–214.

Körner, W., Hanf, V., Schuller, W., Bartsch, H., Zwirner, M., Hagenmaier, H., 1998. Validation and application of a rapid in vitro assay for assessing the estrogenic potency of halogenated phenolic chemicals. Chemosphere 37 (9–12), 2395–2407.

Krishnan, A.V., Starhis, P.S., Permuth, F., Tokes, L., Feldman, D., 1993. Bisphenol-A: an estrogenic substance is released

from polycarbonate flasks during autoclaving. Endocrinology 132, 2279–2286.

Lee, H.B., Peart, T.E., 2000. Determination of bisphenol A in sewage effluent and sludge by solid-phase and supercritical fluid extraction and gas chromatography/mass spectrometry. J. AOAC Int. 83 (2), 290–297.

Ministry of International Trade and Industry of Japan, 1997. *Kagaku Kougyo Toukei Nempo*, Tsusho -Sangyo Chosa-Kai, Tokyo, Japan (in Japanese).

National Institute for Occupational Safety and Health, 1987. Registry of Toxic Effects of Chemical Substances, 1985–86 ed. Washington.

National Institute of Standards and Technology, NIST Chemistry Webbook, 2000a. (http://webbook.nist.gov/cgi/cbook.cgi?ID = C98839 & Units = SI & Mask = 100).

National Institute of Standards and Technology, NIST Chemistry Webbook, 2000b. (http://webbook.nist.gov/cgi/cbook.cgi?ID = C617947 & Units = SI & Mask = 100).

Onodera, S., Yamada, K., Yamaji, Y., Ishikura, S., 1984. Chemical changes of organic compounds in chlorinated water IX. Formation of polychlorinated phenoxyphenols during the reaction of phenol with hypochlorite in dilute aqueous solution. J. Chromatogr. 288, 91–100.

Yamada, K., Urase, T., Matsuo, T., Suzuki, N., 1999. Constituents of organic pollutants in leachates from different types of landfill sites and their fate in the treatment processes. J. Jpn. Soc. Water Environ. 22, 40–45 (in Japanese).

Yamamoto, T., Yasuhara, A., 2000. Determination of bisphenol A migrated from polyvinyl chloride hoses by GC/MS. Bunseki Kagaku 49 (6), 443–447 (in Japanese).

Yamamoto, T., Yasuhara, A., Shiraishi, H., Nakasugi, O., 2000. Bisphenol A in hazardous waste landfill leachates. Chemosphere 42, 415–418.

Yasuhara, A., Shiraishi, H., Nishikawa, M., Yamamoto, T., Nakasugi, O., Okumura, T., Kenmotsu, K., Fukui, H., Nagase, M., Kawagoshi, Y., 1999. Organic components in leachates from hazardous waste disposal sites. Waste Manage. Res. 17, 186–197.

Yasuhara, A., Shiraishi, H., Nishikawa, M., Yamamoto, T., Uehiro, T., Nakasugi, O., Okumura, T., Kenmotsu, K., Fukui, H., Nagase, M., Ono, Y., Kawagoshi, Y., Baba, K., Noma, Y., 1997. Determination of organic components in leachates from hazardous waste disposal sites in Japan by gas chromatography/mass spectrometry. J. Chromatogr. A 774, 321–332.