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Superoxide Radical-Induced Degradation of Polychlorobiphenyls and Chlordanes at Low Temperature

Kazuyoshi Matsunaga, Masaaki Imanaka, Katashi Kenmotsu, Junko Oda,
Seiji Hino, Minoru Kadota, Hirokazu Fujiwara, and Tadashige Mori

Okayama Prefectural Institute for Environmental Science and Public Health,
739-1, Uchio, Okayama 701-02, Japan

Polychlorobiphenyls (PCBs), having unique physical and chemical properties, have been used for many years as an important industrial product such as dielectric fluids, heat-exchanger fluids, plasticizers and flame retardants since 1927. Manufacture, use and disposal of PCB-contaminated materials were prohibited in 1973 in Japan, because it was reported that a disease known as Yusho was induced by ingestion of a commercial rice oil accidentally contaminated by Kanechlor (commercial name in Japan, Kanechlor KC 300, 400, 500 and 600). It has been found that commercial PCBs have also contained polychlorinated dibenzofuranes (PCDFs) formed under pyrolytic conditions. Disposal of hazardous PCBs, therefore, has resulted in considerable environmental problems because of their extreme resistance to degradation. The large amount of PCBs has remained as an unsettled matter in the global community. The acceptable disposal technologies of PCBs are thermal processes (Shaub et al. 1983; Hunt et al. 1984; Tucker et al. 1985), chemical destruction (Brunelle et al. 1985; Sugimoto et al. 1987; Sugimoto et al. 1988), and biochemical degradation (Baxter et al. 1984; Behard et al. 1987).

This paper presents the results of the chemical degradation studies of PCBs and chlordanes in the presence of pyridine, a chain transfer agent, using superoxide ion (O_2^-) produced by the reaction of hydrogen peroxide and sodium metaperiodate at the low temperature (60-75°C). In the synthetic reaction of high molecular compounds, the chain transfer agent with the much higher value of the chain transfer constant was added in order to stop the chain reaction at a certain point. In this degradation method pyridine, the chain transfer agent with the much lower value of the chain transfer constant, was used so as to prolong the life span of O_2^- and/or the induced PCB's radical. The radical degradation of PCBs was finally promoted.

MATERIALS AND METHODS

Send reprint requests to K. Matsunaga at the above address.

All of the Kanechlor and active carbon-impregnated silica gel (Ono et al. 1986) were purchased from Wako Pure Chemical Industries, Ltd. Technical chlordanes were obtained by extraction with hexane from Nakarai's chlordane. Tris(1,3-di-chloro-2-propyl)phosphate(CRP) was purchased from Tokyo Chemical Industry Ltd. Hexane, ethanol and methanol were of commercial pesticide grade. Other reagents were of the highest quality available. Distilled water and 4% sodium sulfate were washed with hexane.

Gas chromatograph-mass spectrometry (GC-MS) was performed with a JEOL JMA-DX303 double-focusing mass spectrometer equipped with a Hewlett-Packard 5890 gas chromatograph and a JEOL JMA-DA5000 mass data analysis system. Gas chromatographic conditions for PCBs, PCDFs, polychlorinated dibenzodioxines(PCDDs) and other hexane extracts such as polar by-produts were as follows: column, fused silica(30 m x 0.32 mm i.d.) DB-1701 capillary column with 0.25 μm coating (purchased from J & W Scientific), column temperatures, 180°C for 1 min isothermal 8 deg/min to 300°C; injector, splitless mode. Mass parameters were as follows: elctron energy, 70 eV; emission current, 300 μA; electron multiplier voltage, 3.0 KeV. ion source, temperature, 250°C; scan range, 30-600 amu, 0.5 sec scan time cycle. Gas chromatographic conditions for volatile organics were as follows: column, megabore column (30 m x 0.54 mm i.d.) GS-Q (J & W Scientific); column temperature, 40°C for 4 min isothermal, 8 deg/min to 200°C, 200°C for 4 min isothermal; injector, splitless mode. Mass parameters were the same as described for PCBs except for a cycle time of 1.5 sec. The degradation rates were calculated from total integrals of peaks-after vs. before degradation of PCBs and other samples.

A Yokogawa Model IC-500 ion chromatography system equipped with a conductivity detector for chloride ion was used. Ion chromatographic conditions were as follows: column, SAM3-125 (10 μm, 12 cm x 0.49 cm i.d.; Yokogawa) equipped with a 3 cm x 0.46 cm i.d. precolumn packed with PAM3-035(10 μm; Yokogawa); eluent, 4 mM sodium carbonate-1.2 mM sodium hydrogencarbonate; flow-rate 2.0 mL/min.

Twenty milligrams of PCBs or chlordanes, dissolved in 2 mL of ethanol, were added to the beaker containing 10 mL of methanol, 2 mL of pyridine and 25 mL of 0.4 M sodium metaperiodate. The white muddy mixture solution was stirred mechanically with a glassed magnetic bar and warmed to about 60°C on the magnetic stirrer having a hot-plate. 50 mL of 3M hydrogen peroxide was succesively added drop by drop to the mixture solution while being stirred. After adding a few milliliters of hydrogen peroxide, the solution temperature initially rose in the range of 68-75°C and then gradually decreased. Therefore, the temperature was almost constant at 70°C when the sample was degraded. When approximately 25 mL of 3M hydrogen peroxide had been added to the reaction medium, an additional 25 mL of 0.4M sodium metaperiodate was added dropwise with the remaining hydrogen peroxide. After the addition of both hydrogen peroxide and sodium metaperiodate, the clear homogenous solution was stirred at a temperature higher than 60°C until the color of the solution turned from yellow to pale green. It was then cooled to room temperature and extracted with two 50 mL portions of hexane. The combined hexane extracts were then washed with 4% sodium sulfate, dried over anhydrous sodium sulfate and concentrated to 2 mL under reduced pressure. The hexane was submitted to GC-MS analysis for the detection of PCBs, hydrocarbons and other degradation products. The combined hexane extracts were colored in pink by dissolving iodine but they were decolored by the concentration under reduced pressure. The aqua layer, on the other hand, was submitted to analysis of chloride ions.

For the analysis of PCDFs and PCDDs, 20 mg of a mixture consisting of the same amount of four Kanechlor (PCB-mix) was degraded as previously mentioned and the decomposition substances were extracted with hexane. Thus, the four hexane extracts were combined from each degradation substances of 20 mg of PCB-mix and concentrated to ca. 0.5 mL under reduced pressure. The hexane was applied to the active carbon-impregnated silica gel column. This column was washed with 200 mL of 25% dichloromethane/hexane (v/v) and then eluted with 200 mL of toluene. The toluene fraction was concentrated to 1 mL and PCDFs and PCDDs were analyzed by the GC-MS. For the measurement of volatile organics, the previously mentioned degradation reaction was performed in a 200-mL four neck flat bottom flask joined to two cylindrical flasks and a thermometer. From the fourth neck a 5 mL reaction solution was taken and poured into the headspace vial every 30 min. The vials were then sealed. Headspace vials were stored in a 70°C water bath. 500 μL of the volatile gases were analyzed by headspace method using GC-MS.

After separating the PCBs and the hexane extracts as previously mentioned, the aqua layer was analyzed for chloride ion concentration by ion chromatography after diluting with distilled water. Carbon dioxide gas produced in superoxide degradation reaction in the above mentioned 200-mL four neck flat bottom flask was introduced to N/10 $Ba(OH)_2$ solution with 50-100 mL/min suction speed and was determined by an aqueous pH titration with N/10 HCl. Using the same 200-mL four neck flat bottom flask, chlorine gas was introduced to 0.1% o-tolidine hydrochloric acid solution with 50-100 mL/min suction speed and was measured by spectrophotometer at 435 nm.

RESULTS AND DISCUSSION

Two milligrams of KC 400, KC 500 and KC 600 dissolved individually in ethanol were degraded by O_2^- that was produced in the reaction between 3M hydrogen peroxide and 0.4M sodium metaperiodate(Knowles et al. 1969). The degradation rate of PCBs in several polar media are summarized in Table 1. 90.1% of the KC 400 sample was degraded at a much lower temperature(60-

Table 1. Effect of Solvent on the Degradation Rate of PCBs

2 mL of PCB ethanol solution	Volume of additional solvent(mL)	Degradation of PCBs in solvents(%)[a] None[b]	Methanol	Ethanol	DMSO[c]
1 KC 400, 2mg	0	90.1	—	—	—
2 KC 500, 2mg	0	46.5	—	—	—
3 KC 600, 2mg	0	50.1	—	—	—
4 KC 600, 2mg	10	—	68.0	65.7	59.5
5 KC 600, 2mg	25	—	65.4	58.8	—
6 KC 600, 2mg	50	—	69.8	41.8	—

[a] Reaction time of a given quantity of H_2O_2 and $NaIO_4$; 30 min.
[b] This word means the absence of an organic solvent except for 2 mL of the ethanol dissolved PCBs.
[c] Dimethyl sulfoxide.

75°C) than 700-1450 °C in the thermal degradation without addition of an organic solvent except for the ethanol dissolved PCBs (entry 1). However the degradation rates of KC 500 and KC 600 were 46.5% and 50.1%, respectively, under the same conditions (entries 2-3) and a little of the oil drop was observed on the surface of the degradation solution of both KC 500 and KC 600. The experimental conditions, therefore, were examined with regard to KC 600. It is considered that the degradation of PCBs depends on the rate-determining step of whether superoxide radical is easily transmitted from the hydrophilic medium to the hydrophobic PCBs. In general, solvent polarity has little effect on the rates of radical reaction. However, it has been reported that methanol, ethanol and dimethyl sulfoxide (DMSO) showed a large effect on the rate of decomposition of tert-butyl o-phenylthioperbenzoate (Pryon ed 1976). This report suggests that the radical generated in the hydrophilic medium transmitted effectively to the hydrophobic substances. In fact, these solvent characteristics had a significant influence on the degradation rate of PCBs as shown in Table 1. Addition of methanol or ethanol to the radical reaction medium increased 15 percent or more the rate of degradation of KC 600 (entries 4-6). Addition of DMSO was less effective than those of methanol and ethanol. The large amounts of methanol or ethanol did not influence the degradation rate and the rate actually decreased in ethanol. In the composition of chlorinated biphenyl before and after degradation of a PCB-mix as shown in Fig.1, penta- to octachlorobiphenyls were very resistive to superoxide degradation as compared to the di- to four-congeners. This obsevation was in conflict with the results of Sugimoto et al.(1988) but it is satisfactory to consider that the rates of degradation depend on solubility of PCB in the reaction system.

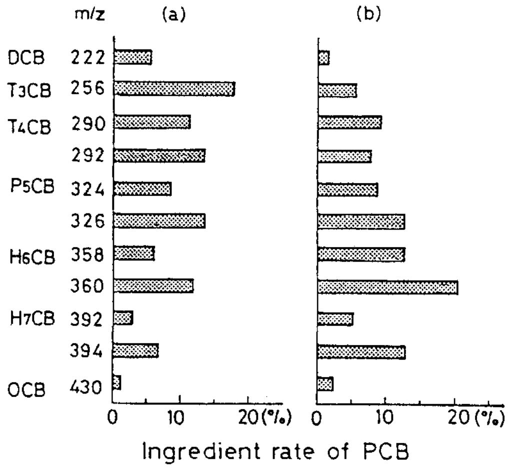

Figure 1. Comparison of the ingredient of chlorinated biphenyl before (a) and after (b) degradation of the PCB-mix by superoxide treatment.

Table 2. Efficiency of Chain Transfer Agent on Degradation of PCBs, Technical chlordanes and CRP

Entry	Compound	Amount mg	Chain transfer agent(2mL)	Degradation rate (%) [a]
1	Chlordane	2	Pyridine	99.23
2	KC 400	2	Pyridine	99.70
3	PCB-mix	2	Pyridine	98.01
4	PCB-mix	20	Pyridine	50.3
5	PCB-mix	20	Pyridine	54.5
6	PCB-mix	20	Pyridine	56.6
7	PCB-mix	20	Pyridine	39.6
8	PCB-mix	20	Pyridine	70.0
9	PCB-mix	20	Dioxane	30.8
10	PCB-mix	20	PEG 200 [c]	31.5
11	PCB-mix	20	PEG 300	26.2
12	PCB-mix	20	PEG 400	28.9
13	PCB-mix	20	PEG 600	25.8
14	Chlordane	20	Pyridine	99.9
15	CRP [b]	2	Pyridine	99.52

[a] All of the entries were degraded after a 30 min reaction time except for entry 7 (15 min) and 8 (2 hour).

[b] Tris(1,3-dichloro-2-propyl)phosphate.

[c] Polyethylene glycol

The chain transfer agent with the much higher value of the chain transfer constant has been used to adjust the polymerization grade of a polymer in general. For instance, n-butylmercaptane and phenylphosphine are the suppressants in the chain reaction (Kambara ed. 1976). From this fact we

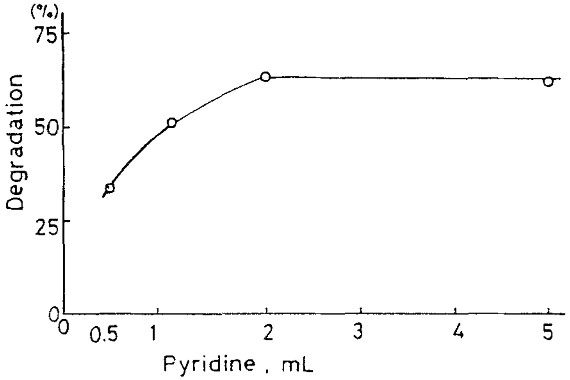

Figure 2. An adeqate amount of pyridine for prolonging the life span of both superoxide and the induced PCB radical in the degradation reaction.

speculated that the application of the agent with the much lower value of the chain transfer constant to the superoxide degradation medium could prolong the life span of both O_2^- and/or the induced PCB radical and that the radical degradation of PCBs might finally be promoted. It was considered that pyridine, dioxane and glycols dissolved in both water and organic solvents were the most suitable reagent to the superoxide degradation. As summarized in Table 2, It was clear that pyridine was much more efficient than dioxane or glycols (see entries 4-6 and 9-13). These findings coincided with the report that O_2^- was stable with an increase of pH (Asada 1976). The degradation rate of chlordanes, KC 400 and a PCB-mix in 2 mg sample was 99.23%, 99.70% and 98.01%, respectively (entries 1-3). The rate of degradation of PCB-mix in a 20 mg sample ranged from 50.3% - 56.6% by GC-MS analysis (entries 4-6). The degradation rate of a 20 mg of PCB-mix increased with exposure time of a given quantity of a H_2O_2 and $NaIO_4$ (entries 6-8). The rate of degradation for technical chlordanes and CRP was also a level of 90%. The optimum volume of pyridine was 2 mL at the degradation step as shown in fig. 2.

Figure 3 shows the cappilary GC-MS chromatograms of 2 mg of each KC 400, the PCB-mix and chlordanes before and after treatment with H_2O_2-$NaIO_4$ in 30 min degradation reaction. The PCBs and the chlordanes were efficiently decomposed by superoxide and their parent hydrocarbons such as biphenyl were not detected by GC-MS analysis with DB-1701 at 60-300°C. PCDFs and PCDDs were under the detection limit of 50 ppb (by GC-MS, scan method) in the degradation products of 80 mg of PCB-mix.

An analysis for volatile organics using the capillary GC-MS analysis with GS-Q did not detect any low molecular aliphatic compounds such as methane, ethane and chlorinated aliphatic compounds, especially chlorinated ethanes and ethenes in samples which were taken every 30 min during the 2 hour degradation reaction.

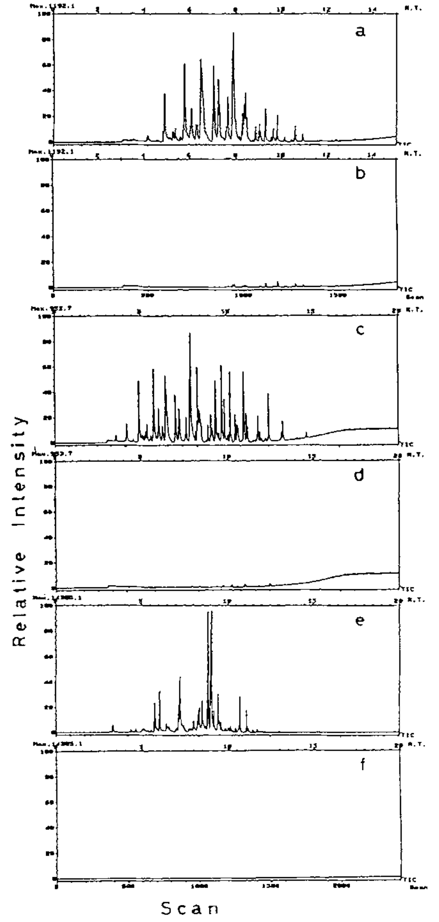

Figure 3. Capillary GC-MS chromatograms of KC 400, PCB-mix and technical chlordanes before and after treatment with superoxide:
(a), (c) and (d); before degradation pattern (2000ppm) of KC-400, PCB-mix and technical chlordanes, respectively.
(b), (d) and (f); degradation pattern of KC 400, PCB-mix and chlordanes, respectively.
Analytical conditions are given in the text.

Chloride ion, which was produced by the degradation of PCB, in the aqua layer after extraction with hexane was determined by ion chromatography and showed 66.2% of theoretical chloride ion yield for a 100 percent degradation of PCB. Cloroine gas was not detected by o-tolidine colorimetric method. The reason why the concentration of chloride ion had not been coincided with the degradation rates of PCB was not clear.
The production of carbon dioxide gas on the superoxide degradation of KC 400 was recognized by the formation of the precipitate of $BaCO_3$ and the value was 8.1% for the theoretically produced CO_2.

The absence of low molecular aliphatic compounds and the production of chloride ion and carbon dioxide suggested the following degradation process that the overall superoxide-induced reaction for PCB might be oxidized to carbon dioxide and chloride ion quickly.

$C_{12}H_6Cl_4 + O_2^- \rightarrow C_{12}H_6Cl_3O_2\cdot \rightarrow\rightarrow$

(Promotion of a chain reaction by pyridine) $\rightarrow\rightarrow CO_2 + Cl^-$

The result agreed that the highly chlorinated PCBs could be degraded completely to inorganic ions as in the reference of Sugimoto et al.(1988). Sugimoto et al.(1988) advocated that superoxide "ion" reacted with polyhaloaromatics by nucleophilic substitution but our result emphasized the action of superoxide "radical" by using a chain transfer agent.

Our new method which is developed for the degradation of polychlorinated compounds by means of superoxide at low temperature is simple and does not demand the larger scale equipment in thermal degradation.

REFERENCES

Baxter RM, Sutherland DA (1984) Biochemical and Photochemical process in the degradation chlorinated biphenyls. Environ Sci Technol 18: 608-610

Behard DL, Wagner RE, Brennan MJ, Haberl ML, Brown JF (1987) Extensive degradation of aroclors and environmentally transformed polychlorinated biphenyls by Alcaligenes eutrophus H850. Appl Environ Microbiol 53: 1094-1102

Brunelle DJ, Mendiratta AK, Singleton DA (1985) Reaction/removal of polychlorinated bihenyls from transformer oil: Treatment of contaminated oil with poly(ethyleneglycol)/KOH. Environ Sci Technol 19: 740-746

Hunt GT, Wolf P, Fennelly PT (1984) Incineration of polychlorinated biphenyls in high efficiency boilers: A viable disposal option. Environ Sci Technol 18: 171-179.

Kambara A, Fujiwara S (1970) Analytical handbook of high molecular compounds. 3rd ed. Asakura Shoten, Tokyo, p 423-430

Knowles DJ, Gibson JF, Pick FM, Bray RC (1969) Electron-spin-resonance evidence for enzymic reduction of oxygen to a free radical, the superoxide ion. Biochem J 111: 53-58

Ono M, Wakimoto T, Tatsukawa R, Masuda Y (1986) Polychlorinated dibenzo-p-dioxins and dibenzofurans. Chemosphere 15: 1629-1634

Pryon WA (1976) Free radicals in biology. ed. vol.1, Academic Press, New York, p 27

Shaub WM, Tsang W (1983) Dioxin formation in incinerators. Environ Sci Technol 17: 721-730

Sugimoto H, Matsumoto S, Sayer DT (1987) Oxygenation of polychloro aromatic hydrocarbons by superoxide ion in aprotic media. J Am Chem Soc 109: 8081-8082

Sugimoto H, Matsumoto S, Sayer DT (1988) Degradation and dehalogenation of polychlorobiphenyls and halogenated aromatic molecules by superoxide ion and by electrolytic reduction. Environ Sci Technol 22: 1182-1186

Tucker SP, Carson GA (1985) Deactivation of hazardous chemical wastes. Environ Sci Technol 19: 215-220

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