Decomposition of Trichlorobenzene with Different Radicals Generated by Alternating Current Electrolysis in Aqueous Solution

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Trichlorobenzenes can be easily decomposed by alternating current electrolysis in aqueous solution. The mechanism of the decomposition was found to be based on selective redox reactions with different radicals—hydrogen atoms and hydroxyl radicals—generated by water electrolysis.

Some of the advantages of electrochemical techniques over other techniques for environmental remediation are environmental compatibility, selectivity, versatility, and amenability. The toxicity of a wide range of pollutants can be substantially decreased by oxidation or reduction processes, especially in water.[1] Inoue et al. reported a method for hydrogenating organic compounds by using water electrolysis with direct current,[2] and Hayakawa developed an electrolysis system that uses high-frequency alternating current to purify water.[3] He showed that impurities could be oxidized in electrolyzed reduced water, something that had never been observed in the conventional direct current electrolysis where the anode and cathode are separated. This unusual phenomenon suggests the possibility of developing a new redox process for environmental remediation by determining its mechanism, but alternating current (AC) electrolysis is such a new technique that the mechanism has not yet been investigated.

We propose a mechanism based on selective redox reactions with different radicals generated by AC electrolysis that allows both oxidation and reduction at the same reaction site between adjacent electrodes. As shown in Figure 1, highly reactive free radicals formed by water electrolysis can be related with the decomposition of organic compounds. In this letter, we present the mechanism of the AC electrolytic decomposition of trichlorobenzene (TCB), an example of a hard-to-degrade organic compound. Analysis of the intermediates of the degradation revealed that the mechanism involves selective redox reactions with short-lived and highly reactive radicals: hydrogen atoms (•H) and hydroxyl radicals (•OH), that are electrochemically formed on the electrodes (Eqs 1 and 2).[4,5] Our experiments showed that these radicals control selectivity of the decomposition and its products.

$$H_2O + e \rightarrow \bullet H + OH^- \tag{1}$$

$$OH^- \rightarrow \bullet OH + e \tag{2}$$

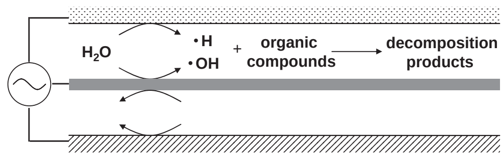

Figure 1. Proposed mechanism of the AC electrolytic degradation of organic compounds.

1,2,3-trichlorobenzene of reagent grade purchased from Kanto Chemicals was used in this study. Water was purified by Milli-Q (Millipore) filters immediately before use. NaOH and NaCl were obtained from Wako Chemicals. Electrolysis was carried out at room temperature with our assembled system, in which a 30-kHz 15-V AC potential of between the electrodes can be controlled by a unit connected with a function generator and amplifiers. Three electrodes were used: the working electrode, the counter electrode, and a ground electrode. Each was a titanium plate plated with platinum ($35 \times 175 \times 1\,\mathrm{mm}^3$, distance between neighboring electrodes $= 25\,\mathrm{mm}$, contact area with electrolytic solution $= 56\,\mathrm{cm}^2$), and arranged vertically in a cell for electrolysis. The cell was a cylindrical glass reactor (about 190 mm long and 95 mm in diameter) with a top.

TCB solutions (0.66 μM) containing NaOH or NaCl (20 mM) were subjected to batch electrolysis in the cell. A 30-kHz anti-phase rectangular impulse at 15-V was applied between the two electrodes and the other was grounded. The evolution of gases accompanying the electrolysis of water and the small increase of temperature with the Joule's heat were observed. The TCB decomposition products were characterized by gas chromatography (GC) with an FID detector (Shimadzu GC-14B) and GC-MS (Agilent Technologies GC/MS system 5972-6890) analysis of the headspace. Free radicals generated by electrolysis in the solution were analyzed by using an X-band electron spin resonance (ESR) spectrometer, the JES-FR30EX (JOEL).

Observation of the TCB decomposition by-products made it clear that two different reactions resulted in selective redox reactions. The formation of 2-ethyl-1-hexanol in the NaOH solution shows the occurrence of both a reductive ring-opening reaction and oxidation of the end methyl group (Figure 2a). That is, it shows that oxidation and reduction of TCB can take place competitively in the degradation, and the barely detected by-product makes it possible to characterize such an unusual process in AC electrolysis. Products other than 2-ethyl-1-hexanol were not observed, presumably because successive radical reactions occurred without forming stable intermediates (e.g., Eq 3). The decomposition rate of TCB after electrolysis for 0.5 h was 29.6%, and about 2% of that was estimated to be converted to 2-ethyl-1-hexanol. The complete decomposition of TCB with only a little by-product is probably due to the complex reaction of hydrogenation and oxidation with hydrogen atoms and hydroxyl radicals formed on the electrodes. As shown in Figure 2b, on the other hand, the formation of $CHCl_3$ in the NaCl solution showed a successive chlorination of TCB with chloride radicals (•Cl). About 43% of the decomposed TCB was estimated to be converted to $CHCl_3$. Toxic intermediates such as $COCl_2$ were not produced in this reaction because TCB in the reductive condition due to the surrounding hydrogen atoms was able to react to chloride radicals without being oxidized (e.g., Eqs 4 and 5).

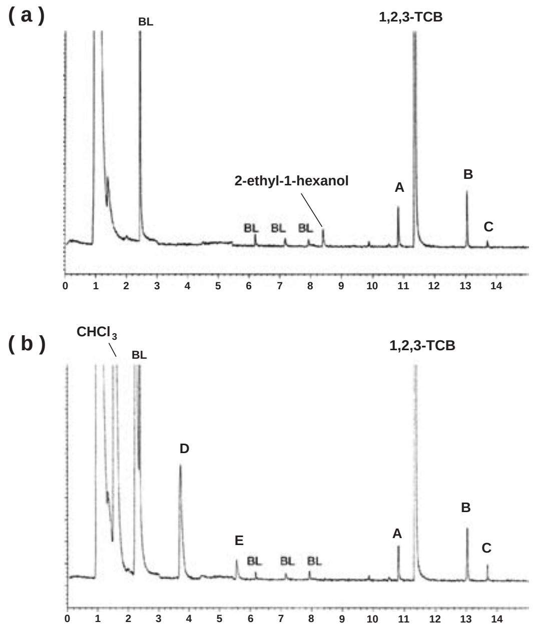

Figure 2. Chromatogram of TCB after electrolysis for 0.5 h (a) in NaOH solution and (b) in NaCl solution. A: isomer of TCBs, B and C: tetrachlorobenzenes, D and E: chloromethanes, BL: blank peak (A, B, and C were impurities of original reagants).

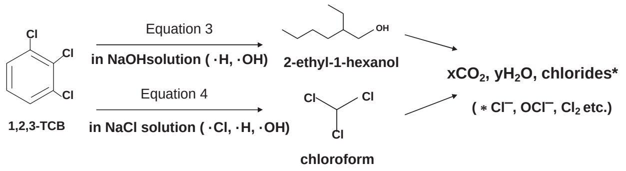

Figure 3. Pathway of the decomposition of TCB with different radicals generated by AC electrolysis in aqueous solution.

$$2C_6H_3Cl_3 + 17{\bullet}H + 17{\bullet}OH \rightarrow C_8H_{17}OH + 4CO_2 + 8H_2O + HCl \quad (3)$$

$$C_6H_3Cl_3 + 3{\bullet}H + 15{\bullet}Cl \rightarrow 6CHCl_3 \quad (4)$$

$$Cl^- \rightarrow {\bullet}Cl + e \quad (5)$$

When the current density in the reactions is assumed to be above 0.1 mA/cm^2 by considering the evolution of gases on the electrodes, the apparent current efficiency in the TCB decomposition can be estimated to be less than 1%. Such low efficiency is mainly due to the fact that most of the radicals formed on the electrodes immediately reacted with each other to produce hydrogen, oxygen, and H_2O.

To obtain information about the radicals formed by the AC electrolysis in NaOH solution, we investigated the ESR spectrum by using the spin-trapping technique with 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO).[6,7] The observation of a spin adduct of the hydroxyl radical (DMPO-OH) proved the existence of hydroxyl radicals. A spin adduct of the hydrogen atom (DMPO-H), however, was not detected. We think this is because the DMPO-H generated was immediately reduced to some species that does not produce an ESR signal at the potential used in this spin-trapping technique.[8] We therefore examined the electrolyzed water again to see the reactivity of hydrogen atoms with easily detected compounds: CCl_4 and isopropyl alcohol. Intermediates in their degradation provided evidence that hydrogen atoms are involved in the degradation of theses compounds (Table 1). The formation of $CHCl_3$ and CH_2Cl_2 from CCl_4 demonstrates successive hydrogenation with hydrogen atoms[9,10] in NaOH solution. In contrast, the formation of oxides such as acetone (CH_3COCH_3) and methyl alcohol (CH_3OH) from isopropyl alcohol ($CH_3CH(OH)CH_3$) under the same conditions is due to successive dehydration with hydroxyl radicals.[11,12] These results indicate that the observed decomposition of organic compounds is based on selective redox reactions with different radicals generated by the AC electrolysis of water.

Table 1. Intermediates in the AC electrolytic degradation of CCl_4 and isopropyl alcohol in NaOH solution

Organic compounds	Intermediates	Active reactant[a]
CCl_4	$CHCl_3$, CH_2Cl_2	•H
$CH_3CH(OH)CH_3$	CH_3COCH_3, CH_3OH	•OH

[a] Active reactant involved in the formation of the intermediates.

In conclusion, we have demonstrated a novel electrochemical technique using AC electrolysis to decompose TCB, and our experiments have revealed that its mechanism is based on selective redox reactions with different radicals generated by water electrolysis. Such hard-to-degrade organic compounds as TCB can be easily decomposed under very mild conditions in water, where hydrogen atoms and hydroxyl radicals generated by water electrolysis promote successive redox reactions of organic compounds. Since AC electrolysis enables selectivity and reaction products to be controlled, it can also be used to synthesize specified compounds and to purify water.

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