Studies on the Carbanions Affected by Neighboring Sulfur Groups. 1. Effect of the Oxidation Number of Sulfur Atom on Ion Pairing and Electron Transfer of the Alkali Metal Fluorenyl Carbanions Substituted in 9 Position with Phenyl Sulfur Groups

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Abstract: Ion-pairing effects derived from the difference in oxidation number of the sulfur atom in the alkali metal fluorenyl carbanions substituted in 9 position with phenyl sulfur groups ($PhSO_nFl^-$, M^+; $n = 0$, 1, and 2) were reflected in the electronic absorption and ^1H NMR spectra and also in the electron-transfer reactions. The solvent-separated $PhSFl^-\|M^+$ ion pairs in THF at 20 °C and the contact $PhSOFl^-,M^+$ ion pairs in MTHF even at 77 K were found. The alkali metal $PhSO_2Fl^-$ carbanions exhibited the different type of electronic absorption band due to an intramolecular charge transfer. In NMR spectra the chemical shift of H_{18} protons also gave information about ion pairing in the carbanions. For the contact ion pairs electron transfer to anthraquinone (AQ) was more facile than for the solvent-separated ion pairs. Electron transfer from the solvent-separated $AQ^-\cdot\|Li^+$ ion pair to $PhSO_2Fl\cdot$ radical was also studied by means of flash photolysis ($k_{tr} = 7.6 \times 10^9$ M^{-1} s^{-1}).

Since chemical reactivity of carbanions is affected by ion pairing and also more or less by neighboring group it is of great importance to make efforts to clarify the relationship between the structure of carbanions and the reactivity. There is considerable literature[1] on the stabilizing effect of carbanions by neighboring sulfur group, but clear understanding of the effect is still lacking. Although the (p-d)π conjugation, back-donation of electrons into vacant sulfur 3d orbitals, has been postulated, recent ab initio studies[2] and LCAO-MO-SCF studies[3] on α-sulfinyl carbanions gave a rather negative version with respect to conjugation effects. Both the +I effect and the +M effect which have been taken into consideration in the sulfinyl and sulfonyl carbanions may also explain the stabilization, but in the former carbanion the +M effect is thought to be weak because of the semipolar property of the S-O bond.

In this paper the countercation, solvent, and temperature effects on ion pairing of alkali metal fluorenyl carbanions substituted in 9 position with sulfur groups ($PhSO_nFl^-$, Figure 1) have been studied using electronic absorption and ^1H NMR spectroscopies. Although ion pairings of the alkali metal carbanions such as fluorenyl,[4] allyl,[5] and benzyl[6] were extensively studied, the effects of the adjacent sulfur groups on carbanions and the relationships between the sulfur groups and ion pairing have not been studied in terms of spectra.

Reactions induced by a one-electron transfer process, one of the interesting reactions of the carbanions, have been focused on considerably recently (e.g., the $S_{RN}1$ reaction[7]); information about the electron transfer from the carbanion adjacent to the sulfur group to various electron acceptors appeared to be fruitful. We studied effect of oxidation state of the sulfur atom and ion-pairing effect on these reactions. The electron-transfer process from acceptor radical anion to free radical, generated by photoejection of an electron from a carbanion in the presence of acceptor, was also studied by means of flash photolysis technique.

Experimental Section

High vacuum line technique was used for solvent purification and for preparation of solutions containing carbanion salts (lithium, sodium, potassium, and cesium).

Purification of Solvents. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME), commercially available, were refluxed over sodium wire for 1 day and distilled from solution containing benzophenone ketyl under reduced pressure. The middle fraction of THF was then stored with sodium benzophenone ketyl on a high-vacuum line (less than 10^{-5} Torr) and DME and 2-methyltetrahydrofuran (MTHF) with sodium-potassium alloy until distillation for preparation of solutions. Hexamethylphosphoric triamide (HMPA) was refluxed over calcium hydride and distilled on a high-vacuum line from a solution containing the sodium salt of pyrene radical anion and then divided into several ampules each equipped with a breakable seal for storage. *N,N*-Dimethylformamide (DMF) for cyclic voltammograph measurements was dehydrated by successive refluxings with anhydrous copper sulfate and barium oxide and then distilled under reduced pressure.

Preparation of 9-Substituted Fluorenes ($PhSO_nFl$-H). 9-Phenylsulfenyl- ($n = 0$) and 9-phenylsulfonylfluorenes ($n = 2$) were synthesized by Bavin's procedure.[8] 9-Phenylsulfinylfluorene ($n = 1$) was prepared by oxidation of PhSFl-H with *m*-chloroperbenzoic acid in chloroform: mp 107 °C; IR (KBr) 1050 cm^{-1} ν_{S-O}. NMR (in $CDCl_3$, δ ppm): H_9, 5.36 (s); H_{Ph}, 6.64, 6.90, 7.03; H_{2-6}, 7.30 (m); H_{18}, 7.66 (m). Anal. Calcd for $C_{19}H_{14}SO$: C, 78.59; H, 4.86. Found: C, 78.78; H, 5.15.

Preparation of Carbanion Salts. Solutions of alkali metal $PhSO_nFl^-$ carbanions were prepared by proton abstraction with the corresponding alkali metal dimeric dianion of 1,1-diphenylethylene or direct metal reduction. Lithium metal was used after successive washings with dry benzene, dry ethanol, and then purified THF. Sodium and potassium metals were used as mirror and cesium metal prepared by the reaction of cesium chloride and calcium metal was also used as mirror.

Measurement of Spectra. Electronic absorption spectra were recorded with a Cary Model 14 spectrophotometer using a 2-mm quartz optical vacuum cell; for some measurements an appropriate spacer was inserted. A quartz Dewar with optical flat windows at both ends was used for the low-temperature measurements and precooled methanol with liquid nitrogen was chosen as cooling liquid. ^1H NMR spectra (100 MHz) were obtained on a JEOL Model JNM-PS-100 spectrometer with probe temperatures of 33 and −78 °C and the chemical shifts are in parts per million downfield from tetramethylsilane as internal standard. NMR sample solutions (ca. 0.05 M) were filtered through a sintered glass filter into an NMR tube attached to the high-vacuum line and sealed off the tube.

Cyclic Voltammograph. Oxidation peak potentials of $PhSO_nFl^-$ carbanions were determined in DMF with a Yanaco Model P8-CV in which tetrabutylammonium perchlorate (TBAP) was used as supporting electrolyte and the saturated calomel electrode (SCE) as reference electrode. Sweep speeds were 0.03 (0.1 V/s) and 0.06 Hz (0.2 V/s). DMF solution containing $PhSO_nFl$-H (ca. 10^{-3} M) and TBAP (10^{-1} M) was deaerated by bubbling nitrogen gas and the platinum electrode was always cleaned before use.

Electron-Transfer Reactions. The reactions were performed in solutions prepared with high vacuum line technique and monitored

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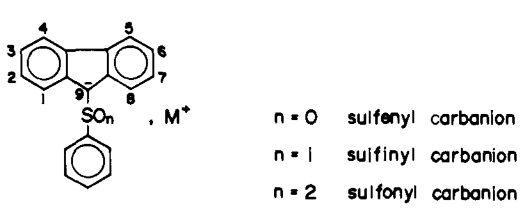

Figure 1. Alkali metal fluorenyl carbanions substituted in 9 position with sulfur groups ($PhSO_nFl^-$).

Table I. Effect of Cation in the Alkali Metal $PhSFl^-$ Carbanions in THF on Increase in Optical Density at 352 nm Caused by Lowering the Temperature

	alkali metal cation			
	Li^+	Na^+	K^+	Cs^+
$OD_{low\ temp}/OD_{20°C}$	2.36	1.93	1.48	1.26[a]
lower temp, °C	−62	−78	−66	−85

[a] At 348 nm.

by a Cary Model 14 spectrometer or a Varian E-4 ESR spectrometer. Electron-transfer reaction of the $AQ^-\cdot$ radical anion to $PhSO_2Fl\cdot$ radical produced by photoejection of an electron from the carbanion in the presence of a large excess of AQ was monitored by kinetic electronic spectroscopy. These reactions were done in a 10-cm cylindical quartz cell with optically flat end windows. Flash energy was 100 J (8 μF, 5 kV), a cutoff filter for wavelength shorter than 350 nm was used, and the flash duration at half peak intensity was about 12 μs.

Results and Discussion

Electronic Absorption Spectra. Alkali Metal $PhSFl^-$ Carbanions. Spectra of the sodium $PhSFl^-$ carbanion in THF observed at 20 and −78 °C are depicted in Figure 2. We assigned the absorption band which appeared at 352 nm to the solvent-separated $PhSFl^-\|M^+$ ion pair or free $PhSFl^-$ ion on the bases of the following observations (fraction of the latter species in the investigated solutions would be less than a few percent by analogy with the data reported for the alkali metal fluorenyl (Fl^-) carbanions,[4] other carbanions,[5,6,9] and radical anions[10]): (1) By addition of 18-crown-6 (6.0 equiv to the Na^+ salt) or HMPA onto the THF solution the absorption band at 352 nm did not shift but optical density increased. The band was independent of used solvents such as THF, DMF, and HMPA. (2) No shift in the absorption maximum (λ_{max}) with the cation was observed except for Cs^+ in THF. (3) The band at 352 nm in THF increased also on lowering the temperature at which the solvation to the countercations becomes more favorable. The band intensity was reversible by changing the temperature. In the visible region similar but small changes with temperature or by addition of solvating agents were also observed, but those were so weak that the effect of crown ether or HMPA could not be estimated. (4) A sharp absorption band at 352 nm due to $\pi\pi^*$ transition (ϵ ca. 10^4 M^{-1} cm^{-1}) and weak absorption bands which appeared in the visible region resembled the behavior of those of the Fl^- carbanions which have been assigned to the solvent-separated $Fl^-\|M^+$ ion pairs or free ion by Šmid et al.[4] It is noteworthy that the stabilizing effect caused by the introduction of phenylsulfenyl group on the fluorenyl carbanion can be estimated to be 1600 cm^{-1} (5.5 kcal/mol) by comparison with the λ_{max} of the same type of transition of $Fl^-\|M^+$ [4] if the stabilizing effect of the sulfenyl group acts mainly upon the ground state of carbanions.

Variation of countercation resulted in the change of the peak height, as shown in Table I. The most extensive increase in optical density at 352 nm on lowering the temperature from 20 °C to about −60 °C was observed for the Li^+ salt. This behavior is reasonable because the solvation of THF is strongest for Li^+ among alkali metal cations used. The increase is in the order $Li^+ > Na^+ > K^+ > Cs^+$. The Cs^+ is not profitable for the solvation by THF owing to a large cationic radius. In fact the variability of optical density was smallest and the λ_{max} appeared at 348 nm, unlike the other cations. This band is assigned to contact $PhSFl^-,Cs^+$ ion pair by a similar behavior to the contact Fl^-,Cs^+ ion pair in THF.[4]

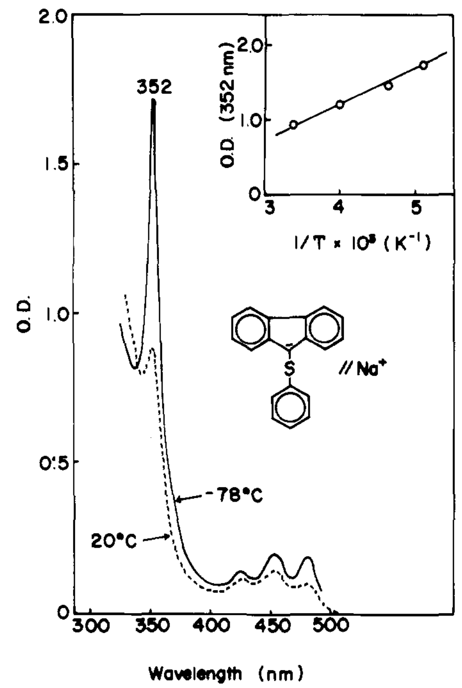

Figure 2. Electronic absorption spectrum of the sodium $PhSFl^-$ carbanion in THF (2-mm cell).

Even at −80 °C the radical anion of phenylsulfenylfluorene, $(PhSFl\text{-}H)^-\cdot$, was not observed, although the ESR spectra of $(Fl\text{-}H)^-\cdot$ radical anions were reported.[11] This is explained by the more stabilizing effect of phenylsulfenyl group on a carbanion (9 carbon is sp^2 carbon) than that on a radical anion (sp^3 carbon). The absorption band ascribable to the contact $PhSFl^-,M^+$ ion pairs could not be detected even in very diluted solution owing to extensive peak overlap. Each unreduced $PhSO_nFl\text{-}H$ and also $Fl\text{-}H$[12] exhibit broad absorption band ranging in wavelength from 250 to 310 nm due to the $\pi\pi^*$ transition of the fluorene ring. However, as depicted in Figure 1, optical density at 352 nm due to the solvent-separated $PhSFl^-\|Na^+$ ion pair increases with decreasing temperature, strongly suggesting the existence of the contact $PhSFl^-,Na^+$ ion pair in the shorter wavelength region in an equilibrium with the solvent-separated ion pair.

Alkali Metal $PhSOFl^-$ Carbanions. Although absorption bands ranging in wavelength from 370 to 450 nm at 20 °C were broad bands due to extensive peak overlap, they separated into three peaks as shown in Figure 3 in glassy MTHF solution at 77 K because the thermal motion of the molecule was suppressed.[13] It is interesting to note that even at 77 K the alkali metal $PhSOFl^-$ carbanions are contact ion pair on the basis of inspection of Figure 4. The intercepts ν_{max}'s on extraporation to $1/r_C \rightarrow 0$ represent the wavenumbers of the solvated free $PhSOFl^-$ carbanion, leading to λ_{max}'s of 395, 418, and 445 nm. These wavelengths agree with the observed λ_{max}'s in HMPA at 20 °C, indicating that in glassy MTHF solution the alkali metal $PhSOFl^-$ carbanions are the contact ion pairs.

In addition to the three absorption bands, a strong band appears in the UV region at 20 °C in THF. This band also shows similar correlation between $1/r_C$ and ν_{max} (*a* in Figure 4), indicating formation of the contact ion pair at 20 °C.

In the ground state the contact ion pair is more stabilized as compared with the solvent-separated ion pair.[14] The three

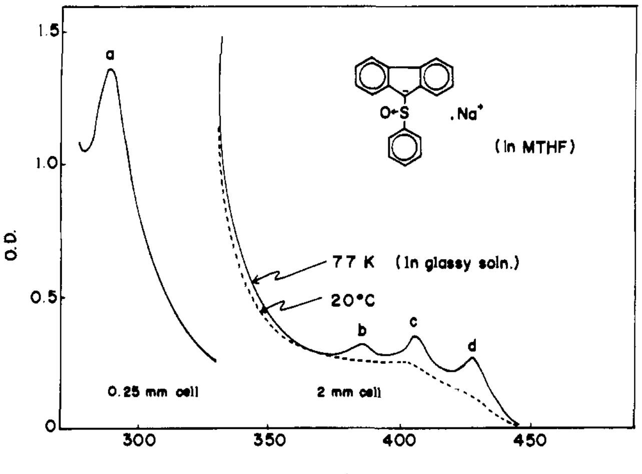

Figure 3. Electronic absorption spectrum of the sodium $PhSOFl^-$ carbanion in glassy MTHF at 77 K (2- and 0.25-mm cell).

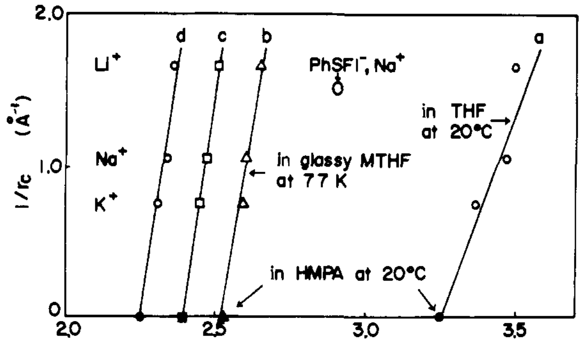

Figure 4. Correlation between wavenumber of absorption maximum and the inverse of the cationic radius for contact $PhSOFl^-,M^+$ ion pairs.

absorption bands of $PhSOFl^-$ carbanions exhibiting in the visible region appear at shorter wavelength than those of $PhSFl^-$ carbanions. This suggests that the sulfinyl carbanions are more stabilized than the sulfenyl carbanions, if the excited state is not so different between the alkali metal $PhSFl^-$ and $PhSOFl^-$ carbanions. This is explicable by an electrostatic attraction between negatively charged oxygen atom and countercation leading to a favorable location of the cation (Figure 5). A similar profile has been reported in the reactions of the sulfinyl carbanions.[15]

Alkali Metal $PhSO_2Fl^-$ Carbanions. In contrast with both spectra shown in Figures 2 and 3 the alkali metal $PhSO_2Fl^-$ carbanions exhibited a single and rather broad absorption band at wavelength less than 450 nm. Their λ_{max}'s were influenced by effects of cation, solvent, and temperature as listed in Table II. However, there is no linear correlation between $1/r_C$ and ν_{max}. In HMPA all the $PhSO_2Fl^-$ carbanions exhibit the λ_{max} at 373 nm and this absorption band can be assigned to the solvent-separated $PhSO_2Fl^-\|M^+$ ion pair or the free $PhSO_2Fl^-$ ion. The λ_{max} in HMPA is located at a little shorter wavelength than the reported value for the sodium $PhSO_2Fl^-$ carbanion in *tert*-butyl alcohol (375 nm),[16] but a strict comparison between them is meaningless because of the solvation of *tert*-butyl alcohol to an anion by hydrogen bonding. Both the lithium and the cesium $PhSO_2Fl^-$ carbanions exhibit the absorption band near 373 nm. This is attributable to relatively weak interactions between $PhSO_2Fl^-$ carbanion and these cations. It seems to be due to surpassing solvation of THF to Li^+ and a large radius of Cs^+. For the sodium salt the λ_{max} locates at the longest wavelength among the alkali metal $PhSO_2Fl^-$ carbanions.

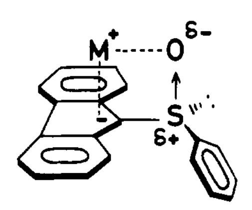

Figure 5. Stabilizing role of the alkali metal cation in formation of contact $PhSOFl^-,M^+$ ion pairs.

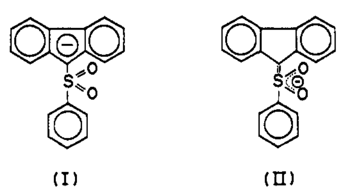

Figure 6. Suggested structure of the alkali metal $PhSO_2Fl^-$ carbanions in the ground state (I) and in the excited state (II).

Table II. Electronic Absorption Maxima of the Alkali Metal $PhSO_2Fl^-$ Carbanions in Solvents (nm)

	THF				
M^+	20 °C	−60 °C	DME	DMF	HMPA
Li^+	377	374			
Na^+	386	387	382	376	373
	380[a]				382[b]
K^+	383	375			373
Cs^+	370				

[a] Added 18-crown-6 (5.3 equiv). [b] Added tetraphenylsodium boride.

These observations strongly suggest that the absorption bands in a shorter wavelength region are due to more solvated species and that the bathochromic shift is found as solvation becomes unfavorable. The observed shift in λ_{max}'s with solvent and temperature and by addition of crown ether for the alkali metal $PhSO_2Fl^-$ carbanions is extraordinary but interesting. The solvation to the cation leading to formation of the solvent-separated ion pair is always accompanied by a bathochromic shift in the cases of other carbanions,[4,5,6,9] phenolate anions,[17] and aromatic radical anions[14,18] excepting the alkali metal aryl thiolate anions in DMF.[19] The hypsochromic shift accompanied by solvation to the cation suggests that the nature of transition of the alkali metal $PhSO_2Fl^-$ carbanions is quite different from the $\pi\pi^*$ transition of both the alkali metal $PhSFl^-$ and $PhSOFl^-$ carbanions. The most reasonable explanation for these λ_{max}'s appearing in the alkali metal $PhSO_2Fl^-$ carbanions is an intramolecular charge-transfer band. In the ground state negative charge is delocalized on the fluorenyl ring including the five-membered pseudo-"aromatic" ring as I and in the excited state in the sulfone moiety (II) in Figure 6. In the ground state the Na^+ is located close to the SO_2 moiety, and, on excitation, as charge moves into this moiety, the cation comes closer to the center of negative charge resulting in greater stabilization. The increase in the size of countercations and solvation by HMPA or other solvating agents decrease such a stabilization. The effect of temperature which resulted in the changes of solvation to the cation is explained in a similar manner. Thus, hypsochromic shifts is observable due to the formation of solvent-separated ion pair or free ion.

Such an intramolecular charge transfer band has been reported for the dimethylsulfonium cyclopentadienyl ylide in which a similar hypsochromic shift is recognized.[20] Since the alkali metal $PhSO_2Fl^-$ carbanions have a strong electron-

Table III. NMR Parameters for Protons in the Sodium Metal $PhSO_nFl^-$ Carbanions in THF[h]

carbanion	Temp, °C	H_{18}	H_{27}	H_{36}[a]	H_{45}[a]	H_{Ph}[b]	J_{12}[c]	J_{23}	J_{34}
$PhSFl^-$	33	7.52 (d-d)[d]	6.97 (t-d)[d]	6.65 (t-d)[d]	8.00 (d-d)[d]	6.85 (m)	8.0	7.5	7.5
	−78[e]	7.22 (m)	6.7 (m)	6.43 (t−d)	7.73 (d)	6.68 (m)		7.5	7.5
$PhSOFl^-$	33	7.66 (m)	6.90 (t)	6.73 (t)	7.92 (d-d)[d]	7.25 (m)		7.5	8.0
	−78[e]	7.50 (m)	6.56 (m)		7.73 (d)	7.18 (m)		7.5	8.0
	33	7.87 (d)	7.05 (m)	6.68 (m)	8.02 (d)	7.32 (m)	9		7
						o 7.80 (d)			
$PhSO_2Fl^-$	31[f]	7.75 (d)	6.97 (t)	6.67 (t)	8.08 (d)	*m* 7.18 (m)	8.0	8.0	8.5
						p 7.3 (m)	6.0 (J_o)		
	−70	7.76 (d)	7.00 (m)	6.63 (m)	7.92 (d)	7.24 (m)	9		7
Fl^- [g]	29	7.376	6.899	6.546	8.004		8.16	6.65	7.85

[a] Determined by decoupling and there are no significant differences among J_{12}, J_{23}, and J_{34} so that both H_{27} and H_{36} triplets are observed with somewhat sharpless peaks. [b] All the H_{Ph}'s are observed in multiplet and overlapped with the fluorenyl protons excepting the $PhSOFl^-$ carbanion. In particular for the H_{Ph} in the $PhSO_2Fl^-$ carbanion the peaks attributable to ortho protons were exhibited downfield so that broad peaks are observed (ca. 40 Hz). [c] In hertz with an error of ±0.3 Hz in the reading. [d] Each small doublet seems to be due to mutual coupling of meta-position protons in the fluorenyl ring. [e] The peaks at −78 °C are broadened considerably. [f] In HMPA. [g] The data reported by Cox, R. H. *J. Phys. Chem.*, **1969,** *73,* 2649. [h] δ, in parts per million downfield from Me_4Si.

withdrawing sulfone moiety and can form a conjugation structure, the sulfone moiety acts as a new chromophore rather than as a substituent perturbing the $\pi\pi^*$ transition of the fluorenyl carbanion.

^{1}H NMR Spectra. The chemical shifts of protons in the alkali metal Fl^- and substituted Fl^- carbanions have been studied extensively by Cox.[21,22] He clearly showed that the effect of the cation should be taken into consideration in correlation of chemical shifts of aromatic anions, which means that ion pairing reflects in the ^{1}H NMR. We determined the chemical shifts of the fluorenyl ring protons in the sodium $PhSO_nFl^-$ carbanions in THF by comparison with the shifts of those in Fl^- carbanions as listed in Table III.

The chemical shifts of H_{18} in the carbanions appear to lower field in order -H ≪ -SPh < -SOPh < $-SO_2Ph$ and have a linear relationship with σ_I[23] of $-SO_nPh$. H_{18} are ortho protons at the 9 position and most sensitive to the π-electron density[24] which is influenced by the oxidation state of sulfur atom and by the ion pairing.

The chemical shifts of H_{18} were also influenced by temperature. Lowering the temperature results in an upfield shift caused by the increase of π-electron density as solvation to the cation is favored.[28] The quantity of the upfield shift was affected by the substituents, i.e., 0.30, 0.16, and 0.11 ppm for -SPh, -SOPh, and $-SO_2Ph$, respectively. The electrostatic attraction force of the sulfonyl carbanion against Na^+ predominates over the solvating power of THF rather than that of sulfenyl and sulfinyl carbanions. These observations are consistent with the electronic absorption spectral data.

In HMPA the line splitting was clear even in the phenyl ring protons, suggesting formation of the solvent-separated or free $PhSO_2Fl^-$ carbanion in this solvent. It is noteworthy that the NMR spectrum of the $PhSO_2Fl^-$ carbanion in HMPA is very close in shape to that of the lithium $PhSO_2Fl^-$ carbanion in THF.

The chemical shifts of protons other than H_{18} were varied with the used carbanions and with conditions, but could not be interpreted clearly.

Oxidation Potentials of $PhSO_nFl^-$ Carbanions. Cyclic voltammographs for the $PhSO_nFl$-H in DMF were irreversible. The reduction peak potential corresponds to the reaction 1 followed by rapid formation of the carbanions by dissociation reaction 2 or by proton abstraction from neutral $PhSO_nFl$-H.[29]

$$PhSO_nFl\text{-}H \xrightarrow{+e^-} (PhSO_nFl\text{-}H)^-\cdot \quad E_{red} \qquad (1)$$

$$(PhSO_nFl\text{-}H)^-\cdot \rightarrow PhSO_nFl^- + H \qquad (2)$$

Table IV. Cyclic Voltammograph of $PhSO_nFl$-H and Fl-H in DMF (V vs. SCE)[a]

substrate	runs[b]	E_{ox}	E_{red}
PhSFl-H	2	−0.42	−1.23
PhSOFl-H	2	−0.12	−1.20
$PhSO_2Fl$-H	3	0.11	−1.19
Fl-H	1	−0.71	−2.69[c]

[a] Irreversible (see text). [b] Measured with different sweep speeds. [c] −2.627 (vs. Ag/AgCl (satd))[30] and −3.130 V (vs. $Ag/AgClO_4$ (0.01 M))[31] have been reported as reversible half-wave reduction potentials.

The carbanions so formed are oxidized to the corresponding free radicals:

$$PhSO_nFl^- \xrightarrow{-e^-} PhSO_nFl\cdot \quad E_{ox} \qquad (3)$$

Pertinent data are listed in Table IV. The sulfonyl carbanion finds it the most difficult to release an electron among the carbanions examined owing to the strong electron-withdrawing character of the sulfone moiety. This is well reflected in electron transfer to anthraquinone as will be discussed in a later section. The fate of the free radicals is not clear but it is most likely that they recombine into neutral dimer.[32] This succeeding reaction would interfere with the reversible cyclic voltammograph.[33] If $\Delta G°$'s for dimerization reaction of the respective $PhSO_nFl\cdot$ are not so different from each other, the E_{ox} values obtained in the irreversible cyclic voltammograph can be used as a relative measure for the ease of electron release from the $PhSO_nFl^-$ carbanions. This is supported by the linear relationship between E_{ox}'s and σ_I values.[23]

Electron Transfer Reaction. Spontaneous Electron Transfer. The difference in oxidation number of sulfur atom in the potassium $PhSO_nFl^-$ carbanions is well reflected in electron-transfer reaction to anthraquinone (AQ, $E_{1/2} = -0.82$ V vs. SCE[34]) as listed in Table V. The formation of $AQ^-\cdot$, K^+ was confirmed by means of electronic absorption and ESR spectroscopies. The ease of the occurrence of electron transfer from carbanions can be discussed in terms of the potential difference between carbanion and acceptor and of ion pairing. The alkali metal $PhSO_nFl^-$ carbanions transferred an electron instantaneously or moderately depending upon the state of the ion pair of the carbanions used.

Both the potassium $PhSFl^-$ and Fl^- carbanions transferred an electron irrespective of the state of the ion pair of the carbanions since there is considerable potential difference

Table V. Effects of Ion Pairing and Oxidation Potential on Electron Transfer

carbanion	solvent	electron transfer from $\mathrm{PhSO_{\mathit{n}}Fl^-}$ to AQ[a]	 from $\mathrm{AQ^-\cdot}$ to $\mathrm{PhSO_{\mathit{n}}Fl\cdot}$[b]	E_{ox}
$\mathrm{PhSFl^-\|K^+ + PhSFl^-, K^+}$[c]	THF	yes (instantaneously)		−0.42
$\mathrm{PhSFl^-\|K^+}$	THF-HMPA (53 vol %)	yes (instantaneously)		
$\mathrm{PhSOFl^-, K^+}$	THF	yes (moderately)		−0.12
$\mathrm{PhSOFl^-\|K^+}$	THF-HMPA (39 vol %)	no	no[d]	
$\mathrm{PhSO_2Fl^-, K^+}$	THF	yes (moderately)		0.11
$\mathrm{PhSO_2Fl^-\|K^+}$	THF-HMPA (25 vol %)	no	yes	
$\mathrm{Fl^-, K^+}$	THF	yes (instantaneously)		−0.71
$\mathrm{Fl^-\|K^+}$	THF-HMPA (16 vol %)	yes (instantaneously)		

[a] Electron-transfer reaction after mixing both the solutions in the dark. [b] Formed by flash photolysis of $\mathrm{PhSO_{\mathit{n}}Fl^-}$ in the presence of AQ. [c] No direct evidence for existence of the contact $\mathrm{PhSFl^-, K^+}$ ion pair (see text). [d] $\mathrm{AQ^-\cdot}$ formed after flash photolysis was stable and $\mathrm{PhSOFl\cdot}$ radicals must have recombined into dimer.

Table VI. Electron Transfer from the Alkali Metal $\mathrm{PhSO_2Fl^-}$ Carbanions to Anthraquinone at 20 °C

$\mathrm{M^+}$	solvent	electron transfer from $\mathrm{PhSO_2Fl^-}$ to AQ
$\mathrm{Li^+}$	THF	yes (slowly)
	THF-HMPA (15 vol %)	no
$\mathrm{Na^+}$	THF	yes (slowly)
	THF-HMPA (8.3 vol %)	yes (very slowly)
$\mathrm{K^+}$	THF	yes (moderately)
	DME	no
	THF-HMPA (25 vol %)	no

Table VII. Electron Transfers from the Potassium Metal $\mathrm{PhSO_2Fl^-}$ Carbanions to Electron Acceptors in DME at −50 °C

electron acceptor	$-E_{1/2}$[a]	electron transfer
naphthalene	2.60	no
pyrene	2.09	no
anthracene	1.92	no
perylene	1.67	no
nitrobenzene	1.12	no
anthraquinone	0.82	no
p-dinitrobenzene	0.53	yes
chloranil	−0.02	yes
acenaphthenequinone	0.92[b]	yes
Koelsch free radical[c]		yes (slow)

[a] Half-wave reduction potential in DMF vs. SCE. [b] Value in acetonitrile. [c] α,γ-Bisdiphenylene-β-phenylallyl.

between the carbanions and AQ. In the cases of $\mathrm{PhSOFl^-}$ and $\mathrm{PhSO_2Fl^-}$ carbanions, however, electron transfer was observed only in the contact ion pairs. For the carbanions which did not transfer an electron spontaneously a flash photolysis experiment was applied with the intention of photoejecting an electron from the carbanion to AQ. The back electron transfer from $\mathrm{AQ^-\cdot\|K^+}$ to $\mathrm{PhSOFl\cdot}$ was not observed but was observed to $\mathrm{PhSO_2Fl\cdot}$. Those are discussed later.

Ion pairing effect on electron transfer was examined further with the $\mathrm{PhSO_2Fl^-}$ carbanions as shown in Table VI. When formation of the more contact $\mathrm{AQ^-\cdot, M^+}$ ion pair was expected, faster electron transfer was observed. This suggests that electron transfer passes through the transition state with a large cation affinity (negative charge is localized in the transition state, thus it is stabilized as the countercation locates in the vicinity of the negative charge). The electron transfer from trityl anion to nitrobenzene[35] and the dissociative electron transfer to 1,2-di(α-naphthyl)ethane[36] proceed through a similar transition state to that of our spontaneous electron transfer.

We examined the possibility of electron transfer from the potassium $\mathrm{PhSO_2Fl^-}$ carbanions to various electron acceptors (A) by monitoring the formation of the alkali metal salts of acceptor radical anions ($\mathrm{A^-\cdot, K^+}$) (Table VII). Electron transfer was observed for $\mathrm{K^+}$ in DME without illumination when the half-wave reduction potential of the acceptor ($E_{1/2}$ in DMF vs. SCE) is less negative than ca. −0.5 V.

$$\mathrm{PhSO_2Fl^-,K^+ + A \xrightarrow[\text{in DME}]{-50\ ^\circ C} PhSO_2Fl\cdot + A^-\cdot K^+} \tag{4}$$

Electron Transfer to Free $\mathrm{PhSO_2Fl\cdot}$ Radical. Electron transfer from the solvent-separated $\mathrm{AQ^-\cdot}$ radical anion to transient free $\mathrm{PhSO_2Fl\cdot}$ radical, the reverse reaction of an electron transfer from carbanion to neutral AQ, was studied by means of flash photolysis technique. Both $\mathrm{PhSO_2Fl\cdot}$ and $\mathrm{AQ^-\cdot\|M^+}$ were produced by photoejection of an electron from $\mathrm{PhSO_2Fl^-\|M^+}$ in the presence of a large excess of AQ. The electron capture is indiscriminate and therefore the electron is initially captured by AQ forming the $\mathrm{AQ^-\cdot}$ radical anion. The rate constant was determined with lithium carbanion in THF containing 15 vol % of HMPA. In this mixture solution the solvent-separated $\mathrm{PhSO_2Fl^-\|Li^+}$ ion pair was clearly formed. The decay of $\mathrm{AQ^-\cdot\|Li^+}$ obeyed good second-order kinetics with $k_{tr} = (7.6 \pm 0.6) \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$ at 20 °C and the same rate constant was obtained with another concentration of $\mathrm{AQ^-\cdot}$ which was attained by changing the flash energy (the standard deviation was estimated from the rate constants determined at three different wavelengths, using the reported value of ϵ[37]). The good second-order kinetics suggests that the $\mathrm{PhSO_2Fl\cdot}$ does not decay through other pathways, for example, dimerization reaction. If the rate constant of dimerization is less than $10^7\ \mathrm{M^{-1}\ s^{-1}}$, the decay of the radical is believed to be due to electron transfer being over 99%. This assumption is not unreasonable since the rate constant of dimerization for 9-hydroxyfluorenyl radical was reported to be $1.4 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$ in benzene.[38] $\mathrm{PhSO_2Fl\cdot}$ seems to be more stable than $\mathrm{HOFl\cdot}$ because of the greater electron-withdrawing power of the sulfone moiety so that it is not necessary to doubt the complete electron transfer.

$$\mathrm{PhSO_2Fl\cdot + AQ^-\cdot\|M^+ \xrightarrow{\mathit{k}_{tr}} PhSO_2Fl\|M^+ + AQ} \tag{5}$$

This is the first experimental value for electron transfer from radical anion to free radical. Electron transfer from sodium naphthalenide to 5-hexenyl free radical was studied in DME by Garst et al.[39] and they estimated the rate constant to be $1.6 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$. These values seem to be close to the diffusion-controlled limit. We are studying the same type of electron transfer in detail.

In conclusion, the ion pairing effects derived from the difference in oxidation number of sulfur atom were clearly reflected in electronic absorption and ^{1}H NMR spectra, oxidation peak potentials, and electron-transfer reactions. It is interesting to note that the stabilizing effect of phenyl sulfur groups is correlated with their inductive effect. However, we could not specify participation of 3d orbitals in the sulfur atom clearly.

Supplementary Material Available: NMR parameters of $PhSO_nFl$-H in THF (Table VIII), the electronic absorption spectrum of sodium $PhSO_2Fl^-$ carbanion in THF (Figure 7), a plot of ν_{max} and $1/r_C$ for the alkali metal $PhSO_2Fl^-$ carbanions (Figure 8), correlation between σ_I and chemical shifts of the protons in the sodium $PhSO_nFl^-$ carbanions (Figure 9), correlation between σ_I and E_{ox} of $PhSO_nFl^-$ carbanions (Figure 10), an oscilloscope trace of the decay of $AQ^-\cdot \| Li^+$ at 545 nm (Figure 11), and the kinetics of reaction 5 (Figure 12) (7 pages). Ordering information is given on any current masthead page.

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Electrochemistry of the Carbon–Halogen Bond. 9-Fluorenyl and Benzhydryl Halides in Dimethylformamide, at Platinum and Vitreous Carbon Electrodes

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Abstract: Electrochemical reductive dehalogenations of 9-fluorenyl and benzhydryl bromides and chlorides at platinum and vitreous carbon electrodes in dimethylformamide initially require two electrons/molecule and afford the corresponding carbanions as short-lived intermediates. The electrogenerated carbanions may be protonated by diethyl malonate to give their corresponding hydrocarbons or, in the absence of added proton donor, react with their starting halides by either proton transfer or displacement of halide ion. Reaction by the first of the latter two pathways leads to the corresponding olefin via an electroactive monohaloethane, whereas reaction involving the displacement of halide ion gives an electroinactive nonhalogenated ethane; the pathway which is followed appears to be determined by the ease with which halide ion is displaced. Reaction by either channel is rapid: the rate constants obtained for the displacement of bromide ion from 9-bromofluorene and benzhydryl bromide are 1×10^5 and $8 \times 10^4\ M^{-1}\ s^{-1}$, respectively, while the rate constant for proton transfer from 9-chlorofluorene to 9-fluorenyl anion is $8 \times 10^3\ M^{-1}\ s^{-1}$. All starting halides give multiple reduction waves on platinum because of either adsorption of halide ion or electrocatalysis from electrode products and adventitious impurities. No specific surface effects are observed with vitreous carbon electrodes.

Introduction

During our recent studies of the electroreduction of diphenyldiazomethane[1] and diazofluorene,[2] anodic waves were observed in the rapid scan cyclic voltammograms which we felt might be due to either carbanion or carbene radical anion intermediates. In order to study the electrochemical behavior of the 9-fluorenyl and diphenylmethyl carbanions and their possible role in the reduction of diazoalkanes, we have attempted to generate these species in situ from alternate precursors, viz., by the electrolytic reductive dehalogenation of

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