

Enhanced Phenol Yield from Radiation-induced Decomposition of Chlorophenols in Deaerated Water by Addition of Cyclodextrin and Glucose

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The yield of phenol, identified as the main product, was enhanced remarkably by addition of cyclodextrins (CDs) and glucose. The effect was found to increase with cavity dimensions. It was suggested that inclusion accelerates hydrogen atom abstraction by the incorporated intermediate radicals.

The host-guest compounds have induced increasing interest in the field of supramolecular chemistry. Large permanent macrocyclic compounds are employed for trapping smaller molecules in cavities of appropriate size. CDs are largely used as hosts for organic molecules. The most important property of CDs is the ability to accommodate guest molecules of the appropriate size in their cavity.¹ We have recently investigated the radiation-induced decomposition of chlorophenols included in CD cavity in deaerated solution.² The CDs were found to retard decomposition and dechlorination. As an extension of the above investigation we have undertaken the study on the products formed from chlorophenols in the presence of CDs and glucose.

The preparation and irradiation of solutions have been already described in the previous paper.² The yields of products were measured by high performance liquid chromatography (HPLC) using a Shodex Ionpak KC-811 column.

The HPLC analysis has indicated that the main products from decomposed chlorophenols in deoxygenated solution are phenol and some substance like chlorophenol dimer. The enhanced phenol yield by additives is remarkable. The effects of CDs, glucose and *t*-butyl alcohol on phenol yield and formation selectivity are summarized in Table 1. The enhanced phenol yield by CDs is the most prominent for *m*-chlorophenol, that is, the ratio of selectivity to the value without additive is 22 or 25, and slightly less for *o*-, and *p*-chlorophenol. The CD addition

enhanced phenol yield in the order of $\alpha < \beta < \gamma$. Glucose is also effective with chlorophenols, but smaller than CDs. The result with *t*-butyl alcohol showed somewhat influence on the yields, even with $5.0 \times 10^{-2} \text{ mol dm}^{-3}$, a value of 100:1 for the *t*-butyl alcohol/*p*-chlorophenol ratio.

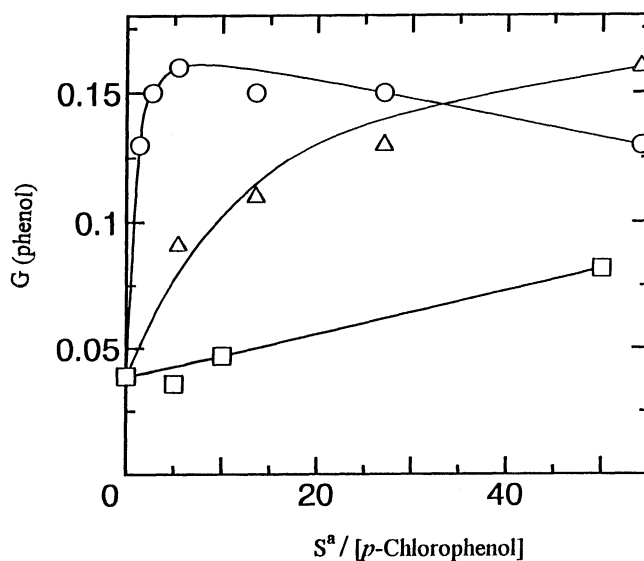


Figure 1. Effect of addition of β -CD (○), glucose (△) and *t*-butyl alcohol (□) on phenol yield from decomposed *p*-chlorophenol, $^a K \times [\text{additive}]$ except for *t*-butyl alcohol, $K = k_1(\text{OH} + \text{glucose}) / k_2(\text{OH} + \textit{t}\text{-butyl alcohol}) = 2.7$.

Table 1. The addition effect of cyclodextrins, glucose and *t*-butyl alcohol on phenol yield from radiation-induced decomposition of chlorophenols

Chlorophenol	G (phenol) / G (decomposed chlorophenol)						
	no addition	α -CD ^a	β -CD ^a	γ -CD ^a	Glucose ^a	<i>t</i> -Butyl alcohol ^a	<i>t</i> -Butyl alcohol ^b
<i>o</i> -Chlorophenol	0.041/0.93 (1.00)	0.21/0.63 (7.6)	0.20/0.56 (8.1)	0.22/0.63 (7.9)	0.13/0.74 (4.0)	—	—
<i>m</i> -Chlorophenol	0.019/0.83 (1.00)	0.17/0.34 (22)	0.19/0.37 (23)	0.23/0.41 (25)	0.11/0.58 (8.3)	—	—
<i>p</i> -Chlorophenol	0.039/0.80 (1.00)	0.14/0.37 (7.8)	0.15/0.41 (7.5)	0.19/0.41 (9.5)	0.12/0.55 (4.5)	0.047/0.82 (1.2)	0.11/0.72 (3.1)

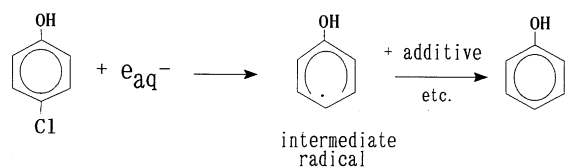
The values in parentheses: ratio of phenol formation selectivity (= ratio of phenol yield to decomposed chlorophenols) to the value without additive, dose: 4 kGy, ^a $5.0 \times 10^{-3} \text{ mol dm}^{-3}$, ^b $5.0 \times 10^{-2} \text{ mol dm}^{-3}$.

In order to know how OH radicals act for the phenol formation, the reactivity differences among the additives toward OH radicals were considered. For this purpose, we defined the standard constant, S , defined by Eq. (1), and the G values of phenol were plotted against the molar ratio of S to p -chlorophenol as shown in Figure 1,

$$S = K \times [\text{additive}] \quad (1)$$

where [additive] is the actual concentration of additives. A constant K , the ratio of k_1 to k_2 was calculated from the rate constants of glucose and t -butyl alcohol to OH radicals, which are $k_1(\text{OH} + \text{glucose} = 1.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})^3$ and $k_2(\text{OH} + t\text{-butyl alcohol} = 5.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})^4$, respectively. That is, K is 2.7 for glucose. For β -CD, k_1 value of glucose was used on the assumption that the both reaction rates are the same. If the OH radicals act similarly in these solutions, all the lines should be on one line. The enhancement of G value by β -CD is the most pronounced. The result by t -butyl alcohol showed a slight increase in G value. It is clear that OH radicals contribute only a little to the phenol formation.

As previously shown, the hydrated electrons are the main active species to decompose chlorophenols in deoxygenated aqueous solution.² Hydrated electrons induced dehalogenation of chlorophenols to produce intermediate radicals as described by Getoff and Solar.⁴ The intermediate radicals abstract hydrogen



atoms from other molecules such as chlorophenol, additive and products to produce phenol molecules as shown by the following scheme.

In the presence of CDs, the intermediate radicals are also considered to be included in CDs. This inclusion may enhance the encountering possibility between the intermediate radicals and CD molecules for the hydrogen atom abstraction, resulting in enhancement of phenol yield. On the other hand, in CD of larger cavity size the intermediate radicals are liable to move in the host cavity to get hydrogen atoms leading to the formation of phenol. The activity of intermediate radicals in CDs are again in the order of cavity size, that is, $\alpha < \beta < \gamma$. These induce the increase in phenol yield by CDs in this order. The high selectivity from m -chlorophenol solution indicates that it fits the cavity well. In the case of glucose, the intermediate radicals also may be included in some complex like the dimers of glucose, resulting in the increase yield.

From the above results, it has been cleared that the high phenol yield by CD addition depended on the ability of inclusion of guest molecules and the cavity dimensions. Glucose was also found to enhance the phenol yield. In contrary, it is difficult for t -butyl alcohol to enhance the phenol product ratio.

References

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