Pulse Radiolysis Study of Ion Pairing of Diphenylpolyene Radical Anions with Tetrabutylammonium and Sodium Cations in Tetrahydrofuran

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Pulse radiolysis of tetrahydrofuran (THF) solutions of all-trans α, ω diphenyl-substituted polyenes, such as 1,4-diphenylbuta-1,3-diene, 1,6diphenylhexa-1,3,5-triene and 1,8-diphenylocta-1,3,5,7-tetraene, has been undertaken in the absence and presence of Bu₄NPF₆ and NaBPh₄. In the presence of the salts, the absorption maxima of the diphenylpolyene radical anions are shifted to shorter wavelengths by ion pairing with Bu_4N^+ and Na⁺ as well as that of the *trans*-stilbene radical anion previously investigated. When $Ph(CH=CH)_n Ph^{-}$ (n = 1-4) is paired with $Bu_4 N^+$, the magnitude of the spectroscopic shift is larger for n = 2-4 than for n = 1. On the other hand, the magnitude of the spectroscopic shift due to the ion pairing with Na⁺ decreases with increasing n and becomes very small in the case of n =3 or 4. The decay of the radical anions, which is due to neutralization reactions with $THF(H^+)$, is retarded by the addition of the salts. The retarding effect of the salts is attributed to the ion pairing of the reactant ions with the counterions derived from the salts. In acetonitrile solution the absorption spectra and the decay rates of the radical anions are not affected by the addition of the salts, demonstrating that the ion pairing is not important in such a polar solvent. Results for the radical anions of pyrene, perylene and triphenylethylene are presented for the sake of comparison. The appreciable spectroscopic shift due to the ion pairing with the large Bu_4N^+ ion was found to be characteristic of the diphenylpolyene radical anions.

In the preceding paper, we have reported a pulse radiolysis study of the effect of Bu_4NPF_6 on the absorption spectra and the decay behaviour of all-*trans* α,ω -diphenyl-substituted polyenes in 1,2-dichloroethane.¹ The absorption maxima of the radical cations are apparently shifted to shorter wavelengths by ion pairing with PF_6^- . The spectroscopic shift was found to be characteristic of the diphenylpolyene radical cations. The present pulse radiolysis study is concerned with the ion pairing of the diphenylpolyene radical anions with Bu_4N^+ and Na^+ in tetrahydrofuran (THF). The diphenylpolyenes examined are 1,4-diphenylbuta-1,3-diene (DPB), 1,6-diphenylhexa-1,3,5-triene (DPH) and 1,8-diphenylocta-1,3,5,7-tetraene (DPO). A comparison is made with the previous results for the *trans*-stilbene (St) radical anion.² Dependence of the spectroscopic shifts of Ph(CH=CH)_nPh⁻⁻ (n = 1-4) due to the ion pairing on the value of n is described. Similar experiments have also been examined in acetonitrile solution in order to reveal the solvent effect on the ion pairing. Results for the radical anions of pyrene (Py), perylene (Pe) and triphenylethylene (TrPE) are also presented for the sake of comparison.

Experimental

THF and acetonitrile (Wako Chemicals) were fractionally distilled and were stored under vacuum over 3A molecular sieves. The diphenylpolyenes, the other aromatic

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solutes and Bu_4NPF_6 were the same as those used in the previous study.¹ NaBPh₄ (Wako Chemicals) was used as received. Bu_4NBPh_4 was prepared from Bu_4NI and NaBPh₄ and recrystallized from an acetone–water mixture. The experimental procedures and the techniques of pulse radiolysis were as described previously.³

The pulse radiolysis experiments were carried out by using 8 ns electron pulses (beam diameter, *ca*. 4 mm) and at room temperature (*ca*. 22 °C). The solute concentration was 5×10^{-2} mol dm⁻³ for DPB and DPH and 3×10^{-3} mol dm⁻³ for poorly soluble DPO. An excess of biphenyl (6×10^{-2} mol dm⁻³) was added to the solution of DPO, where DPO'- is formed by electron transfer from the biphenyl radical anion initially generated. The absorption spectra and the decay rates of DPB'- and DPH'- observed with the 5×10^{-2} mol dm⁻³ biphenyl. The pulse radiolysis of solutions of Pe and TrPE was carried out at a solute concentration of 3×10^{-3} mol dm⁻³ in the presence of 6×10^{-2} mol dm⁻³ biphenyl. Suprasil cells of 10-mm optical path length were used for the measurement of the transient absorption spectra. The second-order rate constants were determined by using Suprasil cells of 1- and 2-mm optical path lengths, as in the previous studies.^{1, 2}

Results and Discussion

Pulse radiolysis of the THF solutions of aromatic compounds results in the formation of the solute radical anions, which is followed by the second-order decay due to neutralization. The formation and decay processes of the radical anions are presented as follows:

$$THF \rightsquigarrow THF'' + e_s^- \tag{1}$$

$$e_{s}^{-} + ArH \rightarrow ArH^{-}$$
(2)

$$THF^{+} + THF \rightarrow THF(H^{+}) + THF(-H)$$
(3)

$$ArH^{-} + THF(H^{+}) \rightarrow ArH(H)^{-} + THF$$
(4)

where ArH denotes an aromatic solute.

The transient absorption spectra and the decay rates of the diphenylpolyene radical anions, observed by the pulse radiolysis, were appreciably affected by the addition of Bu_4NPF_6 and $NaBPh_4$. Fig. 1 shows the spectroscopic shifts of DPB^{--} , DPH^{--} and DPO^- caused by the addition of 6×10^{-3} mol dm⁻³ Bu_4NPF_6 and $NaBPh_4$. The spectroscopic shifts of the radical anions are evidence for the formation of contact ion pairs with the cations derived from the salts, namely Bu_4N^+ and Na^+ . The peak positions of the spectra were unchanged during the decay after the pulse irradiations. The decay rates of the radical anions were decreased by the addition of the salts. The decay rates were constant at salt concentrations (6–10) $\times 10^{-3}$ mol dm⁻³ as well as the peak positions of the spectra. These results mean that the ion pairing is completed within the pulse duration at salt concentrations above 6×10^{-3} mol dm⁻³.

The spectrum for the DPH-NaBPh₄ solution [fig. 1(b)] shows a shoulder at ca. 610 nm. Its decay was slower than that of the main absorption band. No shoulder was observed when NaBPh₄ was replaced by Bu_4NBPh_4 . Furthermore, it was not observed in acetonitrile solution where the ion pairing is not important as described below. The long-lived species having absorption at ca. 610 nm may be a product from the ion pair, DPH⁻/Na⁺

When the pulse radiolysis was carried out in acetonitrile solution, the absorption spectra and the decay rates of the diphenylpolyene radical anions were not affected by the addition of the salts. This result demonstrates that the ion pairing is not important in such a polar solvent. When the solvent was changed from THF to acetonitrile, the absorption maxima of the radical anions in the absence of the salts were shifted to

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Fig. 1. Transient absorption spectra of DPB⁻⁻ (a), DPH⁻⁻ (b) and DPO⁻⁻ (c) in the absence (\bigcirc) and presence of Bu₄NPF₆ (\bigcirc) and NaPh₄(+) in THF at 500 ns after the pulse: the salt concentration is 6×10^{-3} mol dm⁻³.

anion	$\lambda_{\rm max}/{\rm nm}$ in THF			
	free ion	ion pairs with		$\lambda_{\rm max}/{\rm nm}$
		Bu ₄ N ⁺	Na⁺	(free ion)
St'-	500	495	482	491
DPB'-	574	564	555	560
DPH'-	638	625	634	620
DPO'-	693	677	688	670
Py'-	495	495	492	493
Pe ^{·-}	579	577	578	576
TrPE'-	513	508	506	504

Table 1. Peak positions in absorption spectra of free-radical anions and their ion pairs with Bu_4N^+ and Na^+

^a No ion pair is formed in the presence of 6×10^{-3} mol dm⁻³ of Bu₄NPF₆ and NaBPh₄ because of the high polarity of the solvent (see text).

shorter wavelengths. The spectroscopic shift can be attributed to the change in solvent polarity.

The peak positions in the absorption spectra are listed in table 1. The data for St⁻⁻, Py⁻⁻, Pe⁻⁻ and TrPE⁻⁻, obtained by similar pulse radiolysis experiments, are also presented in the table for the sake of comparison. The magnitudes of the spectroscopic shifts of Ph(CH=CH)_nPh⁻⁻ (n = 1-4), caused by the ion pairing and by changing solvent from THF to acetonitrile, depend on the value of n. In fig. 2, the difference in wavenumber between the peak positions is plotted as a function of the value of n. The $\Delta \bar{\nu}$ values for the ion pairing are considered to be a measure of the interaction between the oppositely charged ions. When Ph(CH=CH)_nPh⁻⁻ is paired with Bu₄N⁺, the $\Delta \bar{\nu}$

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Fig. 2. Magnitudes of the spectroscopic shifts of $Ph(CH=CH)_n Ph^{-}$ plotted as a function of the value of *n*. The spectroscopic shifts are caused by the ion pairing with $Bu_4N^+(\bigcirc)$ and $Na^+(\bigcirc)$ and by changing solvent from THF to acetonitrile (+).

value is larger for n = 2-4 than for n = 1. A similar trend is observed for the spectroscopic shift due to the solvent effect. On the other hand, the $\Delta \bar{v}$ value for the ion pairing with Na⁺ decreases with increasing n and becomes very small in the case of n = 3 or 4.

The $\Delta \overline{v}$ values of TrPE⁻⁻ for the ion pairing with Bu₄N⁺ and for the solvent effect are 2×10^2 and 4×10^2 cm⁻¹, respectively. These are close to the values of St⁻⁻. On the other hand, the $\Delta \overline{v}$ value of TrPE⁺⁻ for the ion pairing with Na⁺, 3×10^2 cm⁻¹, is much smaller than that of St⁻⁻. This result may be attributed to the higher steric crowding of TrPE⁺⁻ experienced by the negatively charged centre located on the olefinic double bond. A similar steric effect has been reported in the previous study on the ion pairing of the vinylic radical anions with Na⁺.⁴ The transient absorption spectra of Py⁻⁻ and Pe⁻⁻ are little affected not only by the addition of the salts but also by changing solvent from THF to acetonitrile in contrast to those of the radical anions having olefinic double bonds.

The pulse radiolysis at low salt concentrations was examined with DPH-Bu₄NPF₆ solutions. Below ca. 4×10^{-3} mol dm⁻³ the transient absorption spectrum and the decay rate of DPH⁻⁻ depend more or less on the salt concentration because of the incomplete ion pairing at the end of the pulse irradiations. Fig. 3(*a*) shows the transient absorption spectra for the solution of 5×10^{-2} mol dm⁻³ DPH in the presence of 3×10^{-4} mol dm⁻³ Bu₄NPF₆. The peak position slowly shifts to shorter wavelengths with time after the pulse. This is a result of the slow ion pairing of DPH⁻⁻ occurring at the low concentration of Bu₄N⁺. The observed absorption spectra were analysed into the separate components, that is, the 638 nm band of the free DPH⁻⁻ and the 625 nm band of the paired DPH⁻⁻. The analysis was made by using the absorption intensities at 638 and 625 nm of the observed spectra [fig. 3(*a*)] and the band shapes of the free and paired DPH⁻⁻. The time dependence of 6×10^{-3} mol dm⁻³ Bu₄NPF₆ [fig. 1(*b*)]. It was assumed that each absorption intensity of the observed spectra is the sum of those of the free and paired DPH⁻⁻. The time dependence of the separate component bands are shown in fig. 3(*b*) and 3(*c*). The summation of the separate bands agreed with the

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Fig. 3. Transient absorption spectra for the solution of 5×10^{-2} mol dm⁻³ DPH containing 3×10^{-4} mol dm⁻³ Bu₄NPF₆ (a) and the separate component bands for the free DPH⁻⁻ (b) and for the paired DPH⁻⁻ (c) at 50 ns (\bigcirc), 100 ns (\bigcirc) and 800 ns (+) after the pulse.

original spectra. It is clearly demonstrated that the transient absorption spectra, observed at the low salt concentration, consist of the decreasing free DPH⁻ band and the increasing paired DPH⁻ band. This is evidence for the spectroscopic shifts caused by the ion pairing with Bu₄N⁺.

The results for the Na⁺ ion pairs can be explained by the fact that the interaction between oppositely charged ions in ion pairs decreases with increasing ion sizes. A similar explanation is offered for the negligibly small spectroscopic shifts of Py⁻ and Pe⁻ paired with Bu_4N^+ . Of interest are the results for the ion pairs of $Ph(CH=CH)_nPh^{-}$ with Bu_4N^+ . The apparent spectroscopic shifts for the Bu_4N^+ ion pairs appear to be inconsistent with the view that the large alkyl groups on Bu_4N^+ inhibit the formation of tight ion pairs.⁵ The effect of the solvent polarity suggests that the absorption spectra of $Ph(CH=CH)_nPh^{-}$ are much more susceptible to the electrostatic influence than those of Py⁻ and Pe⁻.

The rate constants for the neutralization reactions of the radical anions in THF were determined in the absence and presence of $6 \times 10^{-3} \text{ mol dm}^{-3} \text{ Bu}_4 \text{NPF}_6$. The reactions occurring in the presence of the salt are presented as follows:

$$ArH^{-}/Bu_4N^{+} + THF(H^{+})/PF_6^{-} \rightarrow ArH(H)^{-} + THF + Bu_4NPF_6.$$
 (5)

The rate constants were also determined for the neutralization reactions occurring in acetonitrile solution

$$ArH^{-} + CH_{3}CN(H^{+}) \rightarrow ArH(H)^{-} + CH_{3}CN$$
(6)

where $CH_3CN(H^+)$ is formed by the proton transfer from the solvent radical cation to the solvent molecule similarly as $THF(H^+)$.⁶ The data are presented in table 2. The molar extinction coefficients, ε_{max} , used for the determination were obtained by comparing the absorption intensities of the radical anions based on the literature value of $\varepsilon_{max}(St^-)$.⁷

The rate constants for the reactions of the free radical anions in THF and acetonitrile, k_4 and k_6 , appear to become smaller for the larger radical anions. The trend may be interpreted in terms of the rate of diffusion depending on the size of the reactant. The neutralization reactions are considered to be diffusion controlled and to be accelerated by the coulombic interaction between the oppositely charged reactants as previously reported for St⁻⁻ and Py^{--,2} The k_6 values are smaller than the k_4 values. This can be attributed to the effect of the solvent polarity since the viscosity of acetonitrile is lower than that of THF.

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		in THF		in CH ₃ CN
anion	$\varepsilon_{\rm max}/{\rm dm^3~mol^{-1}~cm^{-1}}$	$k_4/dm^3 \text{ mol}^{-1} \text{ s}^{-1}$	$k_{5}/dm^{3} \text{ mol}^{-1} \text{ s}^{-1}$	$k_{6}/dm^{3} mol^{-1} s^{-1}$
St ^{- b}	$6.1 \times 10^{4 c}$	$(4.0+0.3) \times 10^{11}$	$(8.2+0.3) \times 10^9$	$(1.5+0.2) \times 10^{11}$
DPB	1.1×10^{5}	$(3.4\pm0.2) \times 10^{11}$	$(9.0 \pm 0.4) \times 10^9$	$(1.4 \pm 0.1) \times 10^{11}$
DPH	2.3×10^{5}	$(2.9 \pm 0.1) \times 10^{11}$	$(7.9 \pm 0.2) \times 10^9$	$(1.3 \pm 0.1) \times 10^{11}$
DPO'-	3.2×10^{5}	$(2.9 \pm 0.1) \times 10^{11}$	$(1.1 \pm 0.1) \times 10^{10}$	$(1.3 \pm 0.1) \times 10^{11}$
Pv ^{·-} ^b	5.0×10^{4}	$(3.5+0.3) \times 10^{11}$	$(3.4 \pm 0.4) \times 10^9$	$(9.9 \pm 0.8) \times 10^{10}$
Pe	7.7×10^{4}	$(2.6 \pm 0.2) \times 10^{11}$	$(6.3 \pm 0.6) \times 10^9$	$(6.4 \pm 0.5) \times 10^{10}$
TrPE'-	3.6×10^{4}	$(2.6\pm0.1)\times10^{11}$	$(6.7 \pm 0.1) \times 10^9$	$(7.6\pm0.8)\times10^{10}$

Table 2. Rate constants for the neutralization reactions of the radical anions^a

^{*a*} The errors are the mean deviations. ^{*b*} The data except those for the acetonitrile solutions were obtained in the previous study [ref. (2)]. ^{*c*} Ref. (7).

The rate constants for the reactions of the Bu_4N^+ ion pairs in THF, k_5 , are one to two orders of magnitude smaller than those for the free radical anions. Not only the ion pairing of the radical anions with Bu_4N^+ but also the ion pairing of THF(H⁺) with PF₆ are considered to be responsible for the retardation of the reactions. This is suggested by the absence of the correlation between the k_5 and $\Delta \bar{\nu}$ values. That is to say, the retarding effect is significant for St⁻, Py⁻ and Pe⁻ rather than for DPB⁻, DPH⁻ and DPO⁻, whereas the interaction between the radical anions and Bu_4N^+ is expected to be larger for the latter radical anions. The k_5 values are suggested to be independent of the sizes of the radical anions. It is considered that the neutralization reactions between the ion pairs are not necessarily diffusion controlled as previously reported for St⁻ and Py⁻.² The rate constants for the neutralization reactions in THF were also determined in the presence of $6 \times 10^{-3} \text{ mol dm}^{-3} \text{ NaBPh}_4$ and were found to be in the range $(1.0-3.3) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. These values were intermediate between the k_4 and k_5 values.

A striking feature observed in the present study is the spectroscopic shifts of the diphenylpolyene radical anions caused by the ion pairing with the large Bu_4N^+ ion. In the preceding paper we reported that the diphenylpolyene radical cations, generated in 1,2-dichloroethane, form the contact ion pairs with PF_6^- resulting in the spectroscopic shifts to shorter wavelengths. The LCMO calculation for linear conjugated polyenes shows that both the end carbons in the radical ions have high charge densities compared with the others. Such a two-centred charge distribution may contribute to the ion pairing of the diphenylpolyene radical ions with the large counterions.

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