Cyclodextrin Addition Effect on Radiation-induced Decomposition of Chlorophenols in Deoxygenated Water

Xixian Huang, Hidehiko Arai, Shinpei Matsuhasi, and Teijiro Miyata
Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute,
Watanuki-machi, Takasaki, Gunma 370-12

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Radiation induced decomposition of chlorophenols in the presence of cyclodextrins (CDs) was studied. CD addition retarded the decomposition and dechlorination of chlorophenols. The effects remarkably depended on the cavity size of CDs and on the molecular shape of chlorophenols.

Cyclodextrins, cyclic oligosaccharides containing six (α-CD), seven (β-CD), or eight (γ-CD), D-(+)-glucopyranose units linked by α-(1,4) bonds, are one of the most important host compounds. A variety of guest compounds comprising ionic species, organic compounds and pharmaceutical drugs can be included in the cavity of CDs in aqueous solution.[1]

Increasing attention was recently devoted to the study of the photochemistry of aromatic molecules in CD cavities.[2] Phenolic compounds were the object of particular interest because of their ability to form hydrogen bonds with the hydroxyl groups of the macrocycle.[3,4] On the other hand, according to Yamamoto et al,[5] β- and γ-CDs significantly reduced the rate constants of the one-electron reduction of biphenyl sulfonates, but α-CD hardly affected the reduction. In this paper, we studied the influence of CDs on the decomposition and dechlorination of chlorophenols in deoxygenated aqueous solutions by gamma-rays.

The *o*-, *m*-, and *p*-chlorophenol aqueous solutions (5×10^{-4} mol dm^{-3}) in the presence of CDs were used. The solutions were deaerated by bubbling with pure helium gas in vials with rubber caps and irradiated by gamma-rays at room temperature. The yields of the produced chloride ion were determined by ion exchange chromatography. The chlorophenol concentrations were measured by high performance liquid chromatography using a C_{18} column (LiChroCART 125-4, Cica MERCK).

The effects of various CDs on the G values of decomposition, G(-chlorophenol), and dechlorination, $G(Cl^-)$, of chlorophenols in deoxygenated solutions are summarized in Table 1. The diameters of the cavities are larger in the order of α-, β- and γ-CDs (4.5, 7.0 and 8.5 Å, respectively). The amounts of the decomposed chlorophenol and produced chloride ion were increased with an increase in the cavity size except for *o*-chlorophenol.

In order to get information on active species responsible for the decomposition, *t*-butyl alcohol addition effect was studied. Table 2 shows the *t*-butyl alcohol effect on the decomposition and dechlorination of *p*-chlorophenol. *t*-Butyl alcohol addition also somewhat retarded the *p*-chlorophenol decomposition and dechlorination, but even addition of 5×10^{-2} mol dm^{-3} only slightly affected the reactions. These results indicate that OH radicals contribute only a little to the decomposition and dechlorination. This is in accord with the results by Getoff and Solar.[6] They reported that 27% of the dechlorination is attributed to OH radicals at the initial stage of irradiation and that about 6% to hydrogen atoms. Then, hydrated electrons are considered to be mainly responsible for the decomposition and

Table 2. The *t*-butyl alcohol effect on the decomposition and dechlorination of *p*-chlorophenol

Molar ratio[a]	G(-chlorophenol)	Ratio[b]	$G(Cl^-)$	Ratio[b]
0	0.93	1.00	0.54	1.00
5	0.95	1.02	0.51	0.95
10	0.95	1.02	0.51	0.95
50	0.88	0.95	0.46	0.86
100	0.85	0.92	0.44	0.82

Dose: 4 kGy.

[a] Molar ratio of *t*-butyl alcohol to *p*-chlorophenol.

[b] Ratio to the value without CD.

Table 1. The cyclodextrin addition effect on the decomposition and dechlorination of chlorophenols

Substance	Additives	G (-chlorophenol)	Ratio[a]	$G(Cl^-)$	Ratio[a]
o-Chlorophenol	no addition	0.93	1.00	0.49	1.00
	α-CD	0.63	0.68	0.27	0.55
	β-CD	0.56	0.60	0.27	0.55
	γ-CD	0.63	0.68	0.29	0.60
m-Chlorophenol	no addition	0.83	1.00	0.41	1.00
	α-CD	0.34	0.41	0.20	0.44
	β-CD	0.37	0.44	0.22	0.53
	γ-CD	0.41	0.50	0.27	0.65
p-Chlorophenol	no addition	0.80	1.00	0.49	1.00
	α-CD	0.37	0.45	0.20	0.40
	β-CD	0.41	0.50	0.22	0.45
	γ-CD	0.44	0.54	0.24	0.50

The concentration of additives: 5×10^{-3} mol dm^{-3}, dose: 4 kGy. [a]Ratio to the value without CD.

dechlorination of chlorophenols in Table 1.

However, the rate constant of glucose to hydrated electrons is very small (3×10^5 $dm^3mol^{-1}s^{-1}$)[7] so that those of CDs are thought to be small. The retardation effect by CDs in Table 1 can be explained by assuming that inclusion into CD cavities protects chlorophenols from the attacks by hydrated electrons. The results in Table 1 also indicate that CDs of smaller cavity strongly include *m*- and *p*-chlorophenols into their cavities. For *o*-chlorophenol, the relation is not clear.

The present study indicates that the CD effect depends on the cavity size of CDs and on the molecular shape of chlorophenols. It means that the CD effect is closely associated with the formation of inclusion complexes between CDs and chlorophenols. A small cavity may allow deep inclusion of guest molecules, while the enlarged cavity dose not enable the guest to be accommodated deeply. On the other hand, the shapes of *m*- and *p*-chlorophenols make a good fitting in the CD cavity. The future research will be worked on the products formed from chlorophenols with CDs.

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