

THE EXPANSION OF THE SULFUR OUTER SHELL

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I. INTRODUCTION

Sulfur belongs to the subgroup VIB and has the configuration $(3s)^2(3p_x)^2(3p_y)(3p_z)$ in the outer shell; this is an *M* shell and has vacant *3d* orbitals which also could be used in bond formation. There is indeed rapidly growing evidence that in certain sulfur compounds such an expansion above the octet does occur.

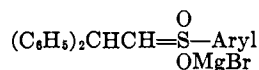
This review reports most (but not all) cases in the literature in which explanations based on expansion have been advanced. In fact, the data presented will be representative and as such are probably fairly complete. However, it is possible that important results may not be included, because the literature of some countries is available to the author only as abstracts.

For both practical and theoretical reasons compounds containing sulfur-oxygen bonds will be reviewed separately.

HISTORICAL

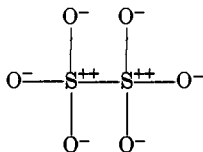
Some of the historical high points have been reviewed by Phillips, Hunter, and Sutton (154).

Before the advent of the Lewis octet theory, the maximum covalency ascribed to sulfur was six, which is its group number in the Periodic System. Later, the Lewis or octet structure was almost generally accepted. Yet the possibility of expansion in second-row elements was never disregarded. In 1930, Ingold and Jessop (95) explained the paraffinic decomposition of sulfones by alkali by invoking a decet structure for sulfur; earlier, Fenton and Ingold (77) had postulated in the paraffinic decomposition of phosphonium salt, addition of the hydroxide ion to the tetrasubstituted phosphorus atom. A few years later certain reactions of sulfones similar to those of the ketone analog were found, such as the addition of Grignard reagents to α, β -unsaturated sulfones (109) and the Michael condensation between benzyl *p*-tolyl sulfone and benzalacetophenone (49); the product of the first reaction was formulated as I:



I

For the second reaction it was considered plausible that the activation of the sulfonyl group on the adjacent methylene group would involve expansion of the valence shell of sulfur. The idea of expansion was also held by Rothstein (160). In 1937 serious doubt as to the validity of the octet theory for elements of the second and later rows of the Periodic Table arose. Pauling and Brockway (153) pointed out that the remarkable stability of dithionic acid, $\text{H}_2\text{S}_2\text{O}_6$, and of hypophosphoric acid, $\text{H}_4\text{P}_2\text{O}_6$, is obviously in conflict with the octet theory, since in the Lewis structures such as



there are similar charges on adjacent atoms. Interatomic distances were also not in accord with the octet formulas (151). Since the late 1930's there have been a very large number of cases which indicate or suggest a swelling of the outer shell of sulfur.

II. THEORETICAL

A. THE NATURE OF THE d ORBITALS

It is worthwhile to recall briefly the nature of d orbitals. The notation will be that of Eyring, Walter, and Kimball (69).

There are five d type orbitals, three of which are shown in figures 1 to 3. The other two, d_{xy} and d_{yz} , are

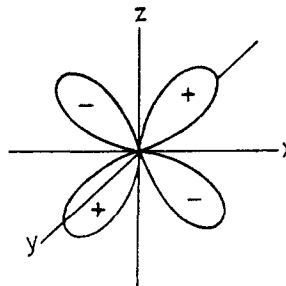


FIG. 1. The d_{xz} orbital

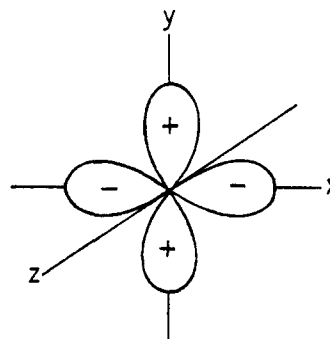


FIG. 2. The $d_{x^2-y^2}$ orbital

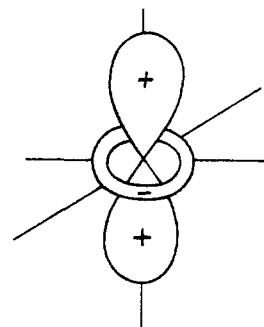


FIG. 3. The d_{z^2} orbital

identical with the d_{xz} orbital, except for the relation to the axes. The four orbitals of similar shape show maxima in four directions and have two nodal planes. The d_{z^2} and $d_{x^2-y^2}$ orbitals are sometimes referred to as d_γ orbitals and the other as d_ϵ orbitals.

B. ENERGY CONSIDERATIONS

Arndt and Eistert (5) pointed out that since argon is chemically inert, the energy of promotion of the electron to a $3d$ orbital should be prohibitive and hence sulfur does not increase its valence shell. Another fact which *a priori* does not support expansion is the nature of the $3d$ electrons. They are too weakly bound and too diffuse; hence they are not well suited for binding and the energy gained by the increased covalency would not make up the energy of promotion. However, modi-

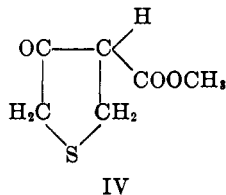
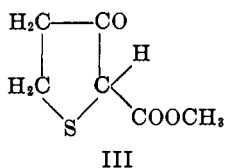
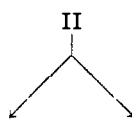
fications occur in molecule formation by polarization due to the attached groups (83), and indeed it is the very electronegative atoms which permit the highest covalency of the central atom. Thus sulfur forms a hexahalide only with fluorine. The function of the electron-attracting groups is to contract the $3d$ orbital (53). Craig and Magnusson (54) have investigated theoretically the problem of the utilization of d orbitals. They described a model in which the ligands are represented by six point positive charges in octahedral disposition. The calculated contraction would permit the $3d$ orbital to be used in covalent binding, of either the σ or the π type. It is interesting that the model indicates that the energy of promotion of the electron to the $3d$ orbital may be increased by the perturbing field. What is important is that the energy resulting from bond formation overbalances the energy of promotion. The hexacovalent compound SF_6 exists because two electrons are promoted to $3d$ orbitals and sp^3d^2 hybridization occurs.

It is to be noted that the energy of $4s$ electrons is similar to that of $3d$ electrons. Yet only in very rare instances (113) does the utilization of $4s$ orbitals come into consideration.

III. EXPANSION IN DIVALENT SULFUR BONDED TO TWO ATOMS

A. SULFIDES

There is abundant evidence that sulfur has a strong activating influence on the hydrogen atoms of an α -carbon atom. Woodward and Eastman (197) found that when α,β' -dicarbomethoxymethyl ethyl sulfide



(II) undergoes the Dieckman cyclization at low temperatures, the product III is formed in larger amounts. This indicates that of the two possible anions (V and

VI), the latter, in which the negative charge is adjacent to sulfur, is the more probable.



V

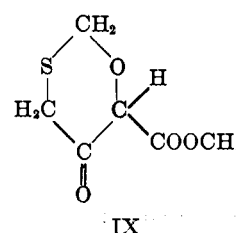
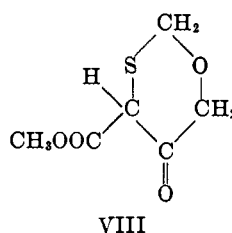


VI

This acidifying effect of sulfur may be even stronger than that of oxygen, a fact contrary to that expected from considerations of inductive effects. Thus, when compound VII undergoes the Dieckman condensation, the product is VIII and not IX (37).

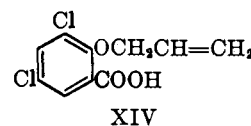
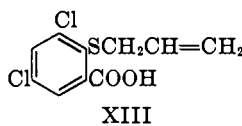


VII

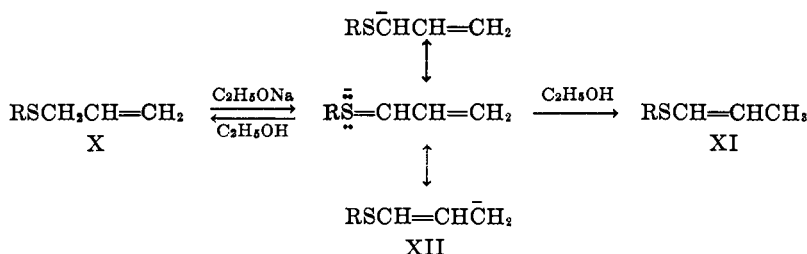


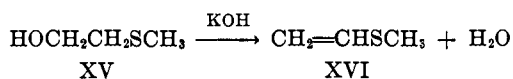
The stabilization of a carbanion by adjacent sulfur is evident from the fact that alkyl or aryl allyl sulfides (X) are readily isomerized by base to the corresponding propenyl sulfides (XI) through the carbanion (XII) (184). Thus, when the reaction is run in deuterioethanol, there is incorporation of two deuterium atoms in the propenyl derivatives, as might be expected from the above mechanism.

Further evidence is the fact that under conditions which isomerize the sulfur compound XIII, the oxygen analog (XIV) is recovered unchanged (185).

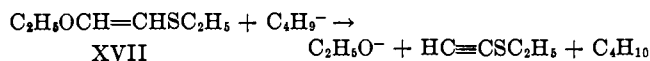


On heating β -hydroxyethyl methyl sulfide (XV) with potassium hydroxide, methyl vinyl sulfide (XVI) is formed (3, 192).

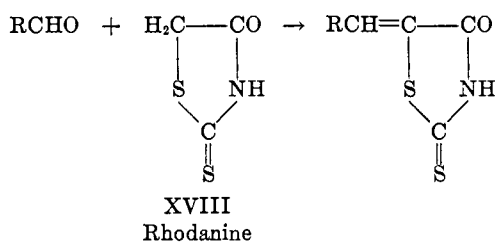




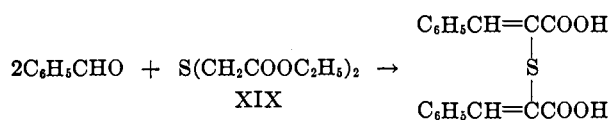
Similarly, on treatment of 1-ethoxy-2-ethylthioethene (XVII) with butyllithium, ethanol is eliminated and a mercaptoacetylene is formed (147, 193).



Regarding the bis-substituted mercapto- and bis-substituted alkoxyethylenes, only the former are able to react with butyllithium (147). Volger and Arens (193) believe that expansion of the sulfur shell contributes to the easy condensation of rhodanine (XVIII) with aldehydes



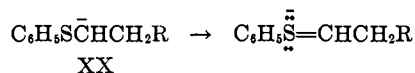
and to the condensation of diethyl thiodiglycolate (XIX) with benzaldehyde.



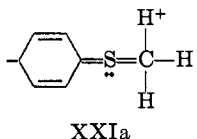
According to Parham and Motter (146) the swelling effect is said to be responsible for the addition of alkyl-lithium compounds to phenyl vinyl sulfide, a reaction not shown by the analogous vinyl ethers.



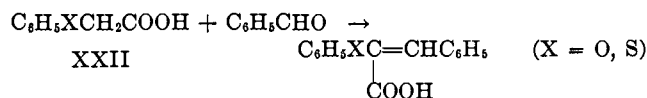
The driving force would be the stabilization of the carbanion XX by sulfur:



The fact that metalation of methyl phenyl sulfide occurs in the methyl group (87) and not in the ring, as in the case of anisole, has been explained (15) by postulating contribution of hyperconjugated structures such as XXIa, which lead to activation of the hydrogen atoms.

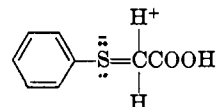


Essentially the same explanation as above has been suggested (16) to account for the higher reactivity of phenylthioglycolic acid (XXII: X = S), as compared with phenoxyacetic acid (XXII: X = O), towards benzaldehyde.



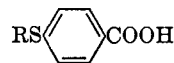
Indeed, if the inductive effect were the dominant factor, the reverse order should have been observed.

However, structures such as



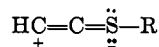
appear to be unimportant because no condensation takes place when phenylthioglycolic acid is replaced by alkylthioglycolic acids (16).

Further, analogous structures have been invoked again (14) to account for the fact that in alkylmercapto-benzoic acids the pK_a decreases when R changes from

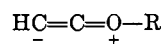


methyl to ethyl to isopropyl, that is, with the decreasing number of hyperconjugated structures. The inductive effect alone should have produced a reverse order. This explanation for these findings, while attractive, should be considered tentative, because there is no abundant evidence that structures in which sulfur is flanked by two double bonds may be very important. Moreover, regarding the case of metalation of methyl phenyl sulfide, it may further be stated that (1) there is no evidence of expansion in the ground state of this compound (122, 124), (2) nuclear metalation is effected by diethylbarium or strontium (88), and (3) when the methyl group is substituted by a higher alkyl group, only nuclear metalation is observed (88).

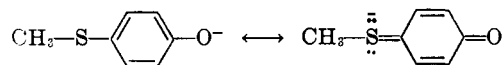
Convincing evidence of expansion of the sulfur shell is furnished by the behavior of aryl- or alkylmercapto-acetylenes towards nucleophilic agents (25, 193). Addition always takes place at the β -carbon atom, whereas in the case of acetylene oxygen ethers the nucleophilic group reacts with the α -carbon atom. In all probability, the mercapto group facilitates the polarization of the triple bond by the approaching nucleophilic reactant, which is also in accord with the increased rate of reaction as compared to acetylene itself.



Only the opposite polarization is possible in the oxygen analog:

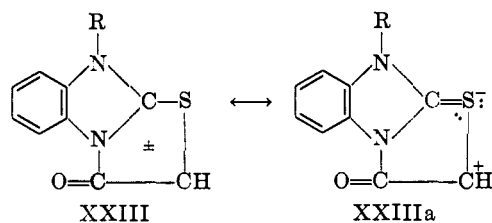


Conjugation of the electron-acceptor type perhaps occurs to some extent in the anion from *p*-alkylmercaptophenols,

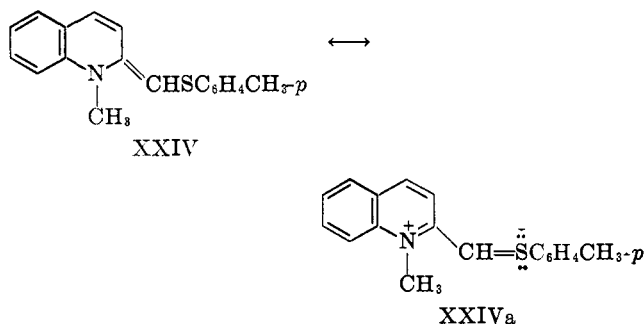


as suggested by measurements of acidity constants by Bordwell and Boutan (30). Spectral evidence of this conjugation seems to be available for the ortho isomer (74).

Duffin and Kendall (64) point out that contribution of structure XXIIIa would explain the ease of attack by nucleophilic reagents at the 5-position of the thiazole nucleus in the anhydro compound (XXIII), a derivative of (2-benzimidazolylthio)acetic acid.



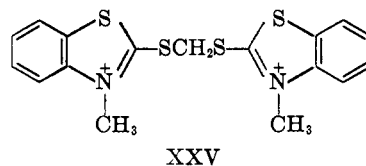
According to Knott (104), the longer transition in the electronic spectrum of the 1,2-dihydroquinoline derivative XXIV appears to be connected with the resonance XXIV \leftrightarrow XXIVa.



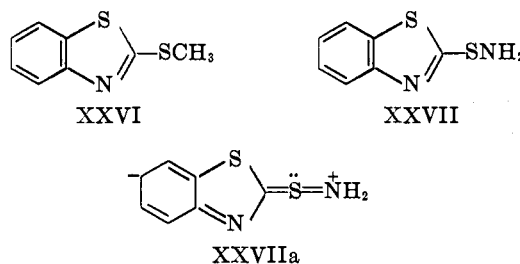
Expansion of course can also lead to deactivation, and Tarbell and Petropoulos (186) have pointed out that hydroxyl or alkoxy groups are far more effective in promoting electrophilic substitution than the analogous sulfur groups. In this connection they mention that coupling of diazonium compounds with thiophenols leads to diazosulfides, $\text{ArSN}=\text{NAr}$, and not to diazothiophenol; also, when thiophenol reacts with tertiary alcohols in the presence of acids, sulfides and not nuclear alkylation products are formed. However, these reactions of thiophenols can hardly be connected to an expansion effect. In fact, there is no evidence of electron-acceptor conjugation in thiophenol (30).

As mentioned earlier, structures in which sulfur is flanked by two double bonds may not be very important. The evidence is as follows: it has been reported that the positive charge of the nitrogen atoms in the

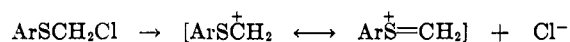
salt XXV cannot resonate with the hydrogen atoms of the central methylene group.



Baltrop and Morgan (18) found that the spectra of 2-methylthiobenzothiazole (XXVI) and 2-sulfenamido-benzothiazole (XXVII) are almost identical, a fact which excludes contributions of structures such as XXVIIa.



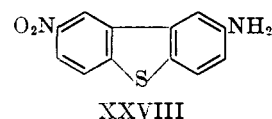
Further, in the hydrolysis of chloromethyl aryl sulfides, a reaction whose rate-determining step appears to be



there is no indication that in the intermediate the positive charge can be spread to the aromatic ring (33).

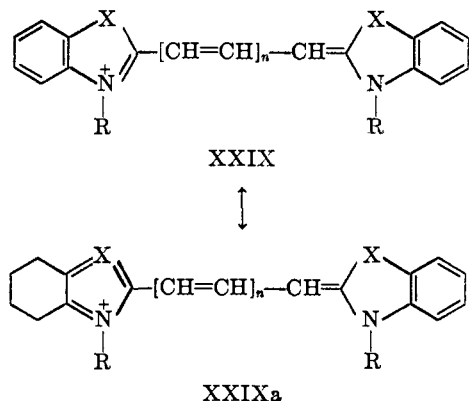
Additional facts are available which prove that sulfur is unable to transmit conjugation.

Although the spectral behavior of *p*-nitro-*p'*-aminodiphenyl sulfide has been interpreted by Szmant and McIntosh (182) as indicative of electron-transmitting ability by the sulfur atom bridge, more extensive work (128, 131, 132, 133) disposes of this conclusion, and also for 3-amino-6-nitrobenzothiophene (XXVIII) (130).

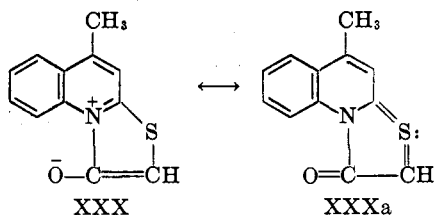


Montanari (137) has presented spectral evidence that sulfur linking two conjugated systems is not a conductor of conjugation. Sanesi and Leandri (167, 168) arrived at the same conclusion by dipole moment measurements on aromatic sulfides. But, according to Knott (103), sulfur can to some extent act as a transmitter of resonance. Thus, in the cyanine dyes (XXIX) ($\text{X} = \text{O}, \text{S}, \text{Se}, \text{or } -\text{CH}=\text{CH}-$) the spectral peaks of dyes from benzothiazole and benzoselenazole lie between those of the analogous dyes from benzoxazole and quinoline. Since structure XXIXa is certainly important when X is $-\text{CH}=\text{CH}-$ and of no significance

when X is oxygen, it is deduced that XXIXa contributes somewhat when X is sulfur or selenium.

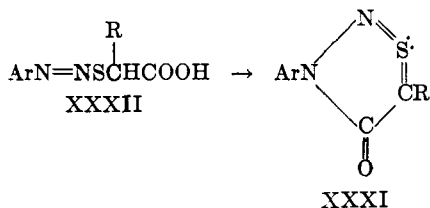


Further, Knott (104), on the basis of comparative studies of spectra and of the effect of solvent polarity on the spectrum, ascribes to the resonance $\text{XXX} \leftrightarrow \text{XXXa}$ the absorption band in the blue region presented

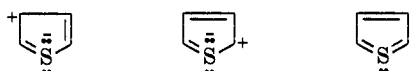


by this derivative of (2-quinolythio)acetic acid. The uncharged structure is said to be less stable than the dipolar one.

Clearly, the evidence for decet structures of sulfur involving two double bonds is scanty. For this reason the assignment of structure XXXI (65) to the anhydro compound obtained from the arylazomercapto acid (XXXII) with acetic anhydride is not convincing.



Thiophene has been the subject of a considerable number of theoretical investigations. In fact, the first suggestion of an expanded shell in double-bonded sulfur was made in connection with thiophene. In 1939 Schoemaker and Pauling (170), on the basis of dipole moment data, postulated that structures such as



would contribute to resonance in thiophene. Ten years later Longuet-Higgins (120) showed that by postulating the utilization of $3d$ orbitals by sulfur in thiophene, one

explains the similarity of this molecule to benzene. In short, while the π molecular orbitals of benzene can be derived from six ethylene molecular orbitals (the two types are shown in figure 4), the π molecular orbitals of thiophene can be constructed by substituting two of the six ethylene orbitals (one of each type) for a pair

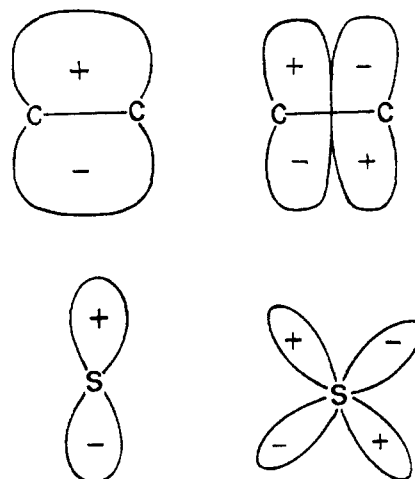


Fig. 4. Ethylenic π molecular orbitals and the corresponding orbitals on sulfur.

of sulfur orbitals of similar symmetry, dimensions, and binding energy (figure 4). More specifically, by pd^2 hybridization two sulfur orbitals will have the correct symmetry and energy to conjugate with the p orbital of the carbon atoms. The third hybrid is mainly of d character and is vacant in the ground state. This

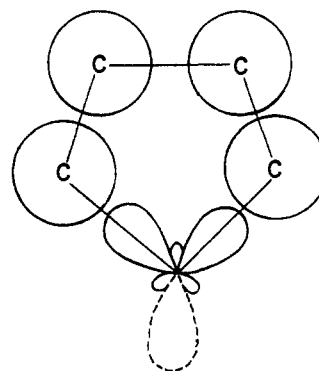


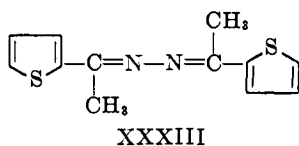
Fig. 5. Schematic representation of the pd^2 hybrid orbitals on thiophene sulfur and of the possibility of conjugation with the p orbital of the carbon atom. The molecular plane is a plane of antisymmetry. The nonbonding orbital on sulfur is vacant.

is schematically illustrated in figure 5, where the molecular plane is also a plane of antisymmetry.

Since the screening effect of $3d$ electrons is small, the effective electronegativity of sulfur in thiophene will be increased and this will lead to a decreased σ -bond polarity of the carbon-chlorine bond in 2-chlorothiophene. In this way, the increased nuclear quadrupole

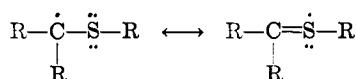
resonance frequency of chlorine in 2-chlorothiophene was accounted for (58).

Expansion in the shell of the sulfur atom of thiophene has also been considered (183) in relation to the spectrum of 2-thienylketazines (XXXIII) and again in relation to the dipole moments of thiophene and furan derivatives (159).



Yet a recent theoretical study of thiophene by Kreevoy (111), in which the $3d$ orbitals of sulfur are neglected, also explains the experimental behavior; the same approach to 1,4-dithiadene gave results in agreement with experimental facts. From these studies it appears that the differences between thiophene and furan are due to deformation of bond angles in the latter and changes in the Coulomb integral of the heteroatom. Therefore, the possibility of the utilization of d orbitals in thiophene should still be considered.

Finally, with regard to the behavior of sulfur, it may be that sulfur can stabilize not only the negative charge on an adjacent carbon atom, but also an unpaired electron (157).



The unshared ninth electron on sulfur would occupy a $3d$ orbital (172).

The use of a d orbital in the excited state of ethylene sulfide has been suggested as a possible explanation for the origin of the near ultraviolet absorption (57).

B. DISULFIDES

Utilization of $3d$ orbitals by sulfur has been suggested in the case of certain disulfides and polysulfides on the

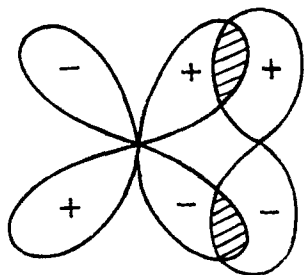
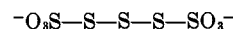


Fig. 6. d_{π} - p_{π} overlap

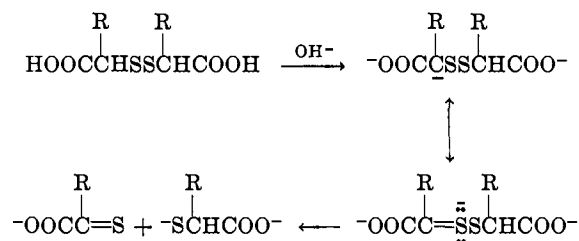
basis of S—S lengths (78, 79). A sulfur p_{π} electron pair would be transferred to a vacant $3d$ orbital of the sulfur partner (figure 6); the partial double-bond character would lead to a shortening of the bond and to a stabilization of the nonplanar configuration with dihedral angle of 90° .

On the basis of sulfur-sulfur distances it would appear that also the middle S—S bonds of the pentathionate ion



and the bonds in orthorhombic sulfur may possess some p_{π} - d_{π} character (78). Another interpretation (118) ascribes distance changes in the S—S bonds to different degrees of s and p character in the hybrid σ -bond orbitals of sulfur; in this hybridization d orbitals do not participate and this is in accord with theoretical expectation, for one would not expect the $3d$ orbitals to be modified so as to be useful (53).

For this reason Mulliken's (139) idea that hybridization of d orbitals may account for the abnormal strength of the simple homocentric σ bonds formed by the elements of the second short period is considered unlikely (53). Yet some evidence exists for the utilization of d orbitals in bonds of π symmetry. Thus, a hyperconjugation effect in disulfides has been pointed out by Bergson (21, 22). Further, it seems that expansion may assist in the alkali cleavage of certain disulfides (150).

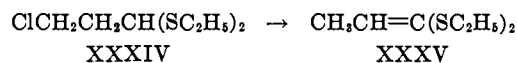


Since this evidence does not refer to the sulfur-sulfur link, it could also have been reported under "sulfides."

The excited state of the weak transition around $250 \text{ m}\mu$ shown by disulfides appears to correspond to a combination of the $4s$ orbital of the two sulfur atoms ($4s_1 + 4s_2$) (113).

C. MERCAPTALS

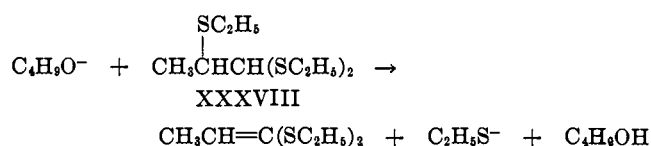
Rothstein (161) found that when β -chloropropionaldehyde diethylmercaptal (XXXIV) is treated with potassium *tert*-butoxide, the metilketene mercaptal (XXXV) is formed; hence the hydrogen atom of the carbon atom adjacent to the sulfur atoms has been removed.



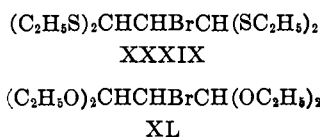
Yet the diethyl acetal analog of XXXIV leads to acrolein diethyl acetal, no metilketene acetal being formed (163). That the effect of sulfur is not inductive was indicated by the behavior of the analogous ammonium salts, which by the action of alkali alkoxide formed allyl derivatives (XXXVI), not the isomeric propenyl ammonium salts (XXXVII) (163):



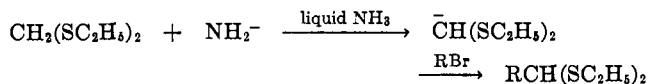
Rothstein (162) reported that treatment of α -ethylthiopropionaldehyde diethyl mercaptal (XXXVIII) with potassium *tert*-butoxide yields the ketene mercaptal.



Additional indication of activation by expansion can be seen in the spontaneous elimination of hydrogen bromide from the tetrasulfur compound XXXIX, whereas the halogen atom in the analogous oxygen derivative (XL) is very stable (165).

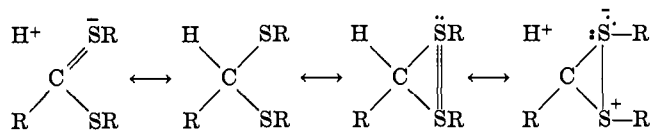


Arens, Fröling, and Fröling (2) report nucleophilic reactions of carbanions derived from thioacetals:



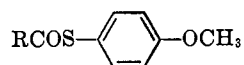
The carbanion is said to be resonance stabilized by the alkylthio group through an expansion effect.

Consistent with the mobility of hydrogen in mercaptals is the interpretation by Fehnel and Carmack (72) of the 235–240 $m\mu$ peak in the ultraviolet spectrum of these compounds. The following polarization was postulated:



D. THIOLESTERS AND THIOCYANATES

The author and Walter (44, 45, 48) have reported spectral evidence that in an excited state of *p*-anisyl thiolesters

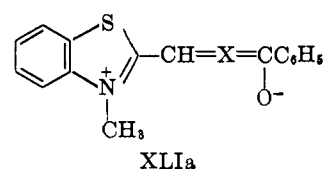
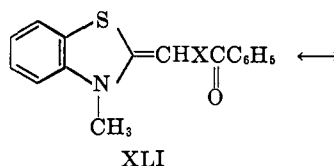


the sulfur atom uses a $3d$ orbital. The gain by the increased delocalization of the π electronic system only slightly overbalances the energy of promotion of an electron to the d orbital and hence expansion does not occur in *o*-anisyl isomers (46). Bordwell and Boutan (30) have criticized this view of the valency expansion of sulfur in thiolesters, but their objections have been answered (46).

Knott (105) pointed out that in the aryl thiolesters

studied by the author, steric hindrance should preclude or hinder structures with a decent configuration on sulfur. This objection too has been answered (46). In fact, the geometrical requirements for d -orbital resonance are not the same as those required in resonating systems of octet structures.

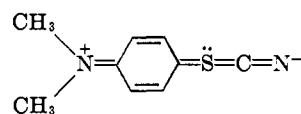
Knott (104) observed in the benzothiazoline derivatives (XLI) that when the X atom is changed from oxygen to sulfur, there is a marked bathochromic shift of the longer electronic transition, a fact suggesting extension of the conjugation to the carbonyl group through a d orbital of sulfur. However, since further bathochromic and hyperchromic shifts result in going to the vinylene analog (XLI: X = $-\text{CH}=\text{CH}-$), it was concluded that in the resonating system (XLI \leftrightarrow XLIa) responsible for the absorption, the sulfur atom is not prone to act as a transmitter of conjugation.



It has been suggested (122) that resonance in the thiolester makes utilization of a d orbital possible by rendering the sulfur atom more positive. However this is unlikely, since this resonance, if it exists, is quite weak (55).

Apparently this utilization of d orbitals by thiolester sulfur occurs only in the excited state and not in the ground state, for Bordwell and Boutan (30) measured the acidity constants for phenols and benzoic acids containing the $\text{CH}_3\text{COS}-$ or the $\text{N}\equiv\text{CS}-$ group and concluded that the phenol conjugation does not extend to the sulfur atom.

On the other hand, the fact that dipole moment data of compounds such as *p*-dimethylaminophenyl thiocyanate indicate some conjugation (42) is not necessarily in conflict with the above results for, because of the large charge separation, a small conjugation produces a relatively large increase in the dipole moment.

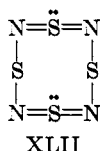


E. INORGANIC COMPOUNDS

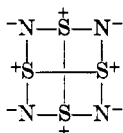
Hybridization of s , p , and d orbitals has been postulated in hydrogen sulfide (143) to account for the result

of the analyses of the hyperfine structure of pure rotational transition of H_2S^{33} , brought about by the interaction of S^{33} nuclear quadrupole moment with the molecular field gradient. Such an analysis indicates a large asymmetry of the coupling constants, although the S—H bonds are practically at right angles. This rules out pure p orbitals for the sulfur bonds.

Sulfur nitride, S_4N_4 , has been considered a resonating hybrid to which the structure XLII would make an important contribution (43, 89).



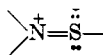
But it appears that the formula of S_4N_4 can be written without the use of any resonance form (118):



This, however, leaves unexplained why the sulfur-nitrogen distance of 1.62 Å. is shorter than the value (1.73 Å.) predicted for a single bond. This situation is again found in $\text{S}_4\text{N}_4\text{H}_4$, a puckered eight-membered ring of alternating sulfur and NH groups, where the sulfur-nitrogen distance is 1.674 Å. Sass and Donohue (169) ascribe this shortening to double-bond character resulting from the donation of unshared p electrons of the nitrogen atom to a vacant d orbital of sulfur, the σ bonds of the nitrogen being almost pure sp^2 in character. This interpretation is also in accord with the lack of basic character of the nitrogen atoms.

Short sulfur-nitrogen bonds in several other compounds are similarly ascribed by Sass and Donohue (169) to double-bond character.

Resonating structures involving the grouping



are believed to contribute to the structure of S_{16}N_2 (90).

IV. EXPANSION IN TRIVALENT SULFUR BONDED TO THREE ATOMS

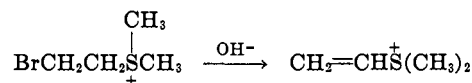
A. SULFONIUM COMPOUNDS

When sulfur is linked by single bonds to three atoms it bears a positive charge. Theoretically this charge should favor the utilization of d orbitals, and indeed there is abundant evidence for expansion in sulfonium compounds. Much of this evidence comes from comparison with the behavior of analogs where mesomeric

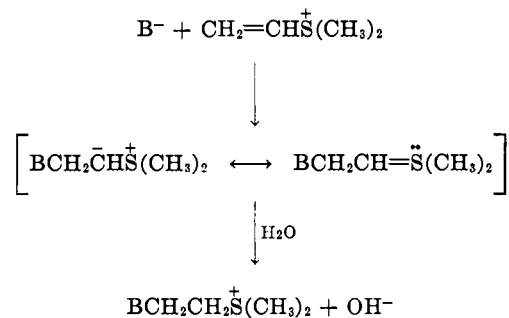
effects cannot occur. These are the ammonium compounds and not the more suitable oxonium compounds, because the latter are usually not available.

1. General evidence

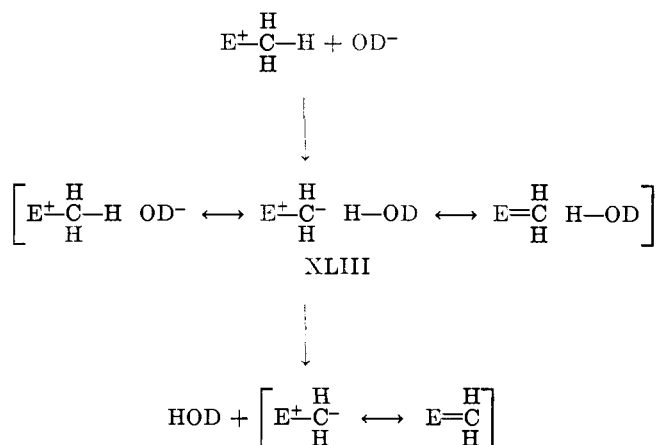
The reaction of 2-bromoethyldimethylsulfonium ion with hydroxyl ions leads to vinyl dimethylsulfonium ion (62):



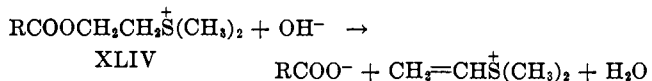
While indeed this is a bimolecular elimination, the analogous bromocholine ion reacts by the $\text{S}_{\text{N}}2$ mechanism (62). The evidence of expansion can also be seen in the reverse reaction: vinyl dimethylsulfonium ion adds a variety of bases very rapidly, whereas vinyltrimethylammonium ion does not (62).



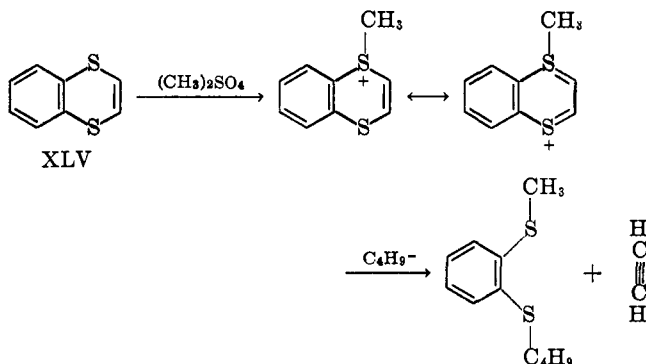
Doering and Hoffmann (60) found that the deuterium-catalyzed exchange of deuterium in deuterium oxide solution goes much faster with tetramethylphosphonium or trimethylsulfonium salts than with the tetramethylammonium salt. The operation of d -orbital resonance in stabilizing the negative charge in the transition state could be disclosed both in the lowering of the heat of activation and in the increase of the entropy term. Thus covalent accommodation of the negative charge lowers the dipole moment of the transition state (XLIII) and hence releases bound solvent molecules.



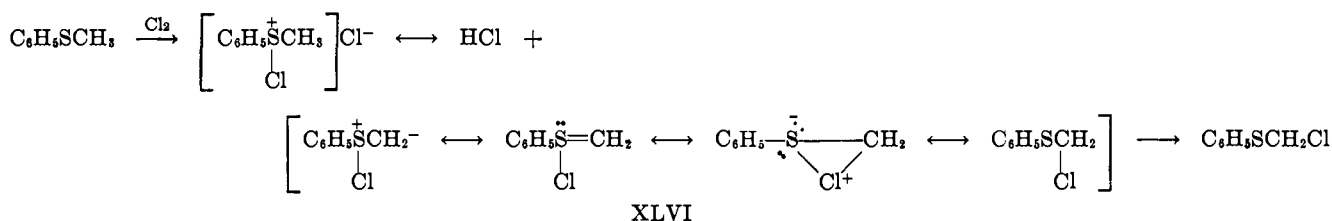
Additional weight to these arguments is provided by the enormous difference in lability toward alkali between the (2-aryloxyethyl)dimethylsulfonium iodides (XLIV: R = aryl) and their ammonium analogs (127), brought about by a more effective loosening of the α -hydrogen in the case of the sulfonium salt:



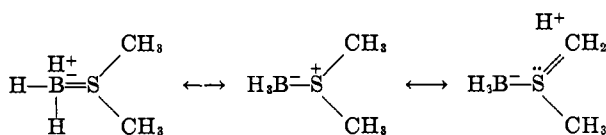
d-Orbital resonance in sulfonium ions has been invoked to account for the reactivity of benzo-1,4-dithiadene (XLV) towards butyllithium when the reaction mixture is treated with dimethyl sulfate (148).



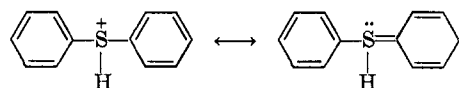
It has also been postulated in the intermediate XLVI in the formation of α -chlorosulfides (35):



Explanations based upon utilization of *d* orbitals by sulfur are available for the unexpected discovery that dimethyl sulfide forms a more stable adduct with borine than dimethyl ether (41, 177). It has been suggested that a filled pseudo- p_π orbital provided by the three hydrogen atoms of the borane group may overlap an empty *3d* orbital of sulfur (177). McDaniel (134), on the other hand, points out the possibility of stabilization due to hyperconjugation with the methyl groups.



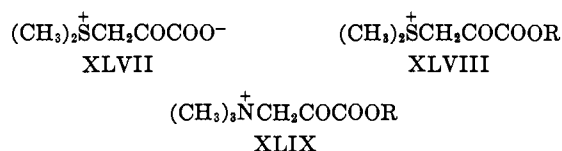
While aromatic sulfides dissolve in sulfuric acid giving deeply colored solutions, diphenyl ether forms a colorless solution. Szmant and Brost (181) ascribe the color to charge-transfer resonance in a diarylsulfonium ion.



The solution of diphenyl sulfide in sulfuric acid is unstable, but di-*p*-nitrophenyl sulfide gives a stable red solution (84) and appears to form a sulfonium salt.

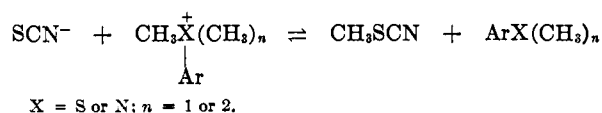
Bordwell and Boutan (29) found that the $(\text{CH}_3)_2\overset{\oplus}{\text{S}}$ group influences the acidity of phenol more than does the $-\overset{\oplus}{\text{N}}(\text{CH}_3)_3$ group. That the effect is in part conjugative can be seen from the fact that among the sulfonium compounds, the para isomer is more than twice as acidic as the meta isomer. Further evidence was provided by the spectral behavior.

Blau and Stuckwisch (23) reported that the methylene group in XLVII or XLVIII (R = CH₃, C₂H₅) can be titrated with alkali, whereas that in the ammonium analog (XLIX) cannot, a finding which they ascribed to *d*-orbital resonance.

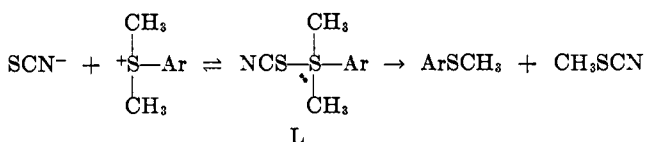


Arylsulfonium and arylammonium ions react with thiocyanate with the formation of methyl thiocyanate, the former reacting much faster. Bolto and Miller (24) point out that if this were an *S_N2* reaction the reverse

order should have been observed, inasmuch as the $-I$ effect of the charged nitrogen is stronger than that of charged sulfur and the carbon-nitrogen bond is weaker



than the carbon-sulfur bond. They ascribe the anomaly to accommodation of the negative charge of SCN⁻ in the outer shell of sulfur,

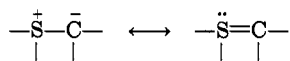


an assumption in agreement with the observed lowering of the activation energy. Yet this interpretation is not satisfactory, since an intermediate such as L is very

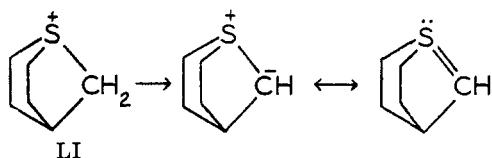
unlikely to exist. The only known case of neutral quadricovalent sulfur is SF_4 , that is, sulfur attached to very electronegative groups. That intermediates such as L do not exist is further suggested by the absence of paraffinic decomposition of sulfonium salts (96).

2. Stereochemistry

Since properly asymmetrically substituted sulfonium salts have been resolved, they cannot have a planar structure. Hence if the d -orbital resonance



occurs, coplanarity is not necessary. That this is so, is shown by the occurrence of deuterium exchange in bicyclo[2.2.1]heptane-1-sulfonium ion (LI), where the sulfur atom is tied up in a nonplanar configuration (60).



The stereochemistry of sulfur flanked by a double bond and having a decet of electrons in the valency group appears to be based on the tetrahedral sp^3 hybridization; this gives rise to the σ bonds. Then, a π bond is formed by donation of electrons from a $2p$ orbital of the carbon atom to a vacant $3d$ orbital of sulfur (figure 6). The availability of two d orbitals for strong π -orbital formation in addition to σ sp^3 bonds is shown by the results of Kimball (99). Formation of tetrahedrally oriented π orbitals has also been theoretically studied by Jaffé (97) and by Giacometti (82).

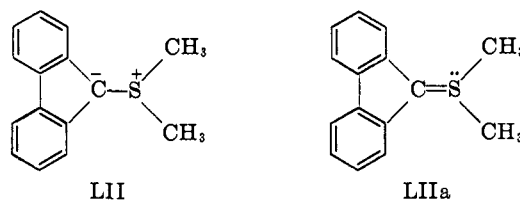
In agreement with these foregoing stereochemical considerations is the fact that in dimethyl-*p*-hydroxyphenylsulfonium ion if the $(\text{CH}_3)_2\overset{\oplus}{\text{S}}-$ group is flanked by ortho substituents, even bulky ones such as bromine, there is no hampering of the conjugation since there is no effect upon the dissociation of the phenol (142). Also, there appears to be no effect spectrally. Clearly, these findings are in striking contrast with the situation in *o*-substituted *N,N*-dimethylaniline.

3. The asserted negative evidence

The fact that sulfonium salts have been resolved was interpreted by Rothstein (164) as an indication that sulfur in sulfonium compounds has the p^3 trigonal pyramidal configuration and an unshared $3s^2$ electron pair. In this situation strong π orbitals with d orbitals of sulfur cannot be formed, as shown by Kimball (99). Impossibility of expansion would explain—according to Rothstein—the resistance of these substances to oxidation and the virtual absence of neutral quadricovalent sulfur. The answer to these objections is straight-

forward: nonplanarity is due to sp^3 configuration and absence of neutral quadricovalent sulfur is not a case in point. In fact, it is not to be expected that utilization of d orbitals by sulfonium sulfur would proceed to the extreme limit of forming a new entity, even a transitory one, such as the would-be intermediate in the paraffinic decomposition.

It is true that dipole moment data (154) do not support structure LIIa for dimethylsulfonium-9-fluorenylidide (LII).



But this is of course not surprising, in view of the large electron delocalization in the sulfonium structure.

B. OTHER COMPOUNDS

There are some other suggestions regarding the utilization of d orbitals by sulfur linked to three atoms.

Dunitz (66) by x-ray analysis found the dithionite anion, $\text{S}_2\text{O}_4^{--}$, to consist of two SO_2^- units joined by a very long S—S bond (2.39 Å.) in an eclipsed configuration with the planes of opposite SO_2 groups 30° from parallel. He made the interesting suggestion that the two halves are joined by overlap of dp hybrid orbitals (figure 7).

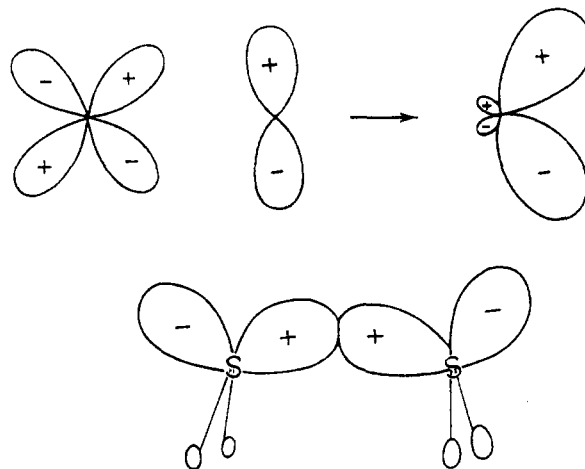


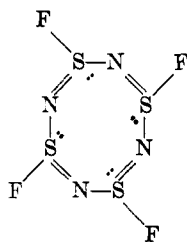
FIG. 7. Formation of dp hybrid orbitals and the possible occurrence of overlap between such hybrids in the dithionite anion.

Yet, according to Lindqvist (118), the unusually long sulfur-sulfur distance can merely be ascribed to p_σ bonds with a reduced s character.

Evidence is available that sulfur dioxide can act as electron acceptor forming charge-transfer complexes (125, 126).

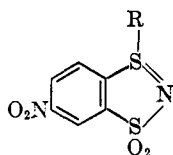
It is probable that the acceptor orbital of sulfur dioxide is the dp hybrid on sulfur (figure 7) postulated by Dunitz (66); thus, in the case of SO_2 -olefin complexes one of the two lobes of this hybrid would overlap one half of the olefin π orbital (26).

Craig (52) thinks that in "thiazyl" halides, such as the tetrameric fluoride,



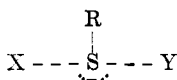
another potentially aromatic character occurs by the overlapping of alternate p_π and d_π orbitals. This resonance has been postulated in the case of $\text{S}_3\text{N}_3\text{F}_3$ and $\text{S}_3\text{N}_3\text{Cl}_3$ (171).

Wagner and Banholzer (194) have reported the synthesis of cyclic sulfinimines (LIII). They ascribed a band in the infrared to the group >S=N- .



LIII

According to Fava, Iliceto, and Camera (70) it is conceivable—although not very probable—that in the transition state for the $\text{S}_{\text{N}}2$ displacement at a divalent sulfur atom, a vacant d orbital of the sulfur atom is used:



However, Parker and Kharasch (149) believe that such a transition state is the most likely one, mainly because sulfur is more prone than oxygen to nucleophilic attack.

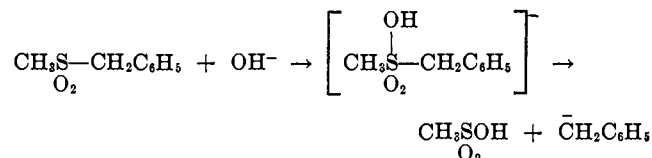
V. EXPANSION IN TETRAVALENT SULFUR BONDED TO FOUR ATOMS

There is no doubt that SF_4 exists (38). Infrared and Raman spectra indicate that the molecule possesses C_{2v} symmetry (59), a finding which is also strongly supported by the nuclear resonance spectrum (50, 51, 138). The five pairs of outer electrons are placed in sp^3d hybrid orbitals, trigonal-bipyramidally directed. The unshared pair occupies an equatorial orbital. The d orbital which is hybridized should be the $3d_{z^2}$ (85).

Apparently this is the only known case of neutral quadricovalent sulfur and may owe its existence to the presence of four very strongly electron-attracting fluorine atoms.

VI. EXPANSION IN SULFUR BONDED TO FIVE ATOMS

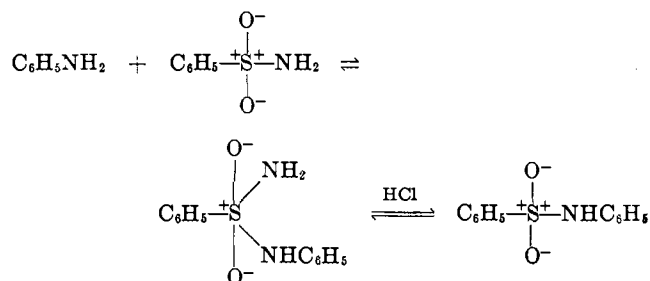
Because sulfone can undergo with alkali the paraffinic decomposition, Ingold and Jessop (95) pointed out that the sulfur atom has a tendency to expand its valence shell:



However, tracer studies make this mechanism unlikely (43a).

Recently the author (47) observed that di- β -naphthyl sulfone has a definite—although weak—Lewis acid character. This sulfone when in highly concentrated benzene solution gives with various aminoazo dyes the same color as is produced by the addition of protons, aluminum chloride, and other Lewis acids [for instance, a red color with *p*-dimethylaminoazobenzene and a green color with 4,4'-bis(dimethylamino)azobenzene]. The only conceivable acceptor orbital can be on sulfur, and this requires expansion. If, in these hypothetical structures, sulfur has the configuration sp^3d , two strong π bonds can be formed (99), so it is feasible that these adducts of sulfones have the trigonal bipyramid configuration.

Sulfur linked to five atoms has been formulated by Kogan and Dziomiko (108) for the intermediate of the reaction by which arylamines can displace the amine groups from arylsulfonamides.



VII. EXPANSION IN SULFUR BONDED TO SIX ATOMS

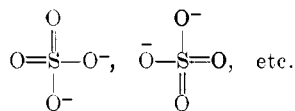
The existence of sulfur hexafluoride is of course beyond dispute. The six pairs of valence electrons are placed in octahedrally directed sp^3d^2 hybrid orbitals. The d orbitals used should be the two d_z orbitals (85).

VIII. THE NATURE OF THE SULFUR-OXYGEN BOND(S) IN SULFOXIDES, SULFONES, AND RELATED COMPOUNDS

A. THEORETICAL INVESTIGATIONS

Moffitt (136), using the molecular orbital method, concluded that in sulfoxides, sulfones, and sulfur oxides the sulfur-oxygen linkage is predominantly a double bond. Pauling (152) arrived at a similar conclusion on

the basis of charge neutralization considerations. For the sulfate ion the π -bond character was found to correspond closely to the resonance formulas



Both investigations indicate that the π -bond character of sulfoxides is smaller than that of sulfones.

Jaffé (97) has discussed the formation of multiple bonds involving d orbitals formed by a tetrahedral central atom. Giacometti (82) has concluded that up to three of the tetrahedrally oriented π orbitals may exist.

When sulfur is attached to the highly electronegative oxygen with compact p_π orbitals, the overlap with the sulfur $3d$ orbital would be small, were it not for the polar character of the σ bond, which by virtue of the fractional positive charge on sulfur will make the d orbital more commensurable with the p orbital and hence will improve the overlap (53). The theoretical study of the contraction of d orbitals by ligands was continued by Craig and Magnusson (54) and indicates that the d orbitals of sulfur are indeed capable of substantial overlap with the $2p_\pi$ orbitals of oxygen, which is even more favorable in a pd hybrid.

B. STEREOCHEMICAL CONSIDERATIONS

Similarly to the case of sulfonium salts, the fact that sulfoxides can be resolved has been often considered as proof of the semipolar character of the sulfur-oxygen bond. Here again this is not necessarily so, because one can have sp^3 hybridization for the σ bonds and concomitant possibility of formation of π orbitals. By another approach, one starts from sp^3d hybridization and lets the oxygen atom share two bonds (75, 114).

C. PARACHOR

Parachor results are believed to support the semipolar linkage for the sulfur-oxygen bonds and are also of historical interest in connection with the controversy. The point is that the double bond present in derivatives of oxygen acids of sulfur and phosphorus lowers the molecular parachor (179). This is again observed in other compounds having sulfur-oxygen bonds (81). However, one has to note that the attachment to sulfur of two atoms larger than hydrogen results in overlapping and therefore in a reduction of the total volume (68).

D. REFRACTIVITY

The first determinations of refractivity in sulfones, sulfites, and sulfates by Strecker and Spitaler (178) were interpreted in favor of the double bond. But no difference was found between sulfoxides and sulfones. Accord-

ing to others (156, 190, 191), data on molecular refractivity do not support the view that the sulfur-oxygen bond is a covalent double bond. The critical point is that the sulfur-oxygen bond refraction is low. Yet as Lumbroso and Passerini (123) have pointed out, the refractivity of A^+B^- compounds is definitely lower than the value expected from A and B refractivities, whereas in a sulfone there is some increase for each sulfur-oxygen bond.

E. BOND LENGTHS

As in the oxygen acids (151), in sulfones the sulfur-oxygen distance is shorter than expected for a single bond (119, 187). In fact, the observed distance in dimethyl sulfone was even shorter than that expected for a double bond (119). The same result was obtained with sulfur dioxide, sulfur trioxide, thionyl chloride, and sulfuryl chloride (145).

F. DIPOLE MOMENT

In 1945 Phillips, Hunter, and Sutton (154) concluded that the sulfur-oxygen bond was not a coordinate link because experimental values of the dipole moment were lower than those predicted for full electron transfer. This deduction is essentially in agreement with more recent work by Lumbroso and Passerini (123) and by Cumper and Walker (56), in which account is taken of the atomic dipoles in thioethers when calculating the expected change in dipole moment in passing to the sulfoxides and sulfones. It appears that the sulfur-oxygen bond is a double link with some coordinate-bond character.

G. THERMAL DATA

The apparent heat of formation from the atoms of the sulfur-oxygen bond, 102.6 kcal./g.-mole, as calculated from data for thionyl chloride and sulfuryl chloride, is indicative of considerable double-bond character in these compounds inasmuch as for a single sulfur-oxygen bond the expected value is 72.4 kcal. (154).

H. INFRARED AND RAMAN SPECTRA

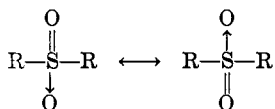
Barnard, Fabian, and Koch (19) observed that the sulfur-oxygen stretching frequency of the sulfur-oxygen linkage was higher in sulfur dioxide, sulfones, and sulfinyl and thionyl halides than it was in sulfur monoxide. The force constant in sulfones appears to be 35-40 per cent stronger than in sulfoxides. It was concluded that the sulfur-oxygen bond is nearly a covalent double bond with some semipolar-bond character, which is relatively more important in sulfoxides than in sulfones. These conclusions are in agreement with theoretical investigations and with the important fact that sulfoxides form stronger hydrogen bonds than do sulfones, as indicated by hydrate and salt formation. As pointed out by these

authors, the observation that the increased strength of the sulfur-oxygen bond is associated with a significant decrease of bond polarity makes untenable the argument that the increased shortness and physical strength of the sulfur-oxygen bonds could be due to their increased polarity rather than to bond-multiplicity.

Other studies (174, 175, 176) indicate that the sulfur-oxygen bond is mainly a double bond, which is weakened in sulfoxides or when the double-bond character is to be shared with other atoms.

Infrared spectroscopy has also been indirectly used in connection with the problem of the sulfur-oxygen bond structure. In *o*-hydroxydiphenyl sulfone the interaction of the ortho hydroxyl group and the sulfone group is much less than that between the hydroxyl and the sulfur-oxygen group in the corresponding sulfoxide (1).

To account for the lack of basic character and the stability of sulfones, Amstutz, Hunsberger, and Chesick (1) proposed that sulfones could be resonance hybrids of the following structures:



This suggestion, which has also been made by Toussaint (187), does not agree with most of the theoretical or related experimental data.

I. OTHER INVESTIGATIONS

Banks and Zimmerman (17), on analyzing the second dissociation constant of sulfoacetic and sulfopropionic acids, treat the sulfonate group as a resonating group. On the other hand, Bell and Rawlinson (20) report kinetic evidence and acidity considerations according to which the bonds in the sulfonate group are essentially single. This is indeed surprising and not easily accounted for.

IX. CONJUGATION IN SULFONES, SULFOXIDES, AND RELATED COMPOUNDS

A. THEORETICAL

Koch and Moffitt (107), on the basis of molecular orbital theory, have studied the possibility of conjugation of the sulfone group with attached unsaturated groups. The π electrons of the SO_2 groups are said to occupy two molecular orbitals: one which has a nodal plane through the sulfur and oxygen atoms, and another which has an additional plane bisecting the $\text{O}-\text{S}-\text{O}$ angle. The first has the correct symmetry to conjugate with p orbitals, whose axes lie in the plane of the sulfur-carbon valences, but since their electrons are strongly bonding and the geometrical conditions are unfavorable, there will be no conjugation (figure 8). The other orbital can conjugate with p orbitals whose axis

is perpendicular to the plane of the sulfur-carbon valences (figure 9); the electrons in it are less strongly bonding. As the sulfur-oxygen bonds are weakened, this may be called ordinary conjugation. It will not occur if the SO_2 group is flanked by only one unsaturated group.

Now, since sulfur has vacant orbitals, donor-acceptor conjugations can also be expected. This is particularly effective under conditions which also lead to ordinary conjugation (figure 10) and becomes weaker if there is only one conjugating group. If the orbitals on the carbon lie on the plane of the sulfur-carbon valences,

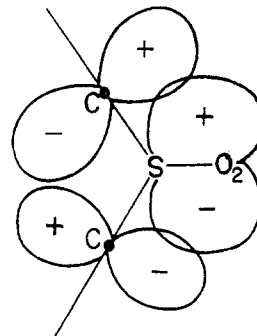


FIG. 8. The strongly bonding π molecular orbital of the sulfone group. Only poor overlap is possible with p orbitals in the plane of the carbon-sulfur valences.

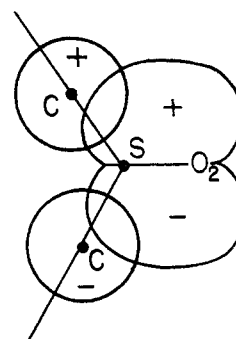


FIG. 9. The less strongly bonding π molecular orbital of the sulfone group. The plane of the paper is another nodal plane. Good overlap is possible with p orbitals perpendicular to the plane of the carbon-sulfur valences.

there can be charge transfer to a vacant hybrid (figure 11); conjugation will be less effective if there is only one unsaturated group.

This theoretical result that conjugation may not affect the sulfur-oxygen bonds explains most of the objections of double-bond formulation.

According to Jaffé (97), the contradictory results about conjugation in sulfones are due to the fact that a central tetrahedral atom will only permit conjugation at the expense of appreciable multiple-bond energy, for, in view of the peculiar character of the d orbital, introduction of a second d_π -bonded atom reduces the double-bond character of the already existing d_π bond. In fact, while a p orbital can π bond in any direction, a d orbital

will more effectively π bond in the plane which goes through the vectors of maximum intensity of the d orbital. Hence, competition will result and conjugation cannot be strong.

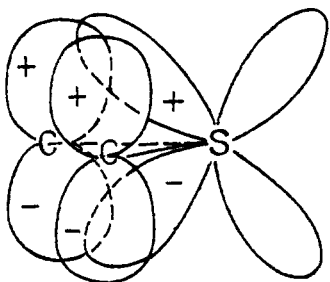


FIG. 10. Schematic representation of the possibility of electron transfer from p orbitals perpendicular to the plane of the carbon-sulfur valences to a vacant d orbital of sulfone sulfur.

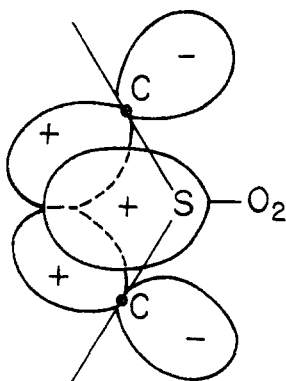


FIG. 11. Schematic representation of the possibility of electron transfer from p orbitals lying in the plane of the carbon-sulfur valences to a hybrid vacant orbital of sulfone sulfur.

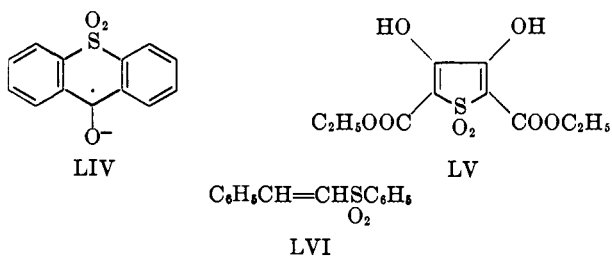
B. CONJUGATION IN SULFONES

1. Sulfones flanked by two conjugatable groups

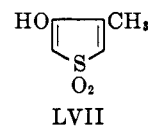
(a) Planar systems

Strong conjugation involving the sulfur-oxygen bonds can be expected with concomitant weakening of these bonds; besides this ordinary conjugation, there will also be a donor-acceptor conjugation, in which charge is transferred to a vacant orbital on sulfur (107).

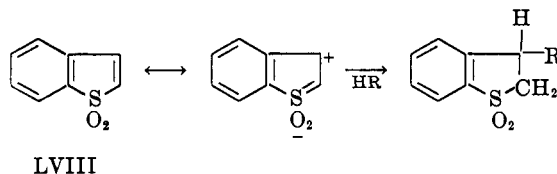
Examples are (107): (i) the semiquinone LIV, a negative radical-ion which is stable and colored (71, 94); (ii) certain 3,4-dihydroxythiophene dioxides (LV), which are powerful acids (67); (iii) styryl p -tolyl sulfone (LVI), which behaves similarly to α,β -unsaturated ketones in certain addition reactions (109).



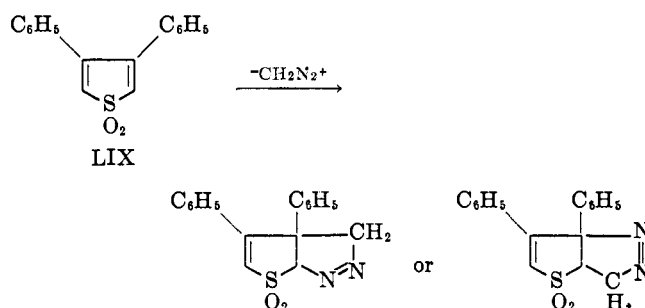
Other possible examples are: (iv) the anion (LVII) from 4-hydroxy-3-methylthiophene sulfone (106), which is deep yellow (9);



(v) benzothiophene 1-dioxide (LVIII), whose 2,3-bond is reactive and undergoes addition reactions with a variety of reagents (27, 34, 116);



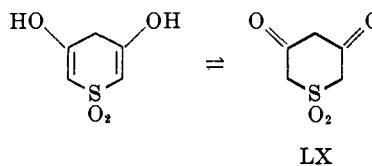
(vi) 3,4-diphenylthiophene dioxide (LIX), which undergoes the nucleophilic addition of diazomethane (7), a behavior not shared by α -monoolefinic sulfones (63);



(vii) the carbanion from benzyl p -tolyl sulfone, as the latter undergoes the Michael condensation with benzalacetophenone (49). Conjugation could assist in the formation of this and certain other carbanions (92).

Some indication of this ordinary conjugation exists for divinyl sulfone, but not for dibenzothiophene dioxide (195). This result has been tentatively ascribed to the lower residual affinity of the phenyl group. With a suitably located donor group there may be some conjugation, as suggested by the ultraviolet spectrum of 3-aminodibenzothiophene dioxide (129).

Cases in which strong conjugation could occur, but apparently does not, are thiophene dioxide, because it is not very stable, and a tautomer of tetrahydrothiopyran-3,5-dione 1,1-dioxide (LX). Thus, the acidity of LX resembles that of alicyclic β -diketones; hence the dissociable proton comes from the β -dicarbonyl portion of the molecule (76).

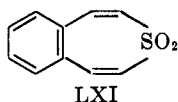


(b) Nonplanar systems

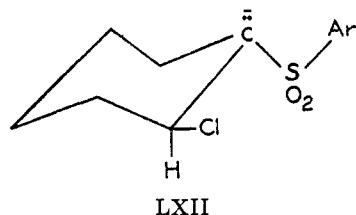
The only conjugation possible is the donation of negative charge to a vacant orbital of sulfur; hence the sulfur-oxygen bonds will not be affected. This explains the intramolecular charge-transfer spectrum of diphenyl sulfone and derivatives (10, 106, 116) and why the stretching frequencies of the sulfur-oxygen bonds in this sulfone are not lower than those observed in dialkyl sulfones (19). The behavior of sulfuric acid solutions (86) is also accounted for.

The nonoccurrence of a bathochromic shift of the main ultraviolet transition when diphenyl sulfone goes from cyclohexane to ethanol solution has been interpreted as semipolar-bond formation (11). Since the transferred negative charge will not reach the oxygen atoms, but will seat on the sulfur atom, not accessible to the solvent molecules, the above interpretation does not appear justified.

Another molecule which can be included here is 3-benzothiepin 3-dioxide (LXI), because its heterocyclic ring is highly puckered. This molecule has little aromatic character (188).

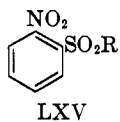
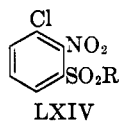
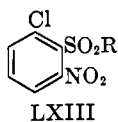


A sulfone flanked by an aromatic group stabilizes a negative charge on an α -carbon atom. Examples are the base-promoted eliminations in *trans*-(2-chlorocyclohexyl) aryl sulfones and related compounds in which the anion (LXII) is formed as an intermediate (91).



It is, however, somewhat surprising that the rate of base-catalyzed deuterium exchange for hydrogen alpha to the sulfone group is similar in cyclopentyl and cyclohexyl sulfones (196). This contrasts with the behavior of ketones and nitro compounds and would suggest that the exo double-bond formation does not occur in the case of sulfones; otherwise the cyclopentyl derivative should have reacted faster (39). Perhaps the rule does not apply to π bonding involving d orbitals.

Conjugation is said to be responsible for the mobility of chlorine and of the nitro group in nucleophilic substitution reactions of compounds LXIII to LXV ($R =$ tolyl) (116, 121).

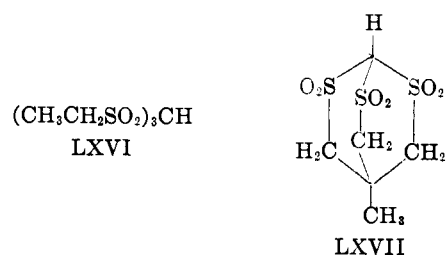


2. Sulfones flanked by only one conjugatable group

It is not necessary to distinguish between the cases in which the conjugatable orbital on the carbon is perpendicular to or lies in the plane of the two sulfur-carbon valences. In both cases only weak donor-acceptor conjugation is possible and the sulfur-oxygen bonds will be unaffected. Incidentally this explains at once why any conjugation of the $-\text{SO}_2-$ group with an aromatic ring may not be affected by the introduction of ortho substituents (101).

The activation of an α -hydrogen atom by the sulfonyl group is of course too well known to warrant documentation; apart from a few aspects undoubtedly connected with expansion, it does not qualify for this review.

The acidity of tris(alkylsulfonyl)methane (LXVI) is indistinguishable from that of hydrogen chloride in water (166). That this in part is due to resonance stabilization of the anion is indicated by the diminished acidity in going to the compound LXVII, in which strain hampers coplanarity of the carbanion (61).



Roentgenographic study of the ammonium salt of tris(methylsulfonyl)methane has shown indeed that the three sulfur atoms and the central carbon atom are coplanar; the $\text{C}_{\text{central}}-\text{S}$ bonds have 25 per cent double-bond character (8).

It is then obvious why trisulfones with an asymmetric carbon atom, $\text{RSO}_2\text{CH}(\text{SO}_2\text{R}')\text{SO}_2\text{R}''$, cannot be resolved; neither can β -disulfones, unless there is no hydrogen atom on the carbon between the two sulfone groups. A properly substituted monosulfone can, however, be resolved; resonance interaction with one sulfone group is not extensive.

Formerly the failure of optical resolution was correctly connected with expansion of the sulfur valence shell but the assumption was wrong; the racemization, as well as the solubility in alkali, was due to enolization (180). Others (4, 6), however, concluded that the sulfonyl group was not enolizable and also that it was incapable of conjugation.

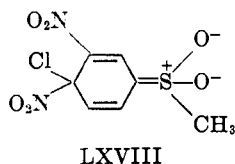
The conjugative effect of the sulfonyl group with adjacent negative charge can be disclosed spectrally in the anion formed by methylene disulfones, β -ketosulfones, and α -carbalkoxysulfones (73).

Theoretically, conjugation in the compounds under study is bound to be weak. Accordingly one can expect

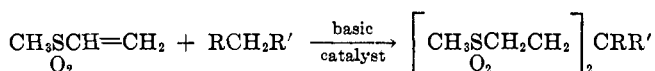
to find cases in which conjugation is detectable and others in which it is not.

Definite evidence of conjugation of the methylsulfonyl group with an aromatic group comes from the effect of this group, when in the para position, upon the dissociation constant of benzoic acid, phenols, thiophenols, and anilines (28, 32). The analogous result has been reported by Kloosterziel and Backer (100). Additional evidence of conjugation with an aromatic ring is provided by dipole moment data (123, 158) and the ultraviolet spectra (73, 75, 102, 106) of properly substituted derivatives. The conjugative effect of the CH_3SO_2 — group is similar to that of the $(\text{CH}_3)_2\text{S}^+$ — group; hence it has been suggested (29) that conjugation in the methylsulfonyl group also involves primarily the sulfur atom. This is, of course, exactly what theory predicts (107). Kinetic evidence of the conjugative ability of the sulfonyl group is also available. This group has been found to activate the deacylation of acetanilides with an ability comparable to that of the cyano group (110).

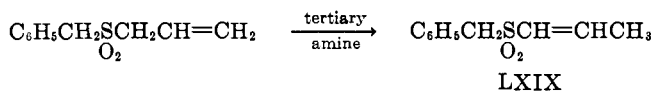
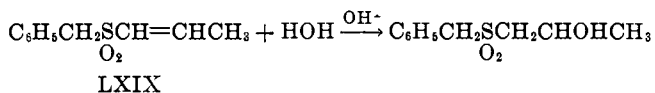
The reaction of 2-nitrochlorobenzene with sodium methoxide is activated by a 4-methylsulfonyl group more efficiently than by a trimethylammonium group, but less efficiently than by a nitro group (93). Since the methylsulfonyl group affects the Arrhenius parameters in much the same way as the nitro group does, it has been inferred by analogy that the methylsulfonyl group has one semipolar bond (decent of electrons) and that the intermediate complex of this nucleophilic substitution has the structure LXVIII.



Further cases of conjugation can be discerned in the following facts: (i) methyl vinyl sulfone reacts with compounds containing active methylene groups in a condensation of the Michael type (116, 189):

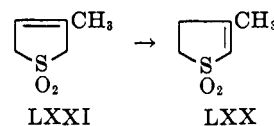


(ii) α, β -unsaturated sulfones such as benzyl propenyl sulfone (LXIX) add nucleophilic reagents and may form from an isomer (7, 98):

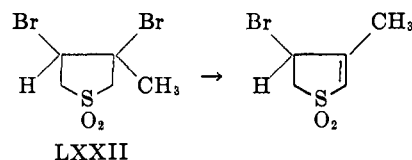


That this conjugation is not strong can be appreciated from the fact that it does not overcome hyperconjugation,

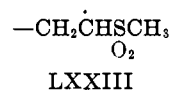
inasmuch as no shift of the double bond occurs in benzyl crotyl sulfone under comparable conditions (7); (iii) 3-methyl-4,5-dihydrothiophene 1,1-dioxide (LXX) is formed from the isomer (LXXI) (7):



(iv) elimination from 3,4-dibromo-3-methyltetrahydrothiophene 1,1-dioxide (LXXII) occurs from the 2,3- and not from the 3,4-position (112):



On the other hand, the following facts could be attributed to lack of conjugation: (i) the absence of acid catalysis in the addition of halogen to vinyl sulfone (135); (ii) the failure of β -sulfonyl ketones to undergo enolization (6); (iii) the very low free-radical stabilization factor of vinyl methyl sulfone (LXXIII) (157).

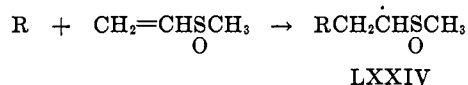


These three examples have been cited by Koch and Moffitt (107). A further example is the lack of reactivity of substituted 2,3-dihydrothiophene 1,1-dioxide towards diazomethane (63) in sharp contrast to the behavior of substituted thiophene 1,1-dioxides (7), as mentioned before.

Dipole moment measurements indicate that there is no conjugation in the ground state of α, β -unsaturated sulfones (13). However, conjugation may exist in an excited state, as suggested by the spectral behavior (12).

C. CONJUGATION IN SULFOXIDES

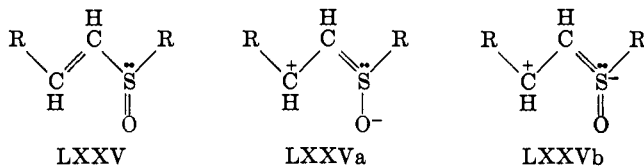
Deuterium exchange in butyl sulfoxide is quite slow (60). Copolymerization studies by Price and Gilbert (155) of the pair styrene-methylvinyl sulfoxide indicate little resonance interaction between the sulfoxide group and the carbon free-radical intermediate (LXXIV) in the polymerization:



Shriner, Struck, and Jorison (173) reported that two sulfoxide groups fail to confer measurable acidity to an adjacent methylene group.

Theoretically the sulfoxide group should be less efficient than the carbonyl group in conjugation, for, as mentioned earlier, if the sulfur *d* orbital is overlapping

the p orbital of oxygen at maximum efficiency, it cannot do so with the p orbital on the α -carbon atom. In other words, structure LXXVa should not be very important. Yet it seems reasonable to conceive of the resonating structure LXXVb, in which charge is drifted into a vacant d orbital of sulfur:



In this connection it is important to note that the conjugating ability of the methylsulfinyl group—as shown by the effect upon the dissociation of a p -phenolic group—is comparable to that of the methylsulfonyl and dimethylsulfonio groups (31). This may be taken as evidence that delocalization is not extended to the oxygen atom of the sulfoxide group. According to Bordwell and Boutan (31), this conjugative effect of the CH_3SO — group is not apparent from the position of the main ultraviolet band of phenyl and p -hydroxyphenyl methyl sulfoxides. However, it should be noted that Bordwell and Boutan (31) consider the main transition as a primary band, whereas it would appear that the band of the



grouping results from the coupling of a transition localized in the sulfur atom with the secondary benzene transition (117).

D. CONJUGATION IN COMPOUNDS OTHER THAN SULFONES AND SULFOXIDES

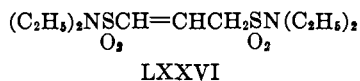
1. Sulfonates

Bryson (40) concluded from a study of the basic strengths of substituted naphthylamines that the sulfonate group is capable of a $-M$ effect. Zollinger extended this conclusion to the benzenesulfonic acids (198).

2. Sulfonamides

Dipole moment data indicate that in sulfanilamide the p -amino group can donate electrons to the sulfamide group (115). Further, measurements of the acidity constant for compounds having a $-\text{SO}_2\text{NH}_2$ group para in benzoic acid and in the anilinium ion indicate the operation of the mesomeric effect (199).

Nicholson and Rothstein (140) report the presence of active hydrogen in the disulfonamide LXXVI.

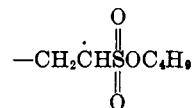


Spectral indication of conjugation in 1,3-disulfamoylpropenes is also available (141).

3. Alkylsulfonates and alkylsulfonates

From the near ultraviolet spectrum of methyl p -toluenesulfonate it has been concluded that the $-\text{SOOCH}_3$ group strongly conjugates with the aromatic system (36).

Copolymerization studies of butyl vinylsulfonate suggest that the alkylsulfonate group does not stabilize the free electron of the α -carbon atom (144):



4. Sulfonyl halides

Raman and infrared spectra for certain saturated and unsaturated sulfonyl chlorides indicate lack of conjugation between the olefinic and the sulfur-oxygen bonds (80). Ultraviolet light absorption studies indicate that conjugation occurs in an electronic excited state of 2-phenylethylene-1-sulfonyl chloride (80).

X. CONCLUSIONS

There is little, if any, doubt that in certain sulfur compounds d orbitals are utilized or can be utilized. Normally this is only possible if, by the very nature of the molecular system, contraction of the $3d$ orbitals occurs. Then these orbitals can take part in σ bonds, localized π bonds, and delocalized π bonds of the aromatic type.

When sulfur is linked to two atoms, the best evidence of electron-acceptor conjugation is found in resonating anionic systems or when the positive charge can be properly accommodated. In sulfonium salts, probably because of the positive charge, sulfur is prone to expansion. With regard to compounds in which sulfur is linked to four or more atoms, as in SF_4 and SF_6 , the very existence of these molecules strongly indicates utilization of d orbitals.

In compounds such as sulfoxides, sulfones, and related structures containing sulfur-oxygen bonds, apart from a few results such as parachor and refractivity data, all the evidence indicates that the sulfur-oxygen bond is a double covalent link, at least to a marked extent, and more in sulfones than in sulfoxides. This is so convincing that one wonders if it is justifiable to extend the parachor and molecular refractivity systems to these classes of compounds.

Theoretical explanations are available for the fact that evidence of conjugation with sulfur-oxygen bonds is apparently conflicting. Further, because of the very nature and manifold degeneracy of d orbitals, geometrical requirements for d -orbital resonance are not

necessarily the same as those required for resonance among octet structures.

The author is grateful to Professor H. Hauptmann and to Professor A. Lüttringhaus for a critical reading of this paper.

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