Effects of Cyclodextrin Complexation on One-electron Reduction and Electron Transfer of Aromatic Sulfonates

Yukio Yamamoto,* Shinji Shiraki and Yuki Kawamura
The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567, Japan

Pulse radiolysis of argon-saturated aqueous solutions of sodium biphenyl-4-sulfonate (BPS^-Na^+) and sodium pyrene-1-sulfonate (PyS^-Na^+) results in the one-electron reduction of the aromatic moieties of the sulfonates by the hydrated electron to give the radical anions, $BPS^{\cdot 2-}$ and $PyS^{\cdot 2-}$. The effects of cyclodextrin (CD) complexation of the sulfonates on the reaction rates of the one-electron reduction have been investigated. The rate constants for the one-electron reduction of BPS^- and PyS^- are significantly reduced by β- and γ-CDs, respectively, through complexation, but are hardly influenced by the other CDs including α-CD. The selective reduction of a mixed sulfonate system has been achieved by using β- and γ-CDs. The electron transfer from $BPS^{\cdot 2-}$ to PyS^- is also retarded effectively by the complexation of PyS^- with γ-CD. The change in the transient absorption spectrum after the pulse irradiation of the PyS^-Na^+ solutions containing γ-CD has suggested that the reduced 2:2 complex is unstable and dissociates into the 1:1 complexes.

Cyclodextrins (CDs) possess hydrophobic cavities and form inclusion complexes with organic molecules in aqueous solution.[1,2] The host–guest stoichiometry depends on the sizes of the CD cavities and of the guest molecules. The hydrophobic association involving two guest molecules in a single cavity accelerates bimolecular reactions such as Diels–Alder reactions,[3–5] photodimerization[6] and excimer formation.[7–10] On the other hand, the 1:1 complexation of reactants with CDs having smaller cavities inhibits bimolecular reactions.

Pulse radiolysis is expected to provide significant information regarding the effects of CD complexation on the reactions of guest molecules. This study is concerned with the one-electron reduction of aromatic sulfonates such as biphenyl-4-sulfonate (BPS^-) and pyrene-1-sulfonate (PyS^-) by the hydrated electron, e_{aq}^-, in the presence of CDs. The one-electron reduction results in the formation of the sulfonate radical anions, $BPS^{\cdot 2-}$ and $PyS^{\cdot 2-}$, whose radical anion sites are located on the aromatic moieties. CD complexation of the sulfonates results in protection against the one-electron reduction. The electron transfer from $BPS^{\cdot 2-}$ to PyS^- is also retarded effectively by the complexation of PyS^- with γ-CD. A selective reduction by using CDs is examined with a solution of an equimolar mixture of the sulfonates.

Formation of CD inclusion complexes has been studied mainly by absorption, circular dichroism, and fluorescence spectra for stable guest molecules. Recently the stability of the complexes of electrochemically generated radical anions with CDs has been investigated by cyclic voltammetry and EPR spectroscopy.[11,12] The present pulse radiolysis study also describes the dynamic behaviour of the reduced 2:2 complex of PyS^- with γ-CD to demonstrate the decrease in stability on introducing a negative charge to one of the guest molecules completely surrounded by the hydrophobic cavity.

Experimental

BPS^-Na^+ was prepared by adding sodium methoxide to a methanol solution of BPS^-H^+, which was synthesized according to a published procedure,[13] and was recrystallized from water. PyS^-Na^+ (Molecular Probes, Inc.) and γ-CD (Wako Chemicals) were used without further purification. α- and β-CDs (both Wako Chemicals) were recrystallized from a water–methanol mixture and from water, respectively. Water was deionized and then distilled. Solutions were saturated with argon or nitrous oxide. The pH was adjusted with NaOH. *tert*-Butyl alcohol (Wako Chemicals) was used after distillation.

The pulse radiolysis was carried out by using 8 ns pulses of 28 MeV electrons from an L-band linear accelerator at room temperature (*ca.* 22 °C). Dosimetry was performed with an aerated aqueous solution of 1×10^{-2} mol dm^{-3} KSCN taking the $G\varepsilon$ value of $(SCN)_2^{\cdot -}$ to be 2.23×10^{-4} m^2 J^{-1}.[14] The dose per pulse was 60–100 Gy producing e_{aq}^- concentrations $(1.7–2.8) \times 10^{-5}$ mol dm^{-3}. The pulse radiolysis set-up has been described in the previous paper.[15]

Results and Discussion

One-electron Reduction of BPS^- *and* PyS^- *by* e_{aq}^-.—The species primarily formed by electron-beam irradiation of aqueous solutions are given in eqn. (1). The yields of these

$$H_2O \rightsquigarrow H, OH, e_{aq}^-, H_3O^+, H_2, H_2O_2 \qquad (1)$$

species are: $G(H) = 0.6$, $G(OH) = 2.7$, $G(e_{aq}^-) = 2.7$, $G(H_3O^+) = 2.7$, $G(H_2) = 0.45$ and $G(H_2O_2) = 0.7$,[16] where the G value is the number of the product molecules per 100 eV absorbed energy. Pulse radiolysis of argon-saturated aqueous solutions of BPS^-Na^+ and PyS^-Na^+ resulted in the one-electron reduction of the aromatic moieties of the sulfonates by e_{aq}^-. The absorption spectrum of e_{aq}^- observed immediately after the pulse was replaced by those of the reduced sulfonates, $BPS^{\cdot 2-}$ and $PyS^{\cdot 2-}$.

Fig. 1 shows the transient absorption spectra at 400 ns after the pulse for the 5×10^{-3} mol dm^{-3} BPS^-Na^+ solution saturated with argon and nitrous oxide. The sharp peak at 405 nm and the broad band at around 620 nm for the argon-saturated solution are analogous to those of the biphenyl radical anion in aqueous and organic solutions.[17,18] The absorption intensities decreased greatly when the solution was saturated with nitrous oxide, which is an electron scavenger. Thus, the absorption is assigned to the one-electron reduction product, $BPS^{\cdot 2-}$, whose radical anion site is located on the biphenylyl group.

$$e_{aq}^- + BPS^- \longrightarrow BPS^{\cdot 2-} \qquad (2)$$

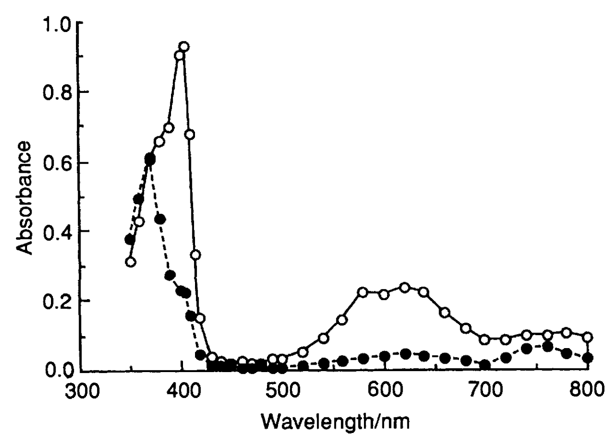

Fig. 1 Transient absorption spectra at 400 ns after the pulse for the BSP^-Na^+ solution saturated with (○) argon and (●) nitrous oxide: $[BPS^-Na^+] = 5 \times 10^{-3}$ mol dm^{-3}

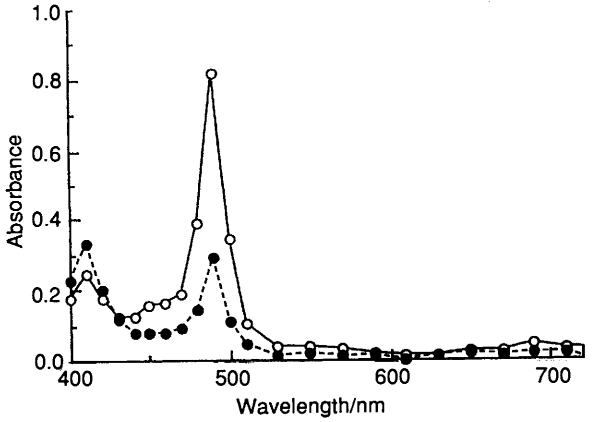

Fig. 2 Transient absorption spectra at 400 ns after the pulse for the PyS^-Na^+ solution saturated with (○) argon and (●) nitrous oxide: $[PyS^-Na^+] = 5 \times 10^{-3}$ mol dm^{-3}

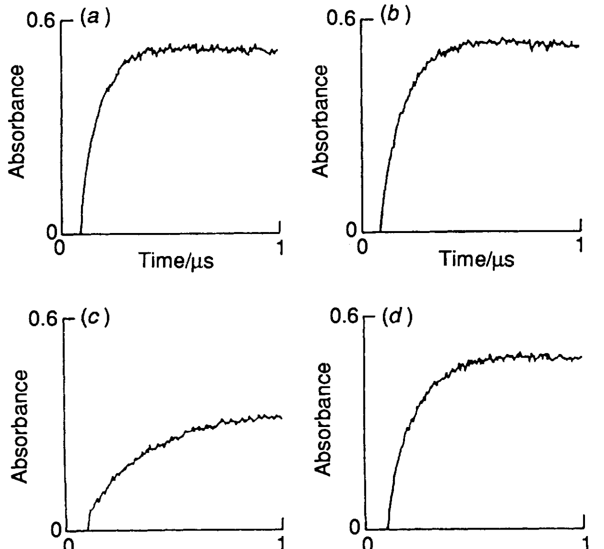

Fig. 3 Increases in the absorption of $BPS^{\bullet 2-}$ for the BPS^-Na^+ solution, saturated with argon, in the (*a*) absence and presence of (*b*) α-, (*c*) β- and (*d*) γ-CDs: $[BPS^-Na^+] = 1 \times 10^{-3}$ mol dm^{-3} and [CD] = 1×10^{-2} mol dm^{-3}

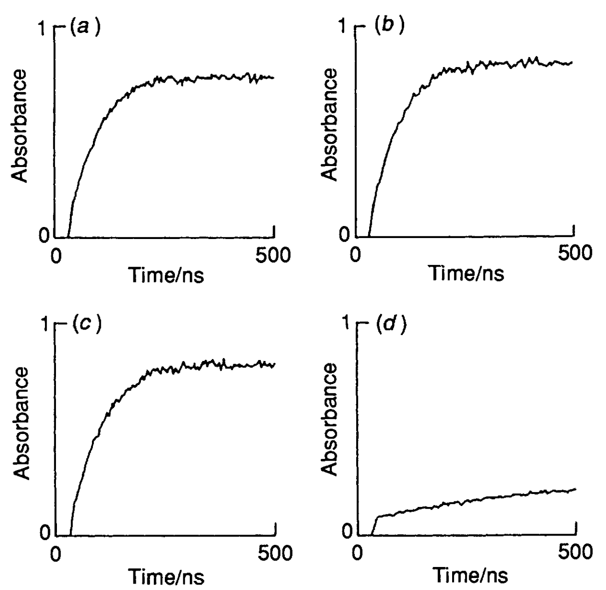

Fig. 4 Increases in the absorption of $PyS^{\bullet 2-}$ for the PyS^-Na^+ solution, saturated with argon, in the (*a*) absence and presence of (*b*) α-, (*c*) β- and (*d*) γ-CDs: $[PyS^-Na^+] = 1 \times 10^{-3}$ mol dm^{-3} and [CD] = 1×10^{-2} mol dm^{-3}

The absorption peak at around 370 nm observed for the nitrous oxide-saturated solution is assigned to the radical species produced from BPS^-. This is also similar to the case of the pulse radiolysis of aqueous and organic solutions of biphenyl.[17,19,20] The increase in absorption intensity at 370 nm and below caused by saturating the solution with nitrous oxide is attributed to the formation of OH-adducts of BPS^-, because OH is a product of the reaction of nitrous oxide with e_{aq}^- [eqn. (3)]. The absorption around 370 nm decreased in the presence

$$N_2O + e_{aq}^- + H_2O \longrightarrow OH + OH^- + N_2 \quad (3)$$

of 1.0 mol dm^{-3} *tert*-butyl alcohol added to the argon-saturated solution as a radical scavenger.

The molar extinction coefficient of $BPS^{\bullet 2-}$ at 405 nm was 4.0×10^4 dm^3 mol^{-1} cm^{-1}, determined by comparison of the absorption intensities of $BPS^{\bullet 2-}$ and e_{aq}^- based on the literature value of e_{aq}^-, 1.85×10^4 dm^3 mol^{-1} cm^{-1} at 715 nm.[21] It is comparable to the molar extinction coefficient of the biphenyl radical anion in tetrahydrofuran.[22] The rise in the 405 nm absorption was consistent with the decay of e_{aq}^-. Their formation and decay behaviour obeyed first-order kinetics. The bimolecular rate constant for reaction (2) was determined to be 9.4×10^9 dm^3 mol^{-1} s^{-1} from the slope of the linear plot of the pseudo-first-order rate constant against BPS^-Na^+ concentration. The decay of e_{aq}^- in the argon-saturated water, not containing BPS^-Na^+, also obeyed first-order kinetics, though not pure. The pseudo-first-order rate constant for the decay of e_{aq}^- in the BPS^-Na^+ solutions gave a good straight line in the range of concentration from 5×10^{-4} to 5×10^{-3} mol dm^{-3} with a small intercept.

Similarly, the one-electron reduction of PyS^- was proved for the PyS^-Na^+ solutions [eqn. (4)]. Fig. 2 shows the transient

$$e_{aq}^- + PyS^- \longrightarrow PyS^{\bullet 2-} \quad (4)$$

absorption spectra at 400 ns after the pulse for the 5×10^{-3} mol dm^{-3} PyS^-Na^+ solution saturated with argon and nitrous oxide. The sharp peak at 490 nm observed for the argon-saturated solution is assigned to $PyS^{\bullet 2-}$; the absorption spectrum is the same as that of the pyrene radical anion generated in organic solvent.[18] The absorption peak at 410 nm, whose intensity increases under the nitrous oxide atmosphere, is assigned to radical species such as OH- and H-adducts of PyS^-. The absorption below 480 nm decreased on addition of 1.0 mol dm^{-3} *tert*-butyl alcohol.

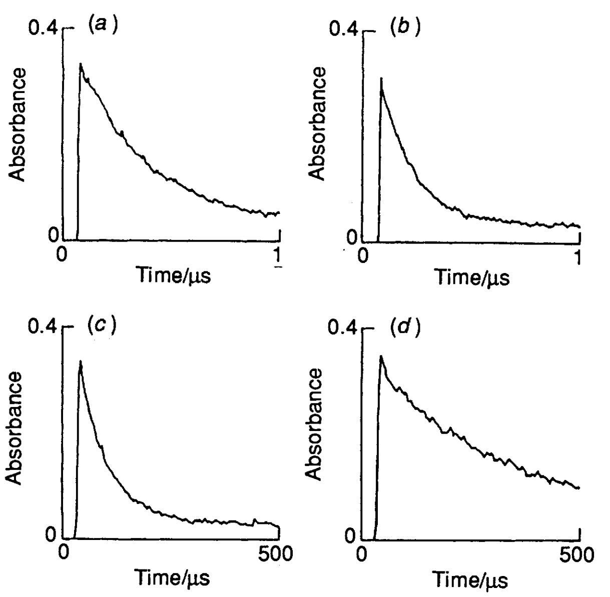

Fig. 5 Decays of e_{aq}^- for the (a) BPS^-Na^+–β-CD, (b) BPS^-Na^+–γ-CD, (c) PyS^-Na^+–β-CD and (d) PyS^-Na^+–γ-CD solutions saturated with argon: [sulfonate] = 1×10^{-3} mol dm^{-3} and [CD] = 1×10^{-2} mol dm^{-3}

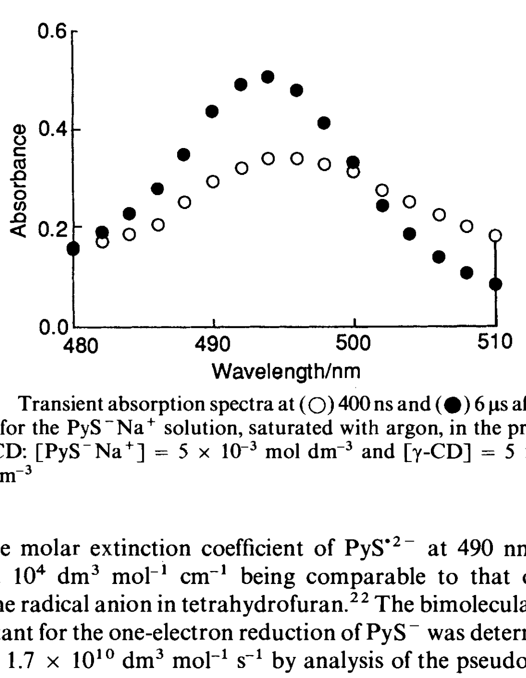

Fig. 6 Transient absorption spectra at (○) 400 ns and (●) 6 μs after the pulse for the PyS^-Na^+ solution, saturated with argon, in the presence of γ-CD: [PyS^-Na^+] = 5×10^{-3} mol dm^{-3} and [γ-CD] = 5×10^{-2} mol dm^{-3}

The molar extinction coefficient of $PyS^{\bullet 2-}$ at 490 nm was 4.7×10^4 dm^3 mol^{-1} cm^{-1} being comparable to that of the pyrene radical anion in tetrahydrofuran.[22] The bimolecular rate constant for the one-electron reduction of PyS^- was determined to be 1.7×10^{10} dm^3 mol^{-1} s^{-1} by analysis of the pseudo-first-order kinetics for the decay of e_{aq}^-. The rate constant for the one-electron reduction of PyS^- is larger than that for BPS^-. This may be due to the difference in electron affinity and/or size between the biphenylyl and pyrenyl groups.

The pH values of the aqueous solution of 5×10^{-3} mol dm^{-3} BPS^-Na^+ and PyS^-Na^+ were 5.8 and 6.0, respectively. This may be due to the presence of sulfonic acids, BPS^-H^+ and PyS^-H^+, as impurities. The pH was not adjusted for the determination of the rate constants since the decay rate of e_{aq}^- was not affected by the adjustment of pH at around 7 with NaOH.

Effects of CDs on the One-electron Reduction.—The one-electron reduction of BPS^- was retarded by β-CD, but hardly affected by α- and γ-CDs. On the other hand, the one-electron reduction of PyS^- was retarded by γ-CD, but hardly affected by α- and β-CDs. The results can be interpreted in terms of protection of the sulfonates against the one-electron reduction through the inclusion complexation, since BPS^- and PyS^- best fit the cavities of β- and γ-CDs, respectively. The effect of the CDs was investigated in the absence of the radical scavenger, *tert*-butyl alcohol, since the excess amount of the organic additive disturbs the CD complexation of the sulfonates.

Figs. 3 and 4 show the effects of α-, β-and γ-CDs on the rise of the absorption of $BPS^{\bullet 2-}$ and $PyS^{\bullet 2-}$, respectively, at the peak positions. A remarkable effect is observed for the BPS^-Na^+–β-CD and PyS^-Na^+–γ-CD solutions. The yields of $BPS^{\bullet 2-}$ and $PyS^{\bullet 2-}$ decrease in the presence of β-and γ-CDs, respectively, as well as their formation rates. This is due to the competitive decay processes of e_{aq}^- whose contribution becomes important in the presence of the CDs retarding the one-electron reduction of the sulfonates. For the PyS^-Na^+ solution containing γ-CD the absorbance at 494 nm reached a maximum, 0.380, at *ca.* 5 μs because of a spectral change occurring after the pulse as described below. Fig. 5 shows the comparison of the decay of e_{aq}^- at 715 nm in the presence of β- and γ-CDs for the BPS^-Na^+ and PyS^-Na^+ solutions to demonstrate that the decay of e_{aq}^- is retarded by the CD complexation of the sulfonates. To avoid coexistence of the dissociated and complexed sulfonates the [CD]/[sulfonate] ratio was kept at 10 and, because of the low solubility of β-CD, the experiments were carried out at a low sulfonate concentration, 1×10^{-3} mol dm^{-3}.

The position of the absorption maximum of $BPS^{\bullet 2-}$ was not affected by the addition of CDs. The bimolecular rate constant was determined to be 1.0×10^9 dm^3 mol^{-1} s^{-1} for the one-electron reduction of the complex of BPS^- with β-CD [reaction (5)]. The pseudo-first-order rate constants were obtained by

$$e_{aq}^- + \text{BPS–β-CD} \longrightarrow \text{BPS}^{\bullet 2-}\text{–β-CD} \quad (5)$$

kinetic analysis of the decay of e_{aq}^- at [β-CD]/[BPS^-] ratios above 10 to avoid contribution of the dissociated BPS^-.

The absorption maximum of $PyS^{\bullet 2-}$ is shifted from 490 nm to 492 in the presence of α- and β-CDs and to 494 nm in the presence of γ-CD. The spectral shift may be due to a decrease in polarity of the medium by the addition of α- and β-CDs or to the hydrophobic environment in the γ-CD cavity. The shape of the absorption spectrum of $PyS^{\bullet 2-}$ in the presence of γ-CD changed with time after the pulse. This is attributed to the dissociation of the reduced 2:2 complex as described below.

Dissociation of the Reduced 2:2 *Complex of* PyS^- *with* γ-*CD.*—It is known that 2:2 complexes are formed between the pyrenyl groups and γ-CD at higher host and guest concentrations.[7,23–26] The 2:2 complexes dissociate into the 1:1 complexes in strongly alkaline solution.[26] This is due to ionic repulsion between the anionic forms of the secondary hydroxy groups of the γ-CDs facing each other to form the 2:2 complexes. Fig. 6 shows the transient absorption spectra for the 5×10^{-3} mol dm^{-3} PyS^-Na^+ solution containing 5×10^{-2} mol dm^{-3} γ-CD. The absorption spectrum in the early stage is rather broad. The absorption below 500 nm slowly increases with time after the pulse and a narrow band appears at 494 nm. After 6 μs the absorption peak decayed without any changes in the shape and the peak position. The broader absorption band in the early stage was not observed in the presence of α- and β-CDs instead of γ-CD. Neither was it observed for the strongly alkaline solutions (pH > 12.7) containing γ-CD, where the narrow band at 494 nm began to build up just after the pulse and decayed without any spectral changes. Therefore, the broader absorption band in the early stage is assigned to the reduced 2:2 complex, which is unstable and dissociates into the 1:1 complexes [reactions (6) and (7)].

$$e_{aq}^- + (\text{PyS}^-)_2\text{–}(\gamma\text{-CD})_2 \longrightarrow (\text{PyS}^{\bullet 2-})(\text{PyS}^-)\text{–}(\gamma\text{-CD})_2 \quad (6)$$

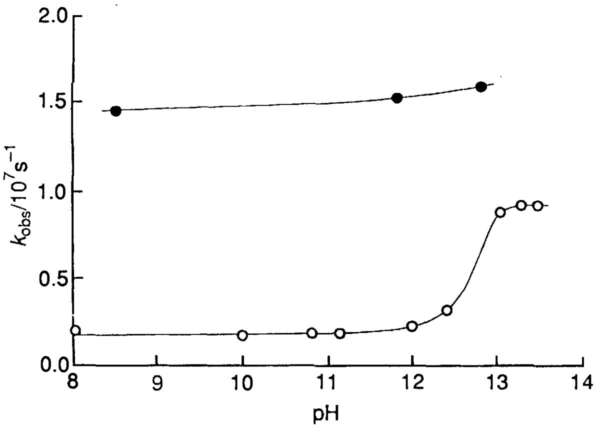

Fig. 7 pH dependence of the pseudo-first-order rate constant for the one-electron reduction of PyS$^-$ in the (○) presence and (●) absence of γ-CD

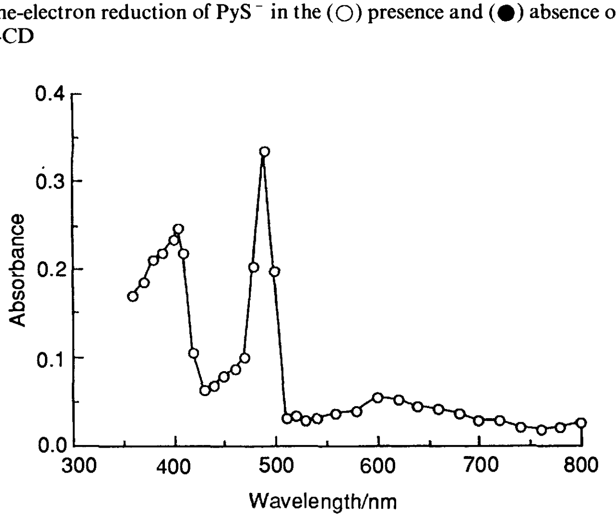

Fig. 8 Transient absorption spectrum at 200 ns after the pulse for the argon-saturated solution of the equimolar mixture of BPS$^-$Na$^+$ and PyS$^-$Na$^+$: [sulfonate] = 1 × 10^{-3} mol dm^{-3} for each

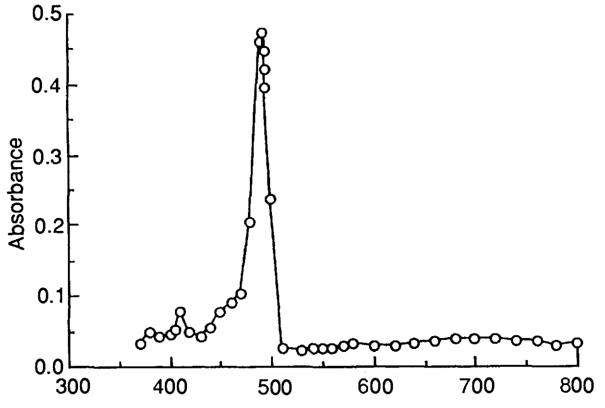

Fig. 9 Transient absorption spectrum at 200 ns after the pulse for the argon-saturated solution of the equimolar mixture of BPS$^-$Na$^+$ and PyS$^-$Na$^+$ in the presence of β-CD: [sulfonate] = 1 × 10^{-3} mol dm^{-3} for each and [β-CD] = 1 × 10^{-2} mol dm^{-3}

$$(\mathrm{PyS}^{\bullet 2-})(\mathrm{PyS}^{-})\text{-}(\gamma\text{-CD})_2 \longrightarrow \mathrm{PyS}^{\bullet 2-}\text{-}\gamma\text{-CD} + \mathrm{PyS}\text{-}\gamma\text{-CD} \quad (7)$$

The dissociation of the reduced 2:2 complex is due to the introduction of the negative charge to one of the guest molecules completely surrounded by the hydrophobic cavities. The reduced 1:1 complex is considered to be more stable than the reduced 2:2 complex, since no spectral changes were observed during the decay. The absorption peak is as sharp as that of the dissociated PyS$^{\bullet 2-}$. These results are attributed to the fact that the pyrenyl group of the 1:1 complex is partially out of the hydrophobic cavity.

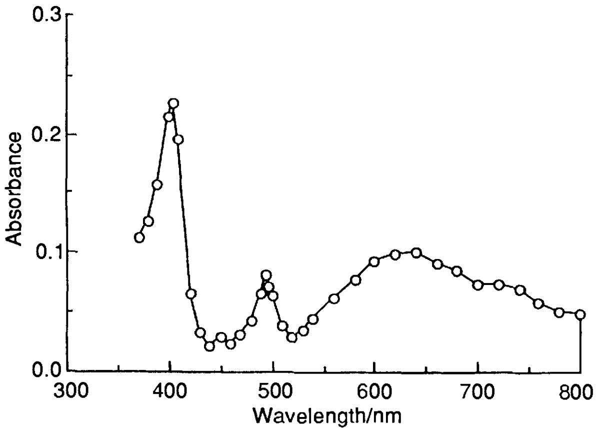

Fig. 10 Transient absorption spectrum at 200 ns after the pulse for the argon-saturated solution of the equimolar mixture of BPS$^-$Na$^+$ and PyS$^-$Na$^+$ in the presence of γ-CD: [sulfonate] = 1 × 10^{-3} mol dm^{-3} for each and [γ-CD] = 1 × 10^{-2} mol dm^{-3}

The decrease in the host–guest affinity by introducing the negative charge to a guest molecule has previously been reported for the electrochemically reduced complex of *p*-nitrophenolate with α-CD.[11] It has also been reported that the benzoate anion is more loosely associated with α-CD than benzoic acid.[27] On the other hand, the anion radicals of dicyanobenzenes associate more strongly than the parent neutral molecules due to the dipole–induced dipole interaction.[12] That is to say, the CD complexes of neutral molecules are stabilized by the one-electron reduction in contrast to those of anions such as *p*-nitrophenolate. The 2:2 complex of PyS$^-$ with γ-CD is the latter case.

The bimolecular rate constant for reaction (6) was determined to be 1.3 × 10^9 dm^3 mol^{-1} s^{-1} by kinetic analysis of the decay of e_{aq}^-. The pseudo-first-order rate constants for the determination were obtained at the PyS$^-$Na$^+$ and γ-CD concentrations up to 5 × 10^{-3} and 5 × 10^{-2} mol dm^{-3}, respectively, to avoid coexistence of the complexes with the other stoichiometries.

Fig. 7 shows the pH dependence of the pseudo-first-order rate constant for the decay of e_{aq}^- in the 1 × 10^{-3} mol dm^{-3} PyS$^-$ Na$^+$ solution in the presence and absence of 5 × 10^{-2} mol dm^{-3} γ-CD. The value drastically increases at pH > 13 in the presence of γ-CD. This can be attributed to the dissociation of the 2:2 complex into the 1:1 complexes, which are much less protected against the one-electron reduction than the 2:2 complex. The bimolecular rate constant pH > 13 was determined to be 9.1 × 10^9 dm^3 mol^{-1} s^{-1} for the one-electron reduction of the 1:1 complex [reaction (8)].

$$e_{aq}^- + \mathrm{PyS}\text{-}\gamma\text{-CD} \longrightarrow \mathrm{PyS}^{\bullet 2-}\text{-}\gamma\text{-CD} \quad (8)$$

Selective One-electron Reduction by Using β- and γ-CDs.— The selective one-electron reduction is expected for a mixed sulfonate solution by using β- and γ-CDs since the rate constants of the CD complexes are one order of magnitude smaller than those of the dissociated sulfonates. Figs. 8, 9 and 10 show the transient absorption spectra for the solution of an equimolar mixture of BPS$^-$Na$^+$ and PyS$^-$Na$^+$ at 200 ns after the pulse in the absence and presence of β- and γ-CDs, respectively. The absorption spectrum for the CD-free solution was an overlap of those of BPS$^{\bullet 2-}$ and PyS$^{\bullet 2-}$. The addition of β- and γ-CDs

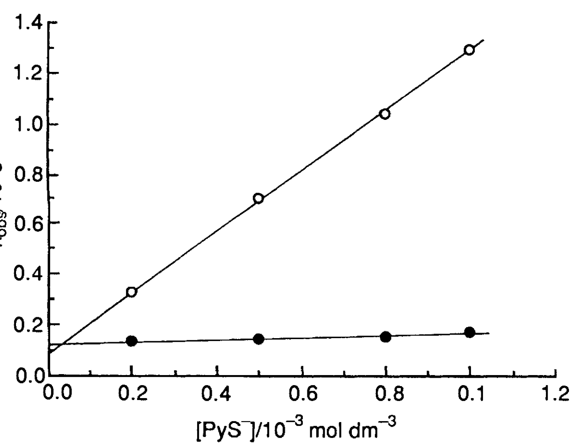

Fig. 11 Plot of the pseudo-first-order rate constants for the electron transfer from $BPS^{\bullet 2-}$ to PyS^- in the (○) absence and (●) presence of γ-CD against PyS^-Na^+ concentration

results in the selective formation of $PyS^{\bullet 2-}$ and $BPS^{\bullet 2-}$, respectively. For the solution containing γ-CD (Fig. 10), the large absorption at around 650 nm is due to a contribution of e_{aq}^- remaining unchanged at the time, 200 ns, after the pulse. On the other hand, for the solution containing β-CD (Fig. 9), the absorption due to e_{aq}^- is negligible because of the larger rate constant for reaction (4) than for reaction (2). The one-electron reduction of BPS^- in the solutions of the mixed sulfonates was followed by electron transfer from the resulting $BPS^{\bullet 2-}$ to PyS^-. The kinetic analysis for the electron transfer reaction is presented below.

Effect of the CD Complexation on the Electron Transfer from $BPS^{-\bullet 2-}$ *to* PyS^-.—The electron transfer reaction was investigated with 1×10^{-2} mol dm^{-3} BPS^-Na^+ solutions containing (2–10) × 10^{-4} mol dm^{-3} PyS^-Na^+ in the absence and presence of 5×10^{-2} mol dm^{-3} γ-CD (pH = 4.8–5.5). The transient absorption spectra for these solutions in the early stage were similar to that for the BPS^-Na^+ solution not containing PyS^-Na^+. The formation of $PyS^{\bullet 2-}$ is due exclusively to electron transfer from the initially produced $BPS^{\bullet 2-}$ to PyS^-. This is similar to the case of the pulse radiolysis of organic solutions of biphenyl containing much lower concentrations of pyrene, where the pyrene radical anion is formed by electron transfer from the initially produced biphenyl radical anion.[15,28] Fig. 11 shows the pseudo-first-order rate constants, obtained by kinetic analysis of the decay of the 405 nm absorption of $BPS^{\bullet 2-}$, plotted against PyS^-Na^+ concentration. From the slope of the plot for the CD-free solutions the bimolecular rate constant for the electron transfer [reaction (9)] was determined to be

$$BPS^{\bullet 2-} + PyS^- \longrightarrow BPS^- + PyS^{\bullet 2-} \quad (9)$$

1.2×10^9 dm^3 mol^{-1} s^{-1}. The bimolecular rate constant for the electron transfer from $BPS^{\bullet 2-}$ to the 2:2 complex of PyS^- with γ-CD [reaction (10)] is estimated to be 5×10^7 dm^3 mol^{-1} s^{-1},

$$BPS^{\bullet 2-} + (PyS^-)_2\text{-}(\gamma\text{-CD})_2 \longrightarrow BPS^- + (PyS^{\bullet 2-})(PyS^-)\text{-}(\gamma\text{-CD})_2 \quad (10)$$

although the slope of the plot is too small to determine an accurate value.

It can be said that the 2:2 complex of PyS^- with γ-CD is more effectively protected against electron transfer than against the one-electron reduction, probably because of a difference in reducing power between $BPS^{\bullet 2-}$ and e_{aq}^-.

Acknowledgements

The authors are grateful to the members of the Radiation Laboratory of this institute for help with the pulse radiolysis experiments.

References

1 M. L. Bender and M. Komiyama, *Cyclodextrin Chemistry*, Springer-Verlag, Berlin, 1978.
2 J. Szejtli, *Cyclodextrins and Their Inclusion Complexes*, Akademiai Kiado, Budapest, 1982.
3 D. C. Rideout and R. Breslow, *J. Am. Chem. Soc.*, 1980, **102**, 7817.
4 N. K. Sangwan and H.-J. Schneider, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1223, and references cited therein.
5 I. Hunt and C. D. Johnson, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1051.
6 F. Hirayama, T. Utsuki and K. Uekama, *J. Chem. Soc., Chem. Commun.*, 1991, 887.
7 A. Ueno, K. Takahashi and T. Osa, *J. Chem. Soc., Chem. Commun.*, 1980, 921.
8 A. Harada and S. Nozakura, *Polym. Bull.*, 1982, **8**, 141.
9 T. Yorozu, M. Hoshino and M. Imamura, *J. Phys. Chem.*, 1982, **86**, 4426.
10 K. Kano, I. Takenoshita and T. Ogawa, *Chem. Lett.*, 1982, 321.
11 K. Kano, K. Mori, B. Uno and T. Kubota, *J. Electroanal. Chem.*, 1990, **283**, 187.
12 K. Kano, K. Mori, B. Uno, M. Goto and T. Kubota, *J. Am. Chem. Soc.*, 1990, **112**, 8645.
13 R. G. Schults, *J. Org. Chem.*, 1961, **26**, 5159.
14 E. M. Fielden, in *The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis*, eds. J. H. Baxendale and F. Busi, D. Reidel, Dordrecht, 1982, p. 49.
15 Y. Yamamoto, S. Nishida, K. Yabe, K. Hayashi, S. Takeda and K. Tsumori, *J. Phys. Chem.*, 1984, **88**, 2368.
16 G. V. Buxton, in *The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis*, eds. J. H. Baxendale and F. Busi, D. Reidel, Dordrecht, 1982, p. 241.
17 K. Sehested and E. J. Hart, *J. Phys. Chem.*, 1975, **79**, 1639.
18 T. Shida, *Electronic Absorption Spectra of Radical Ions*, Elsevier, Amsterdam, 1988.
19 S. Arai and L. M. Dorfman, *J. Chem. Phys.*, 1964, **41**, 2190.
20 F. S. Dainton, T. J. Kemp, G. A. Salmon and J. P. Keene, *Nature*, 1964, **203**, 1050.
21 A. J. Swallow, in *The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis*, eds. J. H. Baxendale and F. Busi, D. Reidel, Dordrecht, 1982, p. 289.
22 J. Jagur-Grodzinski, M. Feld, S. L. Yang and M. Szwarc, *J. Phys. Chem.*, 1965, **69**, 628.
23 N. Kobayashi, R. Saito, H. Hino, Y. Hino, A. Ueno and T. Osa, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1031.
24 W. G. Herkstroeter, P. A. Martic and S. Farid, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1453.
25 W. G. Herkstroeter, P. A. Martic, T. R. Evans and S. Farid, *J. Am. Chem. Soc.*, 1986, **108**, 3275.
26 S. Hamai, *J. Phys. Chem.*, 1989, **93**, 6527.
27 R. J. Bergeron, M. A. Channing and K. A. McGovern, *J. Am. Chem. Soc.*, 1978, **100**, 2878.
28 S. Arai, D. A. Grev and L. M. Dorfman, *J. Chem. Phys.*, 1967, **46**, 2572.

Paper 2/02674K
Received 22*nd May* 1992
Accepted 21*st August* 1992