Volume 1

organic
sulfur
compounds

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ORGANIC SULFUR COMPOUNDS

Edited by

N. KHARASCH

VOLUME I

EDITORIAL PREFACE

In the past two decades, unprecedented world-wide progress has been made in the study of organic sulfur compounds. An avalanche of research papers by chemists, biochemists, pharmacologists, bacteriologists and innumerable industrial scientists, among others, clearly demonstrates the ever increasing importance of organic sulfur chemistry in many disciplines. The studies have not only been extensive; many intensive, theoretical investigations present results which can assist the integration of the work.

Occasionally, as with the penicillins,[1] a suitable joint effort has been made to collate the research results up to a given stage. But in many equally important sectors this has not been done. The resulting sparse coverage of many phases of organic sulfur chemistry in standard review journals is particularly regrettable, because the studies are frequently of immediate interest to many groups of scientists. Volume IX of the second edition of Houben-Weyl's *Methoden der Organischen Chemie*[a] is a major step in the right direction, but the very magnitude of this magnificent German compendium makes frequent up-dating difficult. Even now, this indispensible work is several years behind the advancing front; and even in an oversize book of 1337 pages many major topics have necessarily been completely omitted or given brief treatment. There thus appears to be a definite need for further correlative works on the chemistry of organic sulfur compounds.

The present series of volumes was planned to provide a convenient opportunity for research workers in organic sulfur chemistry to prepare discussions in the areas of their special interests. The articles in Volume I aim to indicate the background to each field of work and, especially, to present the pertinent ideas, specific accomplishments and the problems in each area. The essays are generally brief, authoritative, and current. While they are stated in the technical language required by each field, they should prove to be manageable to any reader with a suitable background in organic chemistry. We believe they will be helpful not only to specialists in organic chemistry, but also to advanced students and to research workers in related areas of study.

In preparing these volumes, we were aware of the valuable monographs and reviews on specific subjects. These are referred to in particular chapters and are also summarized in a special appendix.[3,4] In the individual articles, attention was given to preparing adequate bibliographies to permit easy access to the original literature. To offset, at least in part, the omission of many areas of organic sulfur chemistry in Volume I, the editor has included an annotated bibliography in the Appendix. These notations cite many other areas and recent contributions to organic sulfur chemistry.

In the contributed articles, while a uniform editorial style has been adopted as far as possible, individuality was encouraged by asking authors to develop their material as they desired, without any rigid preset pattern. The selection of a cross-section of

current interests in Organic Sulfur Compounds for the titles of Volume I of this series was a matter of deliberate choice. The alternate possibility of restricting the material to one major aspect, such as reaction mechanisms, synthesis or medicinal interests was also carefully considered, as was also the possibility of including individual monographs, of sufficient scope, as part of the series. The latter alternatives also have quite valuable features, hence Volume I does not preset the contents pattern for later volumes in the series, numbers II and III of which are already in active preparation.

From the editor's viewpoint, the opportunity to participate in the initiation and preparation of the present volume was a rewarding experience—made both possible and enjoyable primarily through the cooperation and encouragement of the contributing authors and the representatives of Pergamon Press. I am deeply indebted to each of these friends; and also to those whose prior commitments prevented their active participation in the preparation of Volume I, but who—nevertheless—took the time to make specific suggestions and to show their interest in the progress of the work. Among the latter, I wish especially to mention Drs. Charles D. Hurd, Marvin Carmack, Wm. E. von Doering, Melvin Calvin, Frederick G. Bordwell, Vincent du Vigneaud, A. N. Nesmeyanov, Robert N. Haszeldine, W. Jenny and Arthur Roe. The need to limit Volume I to a reasonable length necessarily, of course, also omits the contributions of many other leading authors on topics of the greatest interest. It is expected that these will appear in succeeding volumes.

I also wish to express my appreciation to Professors F. Wessely and H. Zorn, of Vienna, and to Dr. W. A. Waters, of Oxford, for their hospitality and kindness in arranging for library facilities for this work, during visits to their institutions, while I was on a Fulbright research appointment in Vienna for the academic year 1959–1960.

The efforts of the editor, the individual contributors, and the many colleagues who helped this undertaking in one way or another, will, I am sure, be amply repaid if the essays in Volume I and in those which follow will activate the critical interests of our readers in the specific details of this intriguing domain of organic chemistry. The most fascinating work lies just ahead.

Los Angeles, California   Norman Kharasch
September 1960

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3. Recent monographs include those of F. Challenger, V. du Vigneaud, E. E. Reid, Young and Maw, etc. Cf. the appendix for the full listing.

4. A list of references to recent reviews which pertain to organic sulfur compounds is given in the appendix.

CONTENTS

THE STRUCTURES OF ELEMENTAL SULFUR†

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Abstract—Although numerous allotropic forms of sulfur have been characterized, only those for which complete structural information is available will be discussed in detail here. It is remarkable that the very familiar "monoclinic sulfur" of elementary chemistry texts has yet to be thoroughly investigated. In fact, of the many varieties of sulfur which have been discovered, only two can be said to have been satisfactorily studied in the structural sense. These are α-sulfur (rhombic sulfur, orthorhombic sulfur, octahedral sulfur) and ρ-sulfur (Aten's sulfur, ε-sulfur, rhombohedral sulfur, trigonal sulfur). There are preliminary reports on some of the other varieties which will be described briefly. The interest in the precise structures of elemental sulfur in relation to interpretation of the reactions of sulfur compounds is also noted.

INTRODUCTION

THE molecular structure of sulfur is governed by two simple geometrical considera-tions: first the bond angle S—S—S, and second the dihedral angle of the grouping S—S—S—S. The importance of this latter was first pointed out by Pauling.[1] In order to grasp its meaning fully let us consider a group of four atoms (Fig. 1(a)) arranged
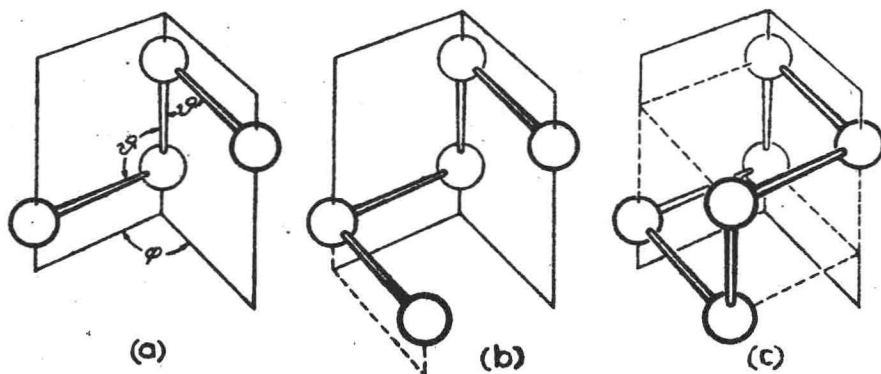
FIG. 1. (a) A group of four atoms with the two bond-angles ϑ, and the dihedral angle, φ, all equal to 90°. (b) The same, with a fifth atom added in the *cis*-position, ϑ and $\varphi=90°$, as above. (c) The same, with a sixth atom added as before. Note that this results in the formation of a regular six-membered ring. Note also the relation of the six atoms to a cube.

so that the two bond-angles, ϑ, are 90°, and the dihedral angle, φ, between the two groups of three atoms is also 90°. (We shall see later that in the case of sulfur the normal values for these angles are both greater than 90°, but we use 90° now merely

for simplicity.) If a fifth atom is added, preserving the conditions that $\vartheta=\varphi=90°$, there are two positions which satisfy these conditions: these may be termed *cis* and *trans*, and in Fig. 1(b) a fifth atom has been added, in the *cis*-position. In Fig. 1(c) a sixth atom has been added, again with $\vartheta=\varphi=90°$, and again in the *cis*-position, and it may be seen that this results in the formation of a regular six membered ring. It may
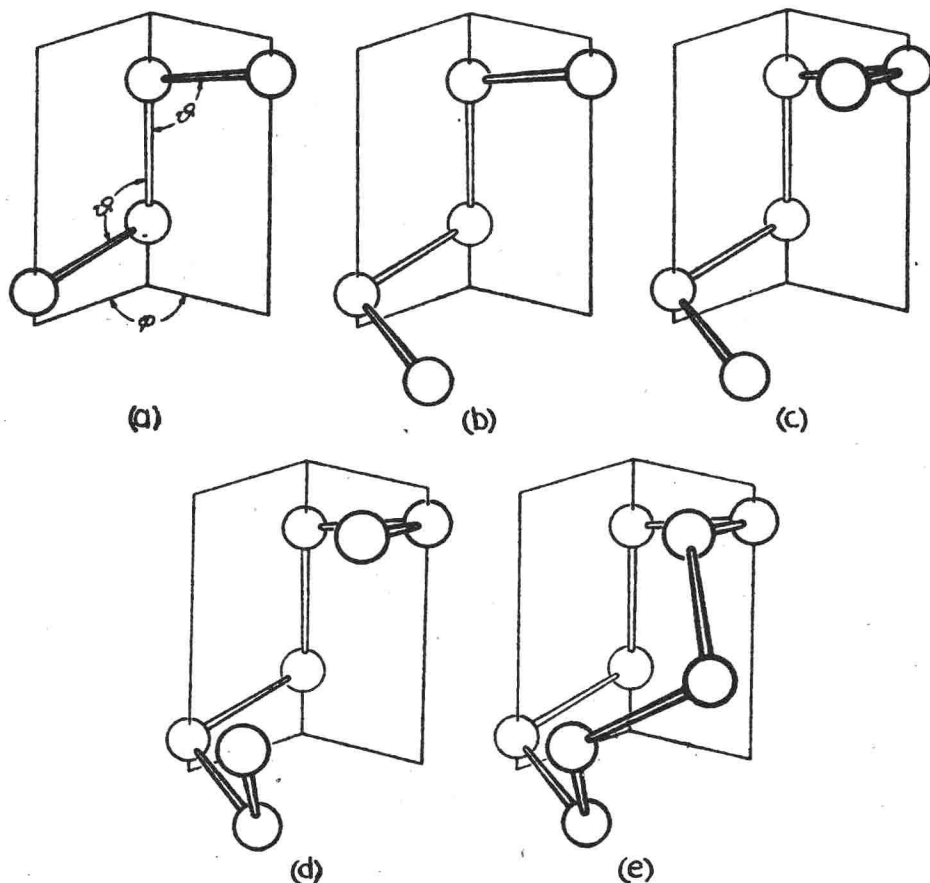
FIG. 2. (a) A group of four atoms with the two bond-angles, ϑ, equal to 105°, and the dihedral angle, φ, equal to 102°. (b) The same, with a fifth atom added in the *cis*-position, ϑ and φ as above. (c) The same, with a sixth atom added, as before. (d) The same, with a seventh atom added, as before. (e) The same, with an eighth atom added, as before. Note that this results in the formation of a regular eight-membered ring.

also be seen, for this special case of $\vartheta=\varphi=90°$, that the six atoms lie at the vertices of a cube.

The ordinary form of a sulfur ring, however, is not S_6, but S_8, as in α- and β-sulfur. The reason for this[1] lies in the normal values for ϑ and φ. The following are some values of the bond-angle, ϑ, which have been reported: 104° in dimethyltrisulfide,[2] 113° in β,β'-bis-iodoethyl trisulfide,[3] 104° and 105° barium tetrasulfide monohydrate,[4] 110°, 106°, 110° and 109° cesium hexasulfide,[5] 104° in dimethanesulfonyl disulfide,[6]

103° in barium tetrathionate dihydrate,[7] and 104° in barium pentathionate dihydrate.[8] The normal S—S—S bond-angle is thus about 105°. Some values which have been found for the dihedral angle, φ, are: 92° in sulfur monochloride,[9] 93° in dimethyltrisulfide,[2, 3] 74° and 77° in barium tetrasulfide monohydrate,[4] 79°, 82° and 61° in cesium hexasulfide,[5] and 94° in the related molecule hydrogen peroxide.[10] The values found in the S_4^{2-} and S_6^{2-} ions appear to be quite a bit smaller than those found in the isolated molecules, in which the normal dihedral angle is apparently a little greater than 90°. As opposed to the above open chain compounds and ions, in a regular n-membered ring (n even) the values of ϑ and φ are of course not independent, for if ϑ is increased, φ must decrease. For example, when the values $\vartheta=105°$ and $\varphi=102°$ are used in the construction of a chain of sulfur atoms, then, if the successive atoms are added in the *cis*-position, ring closure results on the addition of the eighth atom, as shown in Fig. 2. The actual values found in the molecules S_8 and S_6, as described below, represent equilibrium conformations corresponding to minimum strain. The S_8 molecule is less strained than the S_6 molecule because an eight-membered ring having more nearly favorable values of both ϑ and φ is geometrically possible.

α-Sulfur

The crystal structure of α-sulfur was first determined by Warren and Burwell,[11] and later refined by Abrahams.[12] α-Sulfur is orthorhombic, space group D_{2h}^{24}-*Fddd*, with $a=10.44$ Å, $b=12.84$ Å, $c=24.37$ Å, 128 atoms in the unit cell. X-ray analysis shows that the structure is based on the packing of S_8 molecules (sixteen per unit cell). The molecular constants are: S—S bond-length, 2.037 Å, S—S—S bond-angle, 107.8°; S—S—S—S dihedral angle, 99.3°. The molecule may be thought of as two squares of sulfur atoms 0.99 Å apart, the plane of one parallel to the plane of the other, but rotated 45°, as shown in Fig. 3; this figure should be compared with Fig. 2(e). The molecular symmetry is D_{4d}-$\overline{8}2m$, but the symmetry of the environment of a molecule
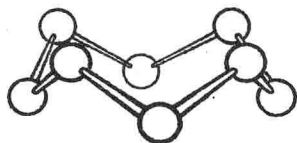

FIG. 3. The S_8 molecule, a regular, staggered, eight-membered ring. Compare with Fig. 2(e).
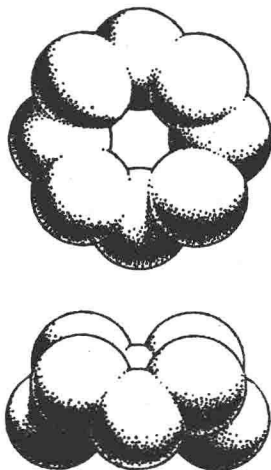

FIG. 4. Two views of the S_8 molecule, made with the van der Waals radius for sulfur as deduced from intermolecular distances in crystalline sulfur.

in the crystal is C_2-2. Each molecule has ten van der Waals contacts with other molecules, two of 3.37 Å, four of 3.50 Å, and four of 3.69 Å. The reason for the spread of 0.3 Å among the closest van der Waals contacts is not known. All other intermolecular S · · · S distances are greater than 3.75 Å. Two views of the S_8 molecule, made with the packing radius of the sulfur atom, are shown in Fig. 4.

β-Sulfur and γ-Sulfur

The structures of β-sulfur (ordinary monoclinic) and γ-sulfur have not been completely worked out, although both are probably based on packing of S_8 molecules. The small heat of transition, α-sulfur → β-sulfur (95 cal/g atom) strongly suggests that, like α-sulfur, β-sulfur is octameric. This observation is, however, complicated by the structural data reported for β-sulfur:[13] space group C_{2h}^5—$P2_1/a$, $a=10.90$ Å, $b=10.96$ Å, $c=11.02$ Å, $\beta=83°16'$, forty-eight atoms in the unit cell. It follows from these data and from space group theory that if β-sulfur consists of S_8 molecules, at least two of them in the unit cell must be centrosymmetric. Since centrosymmetry is impossible for a staggered 8-membered ring, the β-sulfur structure must, if the space group determination is correct, involve either disorder or free rotation, and the final answer must await more comprehensive investigation. γ-Sulfur (nacreous sulfur) is prepared by allowing sulfur to crystallize from a slowly cooled saturated alcohol solution which has been boiled for several hours. Crystals of γ-sulfur are also monoclinic, space group C_{2h}^4—$P2/n$, $a=8.57$ Å, $b=13.02$ Å, $c=8.23$ Å, $\beta=112°54'$, thirty-two atoms in the unit cell.[14] A structure based on packing of S_8 molecules (four per unit cell) together with qualitative intensity considerations has been proposed by de Haan,[14] but no details are as yet available.

ρ-Sulfur

A preliminary note on the structure of ρ-sulfur has been published,[15] and a complete structure determination has since been carried out.[16] ρ-Sulfur is formed, along with α-sulfur and other forms of solid sulfur, when cold concentrated HCl is mixed with saturated $Na_2S_2O_3$, and a toluene extract of the mixture is cooled until crystallization occurs. Crystals of ρ-sulfur are trigonal, space group C_{3i}^2—$R\bar{3}$, $a=10.82$ Å, $c=4.28$ Å, (hexagonal axes), eighteen atoms in the unit cell.[16, 17, 18] The structure is based on packing of S_6 molecules (three per unit cell). The molecular constants are: S—S bond-length, 2.059 Å; S—S—S bond-angle, 102.2°; S—S—S—S dihedral angle, 74°. The bond-angle of somewhat larger than 100° (which is apparently characteristic of S—S—S bonds) results in a decrease in the dihedral angle, as shown in Fig. 5. The
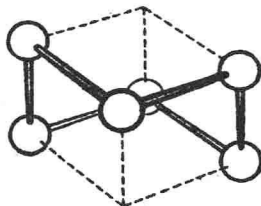
FIG. 5. The S_6 molecule, a regular, staggered, six membered ring. The normal S—S—S bond-angle of about 105° results in a conformation related to an obtuse rhombohedron, rather than a cube (cf. Fig. 1(c)).

symmetry of an isolated molecule is D_{3d}–$3m$, but the symmetry of the environment of a molecule in the crystal is C_{3i}–$\bar{3}$. Each molecule has eighteen van der Waals contacts with other molecules, twelve of 3.50 Å and six of 3.52 Å. All other intermolecular distance are greater than 3.70 Å. The similarity between the packing of S_8 molecules in α-sulfur and S_6 molecules in ρ-sulfur is noteworthy. Two views of the S_6 molecule, made with van der Waals radii, are shown in Fig. 6.

Fibrous sulfur

Fibrous sulfur is obtained by cooling and stretching melted sulfur. The complex equilibrium which exists in liquid sulfur will not be discussed here. Although the structure of fibrous sulfur has not yet been fully worked out, it undoubtedly consists of helical chains similar to those which occur in the metallic forms of selenium and tellurium. As pointed out above, the normal values of the S—S—S bond-angle and the S—S—S—S dihedral angle lead to ring closure at S_8 when successive atoms are added in the *cis*-position. Given, on the other hand, an extended chain of sulfur atoms which
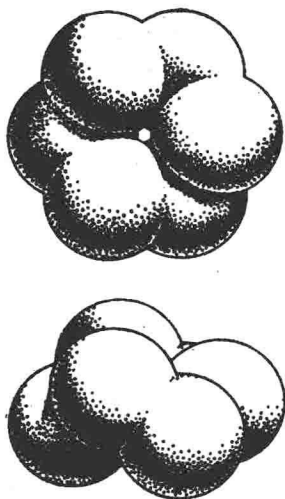
FIG. 6. Two views of the S_6 molecule, showing van der Waals radii, as in Fig. 4.
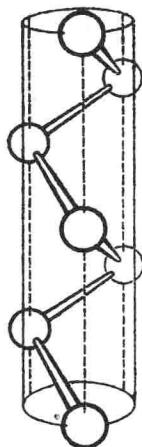
FIG. 7. A helical chain, all *trans*, as found in metallic selenium and tellurium. The fibrous sulfur structure probably differs from these in that there are not exactly three atoms per turn of the helix.

is then stretched, the conformation assumed will be all *trans* so that the maximum length will be attained.

In metallic Se and Te the spirals are exactly threefold, i.e. there are three atoms along the chain in one turn of the helix. Such a helical chain is shown in Fig. 7. The number of atoms per turn in the case of fibrous sulfur is not known: Pauling[1] proposed a structure with three and a half atoms per turn, while Prins et al.[19] have suggested one with three and one-third atoms per turn. Both structures have acceptable values for ϑ and φ. It will be of interest to compare these values for the helical sulfur molecule, when they have finally been established, with those observed in the other forms of sulfur.

CONCLUSION

Although there is still much to be established regarding the structures of most of the forms of solid sulfur, the evidence available at present indicates that an S—S—S bond-angle of about 105° and an S—S—S—S dihedral angle of a little greater than 90° are normal, and that structures which show significant deviations from these values involve strain energy. These two geometrical considerations certainly should be included in discussions concerning reactions of compounds containing the S—S bond, especially with regard to transition states or activated complexes, even though the precise energetics are not now known. Unfortunately the reactions of sulfur compounds have not, as yet, been studied sufficiently to make use of this structural information in a useful manner (cf., however, the chapter by L. Reed, in this volume on the strain effects in α-lipoic acid). As the mechanisms of the reactions of elemental sulfur are more fully elucidated (cf. the chapter by O. Foss on "Ionic Scission of the Sulfur–Sulfur Bond") the structural data will undoubtedly be of increasing importance.

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CHAPTER 2

THE INORGANIC ACIDS OF SULFUR

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(Shell Internationale Research Maatschappij N.V.)

Abstract—No feature of the inorganic acids and oxides of sulfur stands out more prominently from recent research than their tendency to occur in polymeric forms. It seems useful therefore to stop trying to force the ever-increasing number of polymeric molecules into a frame of reference suitable only for the simplest compounds of the group. If, instead, we apply the concepts and terminology of polymer chemistry, we will discover a degree of order unsuspected for so diversified a class of compounds.

For the sake of clarity this survey will be restricted to those acids that are built up solely of sulfur, hydrogen and in most cases, oxygen. Furthermore, reactions of these acids in which other elements than the above play a decisive role chemically will not be considered. This will allow us to focus attention on the genetic relationships within the group. This paper, therefore, consists of the following sections. First, the simple building blocks are listed and new terms are defined. Secondly the three main reaction mechanisms which relate the acids to the building blocks, and to each other genetically are described in general. Finally it is considered how applications of the above generalizations to the known chemistry of the individual acids may lead to their unified classification.
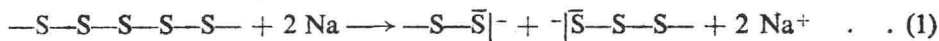
THE BUILDING BLOCKS

A. *The even monomers:* S, SO, SO_2, SO_3, SO_4

As both sulfur and oxygen possess six valency electrons, the sulfur atom and its simple combinations with oxygen, the oxides, are electronically unsaturated and inherently difunctional. Hence their tendency towards polymerization.

The polymeric character and properties of the various forms of elemental sulfur have received much attention lately.[2] The various molecular species are generally believed to interconvert via diradical intermediates. It takes considerable energy to produce diradical chains from the cyclic octamer, which is the stable form at room temperature, as is witnessed by the steep viscosity maximum of molten sulfur at 160° C. The very small concentration of diradicals formed at just below this temperature leads to rapid polymerization to very long chains, which only gradually break down to smaller aggregates as the temperature is increased. As a further illustration of the tendency of sulfur to polymerize we may note the fact that the vapor has to be heated to 2000° C to produce a measurable number of S atoms from the S_2 molecules, which are prevalent at 1000° C. These facts are mentioned to support two points: first, that under the conditions where the chemistry of the sulfur acids takes place, we have to think of elemental sulfur always in terms of sulfur *chains*; second, that radical fissions of these sulfur chains at these low temperatures will be a relatively uncommon process, because of the high activation energy required (25 kcal/mole for the hydrogen polysulfides,[3] or 35 kcal/mole for elementary sulfur[2]).

The energy may be supplied, of course, by reactions with strong reducing agents such as sodium, or strong oxidants as chlorine:

7

$$-S-S-S-S-S- + 2\,Na \longrightarrow -S-\overline{S}|^- + {}^-|\overline{\underline{S}}-S-S- + 2\,Na^+ \quad . \quad . \text{ (1)}$$

$$-S-S-S-S- + Cl_2 \longrightarrow -S-S-Cl + Cl-S-S- \qquad\qquad . \quad . \text{ (2)}$$

In solvents of high dielectric constant, however, a low-energy path for polymerization and depolymerization is provided by reactions with Lewis bases.[4] Under the polarizing influence of these, the sulfur atoms can be visualized as difunctional in that they act "as Lewis acids on one side and Lewis bases on the other one".

$$B \to \overline{\underline{S}} \to \overline{\underline{S}} \to \overline{\underline{S}} \to \overline{\underline{S}}|^- \qquad\qquad . \quad . \quad . \text{ (3)}$$

Thus, the polarized sulfur atom, though only of virtual existence, is the simplest even monomer.

Sulfur monoxide, SO, has been the subject of much investigation. Recent studies have made its existence as a monomer highly doubtful, but its polymers are known.

Sulfur dioxide and sulfur trioxide do occur in monomeric forms, presumably because resonance between double bonded structures exerts a stabilizing influence in these molecules, for which there is no evidence for diradical formation at any temperature at which they are stable. They are classical examples of Lewis acids, as they easily share an electron pair with any suitable donor. The tendency to polymerize by donating an electron pair, themselves, to another molecule of their kind is only incipient in sulfur dioxide, but very pronounced in the trioxide.

Sulfur tetroxide SO_4 has not been isolated in monomeric form, but does exist in the form of polymers.

From these postulated or actually existing even monomers, the great majority of sulfur acids is built up.

B. *The telomers (polymerization initiators)*: H_2O, H_2O_2, H_2S, H_2SO_3, H_2SO_4 *and derived negative ions**

Any number of sulfur atoms or of sulfur oxide molecules, if lined up in an unbranched chain, can be made electronically saturated—according to the octet rule—by accepting one electron pair from a Lewis base:

$$|\overline{\underline{B}}| + \overline{\underline{A}}| + \overline{\underline{A}}| + \cdots \longrightarrow |\overline{\underline{B}}|\overline{\underline{A}}|\overline{\underline{A}}|\overline{\underline{A}}| \cdots \text{ etc.} \quad . \quad . \quad . \text{ (4)}$$

Thus, Lewis bases with sufficient electron donating tendency will act as initiators for these polymerizations. Only those Lewis bases that will lead to formation of the sulfur-hydrogen-oxygen acids will be included in this survey. These are the common simple Brönsted acids, built up from the same elements and, particularly, the corresponding negative ions.

It should be noted that it is again the six-electron valency shell of sulfur and oxygen which leads to the occurrence of simple complimentary pairs of mononuclear Lewis

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* "A telomer is a chemical compound capable of forming the terminal part of the polymer." . . . "In many cases the telomer may be a catalyst for the polymerization reactions, as when dimethylamine is used as a catalyst in the polymerization of ethylene oxide or ethylene imine:"

$$(CH_3)_2NH + n\ CH_2-CH_2 \longrightarrow (CH_3)_2N(CH_2CH_2O)_nH.[5]$$
$$\diagdown\!\!\diagup$$
$$O$$
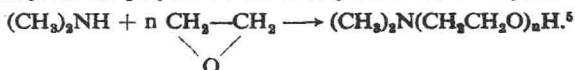
The Lewis bases listed can be looked upon as telomers, in view of this definition.

acids and Lewis bases: S and S⁻, SO_2 and SO_2^-, SO_4 and SO_4^-. This affords at least part of the explanation for the peculiar varieties of inorganic acids of sulfur.

C. The odd monomers: $\cdot SO_2^-$, $\cdot SO_3^-$, $\cdot SO_4^-$

These are three still hypothetical intermediates the occurrence of which we have to assume in particular reduction and oxidation processes. Since $\cdot SO_2^-$, $\cdot SO_3^-$ and $\cdot SO_4^-$ are monofunctional, they cannot form polymers but do form dimers. It is interesting to notice that they are isoelectronic with the well-known odd molecules $\cdot ClO_2$, $\cdot ClO_3$, and the less-firmly established $\cdot ClO_4$. The $\cdot SO_2^-$ radical ion is, furthermore, isoelectronic with $\cdot NO_2^-$, a species present in sodiumnitroxylate, $Na_4N_2O_4$, to the extent of as much as 23 per cent.[6]
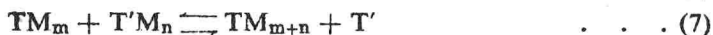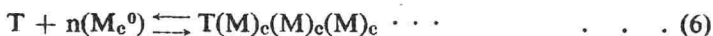
THE MAIN REACTION MECHANISMS

A. The reversible base-catalyzed polymerization of the even monomers

Depending on the molecular form in which the even monomer occurs before the reaction, polymerization can take place in two ways: by addition or by displacement. If the monomer is present as such, the initiating telomer (Lewis base), T, will successively add monomer molecules:

$$T + M + M + M + \cdots + M \rightleftharpoons TMMM \cdots M \qquad . \quad . \quad . \ (5)$$
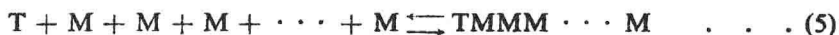
During this process each monomer molecule which adds is so polarized that an effective negative charge is located on the terminating atom and in such a manner that the base strength at the terminating group is sufficient to aquire another monomer-acid.
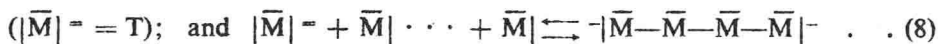
If the starting material is a pure cyclic polymer, M_n^0, or is a chain already terminated by an initiating telomer, further polymerization can occur by displacement:

$$T + n(M_c^0) \rightleftharpoons T(M)_c(M)_c(M)_c \cdots \qquad . \quad . \quad . \ (6)$$

$$TM_m + T'M_n \rightleftharpoons TM_{m+n} + T' \qquad . \quad . \quad . \ (7)$$

In reaction (6) the c—membered rings are successively opened by displacement of one M segment from another one; and in reaction (7), one telomer is displaced by a chain which has another telomer (which may be of the same kind) as a terminating group.

From the equations (5), (6) and (7), it is seen that "high" polymers can be expected at very low telomer concentrations, while increase in telomer (initiator) concentrations will depolymerize the chains by reversal of equilibrium (7).

In those cases where an even monomer is polymerized by its complimentary telomer ion (i.e., for M: M⁻) the chains are symmetrical and can grow with equal ease on both sides:

$$(|\overline{M}|^- = T); \text{ and } |\overline{M}|^- + \overline{M}| \cdots + \overline{M}| \rightleftharpoons {}^-|\overline{M}-\overline{M}-\overline{M}-\overline{M}|^- \quad . \quad . \ (8)$$

B. The dimerizations of the odd monomers

As the odd monomers are monofunctional, dimerization yields electronically saturated compounds:

$$M \cdot^- + M \cdot^- \longrightarrow {}^-M:M^-$$

As this reaction mechanism is a familiar one in organic chemistry, it needs no further elaboration here. The extent of its occurrence depends, of course, on the lifetime of the