Pulse Radiolysis of Aromatic Carboxylates in Aqueous Solution and Effect of Cyclodextrin Complexation on the One-electron Reduction by the Hydrated Electron

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

Pulse radiolysis of Ar-saturated aqueous solutions of biphenyl-4-ylacetate (BPA^-), biphenyl-4-carboxylate (BPC^-), 4-pyren-1-ylbutyrate (PyB^-) and pyrene-1-carboxylate (PyC^-) results in the one-electron reduction of the solutes by the hydrated electron. The transient absorption spectra of the reduced aromatic carboxylates are analogous to those of the radical anions of the corresponding aromatic hydrocarbons, suggesting that the radical anion site is located on the aromatic moieties. The transient absorption spectrum of the reduced BPC^- is shifted to shorter wavelengths with time after the pulse at pH below *ca.* 10. The spectral shift has been attributed to the association of the reduced BPC^- with H^+: $(BP^{\bullet -})COO^- + H^+ \longrightarrow (BP^{\bullet -})CO_2H$, where BP denotes biphenylyl. In the case of biphenyl-2-carboxylate, no absorption bands like those of the biphenyl radical anion were observed. This means that the steric effect of the carboxy group prevents the formation of biphenyl-type radical anions, which have a more coplanar structure than the parent molecule. Effect of cyclodextrin (CD) complexation of the hydrophobic moieties of the carboxylates has been investigated by using α-, β- and γ-CDs. The rate constants for the one-electron reduction of BPA^- and BPC^- are effectively reduced by the addition of β-CD, whose cavity best fits to the biphenylyl group. Similarly, the one-electron reduction of PyB^- and PyC^- is retarded by the best fitting γ-CD. The retarding effect of the CD complexation is greater for BPA^- and PyB^- having $-CH_2-$ and $-(CH_2)_3-$, respectively, between the aromatic and carboxy groups than for BPC^- and PyC^- not having such a spacer. The transient absorption spectrum of reduced PyC^- in the presence of γ-CD is shifted to shorter wavelengths with time after the pulse. Such a spectral shift is not observed for PyB^-. It has been proposed that the 2:2 complex of PyC^- with γ-CD undergoes a structural change upon one-electron reduction.

Cyclodextrins (CDs) form inclusion complexes with various organic molecules in aqueous solution depending on the sizes of their hydrophobic cavities and of the guest molecules.[1,2] The most common of them are α-, β- and γ-CDs consisting of six, seven and eight glucose units, respectively. In the preceding paper we have reported a pulse radiolysis study of the effect of CD complexation on the one-electron reduction of aromatic sulfonates, such as biphenyl-4-sulfonate (BPS^-) and pyrene-1-sulfonate (PyS^-), by the hydrated electron.[3] The transient absorption spectra of the one-electron reduction products, the sulfonate radical anions, 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 sulfonates. The rate constants for the one-electron reduction of BPS^- and PyS^- were appreciably reduced by β- and γ-CDs, respectively, whose cavities best fit to the respective aromatic groups.

The present pulse radiolysis study was undertaken on the one-electron reduction of aromatic carboxylates such as biphenyl-4-ylacetate (BPA^-), biphenyl-4-carboxylate (BPC^-), 4-pyren-1-ylbutyrate (PyB^-) and pyrene-1-carboxylate (PyC^-) in the absence and presence of the CDs. The effect of a $-CH_2-$ or $-(CH_2)_3-$ group as a spacer between the aromatic and carboxylic groups is discussed.

Little information is available on the one-electron reduction of aromatic carboxylates except for benzoate.[4] This paper presents a detailed study on the one-electron reduction of the aromatic carboxylates. It is demonstrated that the radical anion sites of the reduced products are located on the aromatic moieties, similarly to the case of the aromatic sulfonates.[3] A comparison is made for BPC^- and biphenyl-2-carboxylate, the latter of which does not yield the biphenyl-type radical anion upon one-electron reduction.

Results and Discussion

When Ar-saturated aqueous solutions of the aromatic carboxylates are irradiated with electron pulses, the radical anions and neutral radicals are produced by the reactions of the primarily generated e_{aq}^-, OH and H with the solutes [eqn. (1)],

$$H_2O \rightsquigarrow e_{aq}^- \, (2.7),\ OH\ (2.7),\ H\ (0.6) \qquad (1)$$

where the numbers in parentheses represent the radiation chemical yields, *G* values, for the individual species.[5]

Pulse Radiolysis of BPA^-.—Fig. 1 shows the transient absorption spectra at 200 ns and 9 μs after the pulse for the Ar-saturated solution of 5×10^{-3} mol dm^{-3} BPA^- (pH, 7.0). Fig. 2 shows the effects of *tert*-butyl alcohol and N_2O used as radical and electron scavengers, respectively, on the transient absorption spectrum at 200 ns. The absorption bands at 400 and 640 nm disappear when the solution is saturated with N_2O and are assigned to the one-electron reduction product, the radical anion. The spectral shape is analogous to that of the biphenyl radical anion,[6,7] indicating that the radical anion site is located on the biphenylyl group [eqn. (2)], where BP denotes biphenylyl.

$$BPCH_2CO_2^- + e_{aq}^- \longrightarrow (BP^{\bullet -})CH_2CO_2^- \qquad (2)$$

The absorption bands below 380 nm are assigned to the

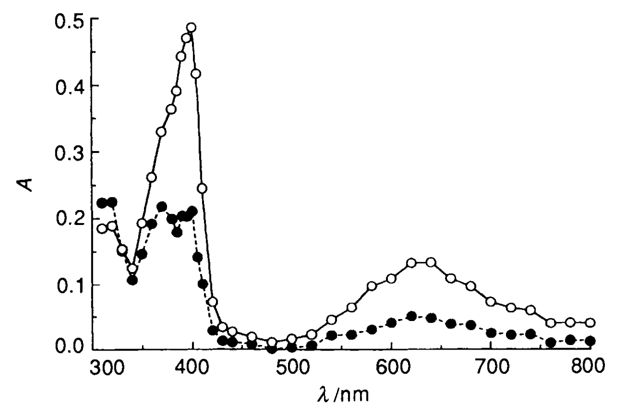

Fig. 1 Transient absorption spectra at (○) 200 ns and (●) 9 μs for Ar-saturated solution of BPA^-; $[BPA^-] = 5 \times 10^{-3}$ mol dm^{-3}

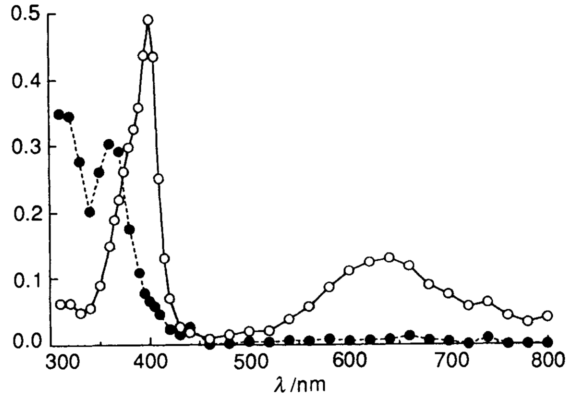

Fig. 2 Transient absorption spectra at 200 ns for BPA^- solutions (○) saturated with Ar and containing 1.0 mol dm^{-3} *tert*-butyl alcohol and (●) saturated with N_2O; $[BPA^-] = 5 \times 10^{-3}$ mol dm^{-3}

neutral radicals, OH- and H-adducts of BPA^-, since they are observed under an atmosphere of N_2O and disappear in the presence of 1.0 mol dm^{-3} *tert*-butyl alcohol. Their absorption intensities are larger for the N_2O-saturated solution than for the Ar-saturated solution, as shown in Figs. 1 and 2, because OH is a product of the reaction of N_2O with e_{aq}^- [eqn. (3)].

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

The molar extinction coefficient of the reduced BPA^- at 400 nm was 3.1×10^4 dm^3 mol^{-1} cm^{-1}, determined by comparison of the absorption intensity with that of e_{aq}^- based on the literature value (1.85×10^4 dm^3 mol^{-1} cm^{-1} at 715 nm).[8] The rise in the 400 nm absorption was consistent with the decay of e_{aq}^- and obeyed first-order kinetics. The rate constant for reaction (2), k_2, was determined to be 3.3×10^9 dm^3 mol^{-1} s^{-1} from the slope of the linear plot of the pseudo-first-order rate constant for the decay of e_{aq}^-, k_{obs}, against BPA^- concentration (pH, 6.7–7.0). The decay of e_{aq}^- was monitored at 800 nm where the absorption due to reduced BPA^- is negligible.

Pulse Radiolysis of BPC^-.—Fig. 3 shows the transient absorption spectra at 200 ns and 9 μs for the Ar-saturated solution of 5×10^{-3} mol dm^{-3} BPC^- (pH, 6.9) together with that at 200 ns for the Ar-saturated solution of 5×10^{-3} mol dm^{-3} biphenyl-2-carboxylate (pH, 7.0). The absorption spectrum at 200 ns for the BPC^- solution is somewhat similar to that for the BPA^- solution. In contrast to the case of the BPA^- solution, the peak positions of the absorption bands at around 400 and 660 nm are shifted to shorter wavelengths with time after the pulse. In the case of the biphenyl-2-carboxylate solution, no absorption band is observed above 350 nm, whereas the absorption of e_{aq}^- rapidly decayed similarly to the cases of the BPC^- solution. This means that the biphenyl-type radical anion is not generated by the one-electron reduction of biphenyl-2-carboxylate. The steric effect of the carboxy group is considered to prevent the formation of the biphenyl-type radical anion, which has a more coplanar structure than the parent molecule.[9]

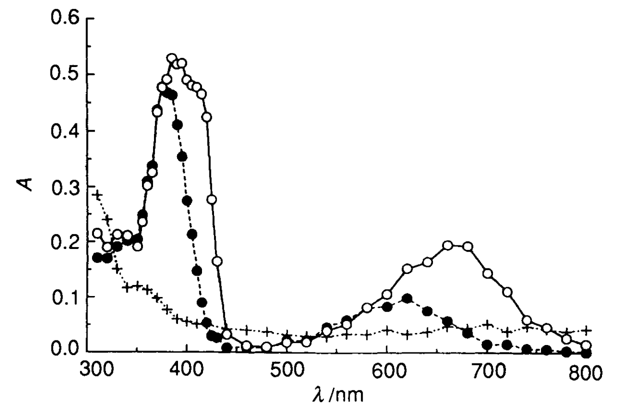

Fig. 3 Transient absorption spectra for Ar-saturated solutions of BPC^- [at (○) 200 ns and (●) 9 μs] and (+) of biphenyl-2-carboxylate (at 200 ns); [carboxylate] = 5×10^{-3} mol dm^{-3}

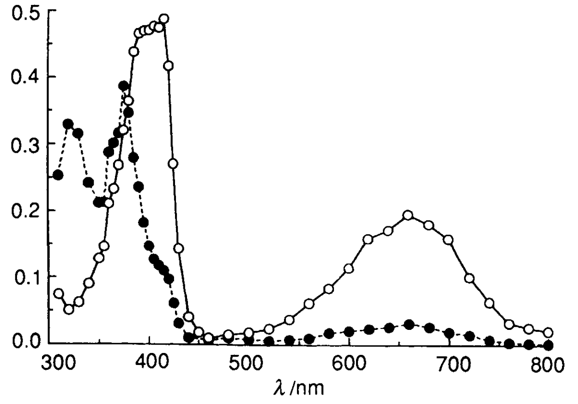

Fig. 4 Transient absorption spectra at 200 ns for BPC^- solutions (○) saturated with Ar and containing 1.0 mol dm^{-3} *tert*-butyl alcohol and (●) saturated with N_2O; $[BPC^-] = 5 \times 10^{-3}$ mol dm^{-3}

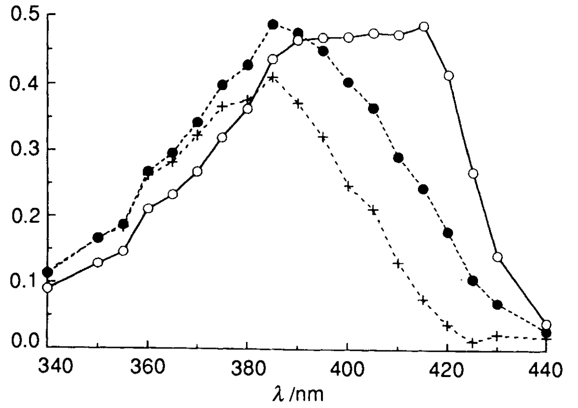

Fig. 5 Transient absorption spectra at (○) 200 ns, (●) 1.5 μs and (+) 6 μs for a BPC^- solution saturated with Ar and containing 1.0 mol dm^{-3} *tert*-butyl alcohol; $[BPC^-] = 5 \times 10^{-3}$ mol dm^{-3}

Fig. 4 shows the effects of *tert*-butyl alcohol and N_2O on the transient absorption spectrum at 200 ns for the BPC^- solution. Similarly to the case of the BPA^-, the effects of the radical and electron scavengers demonstrate that the absorption bands at around 400 and 660 nm are assigned to the one-electron reduction product and those below 380 nm, to the neutral radicals. Fig. 5 shows the spectral change with time after the pulse for the absorption band at around 400 nm in the presence of 1.0 mol dm^{-3} *tert*-butyl alcohol. It can be seen that the decay of the peak at 415 nm accompanies the rise of the peak at 385 nm. Similarly, the absorption band at 660 nm was shifted to 620 nm until 1.5 μs and then decayed without change in peak position irrespective of the presence of *tert*-butyl alcohol.

The effects of the scavengers suggest that the absorption bands at 385 and 620 nm in the later stage are assigned to the biphenyl-type radical anion as well as those at 415 and 660 nm in the earlier stage. The spectral shift with time after the pulse was not observed for the alkaline solutions at pH above *ca.* 10. Therefore, it can be attributed to the association of the radical anion with H$^+$ [eqn. (5)]. The rapid occurrence of reaction (5)

$$\mathrm{BPCO_2^- + e_{aq}^- \longrightarrow (BP^{\bullet -})CO_2^-} \qquad (4)$$

$$\mathrm{(BP^{\bullet -})CO_2^- + H^+ \longrightarrow (BP^{\bullet -})CO_2H} \qquad (5)$$

may be due to an increase in the association constant by the one-electron reduction of BPC$^-$. It is reasonable to consider that, in the case of BPA$^-$, the association constant is little influenced by the one-electron reduction because of the presence of the methylene spacer between the biphenylyl and carboxy groups.

The molar extinction coefficient of the reduced BPC$^-$ at 415 nm was 3.1 × 10^4 dm^3 mol^{-1} cm^{-1}, determined with the alkaline solution to avoid the coexistence of the reduced BPC$^-$H$^+$. k_4 was determined to be 9.0 × 10^9 dm^3 mol^{-1} s^{-1} (pH 6.5–7.0) from the slope of the plot of k_{obs} against BPC$^-$ concentration. The rate constant of BPC$^-$ is about three times larger than that of BPA$^-$ because of the absence of the methylene spacer between the aromatic and carboxy groups as discussed below.

Effects of CD Complexation on the One-electron Reduction of BPA$^-$ and BPC$^-$.—The one-electron reduction of BPA$^-$ and BPC$^-$ is effectively retarded by β-CD. Fig. 6 shows the effects of β- and γ-CDs on the rise of the absorption of reduced BPA$^-$ and BPC$^-$ (pH 6.8–7.0); the rise curves in the presence of α-CD are not presented in the figure because they were quite similar to those for the CD-free solutions. The effect of β-CD is less significant for BPC$^-$ than for BPA$^-$, as discussed below. The k_{obs} values for the 1 × 10^{-3} mol dm^{-3} carboxylate solutions decreased with increasing β-CD concentration and became almost constant at [β-CD] > 5 × 10^{-3} mol dm^{-3}.

The rate constants for the one-electron-reduction of the complexed BPA$^-$ and BPC$^-$ [eqns. (6) and (7)] were

$$\mathrm{BPCH_2CO_2^-\text{–}\beta\text{-}CD + e_{aq}^- \longrightarrow (BP^{\bullet -})CH_2CO_2^-\text{–}\beta\text{-}CD} \qquad (6)$$

$$\mathrm{BPCO_2^-\text{–}\beta\text{-}CD + e_{aq}^- \longrightarrow (BP^{\bullet -})CO_2^-\text{–}\beta\text{-}CD} \qquad (7)$$

determined in the presence of an excess of β-CD (1 × 10^{-2} mol dm^{-3}). The k_6 and k_7 values were 4.4 × 10^8 (pH 7.0–7.4) and 2.5 × 10^9 (pH 6.8–7.0) dm^3 mol^{-1} s^{-1}, respectively. The k_2 : k_6 and k_4 : k_7 ratios are 7.5 and 3.6, respectively, indicating that the effect of the CD complexation is smaller for BPC$^-$ than for BPA$^-$. This can be interpreted in terms of the occurrence of the one-electron reduction of BPC$^-$ through the attachment of e$_{aq}^-$ to the carboxy group being placed outside the CD cavity. On the other hand, in the case of BPA$^-$, the attachment of e$_{aq}^-$ is limited to the biphenylyl group by the presence of the methylene spacer between the biphenylyl and carboxy groups. The attachment of e$_{aq}^-$ to the carboxy group of BPA$^-$ may be as slow as that to the acetate ion with the rate constant of 4.3 × 10^4 dm^3 mol^{-1} s^{-1} reported in the literature.[10] The contribution of the carboxy group to the one-electron reduction of BPC$^-$ is also demonstrated by the result $k_4 > k_2$.

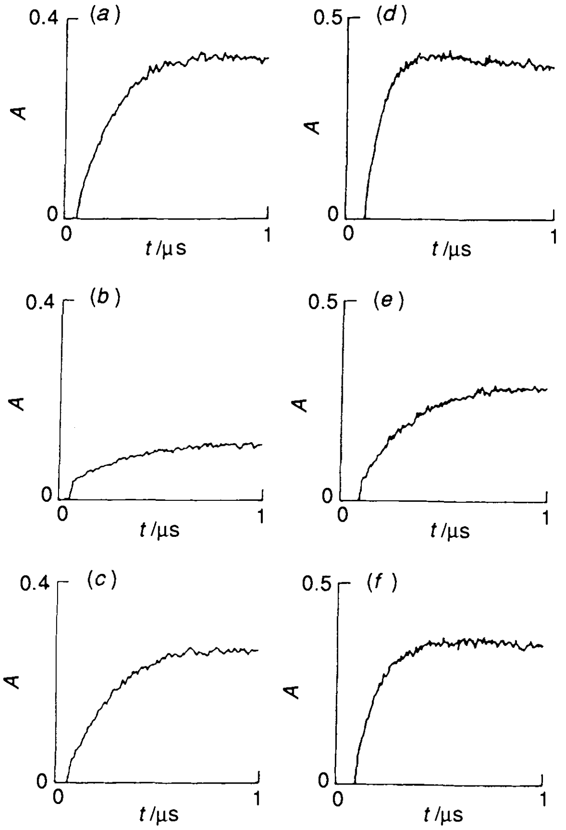

Fig. 6 Rises in the absorption of the radical anions for BPA$^-$ solutions in the (*a*) absence and presence of (*b*) β- and (*c*) γ-CDs and for BPC$^-$ solutions in the (*d*) absence and presence of (*e*) β- and (*f*) γ-CDs; [carboxylate] = 1 × 10^{-3} mol dm^{-3}; [CD] = 1 × 10^{-2} mol dm^{-3}

Pulse Radiolysis of PyB$^-$ and PyC$^-$ and the Effect of the CD Complexation.—In order to confirm the effect of the methylene spacer between aromatic and carboxy groups on the one-electron reduction, a pulse radiolysis study was undertaken for PyB$^-$ and PyC$^-$. Figs. 7 and 8 show the transient absorption spectra for Ar-saturated solutions of 5 × 10^{-3} mol dm^{-3} PyB$^-$ (pH 9.1) and PyC$^-$ (pH 7.1), which are characterized by a strong peak at around 500 nm and a weak one at 410 nm. The PyB$^-$ solution is alkaline because of the low solubility of PyB$^-$H$^+$ at lower pH; the transient absorption spectrum was similar to that of lower pH solutions of dilute PyB$^-$ except for the high absorption intensity. The absorption bands at around 500 and 410 nm were assigned to the radical anions and the neutral radicals, respectively, on the basis of the effects of *tert*-butyl alcohol and N$_2$O. The molar extinction coefficients of the reduced PyB$^-$ and PyC$^-$ at the peak positions were 4.7 × 10^4 (at 490 nm) and 5.2 × 10^4 (at 504 nm) dm^3 mol^{-1} cm^{-1}, respectively. The sharp peaks at around 500 nm are analogous to that of the pyrene radical anion, indicating that the pyrenyl groups are reduced by e$_{aq}^-$ [eqns. (8) and (9)], where Py denotes pyrenyl.

$$\mathrm{Py(CH_2)_3CO_2^- + e_{aq}^- \longrightarrow (Py^{\bullet -})(CH_2)_3CO_2^-} \qquad (8)$$

$$\mathrm{PyCO_2^- + e_{aq}^- \longrightarrow (Py^{\bullet -})CO_2^-} \qquad (9)$$

The one-electron reduction of PyB$^-$ and PyC$^-$ was retarded more effectively by γ-CD than by β-CD as shown in Fig. 9; no apparent effect was observed with α-CD. The k_{obs} values for the 1 × 10^{-3} mol dm^{-3} PyB$^-$ and PyC$^-$ solutions continued to decrease to γ-CD concentrations of 5 × 10^{-3} and 2 × 10^{-2} mol dm^{-3}, respectively. Such a difference in the CD-concentration dependence suggests that the association con-

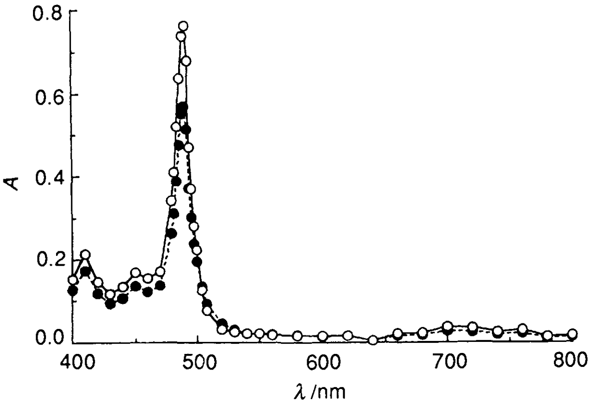

Fig. 7 Transient absorption spectra at (○) 200 ns and (●) 9 μs for an Ar-saturated solution of PyB^-; $[PyB^-] = 5 \times 10^{-3}$ mol dm^{-3}

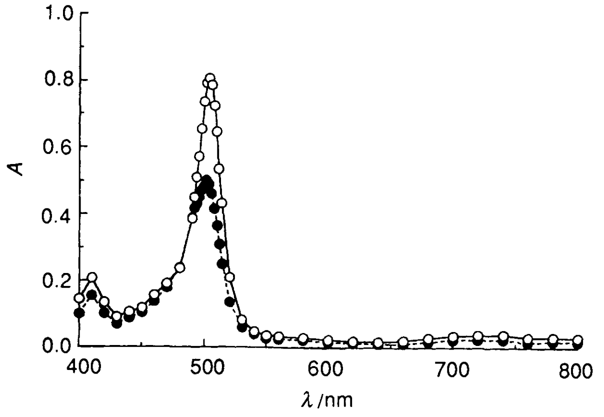

Fig. 8 Transient absorption spectra at (○) 200 ns and (●) 9 μs for an Ar-saturated solution of PyC^-; $[PyC^-] = 5 \times 10^{-3}$ mol dm^{-3}

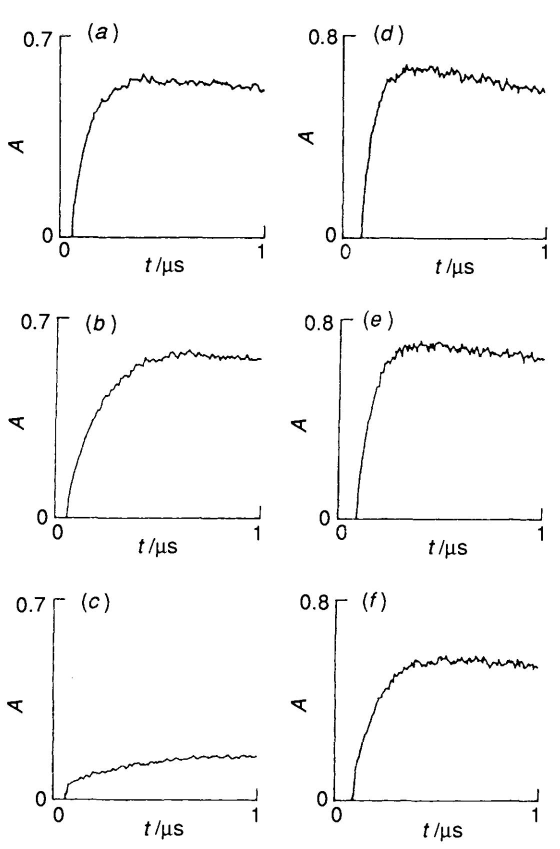

Fig. 9 Rises in the absorption of the radical anions for a PyB^- solution in the (*a*) absence and presence of (*b*) β- and (*c*) γ-CDs and for a PyC^- solution in the (*d*) absence and presence of (*e*) β- and (*f*) γ-CDs; [carboxylate] $= 1 \times 10^{-3}$ mol dm^{-3}; [CD] $= 1 \times 10^{-2}$ mol dm^{-3}

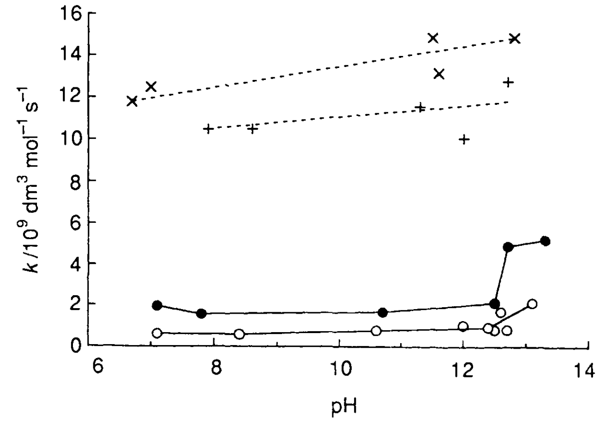

Fig. 10 pH Dependence of the rate constants for the one-electron reduction of (+) PyB^-, (×) PyC^- and the complexes of (○) PyB^- and (●) PyC^- with γ-CD

stant for CD complexation of PyC^- is smaller than that of PyB^-.

The rate constants for the one-electron reduction of PyB^- and PyC^- were determined in the absence and presence of 5×10^{-2} mol dm^{-3} γ-CD. The pH dependences of the rate constants are shown in Fig. 10. The rate constants determined in the presence of γ-CD increase at pH > *ca.* 12. It is known that pyrene derivatives form 2:2 complexes with γ-CD at higher host and guest concentrations.[11-15] The 2:2 complexes dissociate into 1:1 complexes in strongly alkaline solution because of the repulsion between the anionic forms of the secondary hydroxy groups of γ-CD.[15] Thus, the increase in rate constant at high pH is attributed to the dissociation of the 2:2 complexes into 1:1 complexes similar to the case of PyS^-. The rate constants in the lower pH range are for the one-electron reduction of the 2:2 complexes of PyB^- and PyC^- [eqns. (10) and (11)].

$$[Py(CH_2)_3CO_2^-]_2\text{-}(\gamma\text{-CD})_2 + e_{aq}^- \longrightarrow [(Py^{\bullet -})(CH_2)_3CO_2^-]_2\text{-}(\gamma\text{-CD})_2 \quad (10)$$

$$(PyCO_2^-)_2\text{-}(\gamma\text{-CD})_2 + e_{aq}^- \longrightarrow [(Py^{\bullet -})CO_2^-]_2\text{-}(\gamma\text{-CD})_2 \quad (11)$$

The k_9 and k_{11} values are larger than the k_8 and k_{10} values, respectively, over the whole pH range. The $k_8:k_{10}$ and $k_9:k_{11}$ ratios are 17 and 6.2, respectively, at pH around neutrality, suggesting that the one-electron reduction of PyB^- having the methylene spacer is more effectively retarded by the CD complexation than is that of PyC^- not having such a spacer. These results demonstrate that the carboxy group of PyC^- contributes to the one-electron reduction and is placed outside of the CD cavity of the complex, similarly to the case of BPC^- described above.

Spectral Shift for the Reduced 2:2 *Complex of* PyC^- *with* γ-*CD*.—Fig. 11 shows the transient absorption spectra at 200 ns and 6 μs for the 5×10^{-3} mol dm^{-3} PyB^- and PyC^- solutions containing 5×10^{-2} mol dm^{-3} γ-CD. The absorption band for the PyC^- solution is observed at 508 nm immediately after the pulse and is shifted to 498 nm until 6 μs. On the other hand, such a spectral shift with time after the pulse is not observed for the PyB^- solution; the absorption intensity is small because of the effective suppression of the one-electron reduction by the CD complexation.

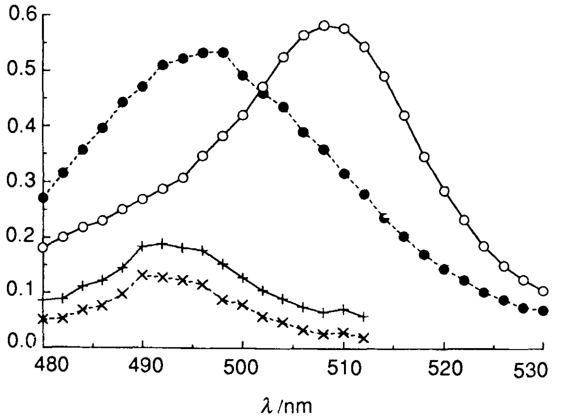

Fig. 11 Transient absorption spectra for solutions of PyC$^-$ [at (○) 200 ns and (●) 6 μs] and of PyB$^-$ [at (+) 200 ns and (×) 6 μs] in the presence of γ-CD; [carboxylate] = 5×10^{-3} mol dm^{-3} and [γ-CD] = 5×10^{-2} mol dm^{-3}

The spectral change with time after the pulse has also been observed for the reduced 2:2 complex of PyS$^-$ with γ-CD as reported previously.[3] In this case, the absorption band of the reduced 2:2 complex, observed immediately after the pulse, is rather broad. Until 6 μs, it becomes narrow and is shifted slightly to shorter wavelengths. The narrow absorption band in the later stage has been assigned to a reduced 1:1 complex since it appears immediately after the pulse in the strongly alkaline solution (pH 12.5) where the 2:2 complex dissociates into 1:1 complexes. Thus, it has been concluded that the reduced 2:2 complex is unstable and dissociates into 1:1 complexes.

On the other hand, in the case of PyC$^-$, the shape of the absorption band is not affected by the addition of γ-CD; only the peak position is slightly shifted, from 504 to 508 nm. Furthermore, for the strongly alkaline solution (pH 12.6) containing γ-CD, the absorption band appeared at 508 nm, not at 498 nm, immediately after the pulse and decayed without change in peak position. On these bases, it seems reasonable to assume that the absorption spectra of the reduced 2:2 and 1:1 complexes have the same peak position at 508 nm and that the spectral shift with time after the pulse is caused by a change in structure of the reduced 2:2 complex but not by dissociation into 1:1 complexes.

In contrast to the cases of PyC$^-$ and PyS$^-$, the reduced 2:2 complex of PyB$^-$ decays with no change in absorption spectrum. The effect of CD complexation on the absorption spectrum of reduced PyB$^-$ is only a very small shift to longer wavelengths. The methylene chain of PyB$^-$ may disturb the formation of the rigid 2:2 complex like those of PyC$^-$ and PyS$^-$. Further spectroscopic study is needed for the reduced CD complexes of pyrene derivatives.

Experimental

BPA$^-$H$^+$ (Tokyo Kasei) was recrystallized from methanol. BPC$^-$H$^+$ (Wako Chemicals) and biphenyl-2-carboxylic acid (Tokyo Kasei) were recrystallized from benzene–methanol mixtures. PyB$^-$H$^+$ and PyC$^-$H$^+$ (both Molecular Probe) were used without further purification. α-, β- and γ-CDs were the same as those used in the previous study.[3] Water was purified by means of the Millipore Milli-Q system. The pH was adjusted with NaOH.

Aqueous solutions of the aromatic carboxylates saturated with Ar or N_2O were irradiated with 8 ns electron pulses at room temp. (*ca.* 22 °C). The techniques of the pulse radiolysis and the method of kinetic analysis were as described previously.[3] The dose per pulse was *ca.* 43–88 Gy (1 Gy = 1 J kg^{-1}) producing e_{aq}^- concentrations *ca.* $(1.2\text{–}2.5) \times 10^{-5}$ mol dm^{-3}.

Acknowledgements

The authors are grateful to the members of the Radiation Laboratory of this institute for help with the pulse radiolysis experiments. This work was supported by a Grant in Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

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 Y. Yamamoto, S. Shiraki and Y. Kawamura, *J. Chem. Soc., Perkin Trans. 2*, 1992, 2241.
4 D. F. Sangster, *J. Phys. Chem.*, 1966, **70**, 1712.
5 G. V. Buxton, in *The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis*, ed. J. H. Baxendale and F. Busi, Reidel, Dordrecht, 1982, p. 241.
6 K. Sehested and E. J. Hart, *J. Phys. Chem.*, 1975, **79**, 1639.
7 T. Shida, *Electronic Absorption Spectra of Radical Ions*, Elsevier, Amsterdam, 1988.
8 A. J. Swallow, in *The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis*, ed. J. H. Baxendale and F. Busi, Reidel, Dordrecht, 1982, p. 289.
9 J. L. Courtneidge, A. G. Davies, T. Clark and D. Wilheim, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1197.
10 J. Rabani, H. B. Steen, H. Bugge and T. Brustad, *J. Chem. Soc., Chem. Commun.*, 1971, 1353.
11 A. Ueno, K. Takahashi and T. Osa, *J. Chem. Soc., Chem. Commun.*, 1980, 921.
12 N. Kobayashi, R. Saito, H. Hino, Y. Hino, A. Ueno and T. Osa, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1031.
13 W. G. Herkstroeter, P. A. Martic and S. Farid, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1453.
14 W. G. Herkstroeter, P. A. Martic, T. R. Evans and S. Farid, *J. Am. Chem. Soc.*, 1986, **108**, 3275.
15 S. Hamai, *J. Phys. Chem.*, 1989, **93**, 6527.

Paper 4/00637B
Received 1*st February* 1994
Accepted 15*th March* 1994