Inclusion Complexation of 4-Biphenylcarboxylate, 4-Biphenylacetate, and 4-Biphenylsulfonate with α-Cyclodextrin, Studied by Pulse Radiolysis

Yukio Yamamoto,* Yoichi Yoshida, and Seiichi Tagawa

The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567

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Inclusion complexation of 4-biphenylcarboxylate (BPC^-), 4-biphenylacetate (BPA^-), and 4-biphenylsulfonate (BPS^-) with α-cyclodextrin (α-CD) has been investigated by a pulse radiolysis method. The one-electron reduction of BPC^- and BPS^- by the hydrated electron was effectively retarded by the 1 : 2 complexation with α-CD as well as by the 1 : 1 complexation with β-CD investigated in our previous study. The retarding effect of α-CD was observed at much higher host concentrations than that of β-CD. No apparent effect of α-CD was observed on the one-electron reduction of BPA^-, but the effect of β-CD was similar to those for BPC^- and BPS^-. The result indicates that the methylene group of BPA^- sterically inhibits the formation of the 1 : 2 complex. The rate constant for the one-electron reduction of the 1 : 2 complex of BPC^- with α-CD was 1.0×10^9 $dm^3\ mol^{-1}\ s^{-1}$, which is smaller than that of the 1 : 1 complex with β-CD, 2.5×10^9 $dm^3\ mol^{-1}\ s^{-1}$. It is demonstrated that the biphenylyl group of the 1 : 2 complex with α-CD is screened from the attack of the hydrated electron more effectively than that of the 1 : 1 complex with β-CD.

Cyclodextrins (CDs) have hydrophobic cavities and form inclusion complexes with organic molecules in aqueous solutions.[1,2] The most common of them are α-, β-, and γ-CDs consisting of six, seven, and eight glucose units, respectively. The host–guest stoichiometry depends on sizes of CD cavities and of guest molecules. In our preceding papers we have reported a pulse radiolysis study of the effects of α-, β-, and γ-CDs on the one-electron reduction of aromatic carboxylates and sulfonates by the hydrated electron.[3,4] The pulse radiolysis of argon-saturated aqueous solutions of the aromatic electrolytes results in the one-electron reduction of the solutes by the hydrated electron. The transient absorption spectra of the reduced products are analogous to those of the radical anions of the corresponding aromatic hydrocarbons, and the radical anion sites are considered to be located largely on the aromatic moieties of the electrolytes. The reaction is effectively retarded when the hydrophobic aromatic moieties are included in the CD cavities. Thus, the rate constants for the one-electron reduction of 4-biphenylcarboxylate (BPC^-), 4-biphenylacetate (BPA^-) and 4-biphenylsulfonate (BPS^-) are appreciably decreased by the complexation with β-CD, the cavity of which best fits the biphenylyl groups. An effective retarding effect is also observed when 1-pyrenecarboxylate, 1-pyrenebutyrate, and 1-pyrenesulfonate are complexed with the best-fitting γ-CD. The pH dependence of the reaction rate supports the formation of the 2 : 2 complexes of the pyrene derivatives with γ-CD at pH below about 12. In this study the complexation of BPC^-, BPA^-, and BPS^- with α-CD was investigated on the basis of the retarding effect on the one-electron reduction of the guest electrolytes. A comparison is made with the previously published results for the effect of the complexation with β-CD.

Experimental

The materials and the experimental procedures were the same as those in our preceding study.[3,4] The pulse radiolysis of the argon-saturated aqueous solutions of BPC^-, BPA^-, and BPS^- was done with 8 ns electron pulses at room temperature (about 22 °C). The dose per pulse was ca. 43—91 Gy (1 Gy=1 $J\,kg^{-1}$). The decay of the hydrated electron was monitored at 800 nm where the absorption due to the one-electron reduction products is negligible.

Results and Discussion

As previously reported,[3,4] the pulse radiolysis of argon-saturated aqueous solution of BPC^-, BPA^-, and BPS^- results in transient absorption spectra consisting of a sharp band at around 400 nm and a broad one in the range from 600 to 700 nm similar to those of the biphenyl radical anion. The rise of the absorption of the biphenyl-type radical anions attends the decay of the absorption of the hydrated electron. In the case of 2-biphenylcarboxyrate, no absorption band is observed above 350 nm, but the absorption of the hydrated electron rapidly decays similarly to the case of the isomer, BPC^-. This means that the steric effect of the carboxy group at the 2-position prevents the formation of the biphenyl-type radical anions, which have a much more coplanar structure than the parent molecules. In other words, the one-electron reduction of the biphenyl derivatives with substituents at the 4-position, such as BPC^-, BPA^-, and BPS^-, results in the formation of coplanar radical anions, the radical anion sites of which are mostly located on the biphenylyl groups

(Chart 1).

Among these biphenyl derivatives, the transient absorption spectrum of the reduced BPC^- shifts to shorter wavelengths with time after the pulse at pH below about 10.[4] The spectral shift has been attributed to the rapid occurrence of the association of the reduced BPC^- with H^+, as a result of an increase of pK_a by the one-electron reduction. The pK_a of the reduced BPC^- should be about 10, while that of the parent BPC^- is 4.5.[5] No spectral shift with time after the pulse is observed for BPA^- and BPS^-. The rise of the absorption of the reduced BPA^- and BPS^- coincides with the decay of the hydrated electron, both of which obey first-order kinetics. In the case of BPA^-, the pK_a is not influenced by the one-electron reduction because of the presence of $-CH_2-$ separating the biphenylyl and carboxy groups in contrast to the case of BPC^-. The absorption changes and the kinetic behaviors of the hydrated electron and of the reduced product are shown in Fig. 1 for the BPA^- solution as an example. The slope of the first-order kinetic plot for the decay of the hydrated electron is almost the same as that for the formation of the reduced BPA^- at least until about 200 ns. Afterwards, the plot for the decay of the hydrated electron slightly deviated from linearity, probably because of a small contribution of long-lived species. The pseudo-first-order rate constants, k_{obs}, for the one-electron reduction of BPC^-, BPA^-, and BPS^- were calculated from the decay of the hydrated electron soon after the pulse irradiation.

Figure 2 shows the effects of α- and β-CDs on k_{obs} for the 1.0×10^{-3} mol dm^{-3} BPC^- solution at around neutral pH. The ratio of the k_{obs} values in the presence and absence of the CDs, $k_{CD}/k_{CD\text{-free}}$, is plotted against the CD concentration. An appreciable decrease in $k_{CD}/k_{CD\text{-free}}$ is observed for α-CD at much higher concentrations than for β-CD. The $k_{CD}/k_{CD\text{-free}}$ ratios at the high α-CD concentrations, 3.0×10^{-2} mol dm^{-3} and above, are smaller than those of the β-CD system. Since the solubility of β-CD is much lower than that of α-CD,[1,2] the maximum concentrations examined are near saturation for both of α- and β-CDs.

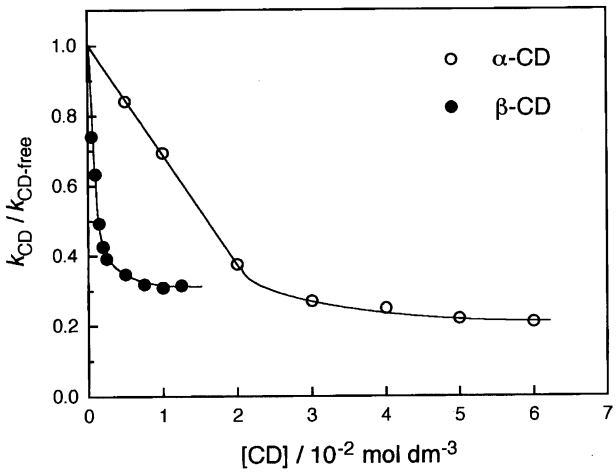

Fig. 2. Plots of $k_{CD}/k_{CD\text{-free}}$ against the CD concentration for the 1×10^{-3} mol dm^{-3} BPC^- solution at around neutral pH, 6.8—7.0 and 6.3—7.0 for the α- and β-CD systems, respectively.

Figure 3 shows the plots of $k_{CD}/k_{CD\text{-free}}$ against the α-CD concentration for the 1.0×10^{-3} mol dm^{-3} BPC^- solution at different pH. The decrease in $k_{CD}/k_{CD\text{-free}}$ in the presence of α-CD is limited at pH 12.4—12.7, but up to pH of about 11, the effect of α-CD is independent of pH. The effect of β-CD for the strongly alkaline solution (pH = 12.4—12.6) was as large as that for the neutral solution.

The pH abruptly diminishing the effect of α-CD coincides with the pK_a of the secondary hydroxy groups of α-CD, 12.1.[6] It is known that the formation of CD complexes consisting of two host molecules is inhibited in strongly al-

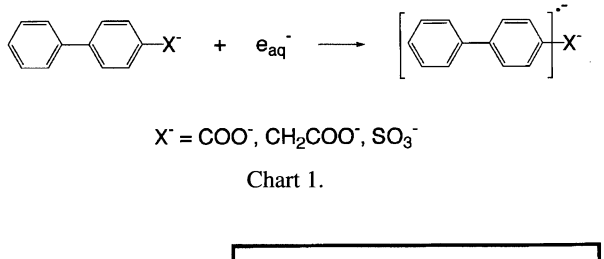

Chart 1.

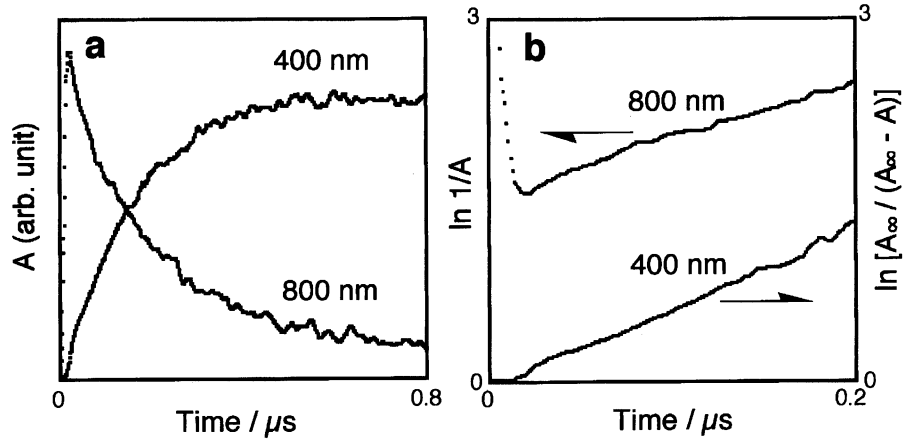

Fig. 1. The absorption changes (a) and the kinetic plots (b) for the decay of the hydrated electron at 800 nm and for the formation of the reduced BPA^- at 400 nm in the argon-saturated aqueous solution of 1×10^{-3} mol dm^{-3} BPA^- solution (A denotes absorbance and A_∞ is the maximum absorbance attained during the formation of the reduced BPA^- at 400 nm).

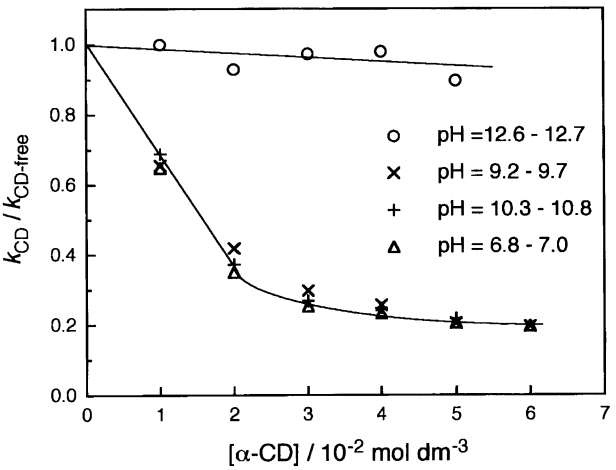

Fig. 3. Plots of $k_{CD}/k_{CD\text{-free}}$ against the α-CD concentration for the 1×10^{-3} mol dm^{-3} BPC^- solution at different pH.

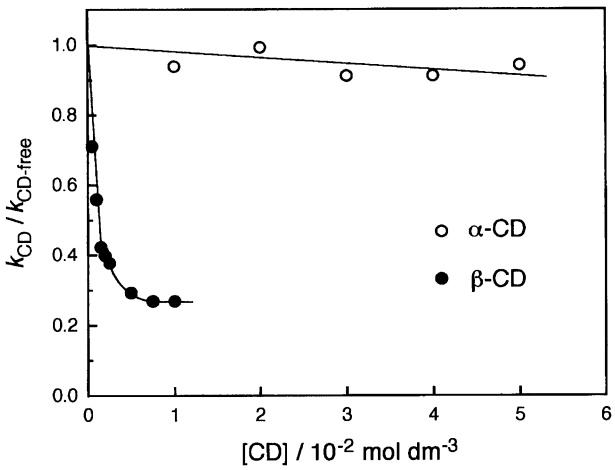

Fig. 4. Plots of $k_{CD}/k_{CD\text{-free}}$ against the CD concentration for the 1×10^{-3} mol dm^{-3} BPA^- solution at around neutral pH, 6.3—6.5 and 6.2—7.0 for the α- and β-CD systems, respectively.

kaline solutions by the ionic repulsion between the anionic forms of the hydroxy groups of the CDs facing to compose the complexes.[7—9] Therefore, the strong retardation effect of α-CD on the one-electron reduction of BPC^- in the neutral solutions can be attributed to the formation of the 1 : 2 complex (Chart 2). The formation of the 1 : 2 complex between BPC^-H^+ with α-CD has recently been demonstrated by a spectrofluorometric study; the guest exists as a neutral species, BPC^-H^+ instead of BPC^-, because the pH of the solution is 3.0, below the pK_a, 4.5.[10]

Figure 4 shows the effects of α- and β-CDs on $k_{CD}/k_{CD\text{-free}}$ for the 1.0×10^{-3} mol dm^{-3} BPA^- solution at around neutral pH. The $k_{CD}/k_{CD\text{-free}}$ is scarcely affected by α-CD, similarly to the case of the strongly alkaline solution of BPC^- (Fig. 3). It is appreciably reduced by β-CD, as previously reported.[4] The result suggests that the methylene group of BPA^- sterically inhibits the formation of the 1 : 2 complex with α-CD (Chart 2).

As shown above, the effect of α-CD on $k_{CD}/k_{CD\text{-free}}$ is very small for the strongly alkaline solution of BPC^- and for the neutral solution of BPA^-. However, it is natural to consider that the 1 : 1 complexes of BPC^- and BPA^- with α-CD are formed in these solutions (Chart 2), as reported for BPC^-H^+.[10] Therefore, the rate constants for the one-electron reduction of the 1 : 1 complexes of BPC^- and BPA^- with α-CD are considered to be as large as those of the dissociated

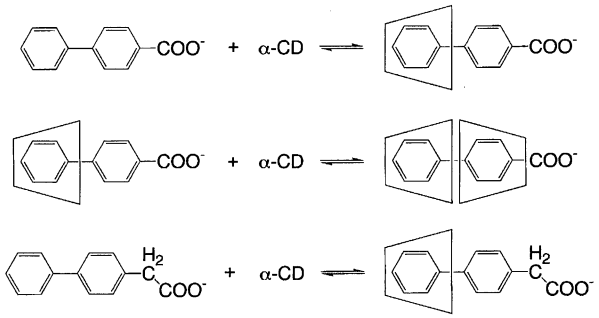

Chart 2.

guests because the biphenylyl groups are partially out of the α-CD cavity in the 1 : 1 complexes.

Figure 5 shows the effects of α- and β-CDs on $k_{CD}/k_{CD\text{-free}}$ for the solutions of 1.0×10^{-3} mol dm^{-3} BPS^-. The $k_{CD}/k_{CD\text{-free}}$ is decreased in the presence of α-CD similarly to the case of the neutral solutions of BPC^-, demonstrating that the 1 : 2 complex between BPS^- and α-CD is formed similarly to the case of BPC^-. The $k_{CD}/k_{CD\text{-free}}$ is appreciably reduced in the presence of β-CD, as previously reported.[3]

The one-electron reduction of BPC^- in the absence and presence of excess amounts of β- and α-CDs can be shown by Eqs. 1, 2, and 3, respectively.

$$BPC^- + e_{aq}^- \rightarrow BPC\cdot^{2-} \quad (1)$$

$$BPC^-\text{–}\beta\text{-CD} + e_{aq}^- \rightarrow BPC\cdot^{2-}\text{–}\beta\text{-CD} \quad (2)$$

$$BPC^-\text{–}(\alpha\text{-CD})_2 + e_{aq}^- \rightarrow BPC\cdot^{2-}\text{–}(\alpha\text{-CD})_2 \quad (3)$$

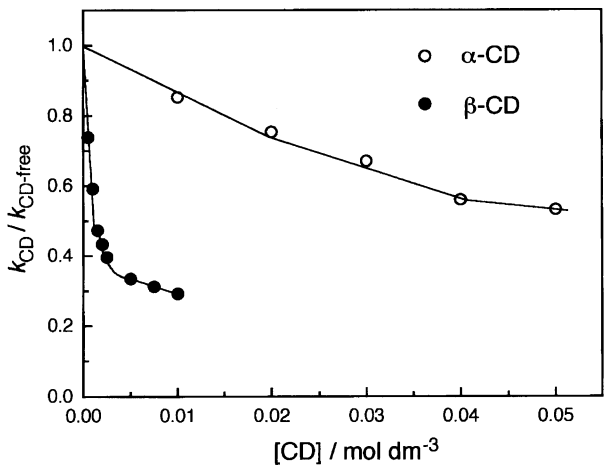

Fig. 5. Plots of $k_{CD}/k_{CD\text{-free}}$ against the CD concentration for the 1×10^{-3} mol dm^{-3} BPS^- solution at around neutral pH, 5.4—5.9 and 5.0—5.6 for the α- and β-CD systems, respectively.

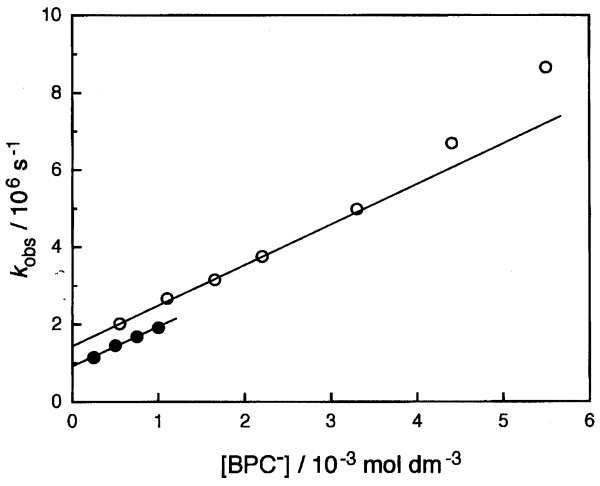

Fig. 6. Plots of k_{obs} against the BPC^- concentration for the solutions containing 6.0×10^{-2} mol dm^{-3} α-CD at pH (○) 6.2—6.9 and (●) 7.3—7.8.

In our preceding study,[4] the rate constants, k_1 and k_2, for the one-electron reduction of BPC^- and of its 1 : 1 complex with β-CD [Eqs. 1 and 2] have been calculated to be 9.0×10^9 and 2.5×10^9 dm^3 mol^{-1} s^{-1}, respectively. In this study the rate constant, k_3, for the one-electron reduction of the 1 : 2 complex of BPC^- with α-CD [Eq. 3] was calculated by analysis of the pseudo-first-order kinetics for the BPC^- solutions containing an excess of α-CD. Figure 6 shows the plots of k_{obs} against BPC^- concentration in the presence of 6.0×10^{-2} mol dm^{-3} α-CD, obtained by two independent experimental runs. The deviation from the linearity at the BPC^- concentrations above about 4×10^{-3} mol dm^{-3} is observed for one of the experimental runs. This can be attributed to the contribution of the more reactive dissociated guest and/or the 1 : 1 complex, which increases with increasing guest concentration. From the slope in the low BPC^- concentration range, k_3 was 1.0×10^9 dm^3 mol^{-1} s^{-1}. The rate constants for the one-electron reduction decrease in the order BPC^-, BPC^-–β-CD, and BPC^-–(α-CD)$_2$ according to the degree of the covering by the CDs.

It is shown in Fig. 5 that the $k_{CD}/k_{CD\text{-free}}$ for BPS^- is not constant at the high α-CD concentrations near saturation. Therefore, the rate constant for the one-electron reduction of the 1 : 2 complex of BPS^- with α-CD could not be measured because of the limit of the solubility of α-CD. The association constant for the 1 : 2 complex of BPS^- may be smaller than that of BPC^-. In our preceding paper,[11] the association constants for the 1 : 1 complexation of BPC^-, BPA^-, and BPS^- with β-CD were calculated from the pulse radiolysis data. However, The association constants for the 1 : 1 and 1 : 2 complexation of BPC^- with α-CD cannot be found by the pulse radiolysis method because of the coexistence of the complexes with different stoichiometry.

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