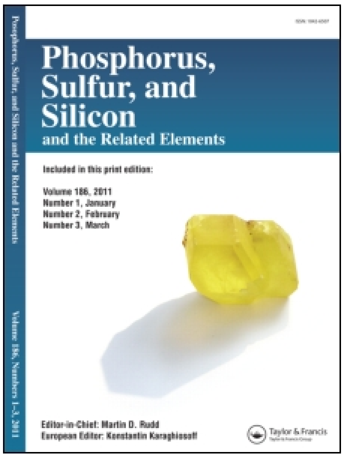


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Why the Central Sulfur or Any Other Atom in Main Group Elements Attracts the Attack of Free Radicals and Nucleophiles?

Shigeru Oae[a]
[a] Institute of Heteroatom Chemistry, Osaka-fu, Japan

To cite this Article Oae, Shigeru(1993) 'Why the Central Sulfur or Any Other Atom in Main Group Elements Attracts the Attack of Free Radicals and Nucleophiles?', Phosphorus, Sulfur, and Silicon and the Related Elements, 74: 1, 349 — 363
To link to this Article: DOI: 10.1080/10426509308038116
URL: http://dx.doi.org/10.1080/10426509308038116

Phosphorus, Sulfur, and Silicon, 1993, Vol. 74, pp. 349–363

WHY THE CENTRAL SULFUR OR ANY OTHER ATOM IN MAIN GROUP ELEMENTS ATTRACTS THE ATTACK OF FREE RADICALS AND NUCLEOPHILES ?

Shigeru Oae

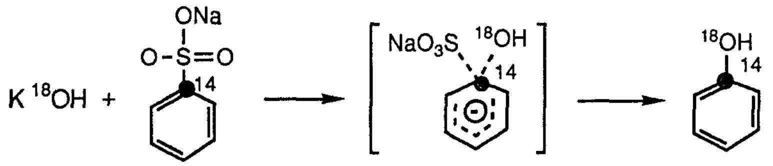
Institute of Heteroatom Chemistry, 2509 Hirao, Mihara-cho, Minamikawachi-gun,
Osaka-fu 587, Japan

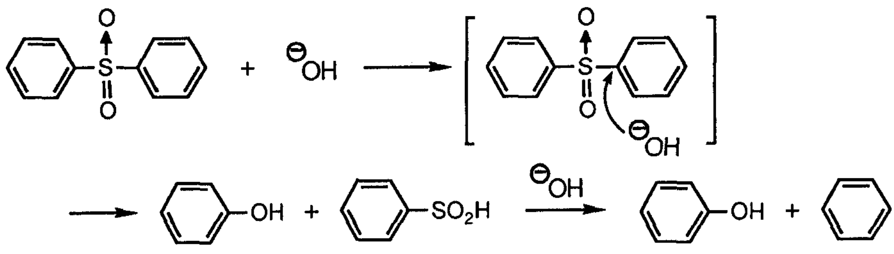
A. INTRODUCTION

This is a mere extension of my lecture, given at ISOCS-14 in Łódź, Poland, September of 1990,[1] and of more philosophical than experimental. Therefore, most of my talk is concentrated on unsolved problems which have remained to be solved in the future.

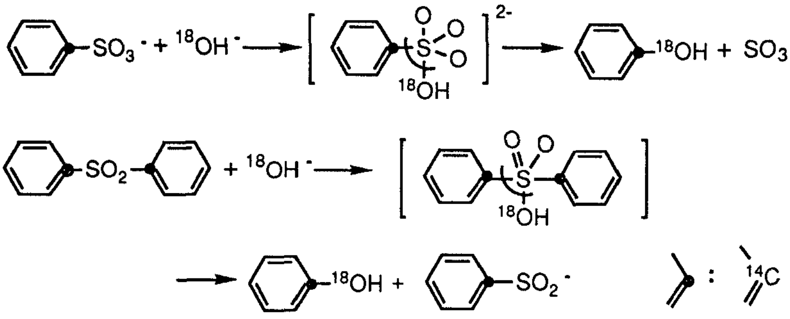
B. WHY SULFUR OR OTHER ATOMS BEYOND SECOND ROW ELEMENTS ATTRACTS ATTACK OF NUCLEOPHILES AND RADICALS ?

Earlier, the alkali fusions of benzenesulfonic acid and diphenyl sulfone with hydroxide ion was shown by us to proceed through the attack of hydroxide ion at the ipso position without any intermediary formation of "benzyne", as shown below.[2,3,4]

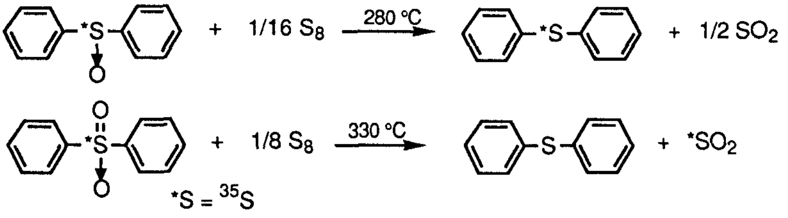




Although the reaction proceeds at somewhat a higher temperature, there is practically no product which originates by the nucleophilic attack of hydroxide ion at other than the ipso position. However, a question remains as to the initial attacking site of hydroxide ion either at the ipso carbon atom(s) of benzene(s) leading to the aromatic nucleophilic displacement of SO_3^- group or $PhSO_2^-$ group or at the sulfur atom of the sulfonate or the sulfone and the subsequent fast ligand coupling, as shown below.



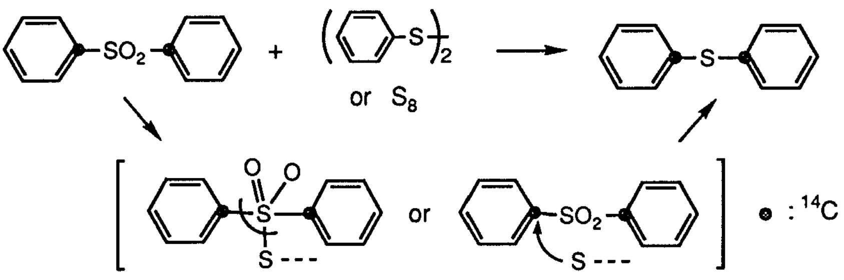
The reactions of diphenyl sulfoxide and sulfone with elemental sulfur are interesting. Both compounds react similarly, affording diphenyl sulfide and sulfur dioxide as shown below.[5]



However, by labelling ^{35}S, the sulfoxide was shown to undergo S-O bond cleavage, while in the case of the sulfone, the reaction appeared to proceed by the homolytic attack of a sulfur species,[6] very probably the triplet S_3 species, which has a distinct red color.[7]

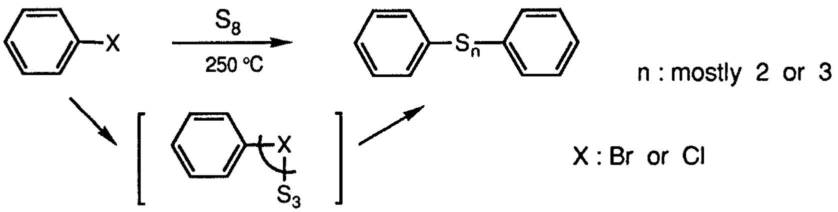
By the use of ^{14}C-labelled diphenyl sulfone at the ipso position, we have found that there were no scrambling of ^{14}C in the resulting diphenyl sulfide.[8]

Here again, a question has remained as to the actual site of the free radical attack, i.e.,

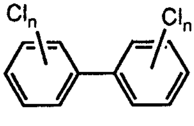


whether at the ipso carbon to result in the homolytic aromatic substitution or the sulfur atom of the sulfone by the red sulfur species and the subsequent fast ligand coupling.

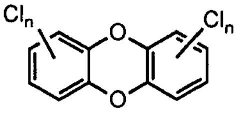
Though in many other aromatic homolytic substitutions with free radicals, the intermediary formations of cyclohexadienyl species have been considered during the reactions, we have found that there was practically no product formed by the homolytic attack at other than the ipso position. Generally, bromo- and chlorobenzenes, having better leaving groups than benzenesulfonyl, were found to undergo the similar displacement more readily, as shown below.[9] In both cases, the reaction mixture turned to deep red,



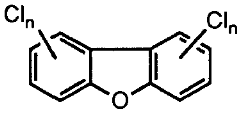
indicating the formation of S_3 species. Only when the reaction became so slow with chlorobenzene, we noticed the formation of a trace amount of hydrogen sulfide, only by the bad smell. This reaction has led to the efficient detoxication of PCB, polychlorodiphenyl and many other polychlorinated aromatic hydrocarbons such as polychlorodibenzodioxine, commonly called as "Dioxine" and polychlorinated dibenzofuran.[10]



PCB

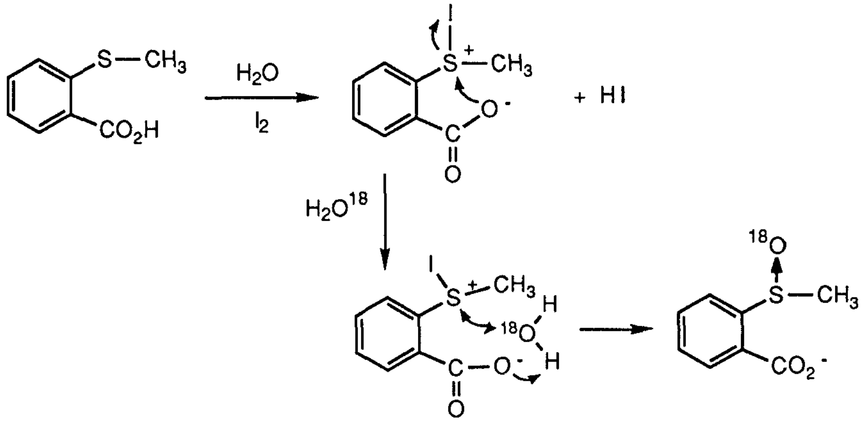


DIOXINE

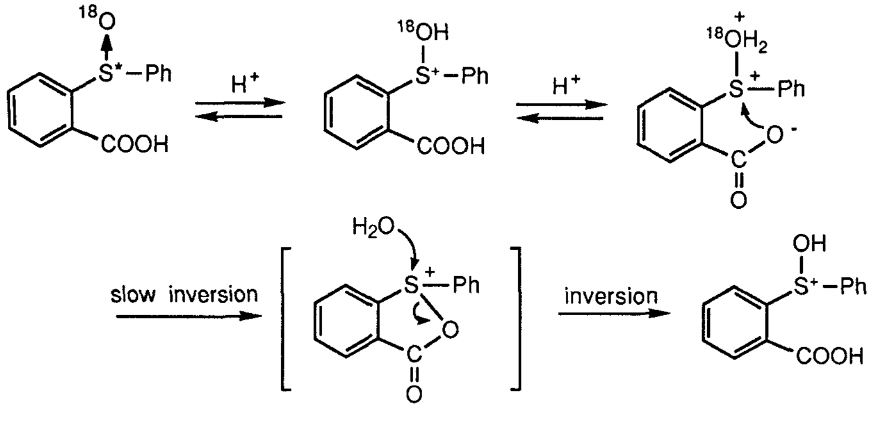


Polychlorodibenzofurane

When a sulfur atom is located in the close vicinity of a nucleophile or a free radicals, it is quite well known that the sulfur atom attracts the attack of these nucleophiles or free radicals. Among numerous examples, only a few examples will be presented here. A strong interaction can be found in the iodine-catalyzed oxidation of *o*-thioanisyl-carboxylic acid in buffer media, as shown below.[11] This is a general acid-base catalyzed reaction, while the *p*-isomer is inert under the condition. Thus, the reaction can be expressed in the following manner, where the solvent kinetic isotope effect, $k_{H_2O}/k_{D_2O} = 2.3$.

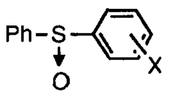


Another would be the facile oxygen exchange reaction of *o*-phenylthiosalicylate sulfoxide in 65.7 % sulfuric acid, as shown below.



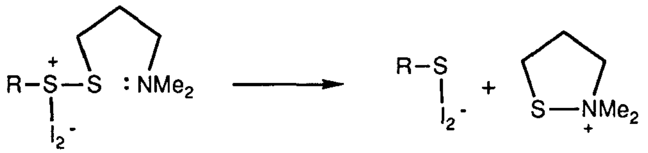
One finds that the *p*-isomer undergo both the ^{18}O exchange and the racemization at nearly the same rates of phenyl *p*-tolyl sulfoxide, while the rate of oxygen exchange is ca. 10^4 times faster than that of the racemization, which is nearly the same as that of the oxygen exchange of phenyl *p*-tolyl sulfoxide, indicating clearly that the interaction of nucleophile and the sulfur atom through the five-membered ring is very much favored, as one see can data in Table 1.[12]

Table 1. Rate Constants of Oxygen Exchange and Racemization of in 65.7 % Sulfuric Acid at 24.8 °C.

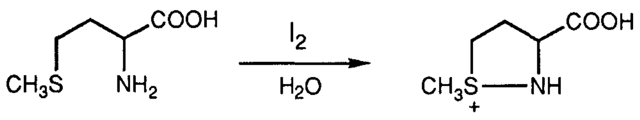


X	$k_{ex} \times 10^5$ (sec^{-1})	$k_{rac} \times 10^5$ (sec^{-1})
o-COOH	3200	0.318
p-COOH	0.736	1.84
o-CH_2COOH	2.01	
p-CH_3	0.768	1.52

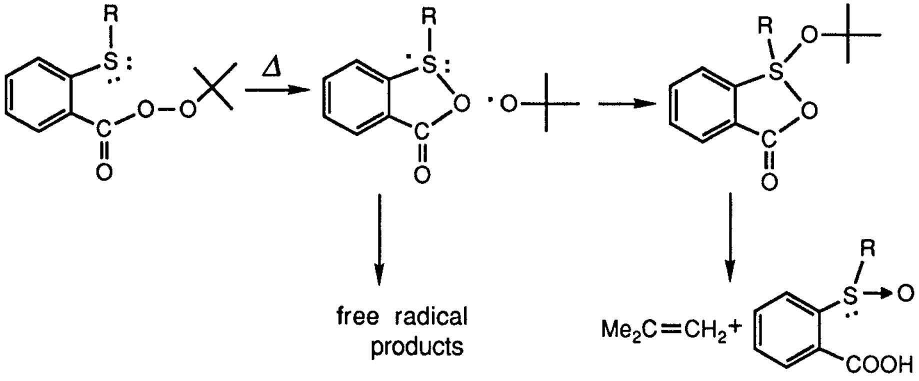
There are many similar examples. Musher, Doi-Takahashi et al. have shown the following reaction.[13]



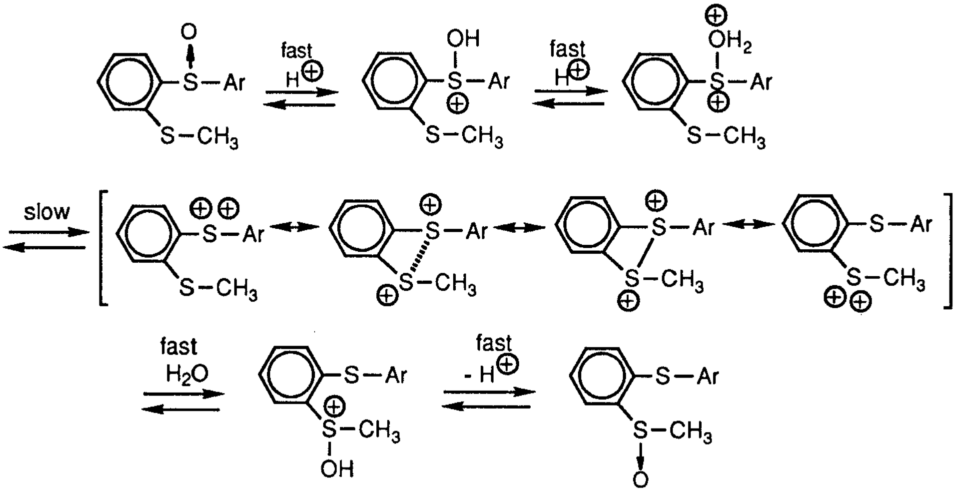
A specially facile ease of the oxidation of methionine may be another one, as shown below.[14]



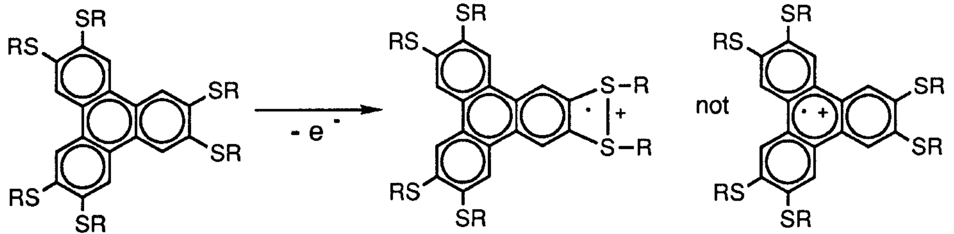
The first observation of hypothetical formation of the sulfurane is also responsible for the facile O-O bond cleavage of *o*-*t*-butylperoxy-methylthioanycilate.[15] Many similar reactions have followed.[15]



Even when the two sulfur atoms are located at *o*-position to each other and capable of forming a four-membered cyclic structure, there was a few cases in which the interaction is substantial. Perhaps the C-S bond is longer and the size of the sulfur atom is larger. Thus, the following oxygen exchange took place as shown below.[16]



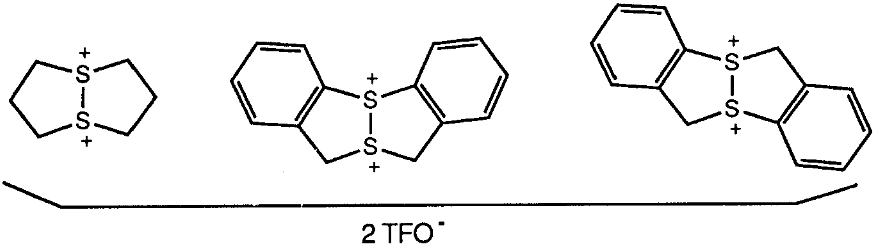
A similar four-membered interaction was observed in the electrolytic oxidation of the following compound.[17]

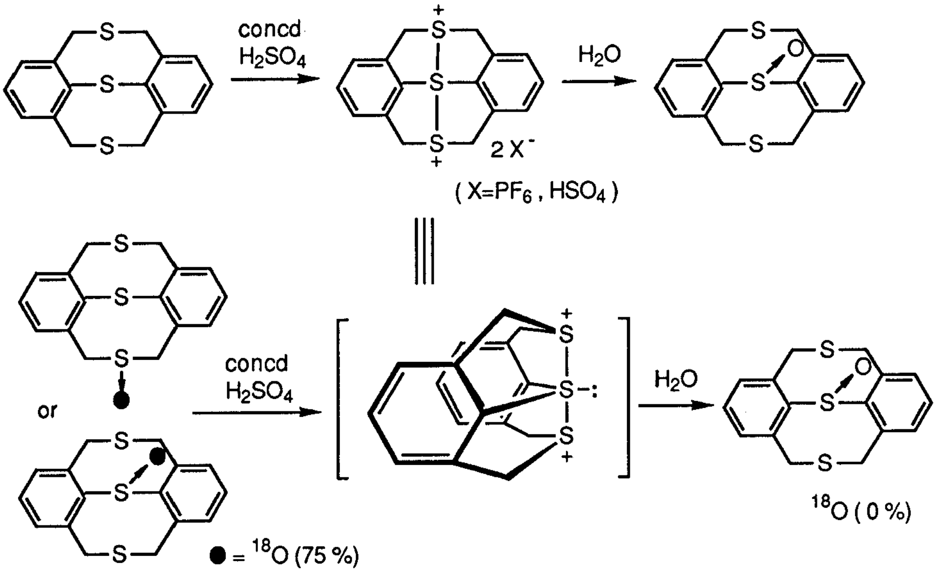


$R = CH_3(CH_2)_5\text{-}$

$R = CH_3(CH_2)_4\text{-}CHD\text{-}$

Numerous examples of five-membered interaction of two sulfur atoms are very well known.[18,19,20,21]





Okuyama et al. were puzzled in explaining the results but suggested that the following mechanistic route involving the nucleophilic attack on sulfur and subsequent transfer of nucleophile,[22] much the same as what we have in our mind. The abridged data of their experiments are shown below in Table 2.

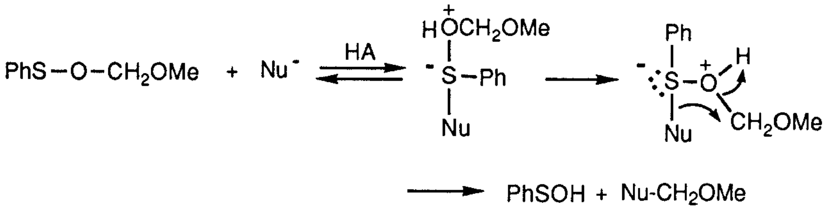
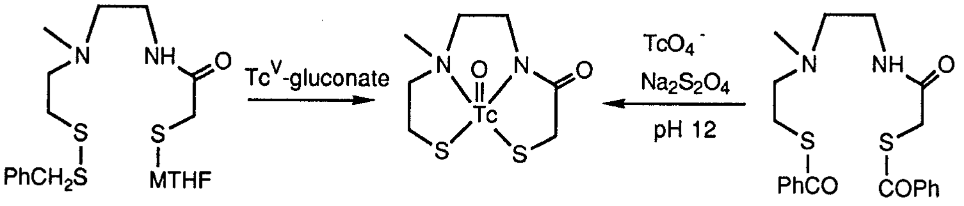


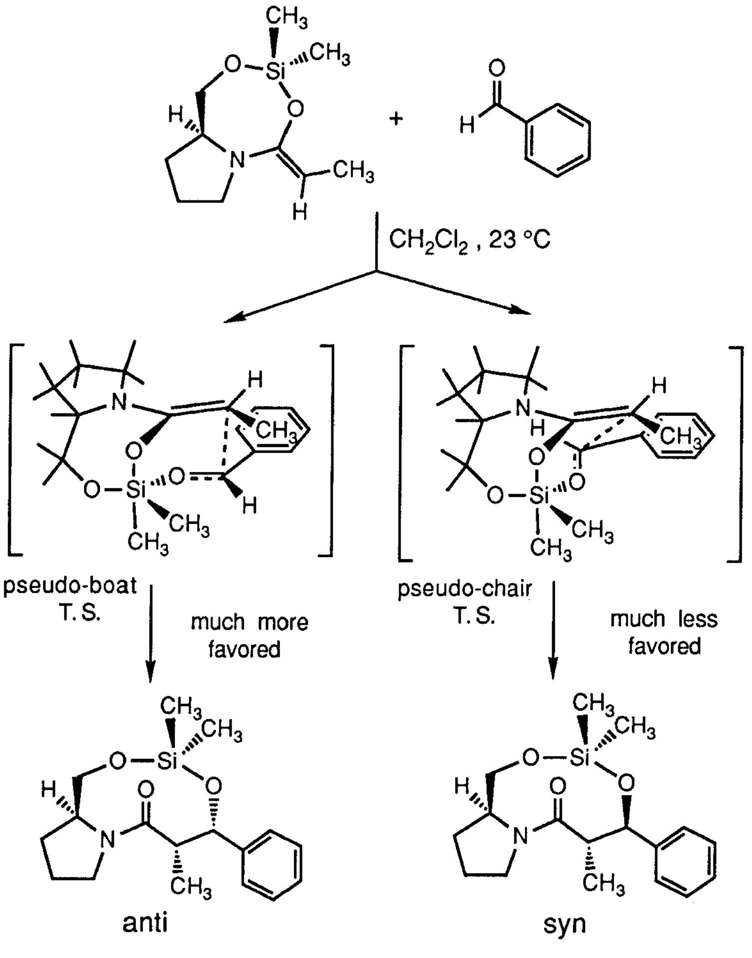
Table 2. Rate Constants for Nucleophilic Catalysis in the Hydrolyses of Ph-S-OCH$_2$OMe, Ph-S(O)-CH$_2$OMe, PhS-OEt, and CH$_3$-I (ionic strength = 0.50 at 25 °C).

Compounds	Ph-S-OCH$_2$OMe	Ph-S(O)-CH$_2$OMe	PhS-OEt	CH$_3$-I
Nucleophiles	k_{Nu}, $M^{-1}s^{-1}$ (rel. value)	k_{Nu}, $M^{-1}s^{-1}$ (rel. value)	k_{Nu}, $M^{-1}s^{-1}$ (rel. value)	k_{Nu}/k_{Cl}
H_2O	2.7×10^{-7}	4.4×10^{-3}	2.4×10^{-3}	0.01
OH^-	4.87×10^{-4}			2.3
Cl^-	0.0015	9.0	17.9	1
Br^-	0.008	54	95.9	2.2
I^-	1.6	950	1160	7.0
SCN^-	73	3500	2950	
$(HOCH_2CH_2)_2S$	3.6	5900	3600	

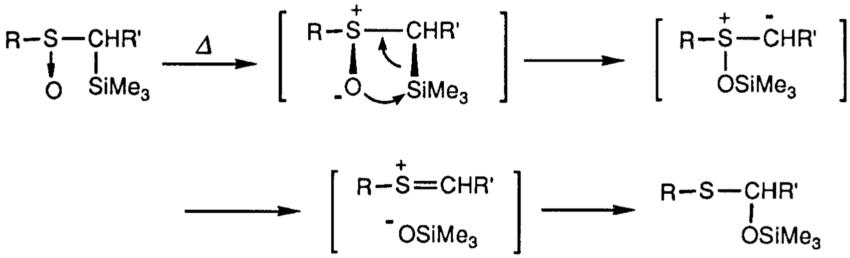
Apparently the cohesive interaction is enhanced by some metal ion. The following is a typical[23] among numerous examples.



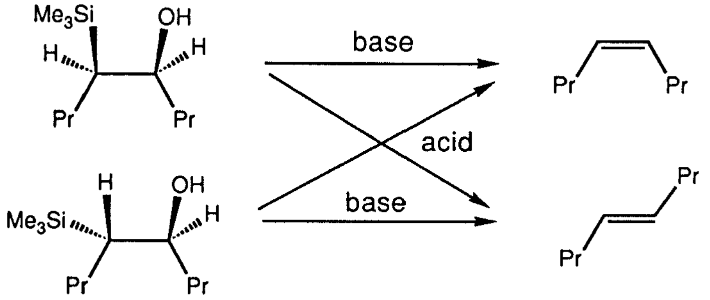
These interactions are not limited only on the sulfur atom but also many other atoms beyond the second row elements. One example is silicon atom which can attract more than mere proton that does not have such a net work of *3d* orbitals for attracting any nucleophile or radical. Thus, the following Aldol type condensation can be achieved so smoothly.[24]



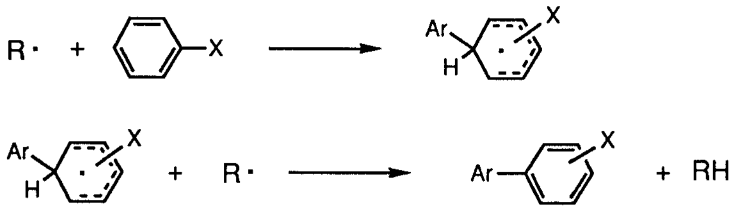
Silo-Pummerer reaction, shown below,[25] may be another one.



Peterson elimination, shown below,[26] is another example.



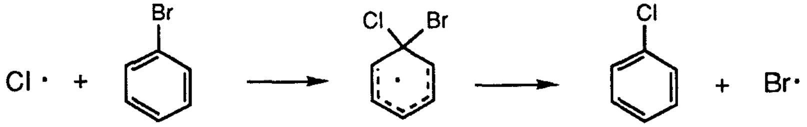
When one looks at the free radical substitution of phenyl group on aromatic compounds,[27] it is easily seen that the substitution at 2-position is more than other ones, if X is an atom beyond the second row element.



Let us look at the works of the late Dick Noyes who studied the following halogen exchange reaction.[28]

$$
\begin{array}{llll}
\mathrm{ArCl} + {}^*\mathrm{Cl}\cdot & \rightleftharpoons & \mathrm{Ar^*Cl} + \mathrm{Cl}\cdot \\
\mathrm{ArBr} + \mathrm{Cl}\cdot & \longrightarrow & \mathrm{ArCl} + \mathrm{Br}\cdot \\
\mathrm{ArI} + \mathrm{Cl}\cdot & \longrightarrow & \mathrm{ArCl} + \mathrm{I}\cdot \\
\mathrm{ArBr} + {}^*\mathrm{Br}\cdot & \rightleftharpoons & \mathrm{Ar^*Br} + \mathrm{Br}\cdot \\
\mathrm{ArI} + \mathrm{Br}\cdot & \longrightarrow & \mathrm{ArBr} + \mathrm{I}\cdot \\
\mathrm{ArI} + {}^*\mathrm{I}\cdot & \rightleftharpoons & \mathrm{Ar^*I} + \mathrm{I}\cdot
\end{array}
$$

Here again, there was not much formation of other products and the suggested mechanism is formulated in the following way.



He has extended the iodine exchange reaction to aliphatic iodides, shown below.[29,30]

$$
\begin{array}{lll}
\mathrm{I^*}\cdot + \mathrm{RI} & \longrightarrow & \mathrm{R}\cdot + \mathrm{I^*I} \\
\mathrm{R}\cdot + \mathrm{I_2^*} & \longrightarrow & \mathrm{RI^*} + \mathrm{I^*}\cdot \\
\mathrm{I}\cdot + \mathrm{I_2^*} & \longrightarrow & \mathrm{II^*} + \mathrm{I^*}\cdot \\
2\,\mathrm{I}\cdot & \longrightarrow & \mathrm{I_2} \\
\mathrm{R}\cdot + \mathrm{I}\cdot & \longrightarrow & \mathrm{RI} \\
2\,\mathrm{R}\cdot & \longrightarrow & \mathrm{R_2} \text{ or } (\mathrm{X} + \mathrm{Y})
\end{array}
$$

$\mathrm{I^*}$ = iodine-131

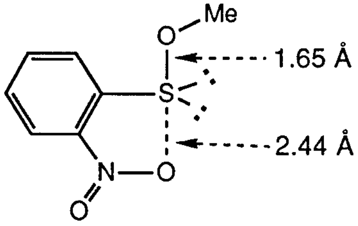
Although the reaction was carried out in polychlorinated hydrocarbons, these are quite different from those of S_N2 or S_N1. Apparently there was practically no product formed by the radical attack of iodine on the other aliphatic moiety.

Thus, when the central atom is beyond the second row in the Periodic Table, this is a quite common phenomenon.

Although the exact attacking site of nucleophiles or free radicals, whether the ipso carbon or the central atom and subsequent ligand coupling, is not clear, the central atom beyond the second row elements in Periodic Table can spread the net work pretty widely using its empty *d* orbitals and would catch any electron-rich nucleophile or free radical, eventually allowing the reaction to proceed.

C. ARE THE SIZE OF COVALENT BOND RADII ADEQUATE ? DOSE THE SIZE OF ORBITAL CHANGE BY CHARGE ?

Although the covalent bond radii, which Pauling assumed,[31] may be quite adequate for all first row elements, they would be somewhat inadequate for atoms of second and third row elements in Periodic Table. It has been so long in my mind since I was writing Sulfur Bonding[32] and hence asked W. C. Hamilton to analyze S-O bond length of *o*-nitrophenylsulfenyl methyl ether. However, the observed value was only slightly shorter than that of the calculated one, as shown below.[33] But, in most cases, the calculated sum

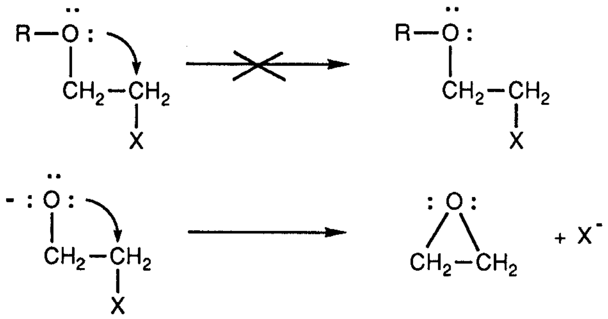


sum of covalent bond radii = 1.70 Å

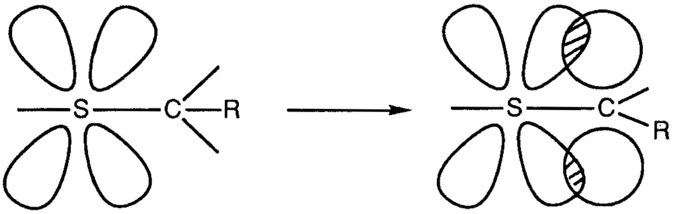
O-S-O angle = 177 °

from covalent bond radii of any particular bond is usually much longer than the observed value.

In the solvolytic reactions of β-heteroatom-substituted alkyl halides or related compounds, the neutral β-alkoxy group, e.g., EtO-, exerts no neighboring group effect, instead reduces somewhat the rate of solvolysis due to the inductive effect of β-oxygen.



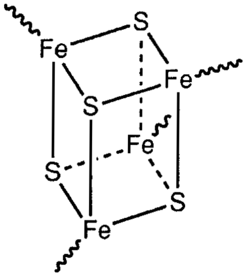
Whereas, the negatively charged β-oxy function, $^{-}$O-, is highly rate-enhancing and shows a large neighboring group effect. This would mean that by putting a negative charge on oxygen, *p* orbitals might diffuse enough to overlap with the vacating *p* orbital or the anti-bonding orbitals on α-carbon.[34] Similarly, by putting a negative charge on α-carbon atom of α-sulfenylcarbanion, the *p* orbital of α-carbon might spread enough to be able to overlap with even the highly diffused *3d* orbitals of adjacent sulfur atom, as shown below.



This unsophisticated concept have led us to uncover the acid-enhancing effect of divalent sulfur groups.[35]

D. WHAT IS THE SPECIAL FUNCTION OF CLUSTER MOLECULAR COMPLEXES LIKE FERREDOXIN ?

Many cluster molecules or complexes are known,[36] but not much works have been carried out why such a molecule, as shown below, is a good redox.



REFERENCES

1. S. Oae, Phosphorus, Sulfur, and Silicon, 59, (1991), 79-113.
2. S.Oae, N. Furukawa, M. Kise and M. Kawanishi, Bull. Chem. Soc. Jpn., 39, (1966), 1212.

3. N. Furukawa and S. Oae, Bull. Chem. Soc. Jpn., 42, (1968), 949.
4. S. Oae, "Organic Sulfur Chemistry: Structure and Mechanism", C. R. C. Press, Chap. 4, (1991).
5. S. Oae and S. Kawamura, Bull. Chem. Soc. Jpn., 36, (1963), 163.
6. S. Oae, Rev. Heteroatom Chem., 1, (1988), 10.
7. B. Meyers, "Current Studies in Inorganic Sulfur Chemistry" at U. S. -Japan Joint Seminar on Organosulfur Chemistry, August-September, Takarazuka, Japan, (1971).
8. S. Oae, Y. Tsuchida and M. Nakai, Bull. Chem. Soc. Jpn., 44, (1971), 451.
9. S. Oae and Y. Tsuchida, Tetrahedron Lett., (1972), 1283.
10. S. Inoue, Ph. D. Thesis at Tokyo Kyoiku Daigaku (predecessor of University of Tsukuba), (1977).
11. W. Tagaki, M. Ochiai and S. Oae, Tetrahedron Lett., (1968), 6131.
12. T. Numata, K. Sakai, M. Kise, N. Kunieda and S. Oae, Chem. Ind. (London), (1971), 576; Int. J. Sulfur Chem., A, 1, (1971), 1.
13. W. K. Musker and J. Takahashi Doi, Rev. Heteroatom Chem., 1, (1988), 120.
14. a) K.-H. Gensch and T. Higuchi, J. Pharm. Sci., 56, (1967), 177; b) D. O. Lambeth and S. W. Swank, J. Org. Chem., 44, (1979), 2632.
15. R. B. Hayes and J. C. Martin, "Sulfurane Chemistry" in "Organic Sulfur Chemistry", edited by F. Bernardi, I. G. Csizmadia and A. Mangini, Elsevier, Chap. 8, (1985).
16. T. Numata and S. Oae, Int. J. Sulfur Chem., A, 1, (1971), 6.
17. N. Boden, R. Borner, R. J. Bushby and J. Clements, Tetrahedron Lett., 32, (1991), 6195.
18. H. Fujihara, J.-J. Chiu and N. Furukawa, J. Am. Chem. Soc., 110, (1988), 1280.
19. H. Fujihara, R. Kawada and N. Furukawa, J. Org. Chem., 52, (1987), 4254.
20. H. Fujihara, R. Akashi and N. Furukawa, Bull. Chem. Soc. Jpn., 60, (1987), 4451; Chem. Lett., (1988), 709.
21. N. Furukawa, Plenary Lecture, ISOCS-15, Caen, France, 1992.
22. a) T. Okuyama, T. Nakamura and T. Fueno, J. Am. Chem. Soc., 112, (1990), 9345; b) T. Okuyama and T. Fueno, ibid., (in print).
23. L. M. Gustavson, T. N. Rao, D. S. Jones, A. R. Fritzberg and A. Srinivasan, Tetrahedron Lett., 32, (1991), 5485.
24. A. C. Meyers and K. L. Widdowson, J. Am. Chem. Soc., 112, (1990), 9672.

25. a) A. C. Brook and D. G. Anderson, Can. J. Chem., 46, (1968), 2115; b) F. A. Carey and O. Hernandez, J. Org. Chem., 38, (1973), 3975; c) F. A. Carey, O. D. Dailey, Jr., O. Hernandez and J. R. Tucker, J. Org. Chem., 41, (1976), 3975; d) E. Vedejs and M. Mullins, Tetrahedron Lett., (1975), 2017.
26. a) P. F. Hudrilik, D. Perterson and R. J. Rona, J. Org. Chem., 40, (1975), 2263; b) P. F. Hudrlik and D. Perterson, J. Am. Chem. Soc., 97, (1974), 1464.
27. O. Simamura, T. Migita, N. Inamoto and K. Tokumaru, Yuriki-Hanno (Free Radical Reactions), Tokyo Kagaku Dojin (1969).
28. R. M. Noyes and D. J. Sibbert, J. Am. Chem. Soc., 75, (1953), 767.
29. J. E. Bujake, Jr. and R. M. Noyes, J. Am. Chem. Soc., 83, (1961), 1547, 1555.
30. S.-W. Wong and R. M. Noyes, J. Am. Chem. Soc., 86, (1964), 3787.
31. L. Pauling, "The Nature of the Chemical Bond", 3rd. Ed., Cornell University Press, Chap. 7, (1960).
32. C. C. Price and S. Oae, "Sulfur Bomding", Ronald Press, (1962).
33. W. C. Hamilton and S. J. LaPlaca, J. Am. Chem. Soc., 86, (1964), 2289.
34. S. Oae, "Historical Development of Sulfur Bonding" in "Org. Sulfur Chemistry", edited by F. Bernardi, I. G. Csizmadia and A. Mangini, Elsevier, Chap. 1, (1985).
35. a) S. Oae, W. Tagaki and A. Ohno, J. Am. Chem. Soc., 83, (1961), 5036; b) S. Oae, W. Tagaki and A. Ohno, Tetrahedron, 20, (1964), 443; c) S. Oae, "Organic Sulfur Chemistry: Structure and Mechanism", C. R. C. Press, Chap. 2, (1991).
36. N. Ueyama and A. Nakamura, "Organic Sulfur Chemistry: Biochemical Aspects", edited by S. Oae and T. Okuyama C. R. C. Press, Chap. 2, (1991).