Supercritical Water Oxidation of a PCB of 3-Chlorobiphenyl Using Hydrogen Peroxide

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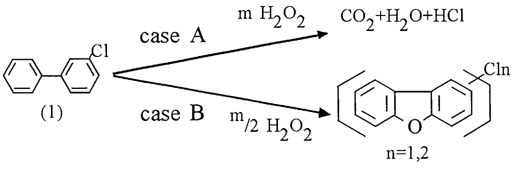
The supercritical water oxidation (SCWO) of a PCB of 3-chlorobiphenyl **(1)** was carried out at a temperature of 673 K and a pressure of 30 MPa with a flow reactor. The initial concentrations of **(1)** and hydrogen peroxide ranged from 1.84×10^{-3} to 8.74×10^{-2} M (1 M=1 mol dm^{-3}), and 0.181 to 2.67 M, respectively. The decomposition of **(1)** was higher than 99.9% so long as hydrogen peroxide was stoichiometrically added.

A large amount of polychlorinated biphenyls (PCBs) had been produced until prohibited by the law from the use and manufacture due to their strong toxicity. Although various methods such as incineration,[1] chemical transformation,[2] and plasma treatment [3] have been examined to decompose PCBs, less satisfactory results have been obtained. Results on SCWO of PCBs using hydrogen peroxide have not been reported so far. We proposed the SCWO using hydrogen peroxide as an alternative for the oxidant of oxygen.[4] In this study, it was found that hydrogen peroxide has a great role in the decomposition of PCBs in supercritical water (SW). This study reports not only our findings from the stoichiometric oxidation of 3-chlorobiphenyl **(1)** in SW using hydrogen peroxide in a flow reactor (Scheme 1, case A), but factors promoting the extent of reaction speculated from reaction products of the oxidation of **(1)** in such a case where half the stoichiometric demand of hydrogen peroxide was used (Scheme 1, case B).



Scheme 1. Reaction of **(1)** with SCWO.

3-chlorobiphenyl **(1)** (Lancaster, 98 wt% purity) was chosen as a reactant to facilitate analysis of reaction products. Figure 1 displays the schematic of a continuous-flow reactor system that we fabricated for our oxidation studies in SW. Hydrogen peroxide as the oxidant was premixed with the water. **(1)** and the aqueous hydrogen peroxide solution were compressed to a desired operating pressure using individual pumps. All experiments were performed at a pressure of 30 MPa and a temperature of 673 K. Pressure control was achieved by a back-pressure regulator within ± 0.15 MPa. The flow rates of **(1)** and the aqueous hydrogen peroxide ranged from 0.1 to 10 and 0.001 to 9.99 ml/min, respectively. The temperature of the reactor was controlled within ± 0.5 K by electric furnaces The fluid temperature was measured with a Hastelloy C-276 sheath thermocouple K class which was placed between the mixing tee and the reactor. The two types of reactor were used; one was 0.351-cm i.d. (0.635-cm o.d.), 45-cm long and another was 0.079-cm i.d. (0.159-cm o.d.), 2-m long. Both reactors were constructed with Hastelloy C-276, and they were set into the second electric furnace. This flow reactor system was designed so that **(1)** and oxidant do not come in contact with each other until they are heated to the desired reaction conditions. It was confirmed that **(1)** can not be decomposed in SW alone. The feed streams were mixed at the reactor inlet using a Hastelloy C-276 mixing tee.

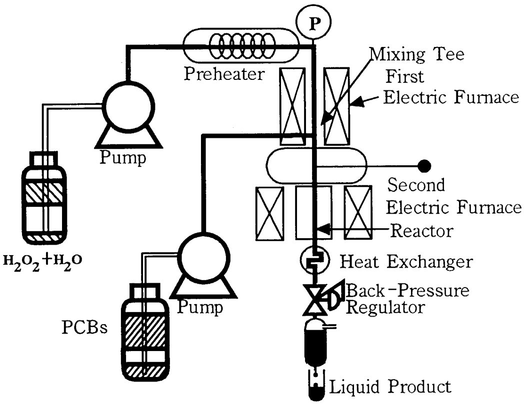


Figure 1. Continuous flow reactor system.

The reactor effluent was cooled quickly in a heat exchanger and depressurized. The liquid effluent was collected in a gas-liquid separator. The reaction products were identified by comparing their mass spectra and GC retention time with those from the authentic standards. 0% of stoichiometric demand is defined as the amount of hydrogen peroxide in the reaction formula as shown in References and Note 5.

Experiments were designed and conducted to compare the efficiencies of hydrogen peroxide for the destruction of **(1)**. The variables considered were residence time and the concentration of hydrogen peroxide. Under the conditions used, water can exist as a supercritical fluid.[6] Oxidation of **(1)** proceeded in the flow reactor.

The pH values of reaction effluent showed between 1.6 to 1.4. Table 1 shows the conversion of **(1)** in each run including case B. As shown in Table 1, the conversion reached more than 99.9% in at least 10.7 seconds. The conversion does not seem to be influenced by the residence time under the conditions examined, but be strongly dependent on stoichiometric demand of the hydrogen peroxide. Further, it is greatly advantageous that, in contrast

Table 1. Experimental conditions and conversion of **(1)**

Run Number	Residence Time (sec)	Percent Excess H_2O_2	(1) Conc. (mM)	H_2O_2 Conc. (M)	Water Conc. (M)	Conversion (%)
1	101.7	18	5.46	0.181	10.68	99.99
2	101.7	41	4.35	0.172	10.16	99.99
3	92.5	240	1.99	0.186	11.18	99.98
4	72.7	376	1.84	0.245	14.47	99.99
5	53.6	545	1.86	0.335	19.81	99.90
6	53.6	222	3.72	0.335	19.81	99.99
7	36.3	57	11.20	0.490	28.94	99.91
8	13.5	55	49.00	2.100	77.77	99.99
9	13.0	110	36.90	2.170	79.69	99.98
10	12.6	9	74.90	2.280	83.53	99.98
11	12.2	24	66.90	2.330	85.45	99.95
12	11.8	12	76.90	2.410	88.33	99.99
13	11.1	22	75.70	2.590	95.05	99.98
14	10.7	95	48.40	2.650	96.97	99.96
15	56.5	-49	24.00	3.180	18.77	85.22

to gas oxidation where the oxidation by oxygen should be carried out at 1023 K,[7] PCBs can be decomposed at a lower temperature of 673 K by the SCWO. The higher conversion at the lower temperature was considered to likely result from the fast thermal decomposition of hydrogen peroxide. Unlike oxygen, hydrogen peroxide is rapidly decomposed during the pre-heating period into hydroxyl radicals (·OH), which are extremely active oxidizing species and promotes the SCWO reaction. The participation of OH radicals in the SCWO may be confirmed by reaction products in the case B of SCWO. When half the stoichiometric demand of hydrogen peroxide was used (run 15), the conversion of PCBs was decreased to 85.22%. Table 2 [8] shows the reaction products in run 15.

Table 2. Reaction products in run 15

Products	Concentration wt %
chlorobenzene	trace
phenol	trace
o-dichlorobenzene	trace
acetophenone	0.3
m-chlorobenzaldehyde	trace
chlorophenol	3.9
m-chloroacetophenone	0.7
m-chlorobenzoic acid	1.0
1-chloronaphthalene	trace
biphenyl	8.5
2-chlorobiphenyl	0.2
dibenzofuran	2.1
3-chlorobiphenyl	70.2
3-chloro-PCDF	0.2
dichlorobiphenyl	2.4
1-chloro-PCDF	0.4
2-chloro-PCDF	5.2
4-chloro-PCDF	2.6
phenanthrene	0.5
xanthone	0.3
2,7-dichloro-PCDF	0.6
2,5-dichloro-PCDF	0.6

Various reaction products were identified, indicating that the oxidation of **(1)** in SW involve a complex set of multiple reactions. The most abundant constituent in the reaction products was polychlorinated dibenzofurans (PCDFs) , which was a mixture of 1-, 2-, 3-, 4-chloro-, and dichloro-PCDFs. Rubey et al., have observed the formation of PCDFs from PCBs in incineration method at 873 K,[9] in which they have propoced the mechanisms by HCl elimination from chlorinated phenyl phenols formed via OH addition to PCBs. Detailed results from thermodynamic and kinetic analyses of OH radical reaction with chlorinated aromatic compounds clearly show several likely routes to the formation of PCDFs involving unimolecular HCl elimination or loss of Cl, in which hydroxyl radical addition to aromatic ring occurs.[10] The PCDFs could be recognized to be an intermediate in oxidation of PCBs with OH radicals.[11] It is, therefore, seemed that OH plays an important role as a reactive species in the SCWO. In the case of run 1-14, furthermore decomposition of the PCDFs were ascertained by the reaction of PCDFs with hydrogen peroxide in SW. As shown in Table 1, it was confirmed that hydrogen peroxide can be an effective oxidant of SCWO but the stoichiometric amount of hydrogen peroxide should be always required in order to accomplish the complete decomposition of PCBs in this method. We demonstrated the continuous decomposition of PCBs by the SCWO using hydrogen peroxide.

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