Determination of Association Constants for Cyclodextrin Inclusion Complexation by Pulse Radiolysis

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(Received May 19, 1995)

The association constants for the inclusion complexation of 4-biphenylcarboxylate and its analogs with β-cyclodextrin are determined by a pulse radiolysis method for the kinetic analysis of the one-electron reduction by the hydrated electron.

Association constants for cyclodextrin (CD) inclusion complexation are mainly determined by a spectrophotometric method analyzing a change in absorption or fluorescence spectrum caused by the complexation.[1,2] They are also determined by a kinetic method when the complexation causes an observable change in reactivities of guest species. This paper describes a new kinetic method by using the pulse radiolysis techniques. The method is based on the retarding effect of the complexation on the one-electron reduction by the hydrated electron and may be used for the determination of the association constants of a wide variety of guest compounds reduced by the hydrated electron.

We have recently reported a pulse radiolysis study of the effect 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 Ar-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 one-electron reduction products are similar to those of the corresponding aromatic hydrocarbon radical anions, and the radical anion sites are considered to be located on the aromatic moieties of the solutes. The reaction is effectively retarded when the hydrophobic aromatic moieties of the solutes are included in the CD cavities. Thus, the rates of the one-electron reduction of 4-biphenylcarboxylate (BPC^-), 4-biphenylacetate (BPA^-), and 4-biphenylsulfonate (BPS^-) are appreciably decreased by the complexation with β-CD, whose cavity best fits to the biphenylyl groups.

The rate constants, k_1 and k_2, for the one-electron reduction of the dissociated guests and their inclusion complexes (Eqs. 1 and 2) were determined by the kinetic analysis of the decay of the hydrated electron in the absence and presence of excess amounts of β-CD, respectively.[3,4] The association constants, K_a, for the inclusion complexation (Eq. 3) were evaluated on the basis of the dependence of the pseudo-first-order rate constant, k_{obs}, for the decay of the hydrated electron on β-CD concentration.

$$BPX^- + e_{aq}^- \longrightarrow BPX^{\bullet 2-} \quad (1)$$

$$BPX^-\text{–β-CD} + e_{aq}^- \longrightarrow BPX^{\bullet 2-}\text{–β-CD} \quad (2)$$

$$BPX^- + \text{β-CD} \rightleftharpoons BPX^-\text{–β-CD} \quad (3)$$

where BPX^- denotes the guest electrolytes (BPC^-, BPA^-, and BPS^-) and BPX^-–β-CD, their inclusion complexes with β-CD.

The pulse radiolysis experiments were carried out at a BPX^- concentration of 1.0×10^{-3} mol dm^{-3} in the β-CD concentration range from 5.0×10^{-4} to 2.0×10^{-3} mol dm^{-3} at room temperature (*ca.* 22 °C). The materials and the experimental procedures were the same as those in the preceding study.[3,4] The k_{obs} value is represented by Eq. 4 where k_0 is the observed first-order rate constant for the decay of the hydrated electron in the absence of BPX^- and is subtracted from k_{obs} for correction.

$$k_{obs} - k_0 = k_1[BPX^-] + k_2[BPX^-\text{–β-CD}] \quad (4)$$

The rate constants, k_1 and k_2, for the one-electron reduction of BPC^- and BPC^-–β-CD were 9.0×10^9 and 2.5×10^9 dm^3 mol^{-1} s^{-1}, respectively.[4] When K_a is assumed, the $k_{obs} - k_0$ values are calculated by using the k_1 and k_2 values and Eq. 4. Figure 1 shows the plot of the experimental values of $k_{obs} - k_0$ against β-CD concentration at pH 6.2 - 6.5 together with the calculated curve for $K_a = 4.7 \times 10^3$ dm^3 mol^{-1} fitting the plot of the experimental data. Thus, the K_a value was evaluated by fitting the calculated curve, obtained by taking an appropriate value as K_a, to the $k_{obs} - k_0$ plot. A similar plot of $k_{obs} - k_0$ against β-CD concentration was obtained by the experiments at pH 9.2 - 9.7. The experimental uncertainty of the K_a value was within ±10%.

Similarly, the K_a value for BPA^- was evaluated to be 3.0×10^4 dm^3 mol^{-1} at pH 6.2 - 6.5. The k_1 and k_2 values used for the evaluation were 3.3×10^9 and 4.4×10^8 dm^3 mol^{-1} s^{-1}, respectively.[4] The uncertainty of the K_a value for BPA^- was somewhat large, about ±20%, because of the small $k_{obs} - k_0$ values as shown in Figure 2, which includes the data for BPS^- discussed below. It is demonstrated that BPA^- has a large K_a value compared with BPC^-. This may be attributed to the methylene spacer of BPA^- which separates the biphenylyl group,

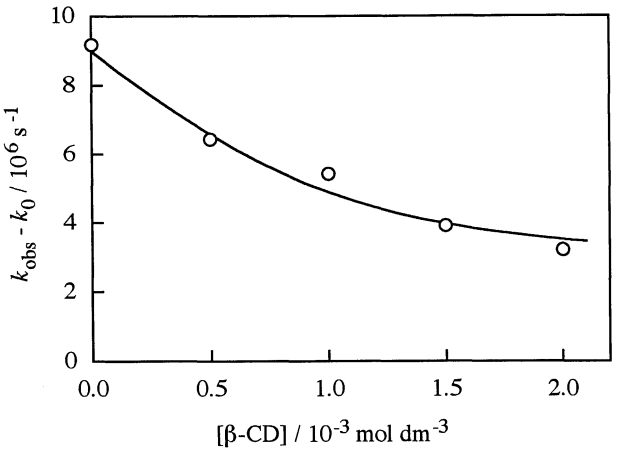

Figure 1 . Plot of $k_{obs} - k_0$ against β-CD concentration for BPC^-; the curve was obtained by taking 4.7×10^3 dm^3 mol^{-1} as K_a.

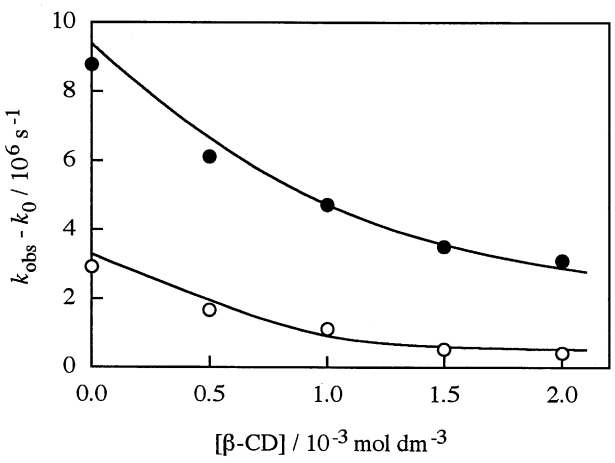

Figure 2 . Plots of $k_{obs} - k_0$ against β-CD concentration for (○) BPA^- and (●) BPS^-; the curves were obtained by taking 3.0×10^4 and 2.8×10^3 dm^3 mol^{-1} as K_a for BPA^- and BPS^-, respectively.

included in the β-CD cavity, from the hydrophilic carboxyl group.

The pulse radiolysis data for BPS^- having no methylene spacer between the biphenylyl and hydrophilic groups were close to those for BPC^- rather than those for BPA^-. The K_a value for BPS^- was evaluated to be 2.8×10^3 dm^3 mol^{-1} by using 9.4×10^9 and 1.0×10^9 dm^3 mol^{-1} s^{-1} as k_1 and k_2, respectively.[3] The $k_{obs} - k_0$ values at pH 5.2 - 5.6 are plotted in Figure 2. No significant difference was observed between the data at pH 5.2 - 5.6 and at pH 7.5 - 8.0. The uncertainty for the K_a value was about ±10%.

The association constants for the 1:1 and 1:2 complexation of BPC^-H^+ with α-CD have recently been determined by a fluorescence spectroscopic method (the guest exists as a neutral species, BPC^-H^+, instead of BPC^- because of the low pH of the solutions, 3.0).[5] On the other hand, it has been reported that the association constant for the 1:1 complexation of BPC^-H^+ with β-CD cannot be determined by the fluorescence spectroscopic method; the effect of β-CD on the fluorescence spectrum of BPC^-H^+ has turned out to be due to the absorption of the light at the exciting wavelength by β-CD. So far as we know, the present determination of K_a is the first for the complexation of BPC^-, BPA^-, and BPS^- with β-CD. The uncertainty for the K_a value may be largely due to the magnitude of the k_0 value. A decrease in dose rate and an increase in optical pathlength are expected to minimize the k_0 value keeping a high absorption intensity of the hydrated electron. Efforts will be made to improve the accuracy in the determination of the association constants by the pulse radiolysis method.

This work was supported by a Grant-in-Aid for Scientific Research (No. 05650826) from the Ministry of Education, Science and Culture, Japan.

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