ORGANIC SULFUR CHEMISTRY

THEORETICAL AND EXPERIMENTAL ADVANCES

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Edited by

F. Bernardi
Istituto di Chimica Organica, Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

I.G. Csizmadia
Lash Miller Chemical Laboratories, 80 St George Street, Toronto, Canada M5S 1A1

A. Mangini
Istituto di Chimica Organica, Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

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LIST OF CONTRIBUTORS

J. BÁLINT
BIOGAL Pharmaceutical Works
DEBRECEN, Hungary 4042

R. BOGNAR
Research Group of Antibiotic Chemistry
Hungarian Academy of Sciences
DEBRECEN, Hungary 4010

G. CAPOZZI
Dipartimento Farmaco-Chimico
Università di Messina
MESSINA, Italy 98100

M. CINQUINI
Istituto di Chimica Industriale
Università di Milano
MILANO, Italy 20133

F. COZZI
Istituto di Chimica Industriale
Università di Milano
MILANO, Italy 20133

A. FAVA
Istituto di Chimica Organica
Università di Bologna
BOLOGNA, Italy 40136

I. HARGITTAI
Research Laboratory for Inorganic Chemistry
Hungarian Academy of Sciences
BUDAPEST, POB 117, Hungary 1431

R.A. HAYES
Roger Adams Laboratory
University of Illinois
URBANA, Illinois, USA 61801

I. KAPOVITS
Institute of Organic Chemistry
Eotvos University (ELTE)
BUDAPEST 8, Hungary 1445

A. KUCSMAN
Institute of Organic Chemistry
Eotvos University (ELTE)
BUDAPEST 8, Hungary 1445

L. LUNAZZI
Istituto di Chimica Organica
Università di Bologna
BOLOGNA, Italy 40136

J.C. MARTIN
Roger Adams Laboratory
University of Illinois
URBANA, Illinois, USA 61801

G. MODENA
Istituto di Chimica Organica
Università di Padova
PADOVA, Italy 35131

F. MONTANARI
Istituto di Chimica Industriale
Università di Milano
MILANO, Italy 20133

S. OAE

Okayama University of Science

Ridai-cho 1-1

OKAYAMA, Japan 700

C. PARADISI

Centro CNR Meccanismi di Reazioni Organiche

PADOVA, Italy 35131

G.F. PEDULLI

Istituto di Chimica Organica

Università di Cagliari

CAGLIARI, Italy 09100

M. RAKOSI

Research Group of Antibiotic Chemistry

Hungarian Academy of Sciences

DEBRECEN, Hungary

I.W.J. STILL

Department of Chemistry

University of Toronto

Erindale Campus

MISSISSAUGA, Ont., Canada L5L 1C6

G. SCORRANO

Istituto di Chimica Organica

Università di Padova

PADOVA, Italy 35131

S. WOLFE

Department of Chemistry

Queen's University

KINGSTON, Ont., Canada K7L 3N6

PREFACE

Organic sulfur compounds represent a special topic in chemistry. On the one hand we tend to consider divalent sulfur to be analogous to divalent oxygen and there is a bit of truth in that analogy. On the other hand sulfur is sufficiently different from oxygen as manifested in its higher oxidation states that occur in some organic compounds as well·as in the existence of hypervalent sulfur compounds. These structural differences always puzzled chemists as far as the interpretation of bonding in sulfur compounds was concerned. Furthermore the reactivity of sulfur compounds, because of the structural characteristics outlined above, is in fact expected to offer some unusual behaviour.

The authors of the present volume attempt to put together a mosaic picture of organic sulfur chemistry in the hope that some understanding will emerge from studies that are concerned with molecular structure, sulfur bonding and chemical reactivity. Furthermore this general area is augmented by a number of special topics including the stereochemistry of optically active organic sulfur compounds, photochemistry of organic sulfur compounds and sulfur containing natural products such as flavonoids.

All in all the Editors of this volume are proud to present this monograph to the world community of chemists as a unified effort of twenty internationally recognized authors specialized in the field of organic sulfur compounds.

F. Bernardi   I.G. Csizmadia   A. Mangini

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Chapter 1

HISTORICAL DEVELOPMENT OF SULFUR BONDING: A VIEW OF AN EXPERIMENTAL
ORGANOSULFUR CHEMIST
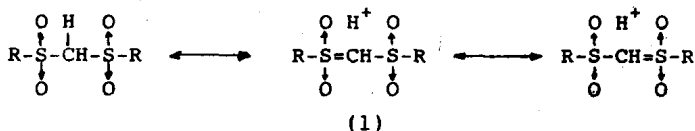
Shigeru OAE
Okayama University of Science
Ridai-cho 1-1
Okayama 700, Japan

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1. INTRODUCTION

Before the Second World War, there was no book which dealt organic sulfur chemistry in general. Only during the World War II, one book, "Organic Chemistry of Sulfur—Tetracovalent Organic Sulfur Compounds", by Suter[1] and a chapter, "Organic Sulfur Compounds", by Connor[2] appeared in Gilman's Advanced Organic Chemistry, Vol I. Neither book, however, contained any remark on bonding characteristics of the sulfur atom, nor did they carry any mechanistic explanation on various reactions involving the organic sulfur compounds, although sulfur atom has been considered capable of expanding its valence shell beyond octet, unlike oxygen atom.[3,4,5] One of a few chemical behaviors,[6,7,8] presumed to involve the expansion of valence shell of the central sulfur atom beyond octet, was the high carbon acidity of bis(sulfonyl)methane (1)[6] before the World War II. Rothstein was the first one of those who

$$\underset{O}{\overset{O}{\underset{\downarrow}{\overset{\uparrow}{R-S}}}}\overset{H}{\underset{}{\overset{}{C}H}}\underset{O}{\overset{O}{\underset{\downarrow}{\overset{\uparrow}{S-R}}}} \longleftrightarrow \underset{O}{\overset{O}{\underset{\downarrow}{\overset{\uparrow}{R-S}}}}=\overset{H^+}{C}H\underset{O}{\overset{O}{\underset{\downarrow}{\overset{\uparrow}{S-R}}}} \longleftrightarrow \underset{O}{\overset{O}{\underset{\downarrow}{\overset{\uparrow}{R-S}}}}\overset{H^+}{\underset{}{C}H}=\underset{O}{\overset{O}{\underset{\downarrow}{\overset{\uparrow}{S-R}}}}$$

(1)

advocated the valence shell expansion in the chemical behaviors of divalent sulfur compounds,[9] though the suggested mechanism had to be corrected somewhat years later.[10]

Although spd hybrid orbitals were discussed early by Hultgren,[11] Kimball was the first who suggested, based on the nature of 3d orbitals, that overlapping between 2p and 3d orbitals in π-bond formation does not require any particular angular arrangement,[12] unlike the 2p-2p or 2p-π overlapping which demands coplanarity for maximum overlapping. However, it was much later when Craig and co-workers pointed out from theoretical considerations,[13,14] and more explicitly by Coulson[14] that highly diffused 3d orbitals could be utilized for hybridization with p- or π-orbitals more effectively if the electron affinity of the sulfur atom is increased, as for example, by

bonding to some highly electronegative groups, such as F in SF_6 or by acquiring a formal positive charge, such as that in a sulfone or a sulfonium group. Thus, following Pauling,[15] the concept of valence shell expansion, using $3dz^2$ orbital to form trigonal bypyramid sp^3d hybridization for SF^4, and the use of both the $3dz^2$ and $3dx^2-y^2$ orbitals to give the hybrid sp^3d^2 orbitals to accomodate octahedral symmetry for SF_6 were postulated.

The small mesomeric moment, 1.25 D, for thiophene and the marked shortening of bonds of thiophene ring were taken to suggest an appreciable contribution of the interaction of sulfur's d-π orbitals in the molecule,[16,17] in keeping with the theoretical treatments of this molecule done somewhat later.[18,19] Meanwhile, Powell and Eyring[20] suggested, based on the observation that the heat of reaction, S_8(ring) $\rightarrow S_x$(chain), is 27.5 kcal/mole per sulfur atom, which is much lower than the dissociation energy of a S-S bond, 63.8 kcal/mole, in the reaction, $S_8 \rightarrow 8S$, that the resonance due to the participation of 3d orbitals is high in both S_8 and S_x chain polysulfur, particularly in S_8, despite the non-planar structure of the molecule. The gradual red-shift of UV absorption as the increase of number of sulfur atoms in the polysulfide linkage in both benzyl and p-tolyl polysulfides observed by Minoura[21,22] has been taken to support the extended conjugation through polysulfide chain as in the conjugated polyenes.[23]

In accordance with the steric insensitivity predicted for 3d orbital resonance,[11,12] a few remarkable experimental data to support the concept came out in early fifties. One is the work of Kloosterziel and Backer to show the lack of steric inhibition of electron-withdrawing conjugative effect of methanesulfonyl group in the acid dissociation of 4-methanesulfonyl-3,5-xylenol.[24] Other examples are the works of Doering and his coworkers on the highly acidic nature of the bridge-head proton of 4-methyl-2,6,7-trithiabicyclo[2,2,2]-octane-2,2,6,6,7,7-hexaoxide,[25] and the facile base-catalyzed hydrogen isotopic exchange of another bicyclo[2,2,1]heptane-1-sulfonium iodide.[26] Yet other representative examples are the higher acidities of p-sulfur group-substituted phenols than those of the m-isomers and the lack of steric inhibition of resonance by bulky m-substituents of p-sulfur group-substituted phenolate ions, observed by Bordwell,[27,28] Oae,[29] Price and coworkers.[30] A large number of literatures have appeared since then to explain many chemical phenomena of organosulfur compounds,[14,22,31-43] on the basis of participation of 3d orbitals. The 3d-orbital resonance effect of dicoordinate sulfur was earnestly advocated by Oae and coworkers in the early sixties[35] since their pio-

neering work on the unusually high kinetic carbon acidity of 4-methyl-2,6,7-trithiabicyclo[2,2,2]octane,[44] however, there were many ambiguous experimental data which were explained uncritically in term of 3d-orbital resonance effect of sulfur. Cautions were warranted against this trend by many theoretical chemists, one typical comment being that of Hoffmann who wrote, "far too often have 3d orbitals been invoked as a kind of theoretical dens ex machina to account for facts apparently otherwise inexplainable.....".[45] The spectroscopic work of Mangini and coworkers on various organic compounds containing divalent sulfur has not shown any evidence of valence shell expansion,too.[46]

The possible involvement of 3d orbital conjugation in various chemical behaviors of organosulfur compounds has begun to be challenged in the late sixties on the basis of molecular orbital calculations first by Wolfe, Csizmadia and coworkers,[47-50] and later by Bernardi et al.,[51] Epiotis et al.,[52] Florey et al.,[53] Musher,[54] along with Streitwieser et al.[55] and Lehn and coworkers.[56] Even in the α-sulfinyl carbanion[50] and the α-sulfonyl carbanion,[57] the participation of 3d orbitals of sulfur has been considered to be rather insignificant according to the prevailing M.O. calculations around that time, despite the long standing postulate of Moffitt and Koch who emphasized the importance of the participation of 3d orbitals of sulfur in the sulfone,[57] and the theoretical reevaluation of the model by Janssen.[58]

The participation of 3d orbitals, once seemingly thoroughly ruled out in the theoretical considerations, is reviving again, using a new basis set for ab initio calculations, especially α-sulfinyl and α-sulfonyl carbanions.[59]

The π-bonding between 3p orbitals of sulfur and 2p orbitals of another atom such as carbon or nitrogen has been considered to be less effective than that between 2p orbitals of oxygen and 2p orbitals of either carbon or nitrogen.[22,60] Numerous experimental results have been accumulated to support the markedly higher π-conjugative effect of oxygen than that of sulfur. While the recent OEMO calculation[61a] and several experimental observations of α-sulfenyl carbocation[61b] seem to refute the above-mentioned consideration, the superior electron-releasing π-conjugative effect of oxygen over that of sulfur in the reactions in somewhat weakly polar solvents and others in neutral systems does seem to remain true. The recent ab initio SCF-MO calculation[62] also support the long standing consideration.

Due to the markedly higher electronegativity and greater polarizability of sulfur atom (2.44) than those of oxygen (3.50), sulfur is an excellent nucleophile. Despite the less basic cheracter of

RS⁻ than that of RO⁻, RS⁻ is far better nucleophile than RO⁻ as summarized later by Pearson in his HSAB theory[63] and also in view of the much higher neighboring group effect of RS- or ⁻S- group than that of RO⁻or ⁻O- group.[64]

Earlier, polycoordinate sulfur molecules such as SF_4 and SF_6 were considered to be made up by hybridization with 3d orbitals of sulfur atom such as $3sp^3d$ and $3sp^3d^2$.[13,14] However, the concept of three center four electron σ-bonding — namely hypervalency —, first postulated by Rundle[65] and Pimentel[66] and developed later by Musher,[67-70] Hoffmann[45] and others,[70-72] has completely displaced the old 3d orbital hybridized model for trigonal bypyramid molecules. The actual isolations of stable sulfuranes by Kapovits et. al.[73] and Martin and his coworkers[74] have firmly established the structure of hypervalent sulfur compounds, i.e., sulfuranes. These discoveries of sulfuranes, together with the concepts of Berry's pseudo-[75] and turnstile rotations,[76] have given an essential guidance to many nucleophilic reactions on polycoordinate sulfur atom such as nucleophilic substitution with retention of configuration on chiral tri-coordinate sulfur[77] and the ligand coupling through σ-sulfuranes.[77] All through the accumulation of these little steps of developments, the organic sulfur chemistry has evolved to the present stage. A new comer in organic sulfur chemistry may think how little it has developed in these decades. However, for those who have walked through the undeveloped jungle of organic sulfur chemistry forest for nearly four decades, organic sulfur chemistry seems to have grown from an acorn to a sizable oak tree. In the following sections, which are divided according to the number of coordination around sulfur, readers are invited to more detailed discussions of the development of organic sulfur bonding.

2. ELEMENTAL SULFUR AND POLYSULFIDES

The stable sulfur molecule, which has a simple crown structure of puckered eight-membered ring, S_8, in the orthorhombic and mono-clinic forms,[78] as well as in the vapor at ordinary temperature,[79] is known to have a dihedral angle of 103° around the S-S linkage, similar to that around the S-S linkage of such a disulfide as p,p'-dibromodiphenyl disulfide.[80] Other polysulfides, such as trisulfides and tetrasulfides are also considered to have similarly linear, non-planar and skewed conformations. Despite the skewed, chain conform-ation, both eight-membered S_8 and polysulfides seem to conjugate just

as efficiently as the planar conjugated polyene systems, as was exemplified by the increase of UV absorption intensity and bathochromic shift with the increase of the number of sulfur atom.[81,82] The rather strong conjugation of S-S linkage and non-coplanarity of
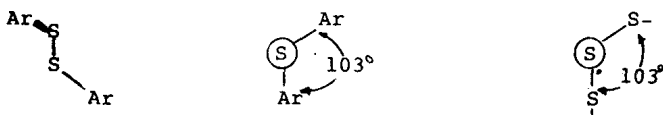
polysulfide chain has been considered to indicate that the conjugation involves participation of 3d orbitals,[20,83] although there was a molecular orbital treatment which suggested that the first UV absorption band of saturated organic disulfides is associated with an electronic transition from the anti-π-orbital (formed by combination of $3p\pi$-atomic orbitals) to the antibonding σ-orbital which is insensitive to the angle.[84] These models for the strong conjugation of S-S linkage, have explained why so few branched molecules of polysulfides have been isolated and the remarkably strong S-S bond, (e.g.,72 kcal for $C_2H_5SSC_2H_5$) as compared to the O-O bond, (e.g.,32 kcal for $C_2H_5OOC_2H_5$), and the Lewis acid nature of sulfur.
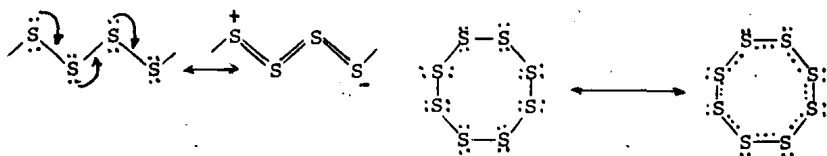
Dissociation energies of a few represntative S-S bonds are listed in the TABLE 1 together with those of O-O bonds. Not only the TABLE 1.

Dissociation Energies of Representative S-S Bonds and O-O Bonds[60,85]

Compound	Bond Dissociation Energy (kcal/mole)	Compound	Bond Dissociation Energy (kcal/mole)
$C_2H_5O-OC_2H_5$	32	PhS-SPh	20-26
HO-OH	48	$(p-CH_3C_6H_4S-)_2$	36-32
HS-SH	72	$(p-MeOC_6H_4S-)_2$	29-35
CH_3S-SCH_3	73	$(p-O_2NC_6H_4S-)_2$	45-52
$CH_3S-SC_2H_5$	72	HSSSH	61-64
$C_2H_5S-SC_2H_5$	70	HS_5H	62-63
$PhCH_2S-SCH_2Ph$	62-68	$-S_n-$ (n=5×10^4)	32
$C_{18}H_{37}S-SC_{18}H_{37}$	60-66	S_8	52-63
		$Alk-S_2-S_2-Alk$	32-36

conjugation of S-S linkage, but also the less repulsion of lone electron pairs due to the longer S-S linkage (2.04 Å) than O-O linkage (1.47 Å) are partly responsible for the higher dissociation energy of S-S bond than that of O-O bond. The low dissociation energy of S-S bond in diaryl disulfides is undoubtedly due to the resonance stabilization of ArS· radical, and the repulsive interaction along the S-S linkage seems to be reduced by the electron-withdrawing two p-nitro groups. However, the very low dissociation energy of S-S bond of unsubstituted diphenyl disulfide is somewhat intriguing. It is interesting to note that S-S bond in polysulfide radical, e.g. RS_2-S_2·, (47.5 ± 2 kcal/mol), is substantially weaker than that in disulfide radical, e.g. CH_3-S·, (53 ± 1 kcal/mol).[86]

The bond length of S-S linkage has been suggested by Davis to be related with the reactivity. According to Davis, the stable S_8 molecule has an average S-S bond of 2.04 Å, the average S-S linkage of S_6 is 2.06 Å, and that of polymeric sulfur, S_x, is 2.07-2.08 Å, while the relative rates of S_8, S_6 and S_x in the reaction with triphenylphosphine have been reported to be 1, 25,300 and more than 10^5, respectively.[87] However, the extraordinarily large difference in rates with the slight variation of bond length is rather difficult to swallow.

The bond distances of S-S linkages in several representative compounds are listed in the following TABLE 2.[88] The extremely short S-S bond length of S_2F_2 has been considered to be due to the additional π-bonding character of the particular S-S linkage.[89] The

TABLE 2

Bond Lengths of S-S Linkages in Several Representative Sulfur Compounds [88]

Compound	Bond Length (Å)	Compound	Bond Length (Å)
FS-SF	1.88	$CF_3S-S-SCF_3$	2.06
$^-O_3S-S^-$	1.97	$PhSO_2-S-SO_2Ph$	2.07
$CH_3SO_2-S^-$	1.98	$ArSO_2-SAr$	2.09
$ClS-SCl$	2.05	$^-O_3S-SO_3^-$	2.14
CF_3S-SCF_3	2.05	$^-O_3S-S-SO_3^-$	2.15
S_6	2.057	$^-S-S^-$	2.25
S_8	2.06	$^-O_2S-SO_2^-$	2.39

relatively short bond lengths of S-S linkages in $CH_3SO_2S^-$ and $S_2O_3^{2-}$

have also been ascribed to the somewhat larger partial double bond character of the S-S bond in these compounds than that in S_8 or ordinary disulfides. Dithionite ion, $^-O_2S-SO_2^-$, has an unusually long S-S bond, i.e. 2.39 Å. This is mainly due to the charge repulsion between the negatively charged oxygen atoms of both terminals. The bond is definitely weak and readily dissociates to two SO_2^- radicals[90] which give a strong e.s.r. signal.[91] The bond energy of S-S linkage is believed to be inversely proportional to the three power of the bond distance.[92] Then, the S-S bond energy of $^-O_3S-S^-$ would be 14% higher than that in S_8 or ordinary disulfides, while that of dithionite ion would be 36% weaker. It is interesting to note that the S-S bond length in polysulfides changes with the substituent as shown in the following three compounds. The S-S bond bound to $-S^-$ is short, while that linked with SO_3^- is long. How these different S-S bond lengths would reflect on the reactivities

$$CH_3SO_2 \underset{\text{2.11Å}}{\rule{2cm}{0.4pt}} S \underset{\text{2.04Å}}{\rule{2cm}{0.4pt}} S\text{-}SO_2CH_3 \qquad {}^-O_3S \underset{\text{2.11Å}}{\rule{2cm}{0.4pt}} S \underset{\text{2.04Å}}{\rule{2cm}{0.4pt}} S\text{-}SO_3^-$$

$$^-S \underset{\text{1.99Å}}{\rule{2cm}{0.4pt}} S \underset{\text{2.11Å}}{\rule{2cm}{0.4pt}} S \underset{\text{2.03Å}}{\rule{2cm}{0.4pt}} S\text{-}S^-$$

in nucleophilic, electrophilic and homolytic reactions on S-S bond? We have to await the answer till some experimental data would come out.

The dihedral angle around S-S linkage in S_8 is known to be 99° and that in ordinary dialkyl disulfides is 103°.[88,93] Deviation from the normal dihedral angle, circa 100°, creates tortional strain and weakens the S-S bond. This can be seen in the lower thermodynamic stability of S_6, in which the dihedral angle is 74.5°, than that of S_8. The better example would be the five-membered 1 2-dithiolane

(2)

4-carboxylic acid (2) of which the dihedral angle is 26.6° ± 10.[94] The S-S bond length of this compound is about 0.04 Å longer than the normal tortion-free S-S bond and hence the S-S bond is weaker than that of the ordinary S-S bond. Indeed, Fava et al. found[95] that the rate of nucleophilic cleavage of S-S bond in 1,2-dithiolane by n-BuS$^-$ is ca. 5,000 times higher than that in open chain dibutyl disulfide, as shown below. Although the rates differ markedly,