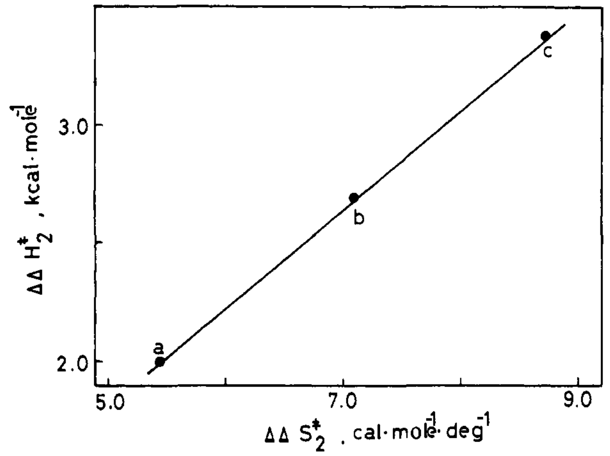

Figure 4. Correlation of $\Delta\Delta S_2^‡$ and $\Delta\Delta H_2^‡$. The quenchers are (a) EA, (b) MPA, (c) DMPA.

activation energy difference and entropy difference between these three quenchers. The activation energy difference and entropy difference between *R–R* and *R–S* pairs increase with increasing bulkiness of the substituents. It also suggests that, although the entropy term compensates for the large activation enthalpy difference, the difference in the activation free energy is still large enough to yield a chiral discrimination in the exciplex formation process. These results lead to the conclusion that, in the transition state of the "equilibrium exciplex" formation process starting from "encounter complex", specific geometry is required between the excited molecule and the quencher.

The modified isokinetic temperature at which the quenching rate constants $k_q(R\text{–}S)$ and $k_q(R\text{–}R)$ coincide was found to be 421 K for all the quenchers studied in this reaction series. Below this temperature, which is in the temperature range of the experiment studied, chiral discrimination in the exciplex formation process is controlled by the activation enthalpy difference, $\Delta\Delta H_2^‡$; i.e., chiral discrimination is most effective for the most bulky quencher, DMPA. Above this temperature, the activation entropy difference, $\Delta\Delta S_2^‡$, controls chiral discrimination in the exciplex formation; i.e., chiral discrimination is most ineffective for the most bulky quencher, DMPA. As a result of this modified isokinetic relationship, linearity between $\Delta\Delta H_2^‡$ and $\Delta\Delta S_2^‡$ was observed as shown in Figure 4. The slope gave the modified isokinetic temperature of 420 K which is in good agreement with the value obtained from Figure 3. This result supports the suggestion that the reaction proceeds by an identical mechanism throughout the reaction series and that the quenching rate ratio $k_q(R\text{–}S)/k_q(R\text{–}R)$ represents the pure steric factor in the exciplex formation process, k_2.

Acknowledgment. The authors wish to express their thanks to Miss Lyne Katsikas, Hahn-Meitner-Institute, Berlin, for her kind corrections of English.

Determination of Rate Constants for Electron Transfer from Radical Anions of Aromatic Compounds to Diaryl Disulfides

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Abstract: Rate constants for electron transfer from the radical anions of aromatic compounds to diaryl disulfides (ArSSAr) have been determined in tetrahydrofuran. By the change of the reduction potentials of the aromatic compounds from −1.04 to −1.91 V (vs. SCE), the rate constants varied from 0.015 to 2.3×10^8 M^{-1} s^{-1}; conventional spectrophotometry has been employed to measure the slow reaction rates, and the xenon-flash photolysis technique has been applied to the fast reaction systems. The reaction including the free ion or the loose ion pair of the thioxanthone sulfone radical anion, $(TO\text{–}SO_2)^{-}\cdot$, was faster than that including the tight ion pair. In the case of the $(TO\text{–}SO_2)^{-}\cdot$, Na^+–PhSSPh system, temperature variation yielded the free energy of activation ($\Delta G^‡ = 18.7$ kcal/mol) and activation entropy ($\Delta S^‡ = -29.1$ eu) at 22.4 °C; the reduction potential of PhSSPh was estimated to be −1.80 V vs. SCE from the $\Delta G^‡$ value. Electron-withdrawing substituents of ArSSAr increase the rates and vice versa; the Hammett reaction constants (ρ) were estimated to be ca. +1.50 and 1.40 for electron transfer from perylene radical anion and $(TO\text{–}SO_2)^{-}\cdot$,$Na^+$ to ArSSAr, respectively. The factors controlling the rates have been examined.

Disulfides react with an electron, yielding transiently the radical anions which dissociate rapidly into the thiolate anions and the thiyl radicals.[1] These processes are recognized to play an important role in enzymatic and radiobiological reactions.[2] The dissociative electron attachment processes are so fast that the pulse radiolysis and the flash photolysis techniques have been employed to clarify the elementary reactions. The rate constants close to the diffusion-controlled limit have been reported for the reactions between the disulfides containing amino and peptide groups and a hydrated electron. However, since the amino and peptide groups attached to the disulfides act as the electron-accepting site, the rates do not reflect the nature of the S–S bonds.[1-3] In order to understand the relation between the electron-acceptor ability and the nature of the S–S bond, it may be necessary to measure the rates of electron transfer from electron donors to disulfides without the amino acid groups.

Ionization potentials and electrophilicities of the disulfides have been explained in terms of the electron densities of the highest occupied molecular orbitals (HOMO) of the S–S linkage.[4,5] On the other hand, electron-acceptor abilities of the disulfides which are related to the nature of the lowest unoccupied molecular orbital (LUMO) of the S–S bond have not been reported.[6]

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(1) Hoffman, M. Z.; Hayon, E. *J. Am. Chem. Soc.* **1972**, *94*, 7950.

(2) Parker, J. E. In "The Chemistry of the Thiol Group"; Patai, S., Ed.; Wiley: London, 1974; Section 11.

(3) Purdie, J. W.; Gillis, H. A.; Kleassen, N. V. *Can. J. Chem.* **1973**, *51*, 3132.

(4) Levitt, L. S.; Levitt, B. W. *Chem. Ind.* (*London*) **1972**, 132.

(5) Happer, D. A. R.; Mitchell, J. W.; Wright, G. J. *Aust. J. Chem.* **1973**, *26*, 121.

(6) Reduction potentials may give information for LUMO, but those values of disulfides have not been estimated because of their irreversible electrochemical processes; thus E_R(ArSSAr) were roughly estimated from peak potentials in cyclic volutammograph of the disulfides.

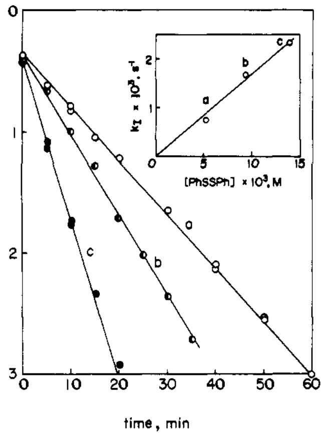

Figure 1. First-order plots for decay of the absorbance (A) of $(TO-SO_2)^{-}\cdot,Na^+$ caused by the addition of PhSSPh in THF at 22.4 °C. [PhSSPh]: (a) 5.1×10^{-3} M, (b) 9.4×10^{-3} M, and (c) 1.4×10^{-2} M. Insert: a pseudo-first-order plot (k_1 vs. [PhSSPh]).

In this report the diaryl disulfides (ArSSAr) were chosen as the subject of the study, since the electronic properties of the S–S linkages of ArSSAr would vary with the substituents on the phenyl rings. It would be anticipated that the rates for electron transfer can be correlated to substituent parameters such as the Hammett constants since the reduction potentials of compounds such as substituted benzonitriles are correlated to this equation.[7,8] Thus, it might be interesting to compare the properties of LUMO with those of HOMO of the disulfides.

As the electron donors, we chose the radical anions of aromatic compounds ($A^{-}\cdot$ (M^+))[9] so as to control the rates of electron transfer by their reduction potentials (E_R(A)); a wide range of the rates could be investigated. When the rate of electron transfer was slow, $A^{-}\cdot(M^+)$ was made upon contact with alkali metal and decay kinetics of $A^{-}\cdot(M^+)$ caused by addition of ArSSAr was followed with conventional spectrophotometry. On the other hand, when the rate was fast, $A^{-}\cdot(M^+)$ was generated by the flash light irradiation of A in the presence of anions and then the decay of $A^{-}\cdot(M^+)$ was followed; $A^{-}\cdot(M^+)$ was efficiently formed by flash photolysis by using aryl thiolate anions ($ArS^{-}(M^+)$). The photoinduced electron-transfer process from $ArS^{-}(M^+)$ to the excited A (A*) was briefly discussed. The effects of ion-pair structures, solvents, substituents of ArSSAr, and reduction potentials of A have been examined.

Results

Slow Electron-Transfer Systems. When E_R(A) is less negative than those of ArSSAr (E_R(ArSSAr) ≈ −1.80 V vs. SCE[6]), the electron transfer from the $A^{-}\cdot(M^+)$ to ArSSAr is endothermic and the slow rate would be anticipated. The radical anion of thioxanthone sulfone ($(TO-SO_2)^{-}\cdot(M^+)$ and $E_R(TO-SO_2) = -1.04$ V), generated upon contact with alkali metal (M), was identified with blue solution and was stable below 60 °C in tetrahydrofuran (THF).[10] The absorption maximum is ca. 600 nm which depends on the countercation; the tight ion pair in THF and free ion in hexamethylphosphoric triamide (HMPA) have been distinguished both by ESR and visible spectra in our previous paper.[10] On addition of an appropriate amount of ArSSAr to THF solution, the absorption band of $(TO-SO_2)^{-}\cdot,M^+$ began to decay, accompanying by the appearance of the absorption bands of $TO-SO_2$ and ArS^{-},M^+.[11] Overall reaction was estimated as reaction 1.

$$A^{-}\cdot + {}^1/_2ArSSAr \xrightarrow{k_{app}} A + ArS^{-} \qquad (1)$$

Table I. Apparent Second-Order Rate Constants (k_{app}) for Electron Transfer from $(TO-SO_2)^{-}\cdot(M^+)$[a] to $(p\text{-}XC_6H_4)_2S_2$ in THF[b]

X in $(p\text{-}XC_6H_4)_2S_2$	M^+	temp, °C	k_{app}, $M^{-1}\ s^{-1}$
H	Na^+	22.4	0.177[d,e]
H	K^+	22.4	0.810
H	free[c]	22.4	0.990
OCH_3	Na^+	22.4	0.030[d]
CH_3	Na^+	22.4	0.054[d]
Cl	Na^+	22.4	1.10
H	Na^+	25.2	0.216[e]
H	Na^+	28.0	0.252[e]
H	Na^+	31.0	0.293[e]
H	Na^+	33.5	0.406[e]

[a] (M^+) represents collectively the tight ion pairs and the free ions. [b] Estimated error is less than ca. 5%. [c] In HMPA. [d] From these values the Hammett reaction constant with 2σ was found to be ca. +1.40. [e] From these values, $E_a = 11.5 \pm 0.4$ kcal/mol, $\Delta G^{\ddagger}$ (at 22.4 °C) = 18.7 kcal/mol, and $\Delta S^{\ddagger}$ (at 22.4 °C) = −29.1 eu.

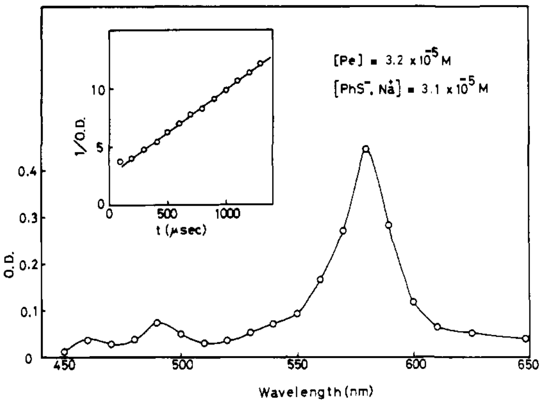

Figure 2. A transient absorption spectrum observed by the flash photolysis of Pe (3.2×10^{-5} M) in THF containing PhS^{-},Na^+ (3.1×10^{-5} M). The light longer than 420 nm was irradiated. The spectrum was plotted 22 μs after each flash. Insert: a second-order plot for decay of $Pe^{-}\cdot$ at 580 nm (length of optical cell is 10 cm).

Figure 1 shows the first-order plots for decay of $(TO-SO_2)^{-}\cdot,Na^+$ on addition of diphenyl disulfide (PhSSPh) in THF; under the condition that [PhSSPh] was ca. 100 times greater than $[(TO-SO_2)^{-}\cdot,Na^+]$, first-order kinetics were held. The slopes, the pseudo-first-order rate constants (k_1), increase with an increase in [PhSSPh]; insert of Figure 1 shows a plot of k_1 vs. [PhSSPh]. The slope yields an apparent second-order rate constant (k_{app}) for reaction 1. In a similar manner, the k_{app} values for $(TO-SO_2)^{-}\cdot,Na^+$–ArSSAr in THF, $(TO-SO_2)^{-}\cdot,K^+$–PhSSPh in THF and $(TO-SO_2)^{-}\cdot$–PhSSPh in HMPA were estimated. They are summarized in Table I. The effects of substituents, countercations, and solvents on k_{app} are seen. Origins of these effects will be examined in the section of discussion.

The rates increase with the rise in temperature (Table I); from an Arrhenius plot of these k_{app} values, the activation energy was estimated to be 11.5 kcal/mol for $(TO-SO_2)^{-}\cdot,Na^+$–PhSSPh system in THF. The free energy ($\Delta G^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation were calculated from the Gibbs–Helmholtz equation: $\Delta G^{\ddagger} = 18.7$ kcal/mol and $\Delta S^{\ddagger} = -29.1$ eu at 22.4 °C.

Fast Electron-Transfer Systems. When A has more negative reduction potential than that of $TO-SO_2$, the reactions of $A^{-}\cdot(M^+)$ with ArSSAr would be anticipated to be fast. In the case of perylene (Pe and E_R(Pe) = −1.67 V[12]),$Pe^{-}\cdot(M^+)$ made upon contact with alkali metal disappeared rapidly on addition of PhSSPh in amounts about equimolar with $Pe^{-}\cdot(M^+)$; after the

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[7] Zuman, P. "Topics in Organic Polarography"; Plenum Press, London, 1970; p 418.

[8] Balahura, R. J.; Wright, G. B.; Jordan, R. B. *J. Am. Chem. Soc.* **1973**, *95*, 1173.

[9] Free ions and tight ion pairs are represented as $A^{-}\cdot$ and $A^{-}\cdot,M^+$, respectively; $A^{-}\cdot(M^+)$ represents collectively both species. Countercations (M^+) are omitted in reaction formulas.

[10] Aruga, T.; Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1979**, *101*, 7585.

[11] Arylthiolate anions are present as the tight ion pairs with alkali-metal ions in THF (Miyashita, T.; Aoki, T.; Matsuda, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 231).

[12] Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous Systems"; Marcel Dekker: New York, 1970; Chapter 5.

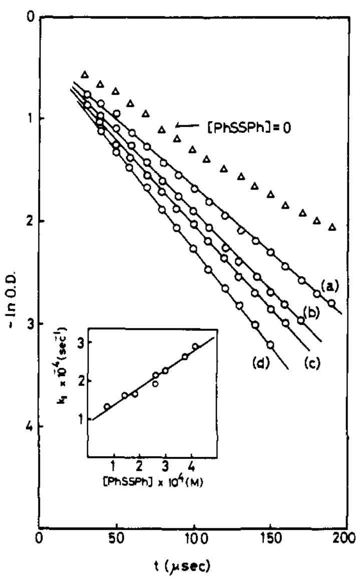

Figure 3. First-order plots for decay of Pe⁻· caused by the addition of PhSSPh. [PhSSPh]: (a) 7.9×10^{-4} M, (b) 1.4×10^{-3} M, (c) 1.8×10^{-3} M, and (d) 2.6×10^{-3} M. Insert: a pseudo-first-order plot.

Table II. Apparent Second-Order Rate Constants (k_{app}) for Electron Transfer from $A^{-}\cdot(Na^{+})$[a] to $(p\text{-}XC_6H_4)_2S_2$ in THF at 23 ± 1 °C[b]

$A^{-}\cdot$	X in $(p\text{-}XC_6H_4)_2S_2$	k_{app}, $M^{-1}\,s^{-1}$
$Pe^{-}\cdot$	H[c]	5.0×10^7
$Pe^{-}\cdot$	Cl[c]	1.1×10^8
$Pe^{-}\cdot$	CH_3[c]	8.2×10^6
$Pe^{-}\cdot$	OCH_3[c]	5.2×10^6
$BPe^{-}\cdot$	H	4.5×10^8
$FO^{-}\cdot$	H	9.6

[a] See Table I. [b] Estimated error is ca. 10%. [c] The Hammett correlation with 2σ yields ρ = ca. +1.50.

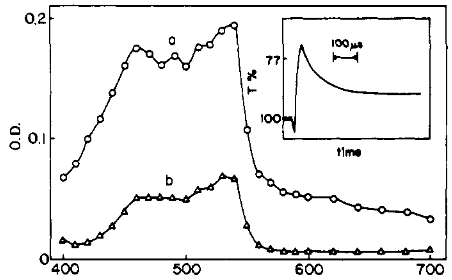

Figure 4. Transient spectra observed by flash photolysis of FO in the presence of PhS⁻,Na⁺ in THF: (a) spectrum at 22 μs after flash and (b) spectrum at 400 μs after flash. Insert: decay curve at 530 nm.

reaction, the absorption bands of Pe and PhS⁻,M⁺ appeared and overall reaction was presumed as reaction 1. The decay rate could not be followed by the conventional method used in the preceding section. Thus, we tried to apply flash photolysis to the rapid reactions; this method is known to be more convenient than the stopped-flow method when the radical anions are involved in the reaction system.[13]

On the flash light irradiation of Pe in the presence of PhS⁻,Na⁺, new transient absorption bands were observed (Figure 2). The intense absorption band at 580 nm was ascribed to Pe⁻·(M⁺)[14] and the weak bands at 490 and 460 nm were attributed to the triplet–triplet absorptions of Pe.[15] The initial concentration of Pe⁻·(M⁺) formed by one flash exposure was estimated to be ca. 8×10^{-6} M from the initial absorbance by using the molar extinction coefficient ($\epsilon = 5.9 \times 10^4\ cm^{-1}\ M^{-1}$ at 580 nm).[14] In such a dilute solution, it has been reported that the fraction of the free Pe⁻· ion was ca. 90%.[14] Since formation of Pe⁻· was observed by irradiation of Pe only, Pe in the excited state (Pe*) may efficiently abstract an electron from ArS⁻,M⁺ which is a good electron donor (reaction 2).[16] The Pe⁻· thus formed began to decay; decay

$$A^{*} + ArS^{-} \xrightarrow{k_q} A^{-}\cdot + ArS\cdot \qquad (2)$$

kinetics of Pe⁻· was mixed order consisting of first- and second-order kinetics. Initial part up to ca. 60% consumption obeyed second order (insert in Figure 2); the slope yielded $k_{II}/\epsilon_{Pe^{-}\cdot}$ in which k_{II} is the second-order rate constant and we found k_{II} to be $4.1 \times 10^9\ M^{-1}\ s^{-1}$ within an experimental error of ±10% by substituting $\epsilon_{Pe^{-}\cdot}$.[14] Since A and ArS⁻,M⁺ were reproduced after cutting off the light, the following two pathways could be thought for the decay of Pe⁻·. Reaction 3 may be exothermic but reaction 1 is

$$\text{path 1:}\quad A^{-}\cdot + ArS\cdot \xrightarrow{k_b} A + ArS^{-} \qquad (3)$$

$$\text{path 2:}\quad 2ArS\cdot \xrightarrow{k_r} ArSSAr \qquad (4)$$

$$A^{-}\cdot + {}^{1}/{}_{2}ArSSAr \xrightarrow{k_{app}} A + ArS^{-} \qquad (1)$$

endothermic for Pe⁻·; thus the k_{II} value close to the diffusion-controlled limit was assigned to k_b.

On addition of an excess of PhSSPh to solution containing Pe and PhS⁻,Na⁺, an amount of Pe⁻· similar to that of the solution without PhSSPh was formed by flash photolysis; this suggests that there is no interaction between A* and PhSSPh. The decay rate of Pe⁻· increased and decay kinetics approached first order (Figure 3);[17] slopes in the first-order plots (k_1) became steeper with an increase in [PhSSPh]. These k_1 values were plotted against [PhSSPh] (insert in Figure 3); the apparent second-order rate constant (k_{app}) for reaction 1 was estimated.[18] This method did not need to estimate the concentration of disulfide formed by reaction 4 after flash photolysis. For other disulfides, the k_{app} values were also estimated in a similar manner (Table II);[19] the corresponding ArS⁻,Na⁺ was used as an electron donor for Pe to simplify the subsequent reactions. The substituent effect for ArSSAr was observed. Appreciable countercation effect in the k_1 values was not observed upon replacing PhS⁻,Na⁺ by PhS⁻,K⁺ in THF. In such a polar solvent as HMPA, some different photochemical reactions occurred; both Pe⁻· and Pe⁺· were observed by the flash photolysis of the Pe solution in the absence of ArS⁻; this phenomenon was attributed to the triplet–triplet annihilation mechanism.[20] Therefore, the k_{app} value in HMPA could not be estimated. The addition of 18-crown-6-ether did not affect the decay rate of Pe⁻· in THF. The k_{app} values for Pe⁻· in Table II are smaller than the diffusion-controlled limit in THF by a factor of $\sim 10^2$–10^3.

The reduction potential of 1,12-benzoperylene (BPe; E_R(BPe) = −1.91 V[12]) is more negative than that of Pe and similar to that of ArSSAr; thus fast electron transfer from BPe⁻· to ArSSAr may be anticipated. Upon flash photolysis of BPe in the presence of PhS⁻,Na⁺ in THF, a transient absorption band attributable to

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(13) Wang, H. C.; Lillie, E. D.; Slomkowski, S.; Levin, G.; Szwarc, M. *J. Am. Chem. Soc.* **1977**, *99*, 4612.

(14) Chang, P.; Slates, R. V.; Szwarc, M. *J. Phys. Chem.* **1966**, *70*, 3180.

(15) Birks, J. B. "Organic Molecular Photophysics"; Wiley: New York, 1973; Vol. 1, p 320.

(16) The quenching of the fluorescence of Pe with PhS⁻,Na⁺ in THF was observed. The Stern–Volmer plot gave a straight line; the slope yields $k_q\tau_0$ = 72 M^{-1} in which k_q is the rate constant for quenching and τ_0 the lifetime of the Pe fluorescence in the absence of PhS⁻,Na⁺. Since τ_0 = 6 ns,[15] k_q was found to be $1.2 \times 10^{10}\ M^{-1}\ s^{-1}$; this value suggests that electron transfer from PhS⁻,Na⁺ takes place efficiently through the excited singlet state of Pe.

(17) In the wavelength region longer than 750 nm, a long-life transient absorption appeared. However, decay kinetics of Pe⁻· was not influenced by the presence of this unidentified long-life species.

(18) The decay curves consisting of first- and second-order kinetics were analyzed with the methods described elsewhere (Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1979**, *101*, 1915).

(19) In the case of both the *p*-methyl and *p*-methoxy derivatives of ArSSAr, the plots of k_1 vs. [ArSSAr] display downward curvature when ArSSAr more than ca. 2×10^{-3} M was added. Thus, the k_{app} values were estimated in the region below 2×10^{-3} M of ArSSAr.

(20) Grellman, K. H.; Watkins, A. R. *Chem. Phys. Lett.* **1971**, *9*, 439.

$BPe^{-}\cdot$ was observed at 550 nm.[21] The $BPe^{-}\cdot$ thus formed began to decay and $k_{II} = 2.2 \times 10^9\ M^{-1}\ s^{-1}$ was estimated from the second-order plot ($k_{II}/\epsilon_{BPe^{-}\cdot}$); the k_{II} value was also attributed to k_b of reaction 3. On addition of PhSSPh to this solution, the decay rate increased and the kinetics obeyed first order. From the slopes of the first-order plots (k_I), the k_{app} value for the reaction between $BPe^{-}\cdot$ and PhSSPh was estimated to be $4.5 \times 10^8\ M^{-1}\ s^{-1}$ (Table II). This k_{app} value is larger than that of $Pe^{-}\cdot$ as would be anticipated from the reduction potentials.

For fluorenone (FO; $E_R(FO) = -1.29\ V^{10}$), it would be anticipated that the electron transfer from $FO^{-}\cdot(M^+)$ to PhSSPh is faster than that from $(TO\text{–}SO_2)^{-}\cdot,M^+$. By flash photolysis of FO in the presence of PhS^-,Na^+, transient bands were observed at 530 and 460 nm (Figure 4); the former band was ascribed to $FO^{-}\cdot,Na^+$ and the latter band was to its associates.[22] The decay curve of $FO^{-}\cdot,Na^+$ at 530 nm consisted of two parts (insert of Figure 4). Initial rapid second-order decay may be attributed to reaction 3 ($k_{II}/\epsilon_{FO^{-}\cdot} = 6.3 \times 10^5\ cm\ s^{-1}$) and later slow decay to reaction 1, since the species decayed slowly were also assigned to $FO^{-}\cdot,Na^+$ and its associates (Figure 4b). They lived for ca. 10 s.[23] On the addition of PhSSPh, the decay rate of later part increased and decay kinetics changed into first order. From a plot of the pseudo-first-order rate constants vs. [PhSSPh], the k_{app} was estimated (Table II).

Upon flash photolysis of $TO\text{–}SO_2$ in the presence of PhS^-,Na^+ in THF, a transient absorption band was observed at ca. 600 nm which was ascribed to $(TO\text{–}SO_2)^{-}\cdot,Na^+$. The decay curve of $(TO\text{–}SO_2)^{-}\cdot,Na^+$ also consisted of two parts; initial rapid second-order decay may be attributed to reaction 3 ($k_{II}/\epsilon_{(TO\text{–}SO_2)^{-}\cdot} = 2.8 \times 10^5\ cm\ s^{-1}$) and later slow decay attributed to reaction 1. The lifetime of $(TO\text{–}SO_2)^{-}\cdot,Na^+$ was surprisingly long (ca. 1 h). On the addition of a large excess of PhSSPh the decay rate of later part increased, but the changes were too small to give precise rate constants.

Discussion

Meaning of k_{app}. The elemental reactions of the overall electron transfer from $A^{-}\cdot$ to ArSSAr (reaction 1) may be expressed as Scheme I. The first step (reaction 5) may be endothermic except

Scheme I

$$A^{-}\cdot + ArSSAr \underset{k_{-e}}{\overset{k_e}{\rightleftharpoons}} A + ArSSAr^{-}\cdot \qquad (5)$$

$$ArSSAr^{-}\cdot \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} ArS^- + ArS\cdot \qquad (6)$$

$$A^{-}\cdot + ArS\cdot \xrightarrow{k_b} A + ArS^- \qquad (3)$$

for BPe; the k_e values are smaller than the diffusion-controlled limit and $k_{-e} > k_e$. If $ArSSAr^{-}\cdot$ was stable, decay of $A^{-}\cdot(M^+)$ after the flash would not be observed. Thus, our observation that $A^{-}\cdot(M^+)$ disappeared completely suggests that $ArSSAr^{-}\cdot$ dissociates rapidly into $ArS^-(M^+)$ and $ArS\cdot$ (reaction 6) and $ArS\cdot$ successively accepts an electron from $A^{-}\cdot(M^+)$ (reaction 3). The rate constant k_b may be close to the diffusion-controlled limit since reaction 3 may be exothermic; the electron affinity of free radicals may be considerably greater. The initial decay of $A^{-}\cdot(M^+)$ which was formed by flash photolysis in the absence of ArSSAr may correspond to reaction 3; the k_b values were estimated from second-order kinetics on the basis of the assumption that $[A^{-}\cdot]$ is nearly equal to $[ArS\cdot]$ at the initial part of the decay curve; $k_b(BPe^{-}\cdot + PhS\cdot) = 2.2 \times 10^9\ M^{-1}\ s^{-1}$ and $k_b(Pe^{-}\cdot + PhS\cdot) = 4.1 \times 10^9\ M^{-1}\ s^{-1}$. In the cases of $FO^{-}\cdot,Na^+$ and $(TO\text{–}SO_2)^{-}\cdot,Na^+$, each ϵ value could not be precisely estimated because of the presence of the associates. By assuming $\epsilon_{FO^{-}\cdot,Na^+} = \epsilon_{(T/\text{–}SO_2)^{-}\cdot,Na^+} = 10^4\ cm^{-1}\ M^{-1}$ at each λ_{max}, we can calculate the rate constants close to the diffusion-controlled limit.

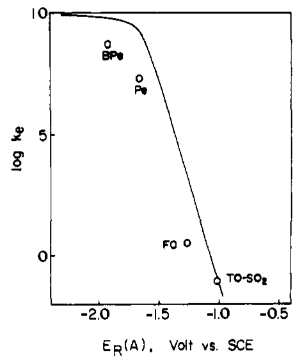

Figure 5. The relationship between the rate constants for electron transfer (log k_e) from $A^{-}\cdot$ to PhSSPh and the reduction potentials of A (E_R(A)). Solid line shows the calculated values from the Rehm–Weller equation.

Before deriving the rate expression for decay of $A^{-}\cdot(M^+)$ in the presence of ArSSAr, we examined the reversibility of reaction 6. For dialkyl disulfides, the reversibility and the rate constants for the dissociation of the disulfide radical anions ($\sim 10^5$–$10^6\ s^{-1}$)[1,3] have been reported. We attempted to observe a similar phenomenon in $ArSSAr^{-}\cdot(M^+)$. By flash photolysis of the arylthiolates ($\sim 10^{-2}$–10^{-4} M) in THF or in alkaline aqueous solution, it would be anticipated that $ArSSAr^{-}\cdot(M^+)$ could be produced by the following reactions: $ArS^-(M^+)(h\nu) \rightarrow ArS\cdot + e^-(M^+)$ and $ArS\cdot + ArS^-(M^+) \rightarrow ArSSAr^{-}\cdot(M^+)$.[24] The observed transient absorption bands were not reactive toward oxygen and were similar to the arylthiyl radicals.[25,26] These findings suggest that the backward reaction of eq 6 is slow and/or that the forward reaction is fast. Therefore, in the derivation of the rate expression for decay kinetics of $A^{-}\cdot$, we assumed that reaction 6 is not reversible. Other reactions such as $ArSSAr^{-}\cdot(M^+) + ArS\cdot \rightarrow ArSSAr + ArS^-(M^+)$ and $2ArS\cdot \rightarrow ArSSAr$ were not taken into consideration as main processes, since the concentrations of $ArSSAr^{-}\cdot(M^+)$ and $ArS\cdot$ in the stationary state may be small. Thus, the steady-state approximation can be applied to $[ArSSAr^{-}\cdot]$ and $[ArS\cdot]$ for the reactions in Scheme I, and eq I can be derived.[27] The reverse

$$-d[A^{-}\cdot]/dt = k_e[A^{-}\cdot][ArSSAr] - k_{-e}[A][ArSSAr^{-}\cdot]$$

$$-d[A^{-}\cdot]/dt = 2k_e[A^{-}\cdot][ArSSAr] \qquad (I)$$

process of reaction 5 is not included in eq I. This was confirmed as follows: with the variation of [Pe] from 10^{-5} to 10^{-4} M keeping other experimental conditions constant, the rate constant k_I did not change. Thus, the k_{app} values in Tables I and II can be related to k_e ($=k_{app}/2$).

Effect of Reduction Potential on k_e. In general, rate constants of electron transfer change with the reduction potentials of the components. Some formular connecting both the values have been proposed.[28-31] In this study, the rate constants for reaction 5 were calculated from a simple relation between $\Delta G^{\ddagger}$ and ΔG° ($=E_R(A) - E_R(ArSSAr)$) proposed by Rehm and Weller.[29] E_R(PhSSPh) can be estimated from the $\Delta G^{\ddagger}$ value for the $(TO\text{–}SO_2)^{-}\cdot,Na^+$–PhSSPh system by assuming $\Delta G^{\ddagger}(0)$ which is defined as $\Delta G^{\ddagger}$ at $\Delta G^{\circ} = 0$; $\Delta G^{\ddagger}(0)$ is usually put equal to 0.10 V.[29] Thus, E_R(PhSSPh) was estimated as −1.80 V. Frequency factor was calculated for the $(TO\text{–}SO_2)^{-}\cdot,Na^+$–PhSSPh system to be 5.7 ×

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10^{12} M^{-1} s^{-1} [32-34] On the basis of these values, the rate constants for electron transfer from $\mathrm{A}^{-}\cdot(\mathrm{M}^{+})$ to PhSSPh were calculated as a function of $E_\mathrm{R}(\mathrm{A})$; they are shown in Figure 5. E_R(PhSSPh) was estimated on the basis of the data of the tight $(\mathrm{TO{-}SO_2})^{-}\cdot,\mathrm{Na}^{+}$ ion pair; on the other hand, $E_\mathrm{R}(\mathrm{A})$'s, estimated electrochemically, were values of the free ions. However, since the difference in $E_\mathrm{R}(\mathrm{A})$ between the free ion and the ion pair was small (ca. 0.01 V),[35] we did not take this difference into consideration. The k_e values observed are in accord with the calculated ones; this suggests that both the experimental procedures and the kinetic analysis based on Scheme I are correct and reliable.

Effects of Solvent and Ion-Pair Structure. The solvent effect on k_e was found for the reaction of $(\mathrm{TO{-}SO_2})^{-}\cdot,\mathrm{Na}^{+}$ with PhSSPh (Table I); as was reported previously,[10] $(\mathrm{TO{-}SO_2})^{-}\cdot,\mathrm{Na}^{+}$ is shown to be a tight ion pair with the countercation in THF, but in HMPA the ion pair dissociates into the free ions. It is shown that k_e value for the reaction involving the free ions is greater than that for the tight ion pair. The countercation effect was also found; k_e for $(\mathrm{TO{-}SO_2})^{-}\cdot,\mathrm{K}^{+}$ is considerably greater than that for $(\mathrm{TO{-}SO_i})^{-}\cdot,\mathrm{Na}^{+}$. Although both the radical anions present as ion pairs, the ion pair with K^{+} is looser than that with Na^{+} because of the size of the alkali-metal cation.[10] On the other hand, the countercation effect was not seen for the reactions of $\mathrm{Pe}^{-}\cdot$ with PhSSPh; this may be attributed to the fact that $\mathrm{Pe}^{-}\cdot$ is shown to be a free ion or loose ion pair irrespective of the countercations in dilute THF solutions.[14,36] Our finding that the rates of electron transfer were reduced by the formation of the tight ion pairs in the reactants is the same tendency reported by Bockrath and Dorfman for electron transfer from the radical anions of aromatic hydrocarbons to alkyl halides.[37] A similar tendency was reported for other electron-transfer reactions.[35,38] According to the interpretation of Bockrath and Dorfman the order of the reactivity (free ion > loose ion pair > tight ion pair) may be determined by the extent of solvent displacement from the solvation shell of the metal cation of the ion pair. The above order also coincides with the decreasing Coulombic interaction between the ions; free radical anions can donate an electron easily.

Substituent Effect. With changing the substituents in the para positions of ArSSAr, the k_e values for the reactions of $(\mathrm{TO{-}SO_2})^{-}\cdot,\mathrm{Na}^{+}$ or $\mathrm{Pe}^{-}\cdot$ varied (Tables I and II). The electron-withdrawing substituents accelerated the rate of electron transfer or vice versa. For the reactions of $\mathrm{Pe}^{-}\cdot$ with ArSSAr, a linear correlation was found between log k_e and the Hammett constants 2σ; a positive reaction constant ρ was obtained (ρ = ca. +1.50). A similar tendency was seen for the reactions of $(\mathrm{TO{-}SO_2})^{-}\cdot,\mathrm{Na}^{+}$ with ArSSAr except for the *p*-chloro derivative (ρ = ca. +1.40). The deviation observed for the *p*-chloro derivative suggests that an unknown reaction other than the reactions in Scheme I takes place simultaneously for $(\mathrm{TO{-}SO_2})^{-}\cdot,\mathrm{Na}^{+}{-}(p\text{-}\mathrm{ClC_6H_4})_2\mathrm{S}_2$ system; however, as unknown reaction may not be so fast as the estimation of the rate constants for the reaction between $\mathrm{Pe}^{-}\cdot$ and $(p\text{-}\mathrm{ClC_6H_4})_2\mathrm{S}_2$ is disturbed.

Inspite of many discussions on the linear free-energy relationship for electron transfer,[27-30] only few electron-transfer systems have been interpreted on the basis of the Hammett correlation.[8,39,40] The sign and magnitude of the ρ value for a reaction may be determined both by the difference in the substituent effects on the total energies between reactant and product and by interactions between the reactants in the transition state. For electron transfer, in general, the latter may be small. In the case of ArSSAr, both ArSSAr and $\mathrm{ArSSAr}^{-}\cdot$ may be stabilized by the electron-withdrawing substituents and vice versa;[4] referring the ρ values for the total energy changes caused by the substituents to $\rho(\Delta G_{\mathrm{ArSSAr}})$ and $\rho(\Delta G_{\mathrm{ArSSAr^{-}\cdot}})$, respectively, we can presume both values are positive. The sign of the ρ value for electron transfer is determined by the following relations: $\rho(k_\mathrm{c}) \gtreqless 0$ for $\rho(\Delta G_{\mathrm{ArSSAR^{-}\cdot}}) \gtreqless \rho$-$(\Delta G_{\mathrm{ArSSAr}})$. Thus, the observed positive ρ value for k_e indicates that $\rho(\Delta G_{\mathrm{ArSSAr^{-}\cdot}})$ is considerably larger than $\rho(\Delta G_{\mathrm{ArSSAr}})$ in the case of ArSSAr; consequently the ρ value reflects the substituent effect on the energy levels of LUMO ($\Delta\mathrm{LUMO} \doteq \Delta G_{\mathrm{ArSSAr^{-}\cdot}} - \Delta G_{\mathrm{ArSSAr}}$). This finding coincides with the facts that the reduction potentials of various compounds are correlated to the Hammett equation.[37,41]

Although the differences in the k_e values between $(\mathrm{TO{-}SO_2})^{-}\cdot,\mathrm{Na}^{+}$ and $\mathrm{Pe}^{-}\cdot$ are about 10^{9} M^{-1} s^{-1}, the ρ values for both the systems are thought to be the same within the estimated errors. This suggests that the exothermicity or endothermicity does not play an important role in determining the ρ values.[42] From the similarity of the absorption spectra of $\mathrm{ArSSAr}^{-}\cdot$ to those of the radical anions of dialkyl disulfides, Shida pointed out that the LUMO of ArSSAr has the σ^* character and that an odd electron is localized on the S–S bond.[43] In the case of HOMO of ArSSAr, stabilization of S–S bond by the electron-withdrawing substituents can be explained on the basis of a decrease in the electric repulsion between the electrons on the S atoms. Our finding suggests that the energy levels of LUMO are also varied by the similar inductive effect on the antibonding orbital having σ^* character. In the MO calculation of dimethyl disulfide, the energy level of LUMO is not sensitive to the CSSC dihedral angle;[44] thus the substituent effect of ArSSAr is not attributed to the change in the energy level caused by the change in the dihedral angle.

Photoinduced Radical Anion Formation. Electron-transfer processes from inorganic anions to excited aromatic compounds have been postulated in the quenching of the fluorescence;[28,45] however, the resulting radical anions of aromatic compounds have not been observed except for some reaction systems.[46] In the case of organic anions such as butyllithium, the radical anions of aromatic compounds have been observed during steady light irradiation as the intermediates of the substitution reactions.[47,48] In this study, we found that $\mathrm{A}^{-}\cdot$ was efficiently formed by the light irradiation in the presence of RS^{-} and that $\mathrm{A}^{-}\cdot$ lived for a long time in solution after cutting off the light when the reduction potentials of A are less negative than that of ArSSAr. For such cases, decays of $\mathrm{A}^{-}\cdot,\mathrm{M}^{+}$ consisted of two processes. The initial part is fast and is attributed to reaction 3; all k_b values estimated are close to the diffusion-controlled limit and the dependence of k_b on $E_\mathrm{R}(\mathrm{A})$ is small. The decay process of later part is attributed to electron transfer from $\mathrm{A}^{-}\cdot,\mathrm{M}^{+}$ to ArSSAr which formed from reaction 4 with competition of reaction 3; the decay rates of the later parts depend on $E_\mathrm{R}(\mathrm{A})$. Since [ArSSAr] formed upon one flash exposure was small, $\mathrm{A}^{-}\cdot,\mathrm{M}^{+}$ such as $(\mathrm{TO{-}SO_2})^{-}\cdot,\mathrm{M}^{+}$ and $\mathrm{FO}^{-}\cdot,\mathrm{M}^{+}$ decayed slowly; thus we could observe colors of these radical anions for a long time. Since A and $\mathrm{ArS}^{-}\cdot,\mathrm{M}^{+}$ are reproduced after cutting off the light, the long-lived radical anions may have some potentials which will be used as strong electron donors in the chemical and electrochemical systems.

Conclusions

The rate constants (k_e) for electron transfer from $\mathrm{A}^{-}\cdot(\mathrm{M}^{+})$ to ArSSAr have been determined. The k_e values for the reactions

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(32) Frequency factor for electron transfer was assumed to be 10^{11} M^{-1} s^{-1} by Marcus.[28] Larger values have experimentally been estimated by other investigations; 7.5 × 10^{12} and 7.0 × 10^{12} M^{-1} s^{-1} are cited in the literature.[33,34] The value estimated in this study rather resembles those values estimated experimentally.

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from various $A^{-}\cdot(M^{+})$ to PhSSPh vary with $E_R(A)$; the k_e values are correlated to the difference between $E_R(A)$ and $E_R(\mathrm{PhSSPh})$. Electron transfer from the free $A^{-}\cdot$ ion or the loose $A^{-}\cdot$ ion pair to PhSSPh was faster than that from the tight $A^{-}\cdot$ ion pair. Electron-withdrawing substituents of ArSSAr increase the electron-transfer rates or vice versa; these reflect the electron-acceptor abilities of the S–S bonds.

Experimental Section

Materials. Thioxanthone *S,S*-dioxide (TO–SO_2) was prepared by the method described in the literature.[49] Perylene (Pe), 1,12-benzoperylene (BPe), fluorenone (FO), and diaryl disulfides (ArSSAr) were purified by recrystallization and/or sublimation. Tetrahydrofuran (THF) and hexamethylphosphoric triamide (HMPA) were stored over the benzophenone ketyl or the pyrene radical anion and distilled before use on a high vacuum line. Arylthiolate anions (ArS^{-},M^{+}) were prepared from the corresponding disulfides upon contact with alkali metal in highly dried THF solution.

Methods. Slow decay kinetics for $(TO\text{–}SO_2)^{-}\cdot,M^{+}$ were followed with a Cary 14 spectrophotometer equipped with a temperature variable cell holder. Fast decay kinetics of $A^{-}\cdot(M^{+})$ were measured with a flash photolysis apparatus of a standard design; the half-duration of xenon flash lamps (Xenon Corp. N851) was ca. 10 μs and flash energy was ca. 100 J. Fluorescence was measured by a Shimazu RF501 fluorescence spectrophotometer. Electrochemical measurements of ArSSAr were made with cyclic volutammography (a Yanako P3V) with a Pt electrode in *N,N*-dimethylformamide solution containing tetra-*n*-butylammonium perchlorate as a supporting electrolyte.

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Dissociation of O^6-(*p*-Methoxybenzyl)guanosine in Aqueous Solution to Yield Guanosine, *p*-Methoxybenzylguanosines, and 4-(*p*-Methoxybenzyl)-5-guanidino-1-β-D-ribofuranosylimidazole

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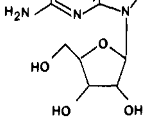
Abstract: The kinetics and products of O^6-(*p*-methoxybenzyl)guanosine (**1**) decomposition in $MeOH/H_2O$ (5:95) at 40 °C have been examined over a wide range of pH values. The decomposition is acid catalyzed below pH 7, but over the pH range 8–13 the rate of decomposition is nearly pH independent. In addition to guanosine, N^2-(*p*-methoxybenzyl)guanosine, 4-(*p*-methoxybenzyl)-5-guanidino-1-β-D-ribofuranosylimidazole, and 7-(*p*-methoxybenzyl)-, 1-(*p*-methoxybenzyl)-, and 8-(*p*-methoxybenzyl)guanosine are produced by the decomposition of **1**. Yields for these nucleoside products are pH dependent. An ionic mechanism involving dissociation of **1** to a *p*-methoxybenzylating agent which reassociates with either anionic and/or neutral guanosine largely accounts for the pH dependence of the product distributions.

As an extension of our previous studies of solvent and leaving-group effects on sites of benzylation of nucleic acid components,[1,2] we have initiated studies of the effects of para-substituent-induced changes in benzylating agent reactivity on the sites of benzylation of guanosine under neutral aqueous conditions.[3] These investigations required preparation of a series of para-substituted benzylguanosine derivatives for product stability studies and for use as chromatographic marker compounds. We observed that, of the several O^6-substituted guanosines we prepared, O^6-(*p*-methoxybenzyl)guanosine (**1**) is markedly unstable in aqueous media and quite unexpectedly undergoes transformation to a variety of nucleoside products. We present here details of the kinetics and products of these novel reactions.



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Results

Preparation of O^6-(*p*-methoxybenzyl)guanosine (**1**) was patterned after Gerster and Robins'[4] procedure for preparation of O^6-benzylguanosine. While this latter compound can be purified by crystallization from water, our attempts to purify **1** by this method led only to the recovery of guanosine as a precipitated solid. The lability of O^6-(*p*-methoxybenzyl)guanosine required alternative procedures for its purification (see Experimental Section) and also prompted our investigation of the kinetics of its decomposition in largely aqueous medium.

Rates of disappearance of **1** in $MeOH/H_2O$ (5:95) at 40 °C were determined spectrophotometrically by monitoring the decrease in absorbance of solutions of **1** at 280 nm as a function of time. Plots of $\ln(OD_t - OD_\infty)$ vs. time were linear for at least 3 to 4 half-times indicating that the decomposition is first order in **1**. Values for the observed first-order rate constants (k_{obsd}) were calculated from the slopes of these plots.

The magnitude of k_{obsd} was found to be pH dependent, and a plot of log k_{obsd} vs. pH is shown in Figure 1. Over the pH range 7–5.5, Figure 1 illustrates that k_{obsd} increases with decreasing pH; the slope of the log k_{obsd} vs. pH plot is approximately −1 in this pH range, indicating that the decomposition of **1** is acid catalyzed below pH 7. However, at pH values greater than pH 8, the rate of decomposition of **1** is nearly pH independent. From least-squares plots of k_{obsd} vs. hydrogen ion activity, it was determined that the experimental values of k_{obsd} could be satisfactorily fit to

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