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Cyclodextrin-Accelerated Oxidation of Iodide by Oxygen in Aqueous Solutions Containing $HClO_4$

SANYO HAMAI
Department of Chemistry, College of Education, Akita University, Tegata Gakuen-machi 1-1, Akita 010, Japan*

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Abstract. The oxidation of iodide to I_3^- by oxygen dissolved in water containing $HClO_4$ has been found to be accelerated by α-cyclodextrin (α-CD). Among α-, β-, and γ-CDs, α-CD is the most effective mediator for the oxidation reaction of iodide by oxygen. The oxidation rate of iodide is first order in the concentrations of α-CD and $HClO_4$, whereas it is second order in the KI concentration.

Key words: α-Cyclodextrin, iodide, oxidation, oxygen, $HClO_4$

1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides composed of 6, 7, and 8 D-glucose units, which are designated as α-, β-, and γ-CD, respectively. Because such CDs have a unique molecular architecture which is shaped like a truncated cone with a hollow cavity, guest molecules of an appropriate size can be accommodated into their hydrophobic cavities to form inclusion complexes [1, 2]. Due to the formation of inclusion complexes, CDs often act as catalysts or as enzyme-like mediators in various kinds of organic reactions [3–8]. There have been few studies of inorganic reactions in which CDs act as catalysts. In addition, to our knowledge, there is no paper on CD-accelerated oxidation of inorganic compounds by oxygen dissolved in solution, although the oxidation of the organic compounds 2,3-dihydroxyindole and formic acid, is accelerated about 2 to 3-fold and modestly by CDs, respectively [9–11].

Iodide has been reported to be oxidized by chromic acid, bromate, and iodate [12, 13]. The initial rate for the oxidation of iodide by nitrous acid increases with O_2 concentration [14]. In this oxidation reaction, nitric oxide is generated from nitrous acid which is recovered through oxidation of nitric oxide by oxygen. However, oxidation of iodide by oxygen has not been reported to date.

It is interesting to examine the interactions between CD and iodide from a viewpoint of comparison with a starch–iodine complex because CDs are degradation products of starch [15]. Aerated aqueous solutions are usually employed for most

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* Part of this work was carried out at Department of Physics, Miyazaki Medical College, Miyazaki 889-16, Japan.

investigations on inclusion phenomena of CDs. Consequently, it is important to know the behavior of oxygen dissolved in water. In this paper, we report on an acceleration effect of α-CD on the oxidation of iodide by oxygen dissolved in water containing $HClO_4$.

2. Experimental

Potassium iodide (Wako Pure Chemical Industries, Ltd.), $HClO_4$ (Wako Pure Chemical Industries, Ltd.), and α- and γ-cyclodextrins (α- and γ-CDs) (Nacalai Tesque, Inc.) were used as received. β-CD (Nacalai Tesque, Inc.) was recrystallized twice from water.

Absorption spectra were recorded on a Shimadzu 260 spectrophotometer. The absorbance, at 360 nm, of a sample solution in a 1-cm path quartz cell was followed spectrophotometrically, immediately after mixing 0.1 mL of a 35% $HClO_4$ solution and 3 mL of an aqueous solution containing both KI and CD. All the measurements were performed at 25.0 ± 0.2 °C.

3. Results and Discussion

Figure 1 shows absorption spectra of a 0.1 mol dm^{-3} KI solution containing 10^{-2} mol dm^{-3} α-CD before and after the addition of $HClO_4$ (0.193 mol dm^{-3} in a final concentration). In the absence of $HClO_4$, an iodide solution containing only α-CD has no absorption peak above ≈270 nm and is stable under our experimental conditions. Upon the addition of $HClO_4$ to the iodide solution with α-CD, new absorption peaks at 287 and 354 nm appear, with the intensity increasing with time. These bands are assignable to the absorption of I_3^- from the similarity to literature data [16]. This finding indicates the oxidation of iodide to I_3^- in aqueous solution containing both α-CD and $HClO_4$. In the presence of α-CD, however, I_3^- forms an inclusion complex with α-CD. In a mixture of water and ethanol (98/2, v/v) containing both 3.0×10^{-5} mol dm^{-3} of I_2 and 1.0×10^{-3} mol dm^{-3} of KI, I_3^- was found to be a predominant species. An equilibrium constant, K, for the formation of the inclusion complex ($I_3^- \cdot \alpha$-CD) of I_3^- with α-CD and a molar absorption coefficient, ϵ, at 360 nm, for $I_3^- \cdot \alpha$-CD can be evaluated according to the Benesi–Hildebrand relation [2(a), 17]:

$$1/(A - A_0) = 1/(\varepsilon - \varepsilon_0)[I_3^-] + 1/(\varepsilon - \varepsilon_0)K[I_3^-][\alpha\text{-CD}] \tag{1}$$

where A and A_0 are the absorbances in the presence and absence of α-CD, respectively, ϵ, and ϵ_0 are the molar absorption coefficients of $I_3^- \cdot \alpha$-CD and I_3^-, respectively. $[I_3^-]$ and [α-CD] represent the initial concentrations of I_3^- and α-CD, respectively. From the absorbance change caused by the addition of α-CD to the water/ethanol (98/2) solutions of I_3^-, ϵ at 360 nm and K were evaluated to be 20 000 mol^{-1} dm^3 cm^{-1} and 39 000 mol^{-1} dm^3, respectively. To analyze the

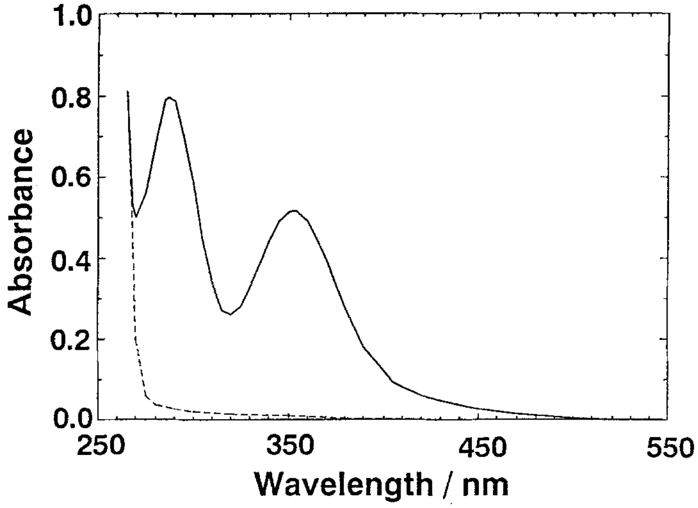

Figure 1. Absorption spectra of an aqueous 0.1 mol dm^{-3} potassium iodide solution containing 1.0×10^{-2} mol dm^{-3} α-cyclodextrin in the absence (- - - - - -) and presence (——) of 0.193 mol dm^{-3} $HClO_4$.

oxidation rates, these values for a water/ethanol (98/2) mixture were used as those for aqueous solutions.

Figure 2 illustrates time courses of the absorbance at 360 nm for 0.14 mol dm^{-3} potassium iodide solutions containing 0.193 mol dm^{-3} $HClO_4$ in the absence and presence of α-CD. The I_3^- concentration in the iodide solution containing both α-CD and $HClO_4$ increases rapidly, while that containing $HClO_4$ alone increases very slightly, indicating that α-CD significantly accelerates the oxidation reaction of iodide. In the oxidation of iodide, an initial period with a fast rate is followed by a period with a constant but slower rate.

Nitrogen- and oxygen-bubbling effects on the oxidation of iodide are exhibited in Figure 3. In an aerated iodide solution with 1.0×10^{-2} mol dm^{-3} α-CD and 0.193 mol dm^{-3} $HClO_4$, the I_3^- concentration increases with time as previously shown. However, upon nitrogen bubbling of the sample solution at point A, the production of I_3^- ceases. When after about 15 minutes oxygen is bubbled at point B, I_3^- is again produced but at a rate considerably faster than that for the aerated sample solution. Like the nitrogen bubbling at point A, the nitrogen bubbling at point C also prohibits the I_3^- production. These experimental results evidently indicate that iodide is oxidized by oxygen dissolved in a sample solution. Therefore, $HClO_4$ does not act as an oxidizing agent for the oxidation of iodide. In the absence of $HClO_4$, the oxidation of iodide did not proceed even if α-CD was added to the iodide solution, so that $HClO_4$ seems to act as an acid. In the absence of α-CD, similar oxygen- and nitrogen-bubbling effects were observed, indicating that iodide is oxidized by oxygen regardless of the existence of α-CD. In the presence of α-CD, hydrochloric acid (0.194 mol dm^{-3}) used in place of $HClO_4$ also generated I_3^- at a rate about

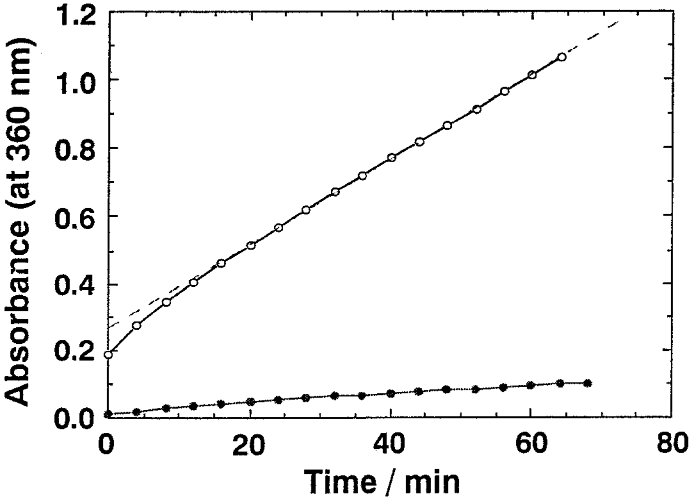

Figure 2. Time course of the absorbance, at 360 nm, for 0.14 mol dm^{-3} potassium iodide solutions containing 0.193 mol dm^{-3} $HClO_4$ in the absence (· · · ● · · ·) and presence (—○—) of 1.0×10^{-2} mol dm^{-3} α-cyclodextrin.

3-fold slower than that for $HClO_4$. In addition, the production of I_3^- was observed in an α-CD solution containing hydriodic acid. These findings strongly suggest that hydrogen iodide is involved in the oxidation reaction of iodide. Combined with the fact that hydrogen iodide is a weaker acid than $HClO_4$, it is most likely that the small amount of hydrogen iodide that is generated by $HClO_4$ is oxidized by dissolved oxygen in the presence of α-CD. Equilibrium constants for the formation of inclusion complexes are affected by ions [18, 19]. The difference in reaction rate between $HClO_4$ and hydrochloric acid is probably due to the difference in the equilibrium constant for the formation of HI·α-CD in solutions containing $HClO_4$ and hydrochloric acid.

In the initial reaction period as shown in Figure 2, it is most likely that there still remains a convection in a sample solution. Consequently, the initial period with a faster reaction rate is observed because oxygen in the air over a sample solution is effectively supplied for the oxidation of iodide in solution. Thus, we devoted our attention to examine the pseudo-zero-order reaction after the initial, fast reaction period. Figure 4 depicts the α-CD concentration dependence on the reaction rate constant, k, for 0.1 mol dm^{-3} iodide/0.193 mol dm^{-3} $HClO_4$ solutions. As shown in Figure 4, the rate constant increases linearly with the α-CD concentration. The rate constant for the solution with 1.0×10^{-2} mol dm^{-3} α-CD is 6.5×10^{-9} mol dm^{-3} s^{-1}, while that for the solution without α-CD is 1.3×10^{-9} mol dm^{-3} s^{-1}. Consequently, 1.0×10^{-2} mol dm^{-3} α-CD accelerates the I_3^- formation rate 5-fold compared to the solution without α-CD. This acceleration effect of α-CD is greater than that (about 3-fold) for the oxidation of 2,3-dihydroxyindole by β-CD [9]. Even in the presence of α-CD, the oxidation

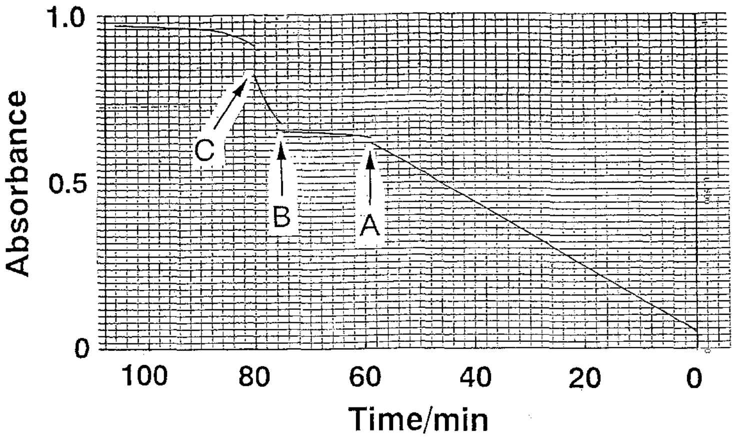

Figure 3. Recorded time course of the absorbance, at 360 nm, for an aqueous 0.1 mol dm^{-3} potassium iodide solution containing 1.0×10^{-2} mol dm^{-3} α-cyclodextrin and 0.193 mol dm^{-3} $HClO_4$. Points A, B, and C represent the times where the nitrogen-, oxygen-, and nitrogen-bubbling of the sample solution were made, respectively.

reaction of iodide is likely to proceed through two reaction paths; that involving α-CD and that not involving α-CD. D-Glucose (6.0×10^{-2} mol dm^{-3}) instead of α-CD (1.0×10^{-2} mol dm^{-3}) did not accelerate the oxidation of iodide, evidently indicating that the formation of an inclusion complex of α-CD plays a critical role in the reaction path involving α-CD. The acceleration effect of α-CD may be due to the formation of a ternary inclusion complex of α-CD with hydrogen iodide and oxygen, which acts as a reaction intermediate. The formation of the ternary inclusion complex may increase the chance of a contact between iodide and an oxygen atom, and promote the oxidation by oxygen. In addition, α-CD probably contributes, to some extent, to the iodide oxidation as a steric effector, which facilitates a sterically appropriate arrangement between oxygen and a substrate [20].

Irrespective of the existence of α-CD, the overall oxidation of iodide is likely to be represented as

$$3I^- + 1/2O_2 + 2H^+ \rightarrow I_3^- + H_2O \qquad (2)$$

To deduce the reaction mechanism, the concentration dependences of $HClO_4$ and KI on the pseudo-zero-order rate for the formation of I_3^- ($I_3^- \cdot \alpha$-CD) were investigated. The I_3^- formation rate was found to be first order in [$HClO_4$] (Figure 5), whereas it was second order in [KI] (Figure 6).

Taking these findings into account, the reaction processes for the oxidation of iodide are tentatively proposed in Scheme 1, where HI·α-CD, HI·α-CD·O_2, $I_2 \cdot \alpha$-CD, and HI·α-CD·H_2O_2 represent an inclusion complex of α-CD with HI, that with HI and O_2, that with I_2, and that with HI and H_2O_2, respectively. Although there is an equilibrium among iodide, iodine, and triiodide, the equilibrium is significantly

$$H^+ + I^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HI \tag{3}$$

$$HI + \alpha\text{-CD} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HI\cdot\alpha\text{-CD} \tag{4}$$

$$HI\cdot\alpha\text{-CD} + O_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} HI\cdot\alpha\text{-CD}\cdot O_2 \tag{5}$$

$$HI\cdot\alpha\text{-CD}\cdot O_2 + I^- + H_2O \xrightarrow{k_4} I_2\cdot\alpha\text{-CD} + OH^- + H_2O_2 \tag{6}$$

$$I_2\cdot\alpha\text{-CD} + I^- \xrightarrow{k_5} I_3^-\cdot\alpha\text{-CD} \tag{7}$$

$$HI\cdot\alpha\text{-CD} + H_2O_2 \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} HI\cdot\alpha\text{-CD}\cdot H_2O_2 \tag{8}$$

$$HI\cdot\alpha\text{-CD}\cdot H_2O_2 + I^- \xrightarrow{k_7} I_2\cdot\alpha\text{-CD} + OH^- + H_2O \tag{9}$$

Scheme 1.

shifted to the formation of triiodide under our experimental conditions, so that any iodine molecule generated is immediately converted to a triiodide ion. Furthermore, the concentration of a free, uncomplexed triiodide ion can be neglected in the presence of α-CD since an equilibrium constant for the formation of $I_3^- \cdot \alpha$-CD is very large (39 000 $\text{mol}^{-1}\ \text{dm}^3$). Assuming that Equation (6) is a rate-determining process, the rate, $d[I_3^- \cdot \alpha\text{-CD}]/dt$, for the formation of $I_3^- \cdot \alpha$-CD is derived under the conditions that $k_{-1} \gg k_2[\alpha\text{-CD}]$, $k_{-2} \gg k_3[O_2]$, and $k_{-3} \gg k_4[I^-]$:

$$\begin{aligned} d[I_3^- \cdot \alpha\text{-CD}]/dt &= 2k_1k_2k_3k_4[H^+][\alpha\text{-CD}][I^-]^2[O_2]/k_{-1}k_{-3} \\ &= k'[H^+][\alpha\text{-CD}][I^-]^2[O_2] \end{aligned} \tag{10}$$

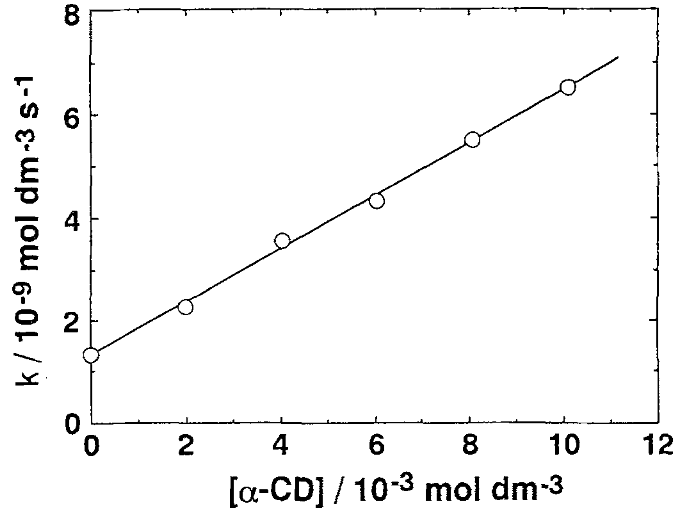

Figure 4. Dependence of k on the α-cyclodextrin concentration for aqueous solutions containing KI (0.1 mol dm^{-3}) and $HClO_4$ (0.193 mol dm^{-3}).

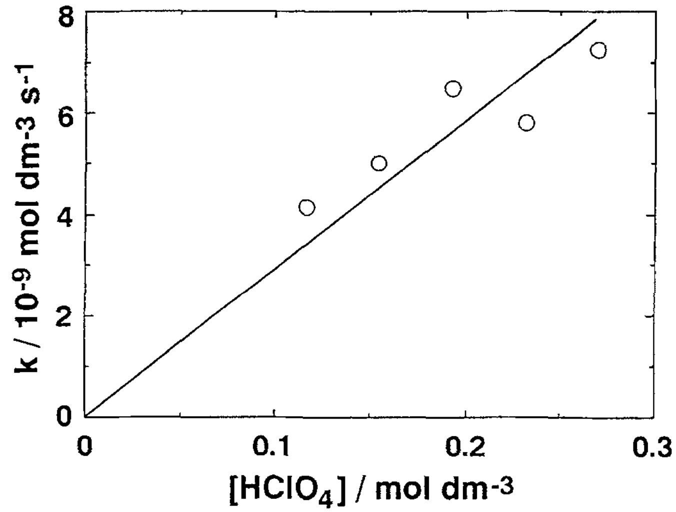

Figure 5. Dependence of k on the $HClO_4$ concentration for aqueous solutions containing KI (0.1 mol dm^{-3}) and α-cyclodextrin (1.0×10^{-2} mol dm^{-3}).

where k' is $2k_1k_2k_3k_4/k_{-1}k_{-3}$. The derived reaction rate is consistent with the experimental results that the I_3^- formation rate is first order in the $HClO_4$ and α-CD concentrations and second order in the KI concentration. From the plot for the concentration dependence of α-CD (Figure 4), the value of k' was estimated to be 2.06 mol^{-4} dm^{12} s^{-1}, using known values of 0.193, 0.10, and 1.3×10^{-3} mol dm^{-3} for $[H^+]$, $[I^-]$, and $[O_2]$, respectively. Similar k' values were also evaluated when the plots for the concentration dependence of $HClO_4$ and I^- were employed.

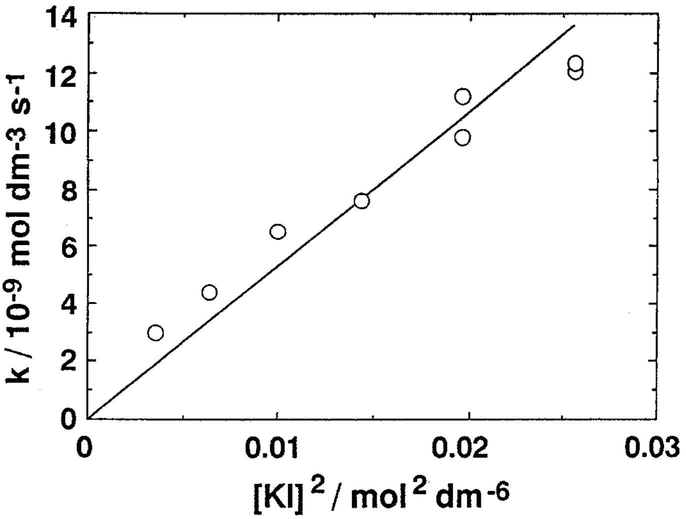

Figure 6. Dependence of k on the KI concentration for aqueous solutions containing α-cyclodextrin (1.0×10^{-2} mol dm^{-3}) and $HClO_4$ (0.193 mol dm^{-3}).

There is the possibility that the catalysis by α-CD is due to its ability to include O_2 in its cavity [21]. When HI·α-CD·O_2 exists, Equations (4) and (5) may be replaced by the following equilibria, respectively.

$$O_2 + \alpha\text{-CD} \rightleftharpoons O_2 \cdot \alpha\text{-CD} \tag{11}$$

and

$$O_2 \cdot \alpha\text{-CD} + HI \rightleftharpoons HI \cdot \alpha\text{-CD} \cdot O_2 \tag{12}$$

However, the final rate equation has the same form as Equation (10), except for the rate constants. α-CD forms an inclusion complex ($I^- \cdot \alpha$-CD) with I^- although an equilibrium constant ($K(I^-)$) for the formation of $I^- \cdot \alpha$-CD is very small [22]. Using 13 mol^{-1} dm^3 as $K(I^-)$, the concentration of $I^- \cdot \alpha$-CD amounts to at most 11.5% of the initial I^- concentration, even at the highest α-CD concentration of 1.0 $\times$ 10^{-2} mol dm^{-3}. If $I^- \cdot \alpha$-CD is related to the oxidation reaction, the oxidation is likely to proceed through the formation of HI·α-CD. In this case, a derived rate equation has the same form as that of Equation (10), with different rate constants.

The cavity diameters of β- and γ-CD are greater than that of α-CD. In the presence of 0.193 mol dm^{-3} $HClO_4$, β- and γ-CDs accelerated the oxidation of iodide by only about 40 and 15% compared to α-CD, respectively, at CD concentrations of 1.0×10^{-2} mol dm^{-3}. These findings are consistent with our proposed reaction scheme where the inclusion complex of CD with hydrogen iodide is formed. A small molecule, hydrogen iodide, is expected to be the most snug fit in the cavity of α-CD among the three CDs. Consequently, the concentration of the α-CD inclusion complex with hydrogen iodide is significantly high, compared to that with β- and γ-CDs, resulting in the most prominent acceleration effect on the oxidation of iodide.

4. Conclusion

We have found that oxygen oxidizes iodide to I_3^- in aqueous solutions containing $HClO_4$. Addition of α-CD to the $HClO_4$ solution of iodide accelerates the oxidation of iodide. α-CD probably works as a mediator through the formation of a ternary inclusion complex of α-CD with hydrogen iodide and oxygen. Of the three CDs, α-CD has the most profound effect on the oxidation of iodide. This result is consistent with the formation of the ternary inclusion complex of α-CD, hydrogen iodide, and oxygen because a small hydrogen iodide molecule is likely to be most favorably bound to the small cavity of α-CD. Since CDs accommodate a variety of substrates to protect guests from other reagents, CDs are often used for retardation or inhibition of oxygenation in the food industries, etc. Taking into account the results in this work, in some cases, conversely, there is the possibility that oxidation by oxygen dissolved in water is promoted by the addition of CDs.

References

1. M. L. Bender and M. Komiyama: *Cyclodextrin Chemistry*, Springer Verlag, Berlin (1978).
2. (a) S. Hamai: *Bull. Chem. Soc. Jpn.* **55**, 2721 (1982). (b) S. Hamai: *J. Phys. Chem.* **93**, 6527 (1989). (c) S. Hamai, T. Ikeda, A. Nakamura, H. Ikeda, A. Ueno, and F. Toda: *J. Am. Chem. Soc.* **114**, 6012 (1992). (d) S. Hamai: *J. Phys. Chem.* **99**, 12109 (1995).
3. R. L. VanEtten, G. A. Clowes, J. F. Sebastian, and M. L. Bender: *J. Am. Chem. Soc.* **89**, 3253 (1967).
4. M. Komiyama, S. Sawata, and Y. Takeshige: *J. Am. Chem. Soc.* **114**, 1070 (1992).
5. R. Breslow and B. Zhang: *J. Am. Chem. Soc.* **114**, 5882 (1992).
6. R. Ueoka, Y. Matsumoto, K. Harada, H. Akahoshi, Y. Ihara, and Y. Kata: *J. Am. Chem. Soc.* **114**, 8339 (1992).
7. T. A. Gadosy and O. S. Tee: *J. Chem. Soc., Perkin Trans. 2* 71 (1995).
8. A. Granados and R. H. de Rossi: *J. Am. Chem. Soc.* **117**, 3690 (1995).
9. F. Cramer: *Chem. Ber.* **86**, 1576 (1953).
10. L. Han, W. Linert, R. Schmid, and R. F. Jameson: *J. Chem. Soc., Perkin Trans. 2* 1907 (1989).
11. O. S. Tee, B. Javed, and S. R. Mikkelsen: *Can. J. Chem.* **68**, 2119 (1990).
12. G. F. Vandegrift and J. Rocek: *J. Am. Chem. Soc.* **99**, 143 (1977).
13. A. F. M. Barton, H. N. Cheong, and R. E. Smidt: *J. Chem. Soc., Faraday Trans. 1* **72**, 568 (1976).
14. M. Kimura, M. Sato, T. Murase, and K. Tsukahara: *Bull. Chem. Soc. Jpn.* **66**, 2900 (1993).
15. R. C. Teitelbaum, S. L. Ruby, and T. J. Marks: *J. Am. Chem. Soc.* **100**, 3215 (1978).
16. H. Isic and W. R. Mason: *Inorg. Chem.* **24**, 271 (1985).
17. H. A. Benesi and J. H. Hildebrand: *J. Am. Chem. Soc.* **71**, 2703 (1949).
18. Y. Kotake and E. G. Janzen: *J. Am. Chem. Soc.* **111**, 7319 (1989).
19. J. Huang and F. V. Bright: *J. Phys. Chem.* **94**, 8457 (1990).
20. K. Takahashi and K. Hattori: *J. Incl. Phenom.* **17**, 1 (1994).
21. A. M. Martre, G. Mousset, and P. Pouillen: *J. Electroanal. Chem.* **281**, 279 (1990).
22. J. P. Diard, E. Saint-Aman, and D. Serve: *J. Electroanal. Chem.* **189**, 113 (1985).