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11 *Short Heading: TBBPA and TCBPA Oxidation by FeTPPS*
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26 **ABSTRACT**

27 Tetrabromobisphenol A (TBBPA) and tetrachlorobisphenol A (TCBPA), commercially used
28 halogenated flame retardants, can be found in leachates from landfills, because hydrophobic
29 interactions with humic acids (HAs), major organic components in landfills, result in an increase in
30 their solubility. The oxidation characteristics of TBBPA and TCBPA in the presence of HA were
31 compared using a catalytic system comprised of a combination of
32 iron(III)-tetrakis(*p*-sulfophenyl)porphyrin (FeTPPS) and KHSO₅ that can mimic the enzymatic
33 reactions that occur in landfills. The levels of degradation and dehalogenation of TBBPA and
34 TCBPA at pH 4 were significantly lower than at pH 8, which is a typical pH value for landfill
35 leachates. In the presence of HA at pH 8, 2-hydroxyisopropyl-2,6 -dihalophenols (2HIP-26DXPs)
36 were detected as major byproducts. These compounds are likely produced via the β -carbon
37 scission of the substrates, and their levels decreased with increasing reaction time. The levels of
38 coupling compounds between 2,6-dihalophenols and TBBPA or TCBPA increased with reaction
39 time. The 27% of Br in the degraded TBBPA and 50% of Cl in the degraded TCBPA were
40 incorporated into the HA as a result of catalytic oxidation via the FeTPPS/KHSO₅ system. These
41 results suggest that TCBPA is incorporated into HA more readily than TBBPA. The coupling
42 compounds between HA and halogenated intermediates from TBBPA or TCBPA were assigned by
43 pyrolysis-gas chromatography/mass spectrometry.

44 **Keywords:** Humic acid, tetrabromobisphenol A, tetrachlorobisphenol A, catalytic oxidation,
45 oxidative coupling, iron(III)-5,10,15,20-tetrakis(*p*-sulfonatophenyl)porphyrin.

46

47 **INTRODUCTION**

48 Tetrabromobisphenol A (TBBPA) and tetrachlorobisphenol A (TCBPA), widely used halogenated
49 flame retardants, can function as endocrine disruptors.^[1,2] These compounds are mainly
50 incorporated into epoxy and polycarbonate resins that are used in the manufacture of printed circuit
51 boards for information technology and other electronic equipment.^[3] TBBPA is a commonly used
52 flame retardant, and the chloro analog TCBPA is also used as an additive to a lesser extent.^[3] The
53 leaching of such halogenated flame retardants from wastes derived from the above materials has
54 been reported to be enhanced in the presence of humic acids (HAs) in landfills via hydrophobic
55 interactions.^[4,5] In general, the log K_{OW} values for brominated phenols (e.g., 5.3 for
56 pentabromophenol^[6]) are larger than those for chlorinated phenols (e.g., 4.08 for
57 pentachlorophenol^[7]). Thus, TBBPA (log K_{OW} 4.5 – 5.3^[8]) may be more hydrophobic than TCBPA,
58 while the log K_{OW} value for TCBPA has not been reported. Such differences between TBBPA and
59 TCBPA are related to the degree of hydrophobic interaction with HAs, their mobility and ease of
60 degradation in landfills.

61 HAs in landfills are mainly generated from organic wastes via microbial processes.^[9,10] Oxidative

62 processes with peroxidase enzymes, as well as anaerobic fermentation accompanying by the
63 generation of CH₄, play important roles in the genesis of HAs in landfills.^[11-13] Peroxidases,
64 classified as members of the cytochrome P-450 family, catalyze the demethylation of lignin and the
65 hydroxylation and polymerization of phenols in organic wastes.^[14] In addition, peroxidases catalyze
66 the oxidation of chlorophenols and their oxidation intermediates are incorporated into polymeric
67 structures in HAs via oxidation coupling.^[15] Thus, the incorporation of chlorophenols into HAs can
68 contribute to their immobilization in soils and ultimate detoxification.^[14,15] Such reactions would be
69 expected to occur in landfills, and these processes might lead to the immobilization and/or the
70 detoxification of halogenated flame retardants, such as TBBPA and TCBPA.

71 On the other hand, it is well known that water-soluble iron(III)-porphyrins are capable of
72 catalyzing the oxidation of chlorophenols,^[16-25] and such structures can be regarded as a model of
73 the active center in oxidative enzymes, such as ligninases and peroxidases.^[26] There have been a
74 few reports of the oxidation of bromophenols by the iron(III)-porphyrin catalysts.^[27-29] However, in
75 the oxidation of halogenated phenols, halogen atom substituents on the phenols affect the levels of
76 dehalogenation via the nucleophilic substitution of H₂O to form quinones.^[30] In the present study, to
77 better understand the metabolic pathways related to halogenated flame retardants in landfills, the
78 oxidation characteristics of TBBPA and TCBPA were compared in an iron(III)-porphyrin/KHSO₅
79 catalytic system in the presence of HA.

80

81 MATERIALS AND METHODS

82 Materials

83 The HA sample used in this study was obtained from Shinshinotsu peat soil, as described in a
84 previous report.^[31] The result of a elemental analysis for the prepared HA was as follows: C 54.5%,
85 H 5.35%, N 2.17%, O 35.1%, S 0.66% and ash 2.22%. The FeTPPS was synthesized according to a
86 previous report.^[32] TBBPA and TCBPA (98% purity) were purchased from Tokyo Chemical
87 Industries (Tokyo), and KHSO₅ was obtained as a triple salt, 2KHSO₅·KHSO₄·K₂SO₄ (Merck,
88 Darmstadt, Hessen, Germany).

89 The 2-hydroxyisopropyl-2,6-dibromophenol (2HIP-26DBP) standard, was synthesized, according
90 to the method by Eriksson et al.^[33] The mass spectral data for the silylated 2HIP-26DBP were as
91 follows, m/z [rel. abundance, fragment ions]: 382 [3.4, M⁺], 367 [17.2, (M – CH₃)⁺], 364 [24.6,
92 (M – H₂O)⁺], 349 [62.0, (M – (CH₃)(H₂O))⁺], 270 [30.8, ((CH₃)₂SiOC₃Br₂)⁺], 139 [26.2,
93 ((CH₃)₂SiOC₅H₅)⁺]. For the synthesis of 2-hydroxyisopropyl-2,6-dichlorophenol (2HIP-26DCP),
94 4-isopropylphenol (0.5 mmole), anhydrous FeCl₃ (1 mmole) and *N*-chlorosuccinimide (1.25 mmole)
95 were dissolved in 5 mL of acetonitrile. After stirring vigorously for 10 h at ambient temperature, 20
96 mL of Na₂S₂O₃ (10% aqueous) was added to quench the reaction. The resulting mixture was
97 acidified by adding 10 mL of aqueous 1 M HCl, and the solution then extracted with ethyl acetate.

98 The yellowish extract was washed with aqueous 0.6 M HCl and then water. After dehydrating with
99 anhydrous Na₂SO₄, the solvent was removed by evaporation under reduced pressure. The obtained
100 residue was dissolved in CH₂Cl₂ and purified using a silica gel column with an eluent composed of
101 CH₂Cl₂/*n*-hexane (1/1, v/v). The obtained material was 4-isopropyl-2,6-dichlorophenol (yield 48%).
102 Mass spectral data for the silylated compound were as follows, m/z [rel. abundance, fragment ions]:
103 276 [16.4, M⁺], 261 [59, (M – CH₃)⁺], 183 [41.2, (M – C₄H₇Cl)⁺]. The
104 4-isopropyl-2,6-dichlorophenol (0.24 mmole) was dissolved in 20 mL of CCl₄, and irradiated with
105 UV-light (254 nm) for 5 min. After stopping the irradiation, 100 μL of Br₂ in CCl₄ (626 mM) was
106 added to the mixture, and this solution was then irradiated for an additional 15 min. After standing
107 for 12 h under the dark at ambient temperature, the solvent was evaporated. The obtained residue
108 was dissolved in 200 mL of 0.025 M aqueous NaOH and the solution pH was adjusted to 9 by
109 adding HCl aqueous. After stirring for 3 days in the dark at ambient temperature, the solution was
110 acidified to pH 2 with aqueous HCl and the 2HIP-26DCP in the reaction mixture was extracted with
111 CH₂Cl₂. After removing the CH₂Cl₂ by evaporation, the residue was collected (yield 23%). Mass
112 spectral data for the silylated 2HIP-26DCP were as follows, m/z [rel. abundance, fragment ions]:
113 292 [6.08, M⁺], 274 [33.7, (M – H₂O)⁺], 259 [73.4, (M – (H₂O)CH₃)⁺], 219 [11.4, (M – (CH₃)₃Si)⁺],
114 183 [54.4, (M – (CH₃)₃Si(HCl))⁺].

115

116 **Test for TBBPA and TCBPA Degradations**

117 A 2 mL aliquot of 0.02 M citrate/phosphate buffer, containing 50 μM TBBPA or TCBPA, 0 or 50
118 mg L^{-1} HA and 0.05 – 5 μM FeTPPS at pH 4 or 8, was placed in a 20-mL L-shaped glass tube.
119 Subsequently, 25 μL of 0.01 M aqueous potassium monopersulfate (KHSO_5) was added, and the
120 tube was then subjected to shaking at 25 $^\circ\text{C}$ in an incubator. After the reaction, 1 mL of 2-propanol
121 was added to the reaction mixture and a 20- μL aliquot of the resulting solution was injected into a
122 PU-980 type HPLC pumping system (Japan Spectroscopic Co.). The mobile phase consisted of a
123 mixture of 0.08% aqueous H_3PO_4 and methanol (22/78 for TBBPA, 25/75 for TCBPA, v/v), and the
124 flow rate was set at 1 mL min^{-1} . A 5C18-MS Cosmosil packed column (4.6 mm id \times 250 mm,
125 Nacalai Tesque) was used as the solid phase, and the column temperature was maintained at 50 $^\circ\text{C}$.
126 The UV absorption of TBBPA or TCBPA was measured at 220 nm. Bromide or chloride ions in the
127 reaction mixture were analyzed by an ion chromatography.

128

129 **Analysis of Oxidation Intermediates**

130 The catalytic oxidation system, described above, was scaled up to 25 mL at pH 8. After reaction
131 periods of 1-, 5-, 10- or 30-min, 1 mL of aqueous, 1 M ascorbic acid was added, and the pH of the
132 solution was adjusted to 11–11.5 by adding aqueous K_2CO_3 (600 g L^{-1}). Subsequently, 5 mL of
133 acetic anhydride was added dropwise to the solution, and 0.5 mL of a 1 mM anthracene solution in

134 hexane/acetone mixture (1/1, v/v) was added as an internal standard (ISTD) for the GC/MS analysis.
135 This mixture was doubly extracted with 15 mL of *n*-hexane, and the extract was then dried over
136 anhydrous Na₂SO₄. After filtration, the extract was evaporated under a stream of dry N₂, and the
137 residue was dissolved in 0.25 mL of *n*-hexane. A 1 μL aliquot of the extract was introduced into a
138 GC-17A/QP5050 GC/MS system (Shimadzu, Kyoto). A Quadrex methyl silicon capillary column
139 (0.25 mm id × 25 m) was employed in the separation. The temperature ramp was as follows: 65 °C
140 for 1.5 min, 65–120 °C at 35 °C min⁻¹, 120–300 °C at 4 °C min⁻¹ and a 300 °C held for 10 min.

141

142 **Separation and Analysis of HA Fraction**

143 The oxidation of TBBPA or TCBPA in the presence of HA was conducted at pH 4 and 8, resulting
144 in the incorporation of brominated or chlorinated intermediates into the HA. The volume of the
145 initial buffer solution was scaled up to 200 mL. In this experiment, the concentrations of HA and
146 TBBPA or TCBPA were fixed at 100 mg L⁻¹ and 100 μM, respectively. The concentrations of
147 TBBPA or TCBPA in the reaction mixtures before and after the oxidation were determined by
148 HPLC. After a 30-min period, 2 mL of 1 M ascorbic acid and 100 mL of 2-propanol were added to
149 the reaction mixture. The HA fraction was then concentrated and deionized by ultrafiltration
150 through a Millipore YM1 ultrafiltration cellulose membrane (molecular weight cut-off of 1 kDa). In
151 the ultrafiltration system, the concentrated HA fraction was washed twice with 100 mL of pure

152 water. The resulting HA fraction was further purified by dialysis against pure water using a
153 Spectra/Por cellulose ester membrane (1 kDa). The HA fraction was then obtained in powdered
154 form by freeze-drying. The prepared samples were analyzed by pyrolysis-gas chromatography/mass
155 spectrometry with online methylation using tetramethylammonium hydroxide (TMAH-py-GC/MS).
156 A 1.0 ± 0.1 mg portion of the powdered sample was placed in a 50 μ L deactivated stainless steel cup.
157 A 25 μ L aliquot of tetramethylammonium hydroxide in methanol (40 mg mL^{-1}) were then added to
158 the cup, and the solvent was removed under reduced pressure. After repeating this procedure 4 times,
159 the cup was introduced into a PY-2020D type Pyrolyzer (Frontier Laboratories Ltd., Koriyama,
160 Fukushima) connected to a Shimadzu GC-17A/QP5050 type GC/MS system. Helium (99.995 %
161 purity) was used as the carrier gas, and flash pyrolysis of the powdered samples were carried out at
162 550 $^{\circ}\text{C}$ for 0.4 min. A Quadrex 100 % dimethylpolysiloxane capillary column (0.25 mm i.d. \times 25 m,
163 0.25 μm film thickness) was employed in the separation of the pyrolysate compounds. The
164 temperature program for the GC oven was as follows: 50 $^{\circ}\text{C}$ for 1 min; 50 – 300 $^{\circ}\text{C}$ at a heating rate
165 of 5 $^{\circ}\text{C min}^{-1}$; 300 $^{\circ}\text{C}$ for 4 min.

166

167 **RESULTS AND DISCUSSION**

168 **Evaluation of Turnover Number**

169 Figures 1 and 2 provide information on the influence of the [FeTPPS] on the concentrations of

170 degraded TBBPA or TCBPA ($\Delta[\text{TBBPA}]$ or $\Delta[\text{TCBPA}]$) and on the $[\text{Br}^-]$ or $[\text{Cl}^-]$ that are released
171 during the oxidation. The degradation and dehalogenation of TBBPA and TCBPA increased with
172 increasing $[\text{FeTPPS}]$ at pH 4, while reached a plateau at pH 8 above $0.5 \mu\text{M}$ of $[\text{FeTPPS}]$. The
173 levels of degradation and debromination at pH 8 were significantly higher than the corresponding
174 values at pH 4. The presence of HA resulted in decrease in the degradation and debromination of
175 TBBPA at pH 4.

176 The efficiencies of TBBPA and TCBPA degradation should be precisely evaluated in terms of
177 moles of degraded substrate per mole of catalyst per minute, that is, as the turnover frequency for
178 the catalyst. However, TBBPA and TCBPA were degraded within 1 min and after this period, a
179 plateau was reached at pH 4 and 8 in the $\text{FeTPPS}/\text{KHSO}_5$ catalytic system. Thus, it was not possible
180 to evaluate the kinetics of degradation and dehalogenation from the present data. Alternatively, the
181 efficiency of degradation for TBBPA or TCBPA was evaluated as mole of degraded substrate per
182 mole of catalyst, that is, the turnover number (TON). The TON values were estimated by dividing
183 $\Delta[\text{TBBPA}]$ or $\Delta[\text{TCBPA}]$ by $[\text{FeTPPS}]$ (Table 1). At pH 4, the TONs for degradation and
184 dehalogenation of TCBPA were significantly higher than those for TBBPA. Such trends are
185 consistent with the levels of degradation and dehalogenation for 2,4,6-trihalophenols in the presence
186 of water-soluble iron(III)-porphyrin catalysts at pH 3 in a previous report and are reported to be
187 dependent on the electronegativity of substituents on the aromatic carbons.^[30] Although the TON

188 values at pH 8 were much larger than those at pH 4, the presence of HA resulted in a decrease in
189 TONs for the degradation and dehalogenation of TBBPA and TCBPA. At pH 4, the majority of
190 acidic functional in HA are protonated species,^[36] and HAs can exist as colloidal forms.^[35] In
191 contrast, acidic functional groups in HAs are almost dissociated at pH 8, and HAs can exist as ionic
192 forms with the large negative electrostatic field.^[34] It has been reported that the lower levels of
193 carboxylic groups in HAs result in the higher adsorption of hydrophobic organic pollutants, such as
194 chlorinated dioxin.^[36] This suggests that the lower levels of the degradation and dehalogenation in
195 the presence of HA at pH 4 can be attributed to the adsorption of TBBPA or TCBPA to the HA.
196 Thus, a higher pH value appears to be preferable for the catalytic oxidation of TBBPA and TCBPA
197 using the FeTPPS/KHSO₅ system, while the presence of HA inhibits the reactions.

198

199 **Oxidation Products**

200 The average pH for landfill leachates is reported to be 8.53.^[4,5] Because TBBPA and TCBPA (pK_a
201 7.5 – 7.6) exist as phenolate anions under such weak alkaline conditions, the mobility of these
202 compounds may be enhanced. In addition, landfill leachates contains several-ten mg L⁻¹ of HAs as
203 dissolved organic carbon, and these also facilitate the mobility of TBBPA and TCPBA.^[4,5] Thus, the
204 oxidation characteristics of TBBPA and TCBPA in the presence of the FeTPPS/KHSO₅ system at
205 pH 8 in the presence of HA should be the focus of scientific attention, in terms of their fates in

206 landfills. To identify the oxidation products produced in the reactions, *n*-hexane extracts of
207 acetylated reaction mixtures were analyzed by GC/MS after for a variety of reaction periods (1 – 30
208 min). Chromatograms of these mixtures are shown in Fig. 3. After a reaction period of 1 min, peaks
209 at 17.8 min (Fig. 3a, ▼) and 13.6 min (Fig. 3b, ◇) were detected as major oxidation products. These
210 peaks were assigned as 2HIP-26DBP and 2HIP-26DCP based on mass spectral data (Fig. 4a and c).
211 However, these peaks were largely decreased after a reaction period of 30 min, while a series of new,
212 small peaks appeared at 56.0 min (Fig. 3a, ●) and 52.6 min (Fig. 3b, ○). As shown in Fig. 4b and d,
213 these peaks were assigned as acetates of coupling compounds produced by reactions between
214 TBBPA or TCBPA and 2,6-dibromophenol (26DBP) or a 2,6-dichlorophenol (26DCP) intermediate.

215 Figure 5a provides information on the kinetics of formation of 2HIP-26DBP and 2HIP-26DCP.
216 The percent conversion of TBBPA or TCBPA to 2HIP-26DBP or 2HIP-26DCP was estimated by
217 dividing the molar concentrations of the products by that for the degraded substrates. 70% of
218 TBBPA and 83% of TCBPA were initially converted into 2HIP-26DBP and 2HIP-26DCP,
219 respectively, while the percent conversion decreased after a reaction time of 1 min. Figure 5b shows
220 the kinetics of formation of coupling compounds between TBBPA or TCBPA and 26DBP or the
221 26DCP intermediate. The peak areas (ratio of the peak areas for the product to ISTD) increase with
222 increasing reaction time. It has been reported that oxidation of TBBPA by δ -MnO₂ or UV-light
223 irradiation leads to β -carbon scission, with the formation of 2,6-dibromo-*p*-benzoquinone as well as

224 2HIP-26DBP.^[33,37] Although 2,6-dibromo-*p*-benzoquinone could be extracted with *n*-hexane after
225 reduction to 2,6-dibromo-*p*-hydroquinone followed by acetylation,^[27,28] this type of compound was
226 not detected in *n*-hexane extracts of reaction mixtures as a result of the catalytic oxidation of
227 TBBPA or TCBPA on the FeTPPS/KHSO₅ system. Although 2HIP-26DBP and 2HIP-26DCP were
228 detected as major products that were produced via β-carbon scission, it is possible that the
229 remaining 26DBP or 26DCP could be present as radical species. Thus, the production of coupling
230 compounds between TBBPA or TCBPA and 26DBP or the 26DCP intermediate can be attributed to
231 coupling between phenoxy radicals derived from TBBPA or TCBPA and radical species derived
232 from the scission of the β-carbons in TBBPA and TCBPA.

233

234 **Halogenated Intermediates in Humic Acid Fractions**

235 It has been reported that halogenated intermediates that are produced as a result of the oxidation of
236 halogenated phenols by the iron(III)-porphyrin catalyst in the presence of HAs can be incorporated
237 into HAs via covalent binding.^[22,29] Thus, the majority of halogenated intermediates from the
238 oxidation of TBBPA and TCBPA may be incorporated into the HA. To characterize the halogenated
239 intermediates that are incorporated into HA as a result of catalytic oxidation via the FeTPPS/KHSO₅
240 catalytic system, TBBPA or TCBPA were oxidized in the presence of HA (initial substrate
241 concentration 100 μM, HA concentration 100 mg L⁻¹), and the HA fractions were then separated. In

242 this experiment, changes in $\Delta[\text{TBBPA}]$ and $\Delta[\text{TCBPA}]$ were monitored by HPLC: 87 μM for
243 TBBPA; 95 μM for TCBPA. The Br and Cl contents in the powdered samples of the HA fractions
244 after reaction with TBBPA and TCBPA (W) were determined: 7.5% for Br; 6.7% for Cl. Based on
245 these results, the percent conversion of tetrahalobisphenol A (TXBPA) to halogenated intermediates
246 incorporated into HA (A) can be calculated as:

$$247 \quad A (\%) = \frac{\frac{W (\%)}{100} \times 0.2 (\text{L}) \times [\text{HA}] (\text{g L}^{-1})}{\Delta[\text{TXBPA}] (\text{M}) \times 0.2 (\text{L}) \times 4 \times (\text{atomic weight of Br or Cl})} \times 100$$

248 The A values were estimated to be 27% for TBBPA and 50% for TCBPA. These results indicate that
249 the level of the incorporation of halogenated intermediates into HA for TCBPA is higher than that
250 for TBBPA.

251 To identify the halogenated intermediates in the HA fractions after oxidation with TBBPA or
252 TCBPA, powdered samples were analyzed by TMAH-py-GC/MS. Figure 6A shows pyrograms for
253 the HA fractions after reaction with TBBPA (i) and TCBPA (ii). The peak number indicates the
254 pyrolysate compounds derived from the pyrolysis of HA and the assignment for these peaks are
255 shown in Fig. 6B, based on the NIST mass spectral library and previous reports on
256 TMAH-py-GC/MS of HAs.^[38,39] The peaks shown by alphabetical symbols ($a - h$) were
257 halogenated pyrolysate compounds related to intermediates from the oxidation of TBBPA and
258 TCBPA. The expected structures were identified based on interpretations of fragment ions from
259 mass spectral data for each pyrolysate compound. The identified fragment ions and predicted

260 structures are summarized in Table 2. These results clearly demonstrate that halogenated
261 intermediates are incorporated into HA via covalent binding as a result of TBBPA or TCBPA
262 oxidation in the presence of the FeTPPS/KHSO₅ catalytic system. Although the brominated
263 intermediates from TBBPA were mainly 2,6-dibromophenol derivatives, a monochloro intermediate
264 (peak *f* in Table 2) was found in the pyrolysate compounds for TCBPA, which is consistent with the
265 result showing that the levels of dechlorination are higher than the corresponding values for
266 debromination. The largest peaks of halogenated intermediates in pyrograms (i) and (ii) in Fig. 6A
267 were peaks *c* and *g*, respectively. These components were structurally similar to the substrates,
268 TBBPA (peak *c*) and TCBPA (peak *g*). The formation of such pyrolysate compounds suggest the
269 coupling of phenoxy radicals from TBBPA or TCBPA with HA.

270 Based on the results described above and the known reactivity of FeTPPS activated by KHSO₅,^[26]
271 possible tetrahalobisphenol A (TXBPA) oxidation pathways in the presence of HAs can now be
272 proposed (Fig. 7). Initially, KHSO₅ reacts with Fe^{III}TPPS in the catalyst to generate high-valent
273 iron-oxo porphyrin cation radicals (O=Fe^{IV}TPPS⁺). This active species reacts with TXBPA to give
274 an iron-oxo species (O=Fe^{IV}TPPS) and a phenoxy radical species (TXBPA[•]). Similarly, phenolic
275 moieties in HA can be oxidized to give phenoxy radicals in the presence of the FeTPPS/KHSO₅
276 catalytic system. The β-carbon scission of TXBPA[•] leads to the production of the 2,6-dihalophenoxy
277 radical (26DXP[•]) and 4-isopropylene -2,6-dihalophenone (4IP-26DXP).^[37]

278 2,6-Dihalobenzo-*p*-quinone was not detected as an oxidation product in the present study,
279 suggesting that 26DXP[•] couples instantaneously with radical species of HA or other radical species
280 to yield further polymerized compounds. On the other hand, the further oxidation of 4IP-26DXP by
281 active species of FeTPPS results in the formation of a 4-isopropyl-2,6-dihalophenolate cation
282 (4IP-26DXP⁺), and the nucleophilic addition of H₂O to 4IP-26DXP⁺ results in the formation of
283 2HIP-26DXP. The findings herein indicate that 2HIP-26DXP is formed at the initial stage of the
284 oxidation and its concentration then decreases. Thus, radical species of 2HIP-26DXP
285 (2HIP-26DXP[•]), which are formed by the active species of FeTPPS, can be covalently incorporated
286 into HA via radical coupling reactions.

287

288 **CONCLUSION**

289 TBBPA and TCBPA were effectively oxidized in the presence of HA at pH 8, which corresponds to
290 the pH values typically found in landfill leachates. Although the levels of dechlorination were
291 significantly higher than those for debromination, the oxidation characteristics of TXBPAs were
292 similar, in terms of oxidation products. 2HIP-26DXPs were detected as major byproducts as a result
293 of the β-carbon scission of substrates in the initial stages of the reaction, and levels of these
294 decreased with increasing reaction time. The halogenated intermediates were incorporated into HA
295 as a result of catalytic oxidation. The content of Br incorporated into HA (27%) was smaller than

296 that for Cl (50%). These results suggest that TCBPA is incorporated into HA more easily than
297 TBBPA as the result of oxidation reactions in landfills by oxidative enzymes that can be mimicked
298 by the FeTPPS/KHSO₅ catalytic system.

299

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303

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418

419 **FIGURE CAPTIONS**

420

421 **Figure 1.** Influence of FeTPPS concentration on the degradation and debromination of TBBPA at
422 pH 4 (a and b) and 8 (c and d) in the absence and presence of HA. [TBBPA]₀ 50 μM, [KHSO₅] 125
423 μM, [HA] 50 mg L⁻¹, reaction time 30 min.

424

425 **Figure 2.** Influence of FeTPPS concentration on the degradation and debromination of TCBPA at
426 pH 4 (a and b) and 8 (c and d) in the absence and presence of HA. [TCBPA]₀ 50 μM, [KHSO₅] 125
427 μM, [HA] 50 mg L⁻¹, reaction time 30 min.

428

429 **Figure 3.** GC/MS chromatograms for *n*-hexane extracts from the reaction mixtures for TBBPA (a)
430 and TCBPA (b) in the presence of HA. [TBBPA]₀ 50 μM, [KHSO₅] 125 μM, [HA] 50 mg L⁻¹.

431

432 **Figure 4.** Mass spectra of the oxidation products shown in Fig. 3. (a) 2HIP-26-DBP (b) coupling
433 product of TBBPA with 26DBP, (c) 2HIP-26-DCP, (d) coupling product of TCBPA with 26DCP.

434

435 **Figure 5.** Kinetics of conversion for TBBPA or TCBPA to 2HIP-26DBP (■) or 2HIP-26DCP (●) (a),
436 and coupling products between TBBPA or TCBPA and 26DBP (■) or 26DCP (●) (b). [TBBPA]₀ 50
437 μM, [KHSO₅] 125 μM, [HA] 50 mg L⁻¹.

438

439 **Figure 6.** (A) Pyrograms of HA fractions from the reaction mixtures as a result of catalytic
440 oxidation with TBBPA (i) and TCBPA (ii), and (B) assigned pyrolysate compounds derived from
441 HA.

442

443 **Figure 7.** Pathways for the production of coupling compounds in the FeTPPS/KHSO₅ catalytic
444 system.

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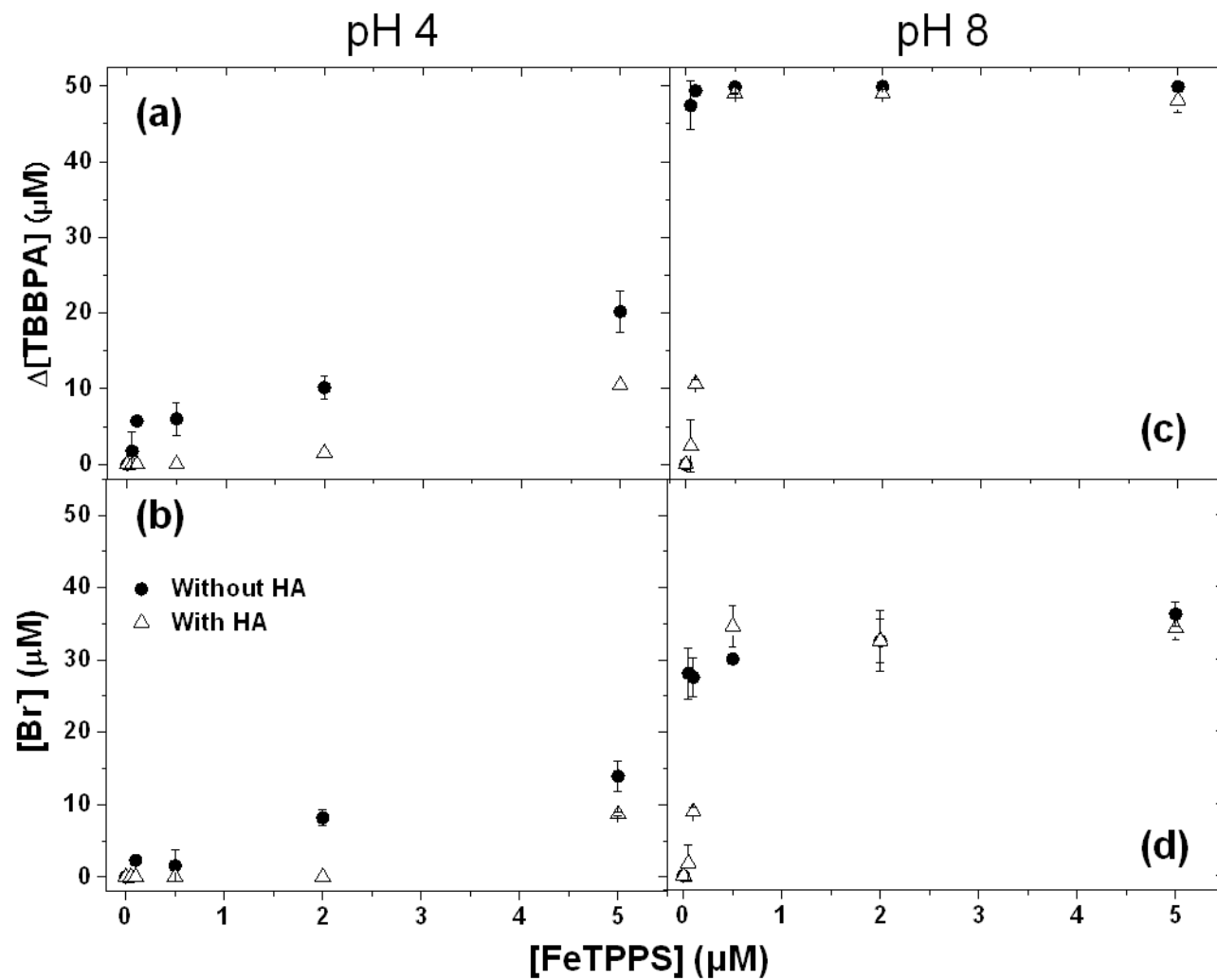


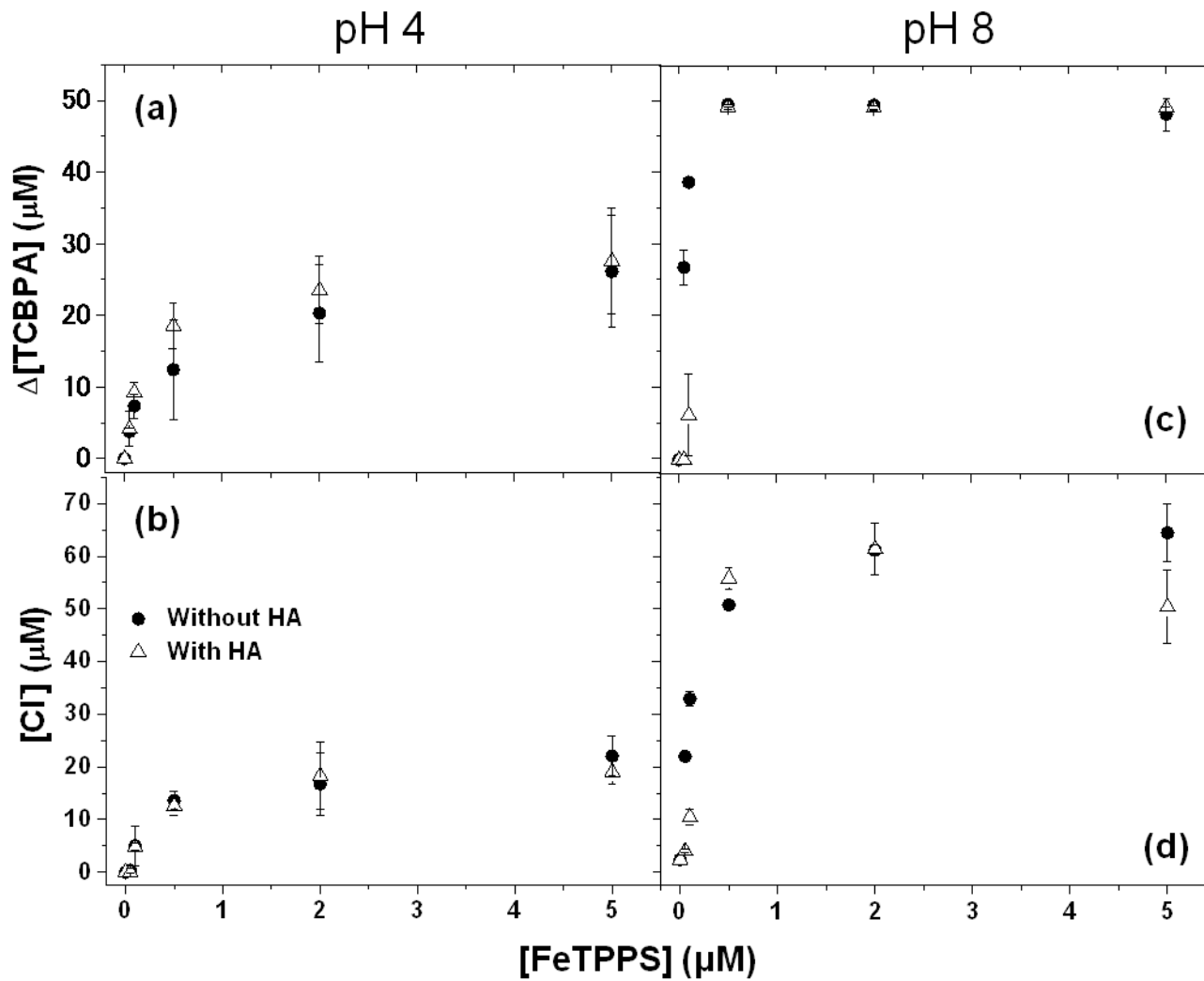
Fig.1 (Mizutani et al.)

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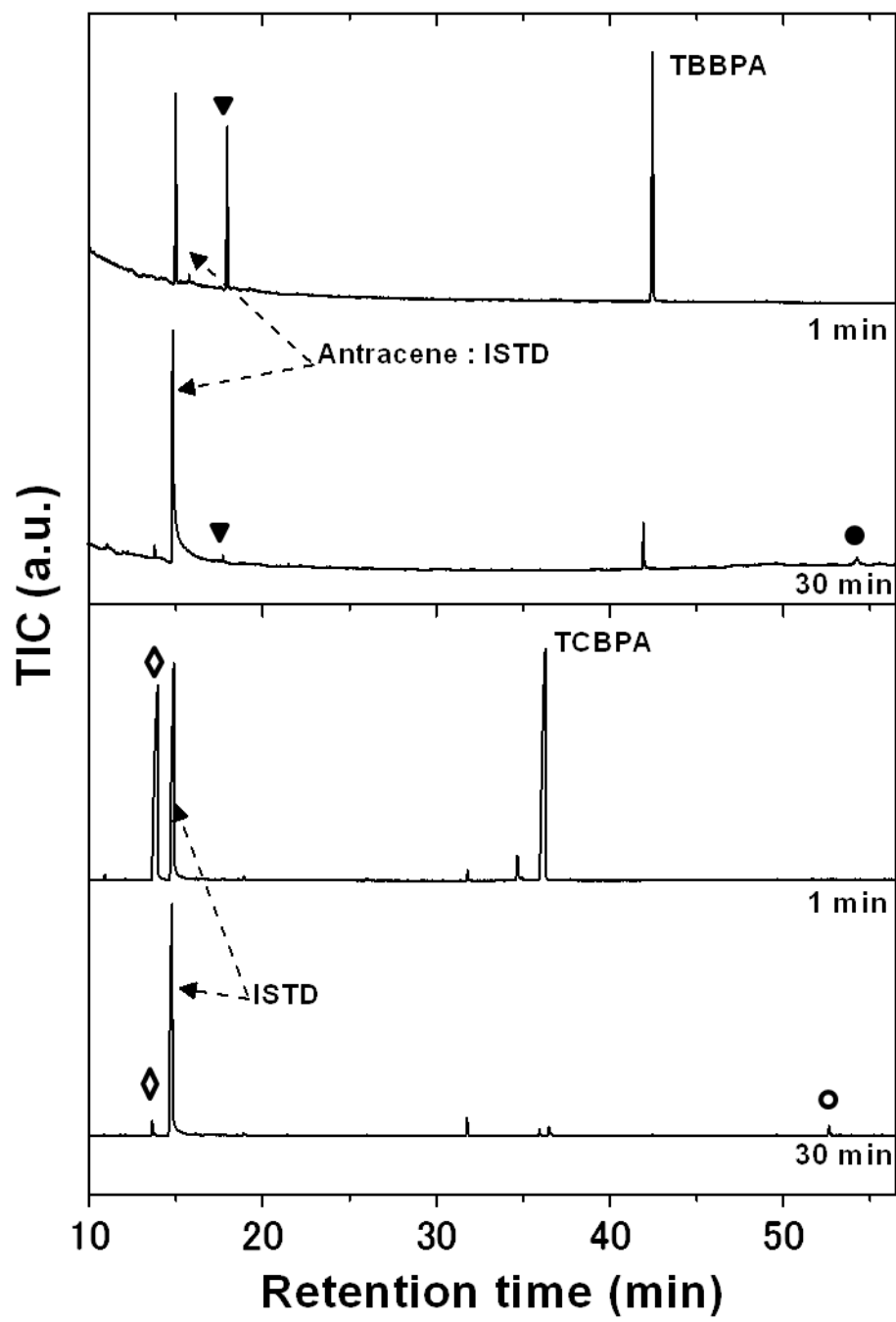
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Fig. 2 (Mizutani et al.)



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Fig. 3 (Mizutani et al.)

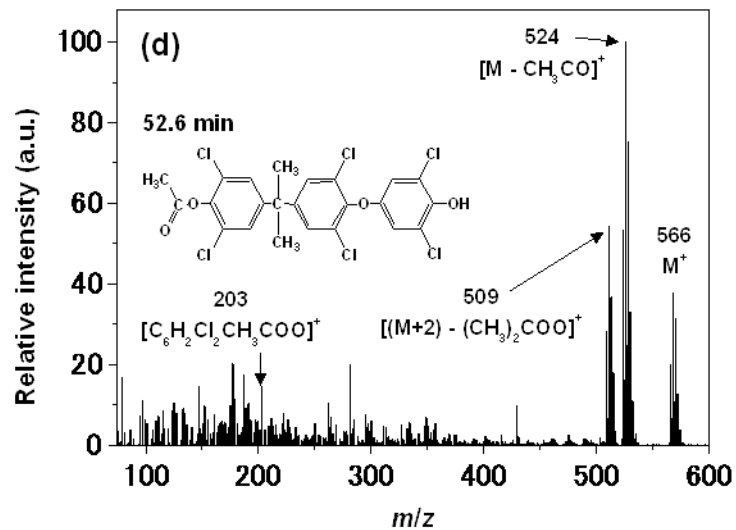
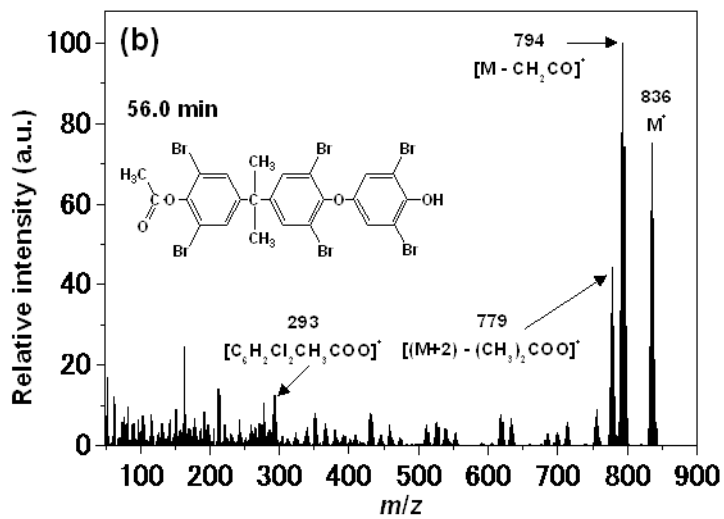
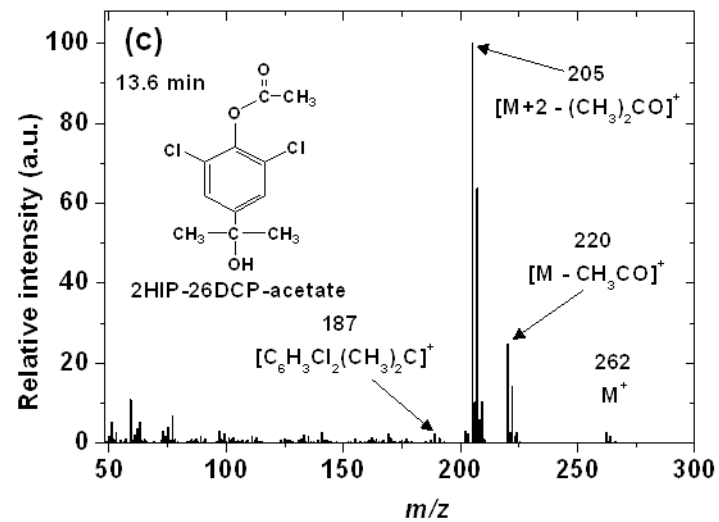
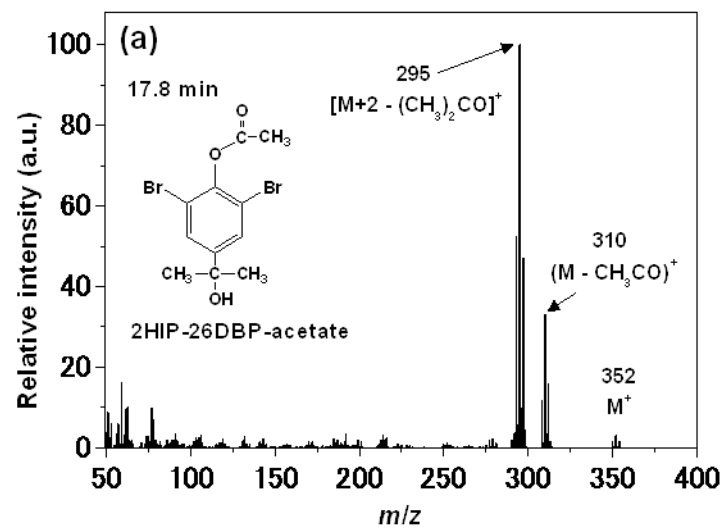
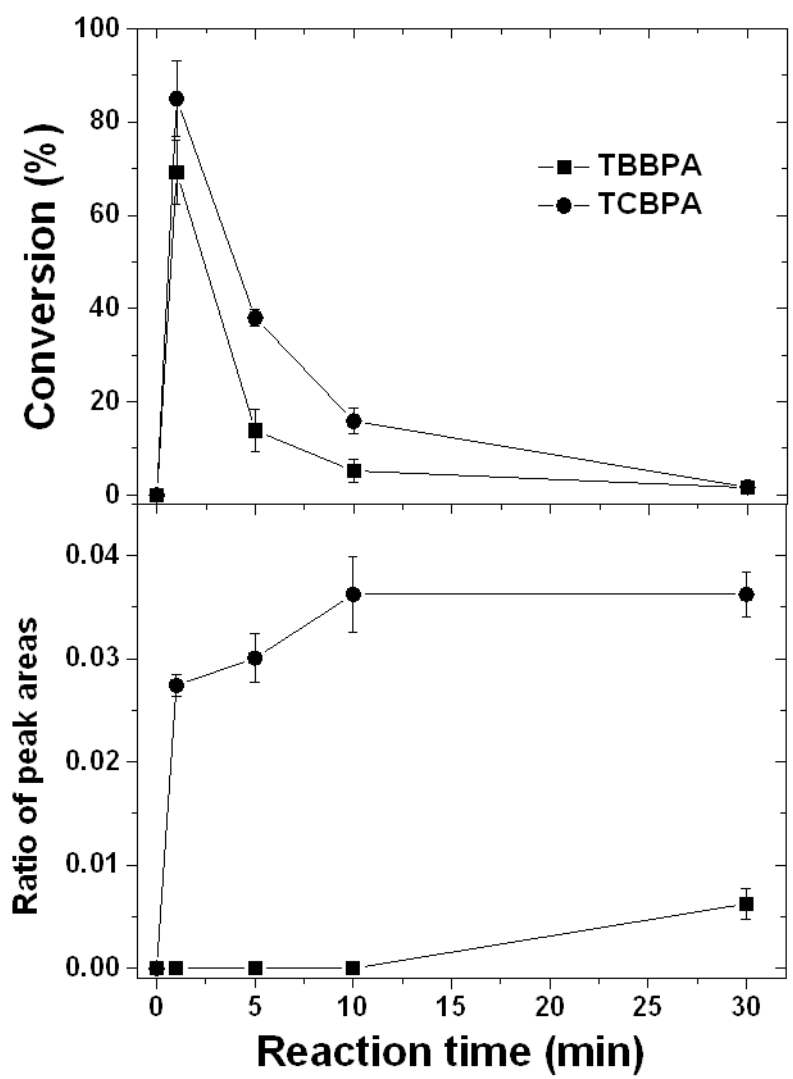


Fig. 4 (Mizutani et al.)



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Fig. 5 (Mizutani et al.)

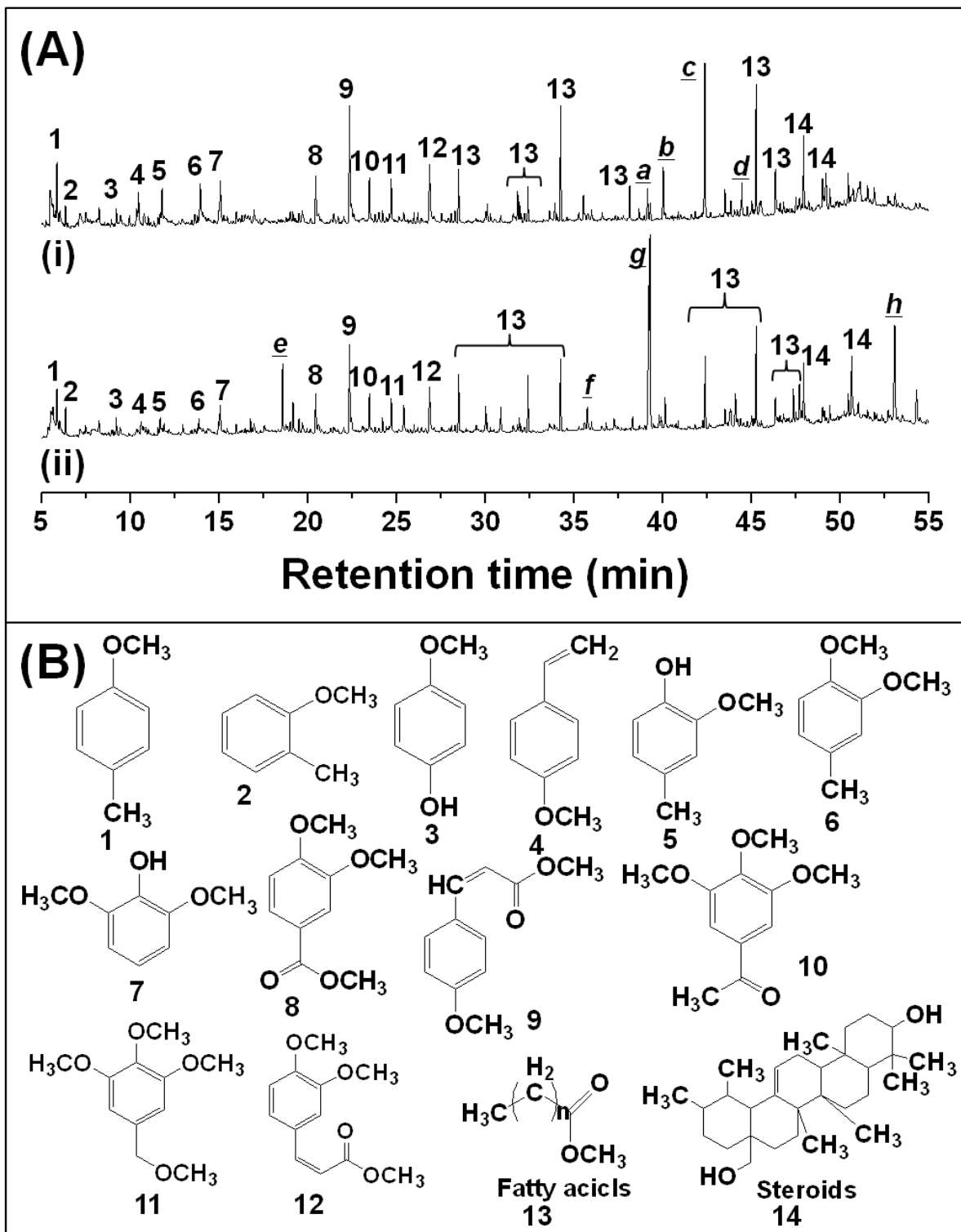
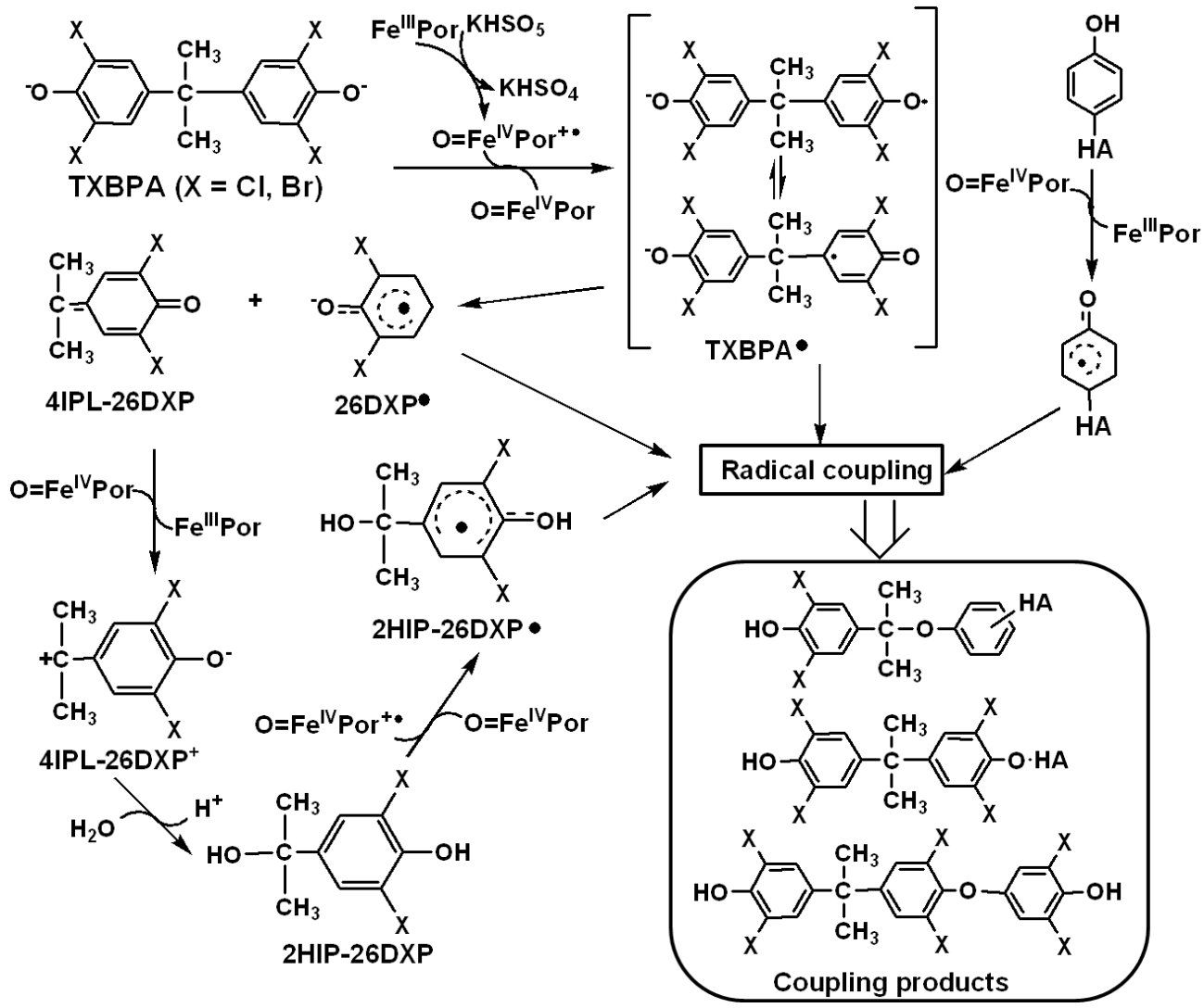


Fig. 6 (Mizutani et al.)

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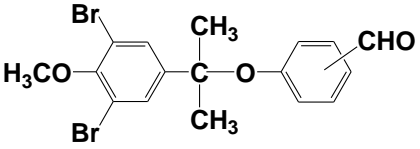
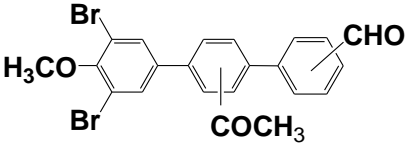
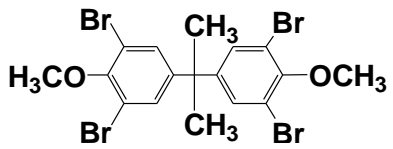
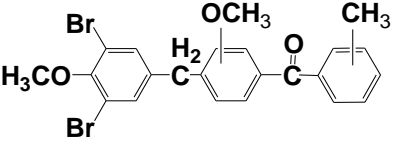
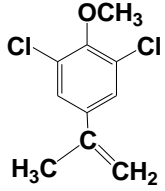
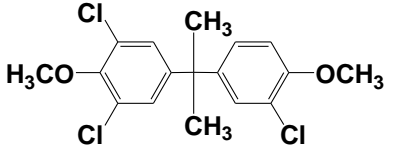
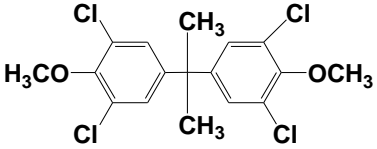
Fig. 7 (Mizutani et al.)

Table 1. Estimation of the turnover number for degradation and dehalogenation of TBBPA and TCBPA.

pH	TBBPA or TCBPA degradation		Dehalogenation	
	Without HA	With HA	Without HA	With HA
<i>TBBPA</i>				
4	4.04±0.54 (5)	2.09±0.23 (5)	2.78±0.41 (5)	1.74±0.06 (5)
8	948±64 (0.05)	106±6 (0.1)	560±71 (0.05)	88.1±6.0 (0.1)
<i>TCBPA</i>				
4	24.8±3.3 (0.5)	37.1±6.4 (0.5)	27.2±3.5 (0.5)	25.2±3.5 (0.5)
8	537±48 (0.05)	62.3±2.8 (0.1)	400±14 (0.05)	82.1±14 (0.1)

Values in parenthesis denote the concentration of FeTPPS (μM) for the estimation of TON.

Table 2. Table 2. Assignments of mass spectra for peaks *a* - *h* from the pyrograms shown in Fig. 6A.

Peaks	m/z [rel. int., fragment identity]	Assigned structures
<i>a</i>	414 [23.0, M ⁺], 399 [100, (M - CH ₃) ⁺], 319 [2.49, (M - CH ₃ Br) ⁺]	
<i>b</i>	492 [53.9, M ⁺], 489 [100, (M - CH ₃) ⁺] 329 [14.2, (M - CH ₃ Br ₂) ⁺]	
<i>c</i>	572 [30.4, M ⁺], 557 [100, (M - CH ₃) ⁺], 477 [2.86, (M - CH ₃ Br) ⁺], 397 [5.03, (M - CH ₃ Br ₂) ⁺]	
<i>d</i>	504 [53.9, M ⁺], 498 [100, (M - CH ₃) ⁺] 329 [14.2, (M - CH ₃ Br ₂) ⁺]	
<i>e</i>	216 [100, M ⁺], 201 [98.9, (M - CH ₃) ⁺], 166 [6.62, (M - CH ₃ Cl) ⁺]	
<i>f</i>	357 [26.8, M ⁺], 342 [100, (M - CH ₃) ⁺], 307 [4.20, (M - CH ₃ Cl) ⁺], 272 [7.55, (M - CH ₃ Cl ₂) ⁺]	
<i>g</i>	392 [22.3, M ⁺], 377 [81.2, (M - CH ₃) ⁺], 342 [2.12, (M - CH ₃ Cl) ⁺], 307 [3.33, (M - CH ₃ Cl ₂) ⁺]	
<i>h</i>	554 [78.2, M ⁺], 539 [100, (M - CH ₃) ⁺], 469 [4.07, (M - CH ₃ Cl ₂) ⁺]	