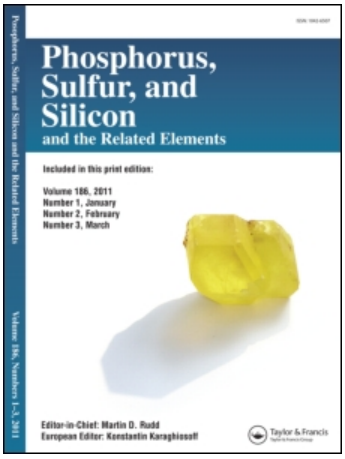

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Nishi, Shin-Ichi and Matsuda, Minoru(1983) 'FORMATION OF THE FREE ION OF FLUORENONE RADICAL ANION IN TETRAHYDROFURAN BY THE FLASH PHOTOLYSIS OF THE SULFONYL CARBANIONS', Phosphorus, Sulfur, and Silicon and the Related Elements, 16: 1, 181 — 185
To link to this Article: DOI: 10.1080/03086648308077766
URL: http://dx.doi.org/10.1080/03086648308077766

Phosphorus and Sulfur, 1983, Vol. 16, pp. 181–185
0308-664X/83/1601-0181/$18.50/0

FORMATION OF THE FREE ION OF FLUORENONE RADICAL ANION IN TETRAHYDROFURAN BY THE FLASH PHOTOLYSIS OF THE SULFONYL CARBANIONS

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(*Received February 7, 1983; in final form March 9, 1983*)

The free ion of fluorenone radical anion $(FlO)^{\cdot-}$ was formed even in tetrahydrofuran (THF) by the flash photolysis of the alkali-metal salts of the sulfonyl carbanion in the presence of neutral FlO and this was attributed to the ion pair structure of the sulfonyl carbanions.

Studies of back-electron-transfer reactions in the dark with a rate constant of k_{-e} such as reaction (1) induced by flash

$$PhSO_2Fl^-(,M^+) + FlO \underset{k_{-e}\,(\text{dark})}{\overset{k_e\,(h\nu)}{\rightleftharpoons}} (FlO)^{\cdot-}(,M^+) + PhSO_2Fl^{\cdot} \qquad (1)$$

photolysis[1] of the solution containing the alkali-metal salt of the carbanion and neutral aromatic ketone give us information about ion-pair structures of the reactant and the product ions. We report here the interesting behavior of the alkali-metal fluorenyl carbanions substituted in the 9-position with a phenylsulfonyl group (see Figure 1; abbreviated as $PhSO_2Fl^-,M^+$ (contact ion pair) and $PhSO_2Fl^-$ (free ion), and $PhSO_2Fl^-(,M^+)$ in reaction (1) represents collectively both the carbanions).[2] As can be seen from Figure 2 and Table I, the direct reduction of neutral fluorenone (FlO) by alkali metal in the absence of $PhSO_2Fl^-(,M^+)$ in THF or hexamethylphosphoric triamide (HMPA) yields the contact $(FlO)^{\cdot-},M^+$ ion pair[3] or the free $(FlO)^{\cdot-}$ ion, respectively, as expected by the nature of the solvents used. Although the absorption maximum (λ_{max}) of the free $(FlO)^{\cdot-}$ ion observed at 570 nm has not been reported, there is no ambiguity about the formation of monomeric free $(FlO)^{\cdot-}$ ion;[4] in diluted HMPA solution, it is not necessary to consider an entity other than the free ion. On the other hand, the alkali-metal fluorenone radical anions in ethereal solvents have been studied,[5-7] particularly by Hirota *et al.*,[5] in detail by means of esr and electronic absorption spectroscopies; according to their assignments, the absorption peaks around 530 nm can be attributed to the monomeric contact $(FlO)^{\cdot-},M^+$ ion pair and/or triple ion, although great complexity results from the coexistence of the radical triple ion as well as the ion quadruplet.[5]

As depicted in Figure 3, photo-ejection of an electron from the $PhSO_2Fl^-,M^+$ ion pairs (10^{-4}–10^{-5} M) in the presence of excess neutral FlO (10^{-3} M) in THF gives two absorption peaks; one can be attributed to the contact $(FlO)^{\cdot-},M^+$ ion pair and the other to free $(FlO)^{\cdot-}$ ion by the fact that the spectra are in full accord with the λ_{max}s which appeared in the directly reduced solutions.[8] Coinciding in behavior with many alkali-metal salts of carbanions[9] and radical anions, the position of the λ_{max}

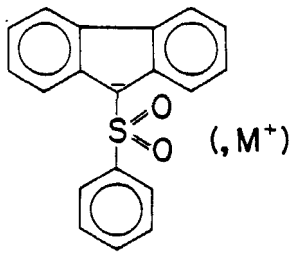

FIGURE 1 Alkali–metal salts of fluorenyl carbanions substituted in the 9-position with a phenylsulfonyl group, $PhSO_2Fl^-$(,M^+), in which (,M^+) represents collectively the contact and the solvent-separated ion pairs and the free ion.

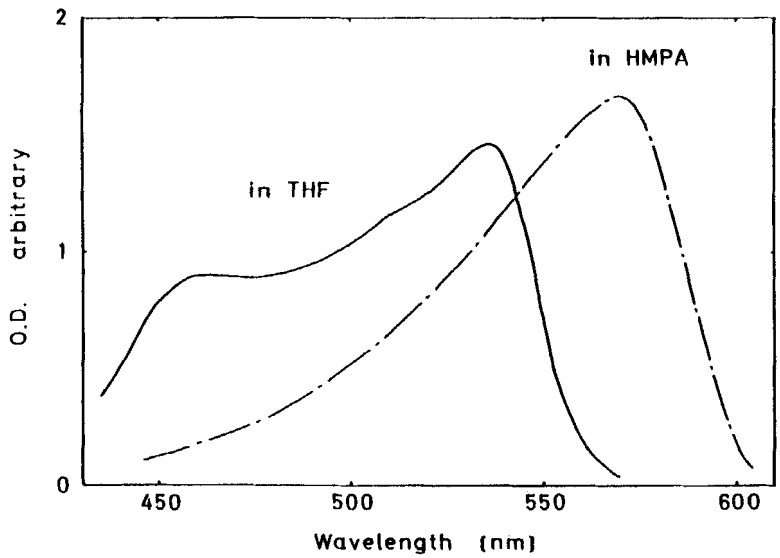

FIGURE 2 Electronic absorption spectra of fluorenone radical anions formed by direct reduction of neutral FlO with potassium metal at 23°C.

of the contact ion pairs formed by flash photolysis was shifted, depending upon the counter alkali–metal cation, and that of the free ions was not altered (see Table I).

It is interesting to note that even in the THF solution of $PhSO_2Fl^-,K^+$ containing potassium tetraphenylboride ($KBPh_4$, 5×10^{-3} M), the absorption peak attributable to the free $(FlO)^{\cdot-}$ ion also appears as a result of photo-ejection, although the ratio of optical densities OD_{570}/OD_{535} decreased from 0.77 to 0.50. In the solvent mixture consisting of THF and HMPA (23 vol%), the λ_{max} attributable to the contact $(FlO)^{\cdot-},K^+$ ion pair was shifted from 535 in THF to 545 nm and a similar shift was observed upon the addition of 18-crown-6 (7×10^{-3} M) to THF (545 and 570 nm; the latter is due to the free $(FlO)^{\cdot-}$ ion), suggesting that in these mixed solvents the contact ion pairs are converted into externally solvated contact ion pairs[10] by the HMPA or crown compounds.

TABLE I

Absorption peaks produced by flash photolysis of the solutions containing $PhSO_2Fl^-(,M^+)$ and neutral FlO[a] at 23°C

Counter cation, M^+	Solvent	Absorption maxima (nm)		
		Contact $(FlO)^-,M^+$	Externally solvated contact $(FlO)^-,M^+,S$	Free $(FlO)^-$
Li^+	THF	525	—	570
Na^+	THF	530	—	570
K^+	THF	535	—	570
K^+	THF-$KBPh_4$[b]	535	—	570
Li^+	THF-HMPA	—	535	570
Na^+	THF-HMPA	—	538	570
K^+	THF-HMPA	—	545	570
K^+	THF-crown[c]	—	545	570
K^+	HMPA	—	—	570
K^+	THF[d,e]	535	—	—
K^+	HMPA[d]	—	—	570

[a] Concentrations of the carbanions; 10^{-4}–10^{-5}.
[b] Potassium tetraphenylboride (4.8×10^{-3} M).
[c] 18-Crown-6 (6.8×10^{-3} M).
[d] Direct reduction of FlO with potassium metal.
[e] Absorption peaks other than that listed herein also appeared.

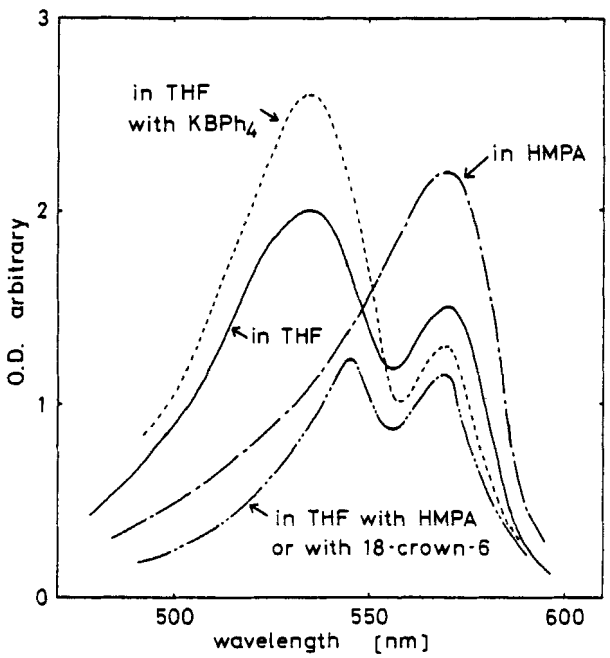

FIGURE 3 Transient absorption spectra obtained by flash photolysis of the sulfonyl carbanions $PhSO_2Fl^-(,M^+)$ in the presence of neutral fluorenone in THF and HMPA (40 μsec after flash). O.D.'s of the absorption bands: 0.12 in THF with $KBPh_4$ at 535 nm; 0.25 in THF at 535 nm; 0.3 in HMPA at 570 nm; 0.08 in THF with HMPA or with 18-crown-6 at 545 nm.

TABLE II

Decay rate constants of fluorenone radical anions (23°C)

Carbanion	k_{-e}/ε (cm s^{-1}) in THF[a]		k_{-e}(M^{-1} s^{-1}) in HMPA
	Contact $(FlO)^{\cdot-},M^+$	Free $(FlO)^{\cdot-}$	Free $(FlO)^{\cdot-}$
$PhSO_2Fl^-,Li^+$	4.1×10^5	5.3×10^5	
$PhSO_2Fl^-,Na^+$	4.6×10^5	6.4×10^5	
$PhSO_2Fl^-,K^+$	4.9×10^5	8.7×10^5	1.3×10^9

[a] ε is molar extinction coefficient of fluorenone radical anions.

From the flash photolyses of the sulfenyl carbanion $PhSFl^-(,K^+)$ and the sulfinyl carbanion $PhSOFl^-,K^+$ [11] in the presence of neutral FlO in THF, only the contact $(FlO)^{\cdot-},K^+$ ion pair was formed. Therefore, the formation of the free $(FlO)^{\cdot-}$ radical anion in THF should be attributable to the characteristics of the sulfonyl carbanions; the alkali-metal cation of the sulfonyl carbanion is located at the sulfonyl moiety which is partially negatively charged owing to an intramolecular charge-transfer interaction between the negative center and the neighboring sulfonyl group[2] and to the inductive effect of the S—O bonds; these tend to prevent the cation from moving toward the $(FlO)^{\cdot-}$.

The back-electron-transfer reactions from the alkali-metal fluorenone radical anions to $PhSO_2Fl^{\cdot}$ are clearly shown by the state of the ion-pair structure of the fluorenone radical anions formed. Decay of the radical anions with a rate constant k_{-e}/ε obeyed second-order kinetics up to *ca.* 80% conversion and was faster from the free $(FlO)^{\cdot-}$ than from the contact $(FlO)^{\cdot-},M^+$ ion pairs in THF (see Table II). The rate constant for the back electron transfer in HMPA was determined in the form of k_{-e} since the molar extinction coefficient of the free $(FlO)^{\cdot-}$ in HMPA was determined.[4]

In conclusion, the free $(FlO)^{\cdot-}$ radical anion was formed even in THF by flash photolysis of the sulfonyl carbanions and this results from the ion-pair structure of the sulfonyl carbanions.

REFERENCES AND NOTES

1. Flash photolysis apparatus and kinetic spectroscopy used in this experiment was described in ref. 2.
2. S. Nishi and M. Matsuda, *J. Am. Chem. Soc.*, **101**, 4632 (1979).
3. Absorption peaks other than that responsible for the monomeric contact $(FlO)^{\cdot-},M^+$ ion pair appeared, but in the present study our interest was focused on the formation of both the monomeric contact $(FlO)^{\cdot-},M^+$ ion pair and the free $(FlO)^{\cdot-}$ radical anion.
4. Molar extinction coefficient of the free $(FlO)^{\cdot-}$ radical anion was determined to be 7.4×10^3 M^{-1}cm^{-1} in HMPA by measuring the optical densities before and after electron transfer from anthracene radical anion to neutral FlO. Esr spectrum of the free $(FlO)^{\cdot-}$ radical anion in HMPA gives g value (2.0038) and hyperfine splitting constants for the free $(FlO)^{\cdot-}$ radical anion (1.73 ± 0.01 ($H_{1,8}$); 0.12 ± 0.005 ($H_{2,7}$); 2.29 ± 0.02 ($H_{3,6}$); 0.63 ± 0.005 ($H_{4,5}$) gauss). No alkali-metal splitting was observed.
5. S. W. Mao, K. Nakamura and N. Hirota, *J. Am. Chem. Soc.*, **96**, 5341 (1974).
6. T. Shida, S. Iwata and M. Imamura, *J. Phys. Chem.*, **78**, 741 (1974).
7. A. G. Evans, J. C. Evans, P. J. Emes and S. I. Haider, *J. Chem. Soc. Perkin 2*, 1121 (1974).

8. The photochemistry of the sulfonyl carbanion could contribute to the observed results; the $(FlO)^{\cdot}$ formed by our xenon flash photolysis may correspond to *ca.* 10 mol % of the $PhSO_2Fl^-(,M^+)$ existing in the ground state. Therefore, the concentration of the $PhSO_2Fl^-(,M^+)^*$ in the excited state may be greater than 10 mol % of the sulfonyl carbanion in the ground state. In general, the ratio of the solvent-separated ion pair in the excited state to that in the ground state becomes progressively greater as the ion pair is excited (e.g.. T. E. Hogen-Esch and J. Plodinec, *J. Am. Chem. Soc.*, **100**, 7633 (1978)). Therefore, the formation of the free $(FlO)^{\cdot}$ from the sulfonyl carbanion may be attributable to the characteristic ion-pair structure of the sulfonyl carbanions (see ref. 2 and the text).
9. T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **87**, 669 (1965); **88**, 307, 318 (1966).
10. L. L. Chan, K. H. Wong and J. Smid, *J. Am. Chem. Soc.*, **92**, 1955 (1970).
11. The alkali-metal salts of sulfenyl carbanions $PhSFl^-(,M^+)$ exist as a mixture of the contact and the solvent-separated ion pairs at room temperature.[2]