

Decomposition of Phenolic Endocrine Disrupting Chemicals by Potassium Permanganate and γ -Ray Irradiation

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The decomposition of phenolic endocrine disrupting chemicals (P-EDCs), such as phenol, 4-*t*-butylphenol (BuP), and bisphenol A (BPA), in aqueous solutions by potassium permanganate (KMnO₄) was studied, and its efficiency was compared with that of hydroxyl radicals (OH•) generated by ⁶⁰Co γ -ray irradiation. Various organic acids and inorganic carbon were formed in the decomposition of P-EDCs due to either KMnO₄ or OH•. They were formed via direct aromatic ring cleavage in the case of KMnO₄ and via OH• addition-substitution reactions, followed by aromatic ring cleavage, in the case of OH•. Comparing the decrease in the P-EDCs based on the number of electrons, the amount of KMnO₄ spent to completely eliminate BuP and BPA was comparable to that of OH•. Although three-times more KMnO₄ was needed for phenol decomposition than OH•, the complete conversion of phenol into organic acids and inorganic carbon was achieved with 720 μ M of electrons in both cases.

Low concentrations of phenol and substituted phenols are found widely in water in nature. Some of these compounds have detrimental effects on water quality and are toxic to aquatic organisms. Petrochemical processes and industrial fermentation produce wastewater containing high concentrations of phenols. Some phenolic compounds, including nonylphenol, bisphenol A, and 2,4-dichlorophenol, have hormonal activity, and are known as phenolic endocrine disrupting chemicals. Bisphenol A and alkylphenols have been detected at high μ M levels ($M = \text{mol dm}^{-3}$) in exudates from waste disposal sites.^{1,2} Effective methods are required to decompose these compounds into low or non-toxic substances, such as organic acids and inorganic carbon.

KMnO₄ decomposes phenol into organic acids or inorganic carbon efficiently.³ In addition, KMnO₄ has various advantages for use in water treatment, such as low cost, ready availability commercially, and ease of handling. In the USA, KMnO₄ is used to remove or decompose phenol in industrial wastewater treatment plants.⁴ A preliminary study examined the use of KMnO₄ in decomposing phenolic endocrine disrupting chemicals in aqueous solutions by analyzing the decrease in the ratio of these compounds after the addition of KMnO₄, using solid-phase micro-extraction/gas chromatography (SPME-GC).⁵ KMnO₄ completely decomposed phenolic endocrine disrupting chemicals, and the rate constants of these were higher than that of phenol, although the decomposition products of these and the comparison of the decomposition efficiency with other oxidants were not investigated.

The hydroxyl radical (OH•) is a very strong oxidizer, and is considered to be the most effective method to remove/decompose phenol in water. Advanced oxidation processes, such as combinations of ozone,^{6–9} hydrogen peroxide,^{8,9} and ultraviolet radiation,^{6–9} and ionizing (X-ray and γ -ray) radiation^{10–12} are commonly used to generate OH•, which can decompose phenol in water effectively. Of these methods, γ -ray irradiation can be used to evaluate the ability of OH• to decompose phenol in water, because this method can produce uniform amounts of OH• in water, and the amount of OH• can be easily estimated from the G-value (moles/100 eV).¹³

This study investigated the efficiency with which KMnO₄ decomposes phenolic endocrine disrupting chemicals, 4-*t*-butylphenol, bisphenol A, and phenol to low/non-toxic substances, such as organic acids and inorganic carbon, and compared it with OH• generated by ⁶⁰Co γ -ray irradiation.

Experimental

Preparation of Solutions Containing Phenolic Endocrine Disrupting Chemicals. Phenol, 4-*t*-butylphenol (BuP), and bisphenol A (BPA) of 99% purity (GL Science, Inc.) were used in this study without further purification. Here, these three compounds are collectively abbreviated as P-EDCs. They were dissolved homogeneously in ultra-pure water (Millipore Milli-Q PLUS, pH 6.5, electric conductivity 18.2 M Ω cm⁻¹) by sonication for 1 h. The concentration of each substance was 50 μ M. A 1.5 dm³ aqueous solution was poured into a 2.0 dm³ glass vessel and aerated by air bubbling for 15 min. 50 cm³ aliquots were placed

into glass vessels (volume: $\phi 40 \times 75$ mm, glass thickness: 1 mm) with screw caps for the decomposition by KMnO_4 and $\text{OH}^\bullet$.

Decomposition of P-EDCs. Aqueous solutions of 0.2 wt % and 2.0 wt % KMnO_4 were prepared by dissolving 99% pure KMnO_4 (Kanto Chemical, Ltd.) in ultra-pure water. These solutions were added to the P-EDC solutions to observe oxidation at room temperature (25 °C). The KMnO_4 concentration in the samples was 10, 20, 40, 80, 120, 180, or 240 μM . The reaction of KMnO_4 with the P-EDC was allowed to proceed to completion for 24 h.

γ -ray irradiation using a ^{60}Co - γ -source was carried out at 25 °C at JAERI, Takasaki. The absorbed dose in water was 33.3, 66.5, 133, 267, 400, 600, 800, or 2,400 Gy at a dose rate of 200 Gy h^{-1} , which was estimated by alanine/ESR dosimetry (ISO/ASTM 51607: "Practice for use of the Alanine-EPR Dosimetry System").

Analysis. A high-performance liquid chromatograph (HPLC: Agilent 1100 series) with a UV/visible detector was used at a wavelength of 280 nm for qualitative and quantitative analyses of P-EDCs and decomposition products with an aromatic ring. These substances were separated using a column (Shodex, RSpak DE-613, 2.1 mm i.d. $\times$ 100 mm long) at 40 °C with water-methanol (25:75) as the eluent at a flow rate of 1.0 $\text{cm}^3 \text{min}^{-1}$. The identification and quantitative analysis of the substances were based on comparisons of their retention times and the peak areas with reference substances.

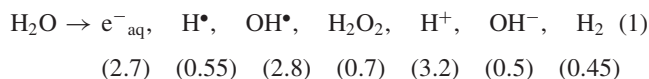
An ion chromatograph (IC: Metrohm 761 Compact IC) with an anion suppressor was used for qualitative and quantitative analyses of organic acids. The anions were separated using a column (Shodex, IC SI 90-4E, 4.0 mm i.d. $\times$ 250 mm long) at room temperature (25 °C) with a mixture of 1.8 mM Na_2CO_3 and 1.7 mM NaHCO_3 as the eluent at a flow rate of 1.2 $\text{cm}^3 \text{min}^{-1}$. The organic acids forming the decomposition products were identified and quantitatively analyzed by comparing their retention times and the peak areas with reference substances.

Inorganic carbon was determined by measuring the total organic carbon (TOC) concentration, where inorganic carbon was calculated by subtracting the TOC from the carbon concentration of the initial P-EDC sample (Phenol, 300 μM ; BuP, 500 μM ; and BPA, 750 μM). The TOC concentration was measured with a TOC analyzer (Shimadzu TOC Vwp). Potassium phthalate and an equimolar mixture of $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ were used as calibration standards to evaluate the total carbon and inorganic carbon, respectively. The complete oxidation of TOC to carbon dioxide was carried out with sodium peroxodisulfate and exposure to UV light at 85 °C. The concentration of CO_2 formed was measured with a non-dispersive infrared detector.

Results and Discussion

KMnO_4 can receive one, three, or five electrons when oxidized in alkaline, neutral, and acidic solutions, respectively. In this study, KMnO_4 could receive three electrons, because the decomposition of P-EDCs by KMnO_4 was carried out in a neutral solution.

The primary products of water formed by γ -ray irradiation (neutral pH) were as follows:¹³



The values in parentheses are the numbers of molecules generated per 100 eV of absorbed energy, the G-value, and

are used to calculate the concentrations of the formed species. Of these species, H_2O_2 , H^+ , OH^- , and H_2 are stable, while e^-_{aq} , $\text{H}^\bullet$, and $\text{OH}^\bullet$ react with organic compounds rapidly. In the presence of oxygen, e^-_{aq} and $\text{H}^\bullet$ are converted to $\text{O}_2^{\bullet-}$ and $\text{HO}_2^\bullet$, and make an insignificant contribution to the degradation of phenols.^{14,15} Therefore, $\text{OH}^\bullet$, which received one electron, had the most important role in destroying P-EDCs. From these assumptions, the decomposition of P-EDCs by KMnO_4 and $\text{OH}^\bullet$ in water can be compared in terms of the number of electrons received.

The P-EDC samples decomposed using KMnO_4 and $\text{OH}^\bullet$ were analyzed by HPLC to measure the decomposition products with an aromatic ring. Figure 1 shows HPLC chromatograms with 120 μM of electrons of KMnO_4 (KMnO_4 : 40 μM) and $\text{OH}^\bullet$ (absorbed dose: 400 Gy). Peaks (e), (m), and (s) are due to residual phenol, BuP, and BPA, respectively. For KMnO_4 decomposition, peaks (f), (g), and (t) appeared in the chromatograms of the P-EDCs. Peaks (f) and (g) resulted from colloidal MnO_2 formed by the reaction of KMnO_4 with P-EDCs. No decomposition products with aromatic rings were observed in the KMnO_4 decomposition, except for unidentified peak (t) in the chromatogram of BPA. This compound might be formed via a side reaction, because the peak is very small. Conversely, several aromatic compounds were observed in the chromatogram of each P-EDC sample decomposed with $\text{OH}^\bullet$. Decomposition products with large peak areas were identified as catechol (d), hydroquinone (c), and 4-*t*-butylcatechol (BuCa, (l)), while the other peaks (a, b, h-k, and n-r) could not be identified. The very large peak (r) in BPA might be a hydroxylated BPA compound, since various hydroxylated compounds were seen in the decomposition of phenol and

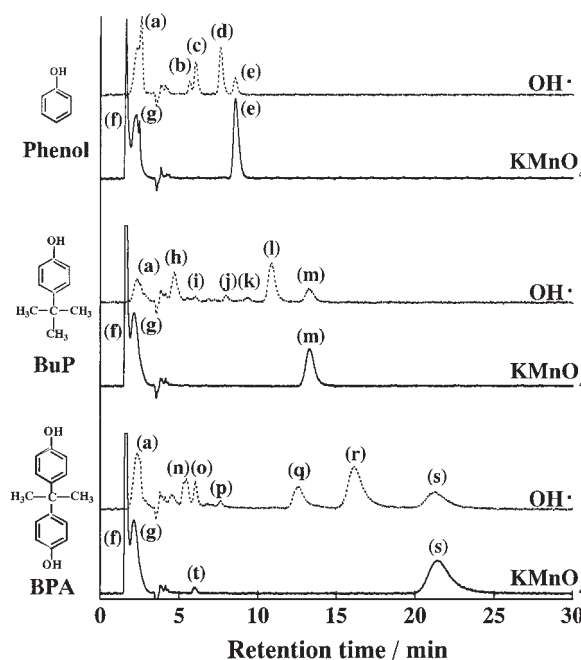


Fig. 1. HPLC chromatograms of P-EDC samples decomposed using KMnO_4 and $\text{OH}^\bullet$ with 120 μM of electrons. $\lambda = 280$ nm. Peaks: (c) hydroquinone, (d) catechol, (e) phenol, (f) and (g) colloidal MnO_2 , (l) BuCa, (m) BuP, (s) BPA, (peaks a, b, h-k, n-r, and t) unknown.

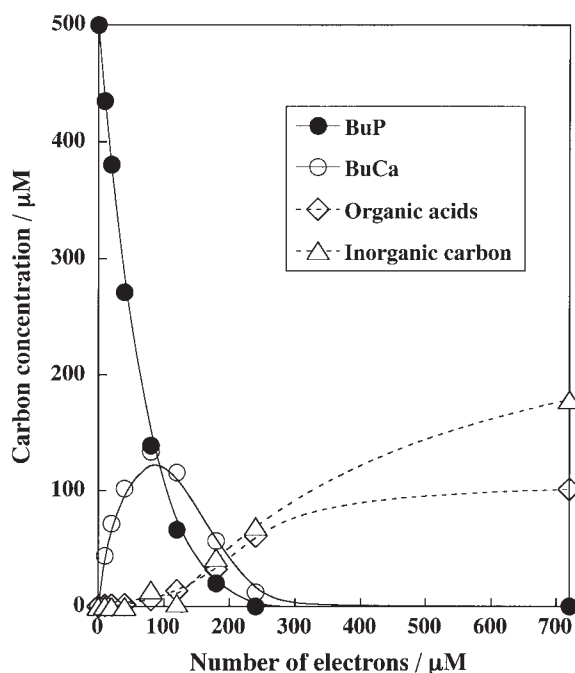


Fig. 2. Decrease in BuP and the formation of decomposition products (BuCa, total organic acids, and inorganic carbon) for $\text{OH}^\bullet$ as a function of the number of electrons. The concentrations of BuP and the products are expressed in terms of the carbon concentration.

BuP. These results demonstrate that the decomposition of P-EDCs by KMnO_4 and $\text{OH}^\bullet$ differs, and few aromatic compounds are formed with KMnO_4 .

Organic acids, such as formic, malic, maleic, acetic, and oxalic acid, as well as inorganic carbon were identified in P-EDC samples decomposed using KMnO_4 and $\text{OH}^\bullet$. As an example, Fig. 2 summarizes the decomposition of BuP with $\text{OH}^\bullet$. The figure shows the decrease in BuP and the formation of decomposition products, i.e., BuCa, total organic acids, and inorganic carbon for $\text{OH}^\bullet$, in terms of the carbon concentration as a function of the number of electrons. A hydroxylated compound, BuCa, was formed early in the decomposition; then, the concentrations of total organic acids and inorganic carbon increased as BuCa decreased. Similar results were obtained for phenol and BPA. These results show that the decomposition of P-EDCs by $\text{OH}^\bullet$ consists of $\text{OH}^\bullet$ addition-substitution reactions and a subsequent cleavage of the aromatic ring to form organic acids and inorganic carbon. In contrast, KMnO_4 cleaves the aromatic ring directly to form organic acids and inorganic carbon, since few decomposition products with an aromatic ring were seen.

Figure 3 shows the decrease in P-EDCs for KMnO_4 and $\text{OH}^\bullet$ as a function of the number of electrons. There is an apparent difference in the decomposition curves of the P-EDCs with KMnO_4 ; BuP and BPA were decomposed more rapidly than phenol with the same number of electrons. In contrast, the decomposition curves of the P-EDCs with $\text{OH}^\bullet$ were quite similar. The amount of KMnO_4 required for the complete elimination of BuP and BPA was comparable to the amount of $\text{OH}^\bullet$, while three-times more KMnO_4 than $\text{OH}^\bullet$ was needed for phenol.

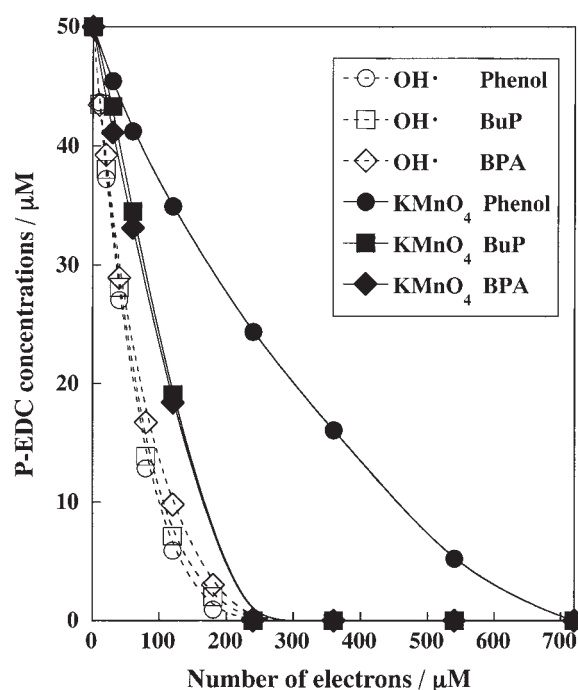


Fig. 3. Decrease in P-EDCs for KMnO_4 and $\text{OH}^\bullet$ as a function of the number of electrons.

To evaluate the formation of organic acids and inorganic carbon by KMnO_4 and $\text{OH}^\bullet$, the conversion ratios (CR) of organic acids and inorganic carbon to the initial P-EDCs were defined as follows:

$$CR_{OA} = A/T \times 100(\%), \quad (2)$$

$$CR_{IC} = B/T \times 100(\%), \quad (3)$$

$$CR_{OA+IC} = (A + B)/T \times 100(\%), \quad (4)$$

where A is the carbon concentration for all the organic acids (μM), B is the concentration of inorganic carbon (μM), and T is the initial carbon concentration of the P-EDCs (phenol, $300 \mu\text{M}$; BuP, $500 \mu\text{M}$; and BPA, $750 \mu\text{M}$).

The total conversion ratio, CR_{OA+IC} , for KMnO_4 and $\text{OH}^\bullet$ as a function of the number of electrons, is shown in Figs. 4(a) and (b), respectively. In the decomposition of P-EDCs by KMnO_4 , the CR_{OA+IC} for phenol increased almost linearly with the number of electrons, while CR_{OA+IC} for BuP and BPA started to increase after the P-EDCs were completely eliminated (see Figs. 3 and 4(a)). These results indicate that KMnO_4 reacts not only with phenol, but also with the organic decomposition products simultaneously, while KMnO_4 reacts only with BuP and BPA in the early stage, then with their decomposition products. In the case of $\text{OH}^\bullet$ (Fig. 4(b)), the formation of organic acids and inorganic carbon for each P-EDC was not observed in the early stage, because $\text{OH}^\bullet$ is rapidly used for addition-substitution reactions, as shown in Fig. 2. The decomposition curves of the P-EDCs are quite similar, as shown in Fig. 3, suggesting that their substituent groups do not influence the addition-substitution reactions of $\text{OH}^\bullet$ for each P-EDC. In the later stage of decomposition, however, CR_{OA+IC} is in the order: phenol > BuP > BPA. This means that hydroxylated phenols are decomposed more easily than

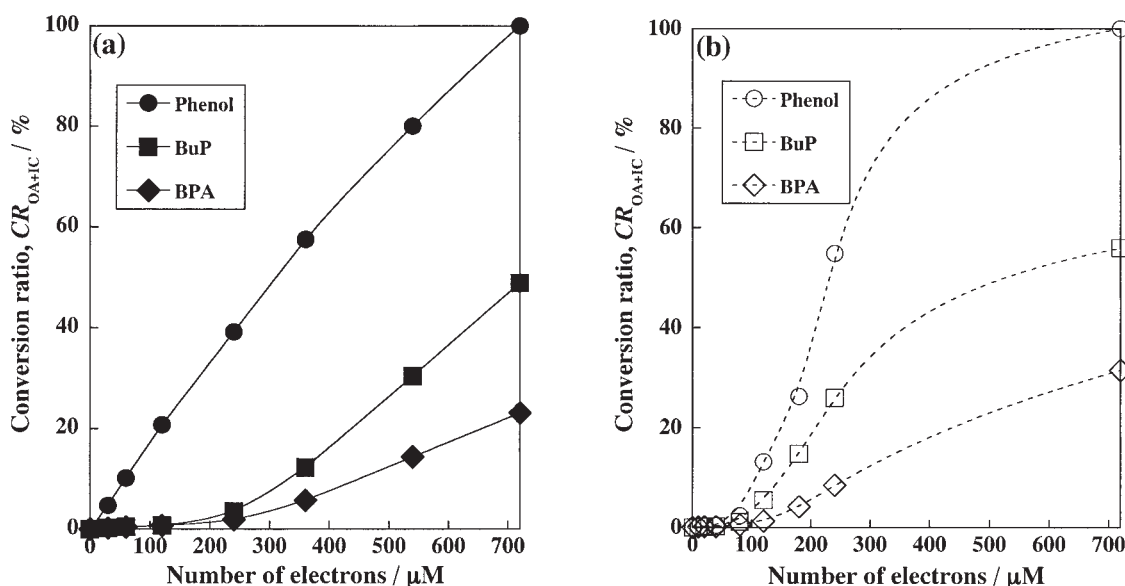


Fig. 4. Conversion ratio, CR_{OA+IC} , for KMnO_4 (a) and $\text{OH}^\bullet$ (b) as a function of the number of electrons. See text for the definition of the conversion ratio.

Table 1. Conversion Ratios CR_{OA} , CR_{IC} , and CR_{OA+IC} , for the Decomposition of P-EDCs with 720 μM of Electrons Using KMnO_4 and $\text{OH}^\bullet$ ^{a)}

	KMnO_4			$\text{OH}^\bullet$		
	CR_{OA}	CR_{IC}	CR_{OA+IC}	CR_{OA}	CR_{IC}	CR_{OA+IC}
Phenol	79	21	100	36	64	100
BuP	37	12	49	20	36	56
BPA	17	8	25	18	13	31

a) See text for the definitions of the conversion ratios.

hydroxylated BuP or BPA.

The conversion ratios CR_{OA} , CR_{IC} , and CR_{OA+IC} for 720 μM of electrons of KMnO_4 and $\text{OH}^\bullet$ are summarized in Table 1. As shown in Table 1, CR_{OA+IC} of each P-EDC at 720 μM KMnO_4 is comparable to that of $\text{OH}^\bullet$. Especially, the complete conversion of phenol into organic acids and inorganic carbon was achieved in both cases. On the other hand, the CR_{OA+IC} values in BuP and BPA were lower than that of phenol. Since the carbon number of these molecules is higher than that of phenol, larger amounts of the oxidants were needed for their complete conversion into organic acids and inorganic carbon. The percentage of inorganic carbon produced by $\text{OH}^\bullet$ was higher than that produced by KMnO_4 . This can be explained by the fact that $\text{OH}^\bullet$ has the highest redox potential.

Conclusions

In order to evaluate the use of KMnO_4 to decompose P-EDCs (phenol, BuP, and BPA) in aqueous solutions, the decomposition efficiency of the P-EDCs with KMnO_4 was compared with that using $\text{OH}^\bullet$ generated by ^{60}Co γ -ray irradiation. Some hydroxylated compounds, several organic acids, and inorganic carbon were identified as decomposition products by HPLC, IC, and TOC. These analyses indicated that decompo-

sition with KMnO_4 causes direct aromatic ring cleavage to form organic acids and inorganic carbon, while decomposition with $\text{OH}^\bullet$ proceeds through two steps: the addition-substitution of $\text{OH}^\bullet$ and the subsequent cleavage of the remaining aromatic rings. The amount of KMnO_4 spent to completely eliminate BuP and BPA was comparable to the amount of $\text{OH}^\bullet$ based on the number of electrons. Although three-times more KMnO_4 than $\text{OH}^\bullet$ was needed to completely eliminate phenol, the complete conversion of phenol into organic acids and inorganic carbon was achieved with 720 μM of electrons in both cases. These results demonstrate that KMnO_4 is as effective as $\text{OH}^\bullet$ generated by γ -ray irradiation for decomposing P-EDCs into low/non-toxic substances in water.

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