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# Ion Pairing of Radical Ions of Aromatic Alkenes and Alkynes Studied by Pulse Radiolysis

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Pulse radiolysis of 1,2-dichloroethane solutions of *trans,trans*-1,4-bis(2-phenylethenyl)benzene and 1,4-bis(2-phenylethynyl)benzene was undertaken in the presence of $Bu_4NPF_6$ (Bu=butyl) to investigate the effect of ion pairing of the solute radical cations with $PF_6^-$. It was also undertaken for the tetrahydrofuran solutions of the above compounds in the presence of $Bu_4NPF_6$ and $NaBPh_4$, where the solute radical anions are generated and form ion pairs with $Bu_4N^+$ and $Na^+$. The decay of the radical ions, which is due to neutralization, is retarded by the ion pairing. The rate constants for the neutralization reactions in the free-ion and ion-paired states were determined. Also presented are the data for the radical ions of *trans*-stilbene, diphenylacetylene, *trans,trans*-1,4-diphenyl-1,3-butadiene, and diphenylbutadiyne. The radical ions of the aromatic alkynes are less stabilized by the ion pairing than those of the aromatic alkenes having the same carbon skeletons probably because of more extensive charge delocalization of the former radical ions. Spectral shifts to shorter wavelengths caused by the ion pairing are appreciable for the radical anions. Dependence of the spectral shifts on the size of the radical anions is described.

Extensive spectrophotometric studies of ion pairing have been undertaken for aromatic radical anions formed by alkali-metal reduction.[1,2] The absorption maxima of the anionic species are shifted to shorter wavelengths when they form contact ion pairs with the alkali-metal cations. The magnitude of the spectral shifts decreases as the interionic separation, or the radius of the cations, increases. Thus, the absorption maxima of solvent-separated ion pairs are essentially the same as those of free anions. The effect of ion pairing has also been studied for negatively charged species generated by pulse radiolysis. The rate constants for the reactions of solvated electrons, aromatic radical anions, and carbanions have been determined for the free-ion and ion-paired states.[3–7]

We have previously reported pulse radiolysis studies of salt effects for aromatic radical cations and anions, which are formed in 1,2-dichloroethane and tetrahydrofuran (THF) solutions, respectively.[8–12] In the solutions containing $Bu_4NPF_6$ (Bu=butyl) and $NaBPh_4$ (Ph=phenyl) the radical ions form ion pairs with the counter ions derived from the salts, such as $PF_6^-$, $Bu_4N^+$, and $Na^+$. The decay of the radical ions, which is due to neutralization, was retarded by the ion pairing. Spectral shifts to shorter wavelengths by the ion pairing were appreciable for the radical anions. For the radical anions of all-*trans* $\alpha,\omega$-diphenyl-substituted polyenes, $Ph(CH=CH)_nPh$ ($n$=1—4), the magnitude of the spectral shifts varied with the value of $n$ depending on the kind of the counter ions, $Bu_4N^+$ and $Na^+$.[12] As the value of $n$ increased, the magnitude of the spectral shift increased for the ion pairs with $Bu_4N^+$ and decreased for the ion pairs with $Na^+$. Small spectral shifts were also observed for the radical cations of $Ph(CH=CH)_nPh$, when paired with $PF_6^-$.[11] We are interested in the ion pairing of the radical ions having long conjugated $\pi$-electron systems.

The present pulse radiolysis study has been undertaken for the radical ions of *trans,trans*-1,4-bis(2-phenylethenyl)benzene (DStBz) and 1,4-bis(2-phenylethynyl)benzene (DPEBz). Also presented are the data for the radical ions of other aromatic alkenes

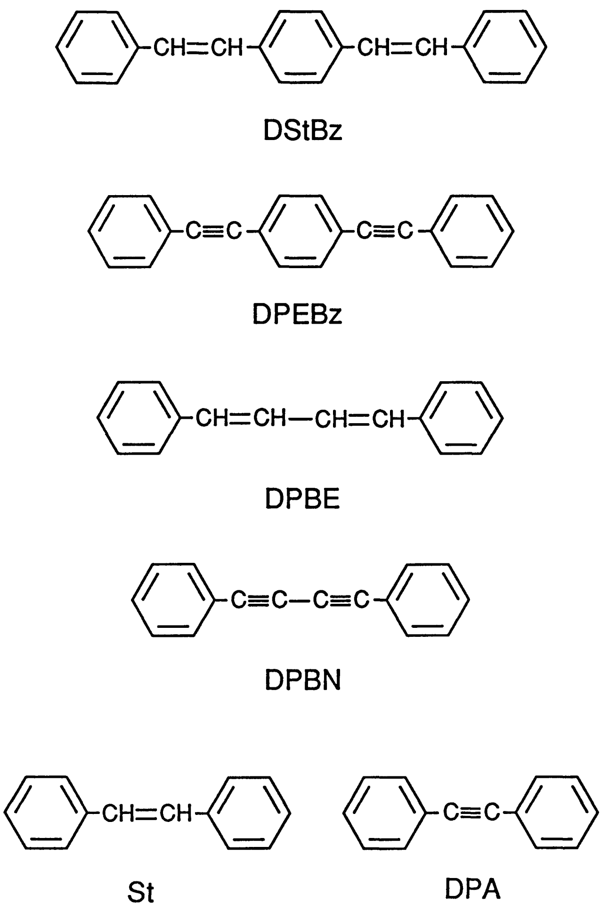

Fig. 1. Structures of the aromatic alkenes and alkynes.

and alkynes such as *trans*-stilbene (St), diphenylacetylene (DPA), *trans,trans*-1,4-diphenyl-1,3-butadiene (DPBE), and 1,4-diphenylbutadiyne (DPBN). The structures of these compounds are shown in Fig. 1. The second-order rate constants for the neutralization reactions of the radical ions were determined in the absence and presence of the salts. The effect of the ion pairing is compared between the radical ions of the aromatic alkenes and alkynes having the same carbon skeletons. The results of the previous studies on the ion pairing of the various aromatic radical ions are summarized in the present paper.

## Experimental

1,2-Dichloroethane, THF, $Bu_4NPF_6$, and $NaBPh_4$ were the same as those used in the previous studies.[8–12] DStBz and DPEBz were prepared by literature procedures[13,14] and recrystallized from benzene and a benzene-hexane mixture, respectively. DPA (Tokyo Kasei) and DPBN (Aldrich) were purified by recrystallization from hexane. The experimental procedures and the techniques of pulse radiolysis have been described in the previous paper.[8] The pulse radiolysis experiments were carried out by using 8 ns electron pulses and at room temperature. The molar extinction coefficients of the radical ions were determined by comparing the absorption intensities based on the values of the St radical ions as in the previous studies.[8–12]

## Results

The pulse radiolysis of 1,2-dichloroethane solutions of the aromatic alkenes and alkynes was carried out at a solute concentration of $3\times10^{-3}$ mol dm$^{-3}$ in the presence of $6\times10^{-2}$ mol dm$^{-3}$ biphenyl as in the previous studies.[8–12] The solute radical cations are produced by charge transfer from the biphenyl radical cation initially formed. The decay of the radical cations, $S^{+\cdot}$, is due to neutralization with $Cl^-$, a product of electron attachment to the solvent.

$$S^{+\cdot} + Cl^- \longrightarrow \text{neutral product}, \qquad (1)$$

where S denotes the aromatic solute.

Figures 2 and 3 show the transient absorption spectra measured for the solutions of DStBz and DPEBz, respectively, in the absence of the salt. The absorption spectra did not change during the decay, and all observed peaks are assigned to $DStBz^{+\cdot}$ and $DPEBz^{+\cdot}$. When $6\times10^{-3}$ mol dm$^{-3}$ $Bu_4NPF_6$ was added, the peaks of the absorption spectra were slightly shifted to shorter wavelengths, and the decay of the absorption was retarded. The absorption spectra measured in the absence and presence of the salt are those of the free-radical cations and their ion pairs with $PF_6^-$, respectively.

The pulse radiolysis was also carried out for the solutions of DPA and DPBN. The absorption spectra of $DPA^{+\cdot}$ and $DPBN^{+\cdot}$ agreed with those reported in literature.[15] The absorption maxima of the radical cations and the magnitudes of the spectral shifts caused by the ion pairing are listed in Table 1 together with those of $St^{+\cdot}$ and $DPBE^{+\cdot}$ measured in the previous studies.[10,11]

The decay of the absorption of the radical cations obeyed second-order kinetics, suggesting that it is due exclusively to the neutralization. The rate constants, $k_1$ and $k_2$, for the neutralization reactions were determined in the absence and presence of the salt, respectively. The data are listed in Table 2. In the presence of the salt the neutralization reactions occur

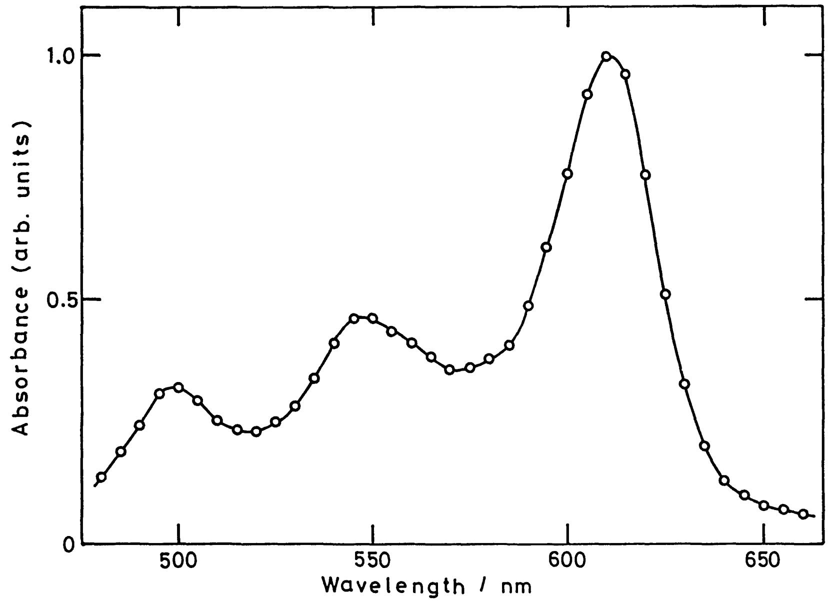

Fig. 2. Transient absorption spectrum of $DStBz^{+\cdot}$ in 1,2-dichloroethane (at 400 ns).

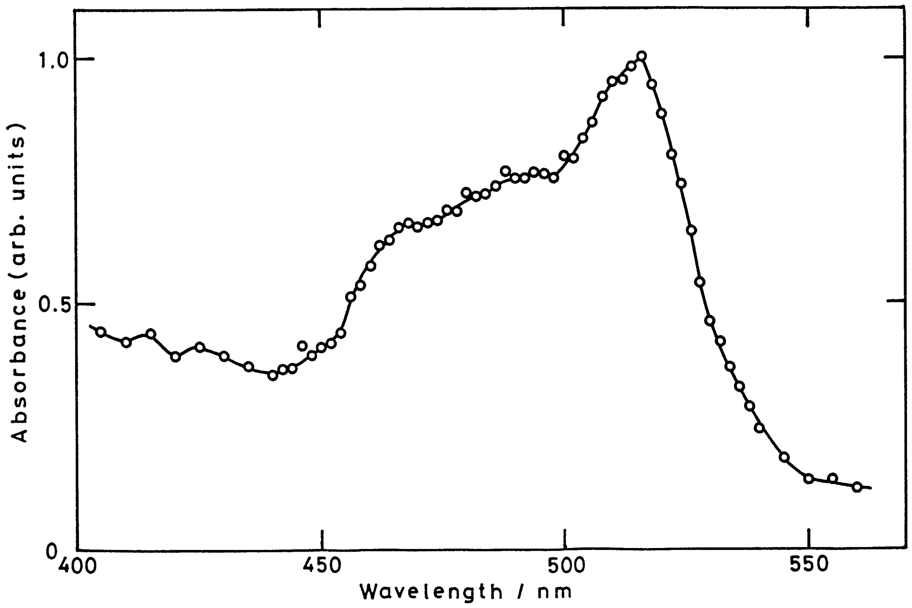

Fig. 3. Transient absorption spectrum of DPEBz$^{+\cdot}$ in 1,2-dichloroethane (at 400 ns).

Table 1. Positions of Absorption Maxima of the Free-Radical Cations and Spectral Shifts Caused by Ion Pairing with $PF_6^-$

| Cation | $\lambda_{max}$ | $\Delta\lambda$ | $\varepsilon_{max}$ |
|---|---|---|---|
| | nm | nm | $dm^3\,mol^{-1}\,cm^{-1}$ |
| St$^{+\cdot}$ | 480 | <2 | $6.5\times10^4$ |
| DPBE$^{+\cdot}$ | 546 | 4 | $1.2\times10^5$ |
| DStBz$^{+\cdot}$ | 610 | 2 | $1.1\times10^5$ |
| DPA$^{+\cdot}$ | 422 | 0 | $3.9\times10^4$ |
| DPBN$^{+\cdot}$ | 482 | 0 | $1.7\times10^4$ |
| DPEBz$^{+\cdot}$ | 515 | 3 | $7.1\times10^4$ |

Table 2. Rate Constants for the Neutralization Reactions of the Radical Cations in the Free-Ion ($k_1$) and Ion-Paired ($k_2$) States

| Cation | Rate constant/$dm^3\,mol^{-1}\,s^{-1}$ | | $k_1/k_2$ |
|---|---|---|---|
| | $k_1$ | $k_2$ | |
| St$^{+\cdot}$ | $(1.6\pm0.2)\times10^{11}$ | $(3.3\pm0.2)\times10^{10}$ | 5.0 |
| DPBE$^{+\cdot}$ | $(1.6\pm0.1)\times10^{11}$ | $(2.9\pm0.1)\times10^{10}$ | 5.5 |
| DStBz$^{+\cdot}$ | $(8.9\pm0.7)\times10^{10}$ | $(1.7\pm0.2)\times10^{10}$ | 5.2 |
| DPA$^{+\cdot}$ | $(1.2\pm0.2)\times10^{11}$ | $(4.4\pm0.5)\times10^{10}$ | 2.7 |
| DPBN$^{+\cdot}$ | $(1.5\pm0.2)\times10^{11}$ | $(6.4\pm0.4)\times10^{10}$ | 2.3 |
| DPEBz$^{+\cdot}$ | $(1.4\pm0.1)\times10^{11}$ | $(4.3\pm0.2)\times10^{10}$ | 3.3 |

between the ion pairs.

$$S^{+\cdot}/PF_6^- + Bu_4N^+/Cl^- \longrightarrow \text{neutral product.} \qquad (2)$$

The $k_1/k_2$ ratios are presented as a measure of the salt effect. It can be seen that the $k_1/k_2$ ratios of the radical cations of the aromatic alkynes are small compared with those of the aromatic alkenes having the same carbon skeletons.

Table 3. Positions of Absorption Maxima of the Free-Radical Anions and Spectral Shifts Caused by the Ion Pairing with $Bu_4N^+$ and $Na^+$

| Anion | $\lambda_{max}$ | $\Delta\lambda$/nm ($\Delta\bar{\nu}/10^2\,cm^{-1}$) | | $\varepsilon_{max}$ |
|---|---|---|---|---|
| | | Counter ions | | |
| | nm | $Bu_4N^+$ | $Na^+$ | $dm^3\,mol^{-1}\,cm^{-1}$ |
| St$^{-\cdot}$ | 500 | 5 (2) | 20 (8) | $6.1\times10^4$ |
| DPBE$^{-\cdot}$ | 573 | 9 (3) | 18 (6) | $1.1\times10^5$ |
| DStBz$^{-\cdot}$ | 634 | 14 (4) | 6 (2) | $1.5\times10^5$ |
| DPA$^{-\cdot}$ | 449 | 5 (3) | 13 (7) | $5.6\times10^4$ |
| DPBN$^{-\cdot}$ | 494 | 6 (2) | 14 (6) | $1.1\times10^5$ |
| DPEBz$^{-\cdot}$ | 519 | 7 (3) | 3 (1) | $1.1\times10^5$ |

Similar experiments were carried out for the THF solutions of DStBz and DPEBz containing $6\times10^{-2}$ mol dm$^{-3}$ biphenyl, where the solute radical anions are produced by electron transfer from the biphenyl radical anion and are neutralized by the solvent cation.

$$S^{-\cdot} + THF(H^+) \longrightarrow \text{neutral product.} \qquad (3)$$

When $6\times10^{-3}$ mol dm$^{-3}$ $Bu_4NPF_6$ and $NaBPh_4$ were added, the absorption maxima of the radical anions were appreciably shifted to shorter wavelengths. Figures 4 and 5 show the transient absorption spectra measured for the solutions of DStBz and DPEBz, respectively, in the absence and presence of $Bu_4NPF_6$. The absorption spectra did not change during the decay. The pulse radiolysis was also carried out for the solutions of DPA and DPBN. The absorption spectra of DPA$^{-\cdot}$ and DPBN$^{-\cdot}$ in the absence of the salts agreed with those reported in literature.[15] The absorption maxima of the radical anions are listed in

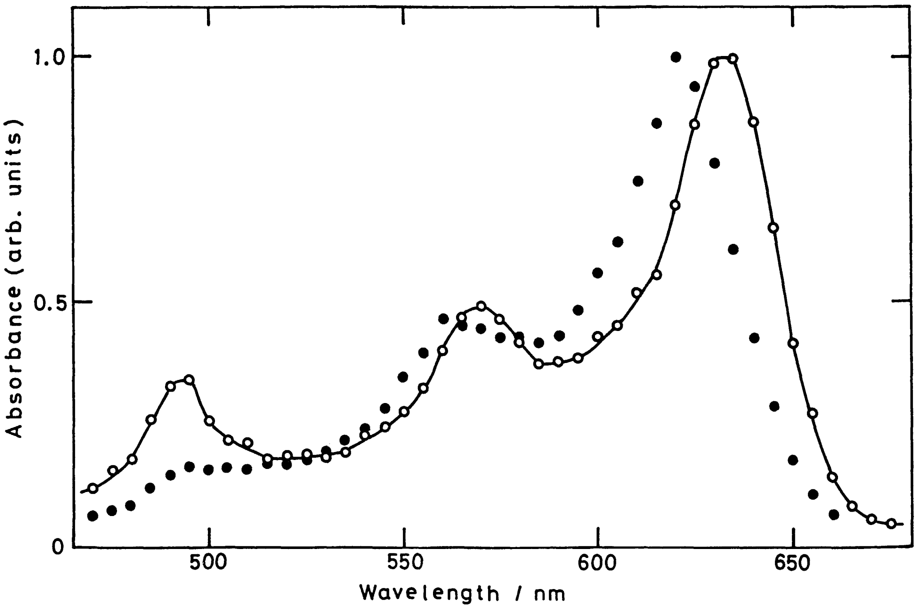

Fig. 4. Transient absorption spectra of $\mathrm{DStBz^{-\cdot}}$ in the absence (○) and presence (●) of $6\times10^{-3}$ mol dm$^{-3}$ $\mathrm{Bu_4NPF_6}$ (at 400 ns).

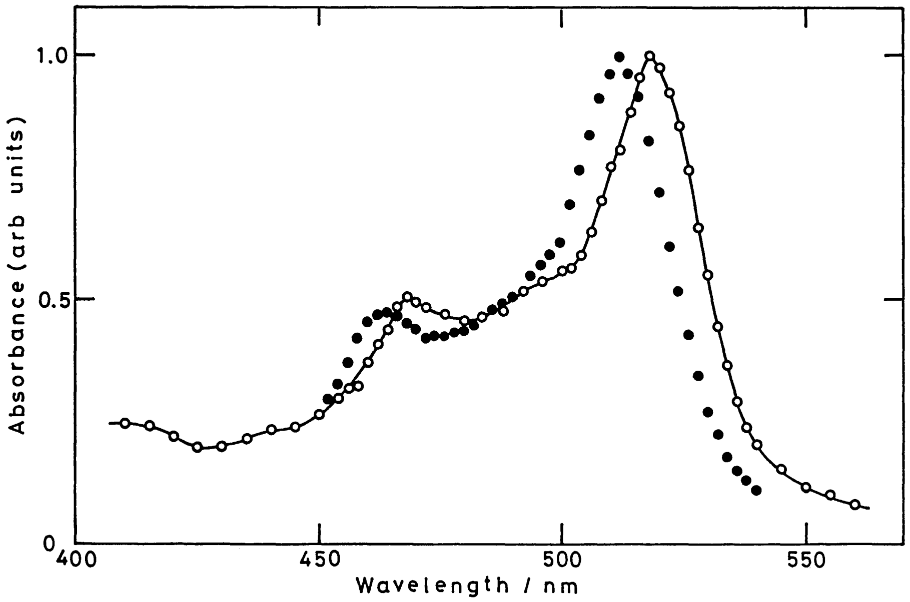

Fig. 5. Transient absorption spectra of $\mathrm{DPEBz^{-\cdot}}$ in the absence (○) and presence (●) of $6\times10^{-3}$ mol dm$^{-3}$ $\mathrm{Bu_4NPF_6}$ (at 400 ns).

Table 3 together with those of $\mathrm{St^{-\cdot}}$ and $\mathrm{DPBE^{-\cdot}}$ measured in the previous studies.9,12)

The rate constants for the neutralization reactions of the radical anions are listed in Table 4. The $k_3$ and $k_4$ values were determined in the absence and presence of $6\times10^{-3}$ mol dm$^{-3}$ $\mathrm{Bu_4NPF_6}$, respectively. The $k_4$ values are the rate constants for the reactions between the ion pairs.

$$\mathrm{S^{-\cdot}/Bu_4N^+ + THF(H^+)/PF_6^-} \longrightarrow \text{neutral product.} \quad (4)$$

Table 4. Rate Constants for the Neutralization Reactions of the Radical Anions

| Anion | Rate constant/dm$^{-3}$ mol$^{-1}$ s$^{-1}$ | | $k_3/k_4$ |
|---|---|---|---|
| | $k_3$ | $k_4$ | |
| $\mathrm{St^{-\cdot}}$ | $(4.0\pm0.3)\times10^{11}$ | $(8.2\pm0.3)\times10^{9}$ | 49 |
| $\mathrm{DPBE^{-\cdot}}$ | $(3.4\pm0.2)\times10^{11}$ | $(9.0\pm0.4)\times10^{9}$ | 38 |
| $\mathrm{DStBz^{-\cdot}}$ | $(2.5\pm0.1)\times10^{11}$ | $(5.4\pm0.2)\times10^{9}$ | 47 |
| $\mathrm{DPA^{-\cdot}}$ | $(2.9\pm0.1)\times10^{11}$ | $(7.9\pm0.2)\times10^{9}$ | 37 |
| $\mathrm{DPBN^{-\cdot}}$ | $(3.3\pm0.1)\times10^{11}$ | $(1.0\pm0.1)\times10^{10}$ | 33 |
| $\mathrm{DPEBz^{-\cdot}}$ | $(1.7\pm0.1)\times10^{11}$ | $(5.3\pm0.2)\times10^{9}$ | 32 |

The $k_3/k_4$ ratios of the radical anions are much larger than the $k_1/k_2$ ratios of the radical cations. The rate constants determined in the presence of $NaBPh_4$ were intermediate between the $k_3$ and $k_4$ values.

It can be seen for the absorption spectra of $DStBz^{-\cdot}$ that the peak at 495 nm becomes smaller in the presence of $Bu_4NPF_6$ (Fig. 3). This was also observed in the case of $NaBPh_4$. Furthermore, the intensity of the 500-nm band of $DStBz^{+\cdot}$ was decreased by 20% in the presence of $Bu_4NPF_6$. However, the extinction coefficients of $DStBz^{+\cdot}$ and $DStBz^{-\cdot}$ at the main absorption peaks were not affected by the addition of the salts.

## Discussion

The interaction between oppositely charged species of ion pairs, or the magnitude of spectral shifts caused by the ion pairing, decreases as the ion size increases.[1,2] The charge distribution of the large aromatic radical ions is considered to be responsible for the effect of the ion pairing rather than the apparent size of the charged species. The retardation of the neutralization reactions and the spectral shifts caused by the ion pairing are considered to be the measure of the interaction between the radical ions and the counter ions derived from the salts. Here the ion pairing of the radical ions of the aromatic alkenes and alkynes is discussed by considering the charge distribution and the length of the conjugated π-electron systems.

**Radical Cations.** The neutralization reactions of the radical cations of the aromatic alkenes and alkynes with $Cl^-$ in the free-ion state are considered to be diffusion controlled and be accelerated by Coulombic attraction between the oppositely charged reactants. This is similar to the case of the radical cations of biphenyl, anthracene, triphenylethylene, and $Ph(CH=CH)_nPh$ ($n$=1—4).[10,11] The rate constants, $k_1$, of these radical cations are close to each other, lying in the range $(8.6—19)\times10^{10}$ $dm^3\,mol^{-1}\,s^{-1}$. In general, $k_1$ decreases as the ion size increases because of the slow rate of diffusion of the large radical cations.[10,11] A similar trend is observed for $k_3$ of the radical anions.[9,12]

In the presence of the $Bu_4NPF_6$, the rate constants of the radical cations of the aromatic alkenes decrease by a factor of about 5: the $k_1/k_2$ ratios are in the range 5.0—5.5. On the other hand, the $k_1/k_2$ ratios of the radical cations of the aromatic alkynes are in the range 2.7—3.3. It is suggested that the alkyne radical cations are less stabilized by the ion pairing with $PF_6^-$ than the alkene radical cations having the same carbon skeletons. This can be explained as follows. The positive charge of the alkyne radical cations is cylindrically distributed around the triple bonds, whereas the charge distribution of the alkene radical cations is restricted to the direction perpendicular to the molecular planes. The charge of the alkyne radical cations may be spread over the aromatic rings more extensively than that of the alkene radical cations, for which the aromatic rings and the olefinic moieties are not completely coplanar. The charge delocalization of the alkyne radical cations results in a lowering of the interaction with $PF_6^-$.

As reported previously,[10,11] the neutralization reactions of the radical cations of pyrene, perylene, and tetraphenylethylene in the free-ion state are not diffusion controlled: the $k_1$ values are $9.4\times10^9$, $7.2\times10^9$, and $2.8\times10^9$ $dm^3\,mol^{-1}\,s^{-1}$, respectively, and are one order of magnitude smaller than those of the other radical cations. Furthermore, the salt effect is negligibly small for these radical cations: the $k_1/k_2$ ratios are nearly unity.[10,11] It can be said that these radical cations have smaller reactivities or interactions with the anions, $Cl^-$ and $PF_6^-$, than the other radical cations. The result for the tetraphenylethylene radical cation has been interpreted in terms of steric crowding of the phenyl groups, which surround the positive charged center located on the olefinic double bond. For the radical cations of pyrene and perylene the charge delocalization over the large condensed-ring aromatics may be responsible for the small reactivities or interactions with the anions. Formation of a complex has been proposed for the slow neutralization reactions of the radical cations of pyrene and perylene, $P^{+\cdot}$.[10,11]

$$P^{+\cdot}+Cl^- \underset{k_d}{\overset{k_c}{\rightleftarrows}} P^{+\cdot}/Cl^- \xrightarrow{k_n} \text{neutral product.} \tag{5}$$

The $k_1$ values correspond to $k_nk_c/k_d$.

Although both the radical cations and $Cl^-$ are paired with the counter ions from the salt, the retardation of the neutralization is due largely to the ion pairing of the radical cations as reported previously.[10,11] This is based on the result that the $k_1/k_2$ ratios depend on the kind of the radical cations and are close to unity for the radical cations of pyrene, perylene, and tetraphenylethylene.

Spectral shifts by the ion pairing are observed only for the radical cations having long π-electron systems, such as $DStBz^{+\cdot}$, $DPEBz^{+\cdot}$, and $Ph(CH=CH)_nPh^{+\cdot}$ ($n$=2—4), although very small spectral shifts, $<2$ nm, are also observed for $St^{+\cdot}$ and the triphenylethylene radical cation.[10,11] An explanation for the spectral shifts of these large radical cations may be the charge localization induced by $PF_6^-$ in the long π-electron systems, resulting in formation of contact ion pairs.[11] It is also possible that the absorption spectra of the radical cations having long π-electron systems are sensitive to the counter ion and are shifted without forming contact ion pairs.

**Radical Anions.** The appreciable spectral shift by the ion pairing is characteristic of the radical anions. The magnitude depends on the size of the radical anions and on the kind of the counter ions. A dependence of the spectral shift on the size of the radical anions, similar to that for Ph(CH=CH)$_n$-Ph$^{-\cdot}$,[12] can be seen in Table 3, although the trend is not clear when the magnitude is small. It is suggested that a large radical anion has a strong interaction with a large counter ion while a small one does with a small counter ion. This may be particular to the radical anions having long π-electron systems.

The neutralization reactions of the radical anions with THF(H$^+$) in the free-ion state are considered to be diffusion controlled. The rate constants, $k_3$, are in the range (1.7—4.0)$\times 10^{11}$ dm$^3$ mol$^{-1}$ s$^{-1}$, including $k_3$ of the radical anions of biphenyl, anthracene, pyrene, perylene, triphenylethylene, and Ph(CH=CH)$_n$Ph ($n$=1—4).[9,12] They are larger than $k_1$ for the diffusion controlled reactions of the radical cations in 1,2-dichloroethane. This is due mainly to the difference in the solvent viscosity as reported previously.[10] The viscosities of 1,2-dichloroethane and THF at 22 °C are 0.0081 and 0.0048 Pa s, respectively. Corrected for the solvent viscosities, $k_1$ and $k_3$ become almost the same.

Contrary to the radical cations, the radical anions of pyrene and perylene have $k_3$ comparable to those of the other radical anions.[9,12] It has been suggested that the neutralization reactions of the radical anions with THF(H$^+$) are less selective than those of the radical cations with Cl$^-$ because of the strong electrophilicity of THF(H$^+$), which is essentially a proton.

The neutralization reactions of the radical anions are significantly affected by the addition of Bu$_4$NPF$_6$. The $k_3/k_4$ ratios are one order of magnitude larger than the $k_1/k_2$ ratios of the radical cations. It has already been demonstrated that the salt effect on the neutralization reactions is due mainly to the ion pairing of THF(H$^+$) with PF$_6^-$ rather than to that of the radical anions with Bu$_4$N$^+$.[8] Therefore, the large retarding effect for the radical anions can be attributed to the strong interaction of the charge-localized THF(H$^+$) with PF$_6^-$.

The $k_3/k_4$ ratios of the radical anions of the aromatic alkynes are slightly smaller than those of the aromatic alkenes having the same carbon skeletons. This shows that the alkyne radical anions are less stabilized by the ion pairing than the alkene radical anions. This is similar to the radical cations paired with PF$_6^-$. The dependence of $k_4$ on the kind of the radical anions suggests that the ion pairing of the radical anions with Bu$_4$N$^+$ is partly responsible for the retardation of the neutralization reactions but to a less extent compared to the ion pairing of THF(H$^+$) with PF$_6^-$.

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### References

1) J. Smid, "Ion and Ion Pairs in Organic Reactions," ed by M. Szwarc, Wiley-Interscience, New York (1972), Vol. 1, p. 85.

2) M. A. Fox, *Chem. Rev.*, **79**, 253 (1979).

3) B. Bockrath and L. M. Dorfman, *J. Phys. Chem.*, **77**, 1002 (1973).

4) B. Bockrath and L. M. Dorfman, *J. Phys. Chem.*, **77**, 2618 (1973).

5) B. Bockrath and L. M. Dorfman, *J. Am. Chem. Soc.*, **96**, 5708 (1974).

6) J. R. Langan and G. A. Salmon, *J. Chem. Soc., Faraday Trans. 1*, **78**, 3645 (1982).

7) J. R. Langan and G. A. Salmon, *J. Chem. Soc., Faraday Trans. 1*, **79**, 589 (1983).

8) Y. Yamamoto, S. Nishida, K. Yabe, K. Hayashi, S. Takeda, and K. Tsumori, *J. Phys. Chem.*, **88**, 2368 (1984).

9) Y. Yamamoto, S. Nishida, X.-H. Ma, and K. Hayashi, *J. Phys. Chem.*, **90**, 1921 (1986).

10) Y. Yamamoto, S. Nishida, and K. Hayashi, *J. Chem. Soc., Faraday Trans. 1*, **83**, 1795 (1987).

11) Y. Yamamoto, T. Aoyama, and K. Hayashi, *J. Chem. Soc., Faraday Trans. 1*, **84**, 2209 (1988).

12) T. Aoyama, Y. Yamamoto, and K. Hayashi, *J. Chem. Soc., Faraday Trans. 1*, **85**, 3353 (1989).

13) K. Sonogashira, Y. Tohda, and N. Hagihara, *Tetrahedron Lett.*, **1975**, 4467.

14) T. W. Campbell and R. N. McDonald, *J. Org. Chem.*, **24**, 1246 (1959).

15) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 4372 (1966).