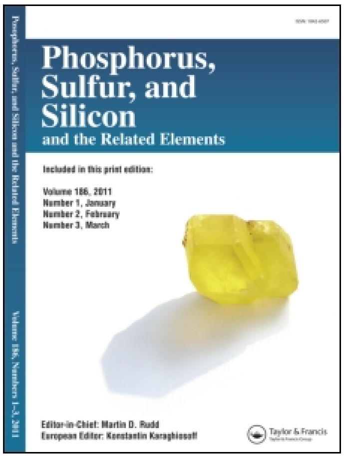


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE REACTION OF HYDROGEN SULFIDE WITH SULFOXIDES

Y. Mehmet[a]; J. B. Hyne[a]
[a] Alberta Sulphur Research Ltd., The University of Calgary, Calgary, Canada

To cite this Article Mehmet, Y. and Hyne, J. B.(1976) 'THE REACTION OF HYDROGEN SULFIDE WITH SULFOXIDES', Phosphorus, Sulfur, and Silicon and the Related Elements, 1: 1, 47 — 54

To link to this Article: DOI: 10.1080/03086647608070711

URL: http://dx.doi.org/10.1080/03086647608070711

Phosphorus and Sulfur
1976, Vol. 1, pp. 47-54

THE REACTION OF HYDROGEN SULFIDE WITH SULFOXIDES

by

Y. Mehmet and J. B. Hyne

Alberta Sulphur Research Ltd., The University of Calgary, Calgary, Canada

Received January 14, 1974

ABSTRACT

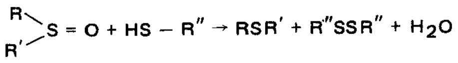
The reaction of hydrogen sulfide with a series of dialkyl sulfoxides yielding sulfur, water and the corresponding dialkyl sulfide has been examined.

$$H_2S + RSOR' \rightarrow H_2O + 1/8\, S_8 + RSR''$$

The kinetics indicate the existence of important intermediates. These have been confirmed spectroscopically and shown to be ionic in character by conductimetric studies. A mechanism is proposed which accommodates the requirement for participation of ionic intermediates. Some suggestions are offered for the process whereby the S_8 species is built up from molecularly distinct sulfur atoms.

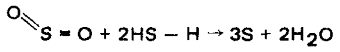
Introduction

The oxidizing properties of sulfoxides, particularly that of dimethyl sulfoxide are well known;[1,2] in these reactions, the sulfoxide is normally reduced to the corresponding sulfide. The reaction of sulfoxides with H_2S may be considered to fall within the broader scope of the generalized reaction between the >S = O and –SH functional groups. The reactions of organic sulfoxides with thiols have been investigated by others[3-9] and yield the corresponding disulfides.



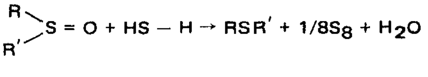
$$\begin{matrix}R\\R'\end{matrix}\!\!>S=O + HS-R'' \rightarrow RSR' + R''SSR'' + H_2O$$

The generalized reaction also encompasses the industrially important Claus reaction between H_2S and SO_2 when R″ = H, and R and R′ are considered to have been replaced by a single oxygen atom.



$$O\!\!\diagdown S=O + 2HS-H \rightarrow 3S + 2H_2O$$

Both from a general chemical interest and from an applied standpoint it is therefore of some importance to examine the particular reaction of hydrogen sulfide with sulfoxides.



$$\begin{matrix}R\\R'\end{matrix}\!\!>S=O + HS-H \rightarrow RSR' + 1/8S_8 + H_2O$$

This paper reports the results of a study of the variation of sulfoxide structure on the kinetics of the reaction and presents spectroscopic and conductimetric evidence for the involvement of ionic intermediates. The experimental findings are incorporated in a proposed mechanism.

Experimental Section

Materials

Dimethyl Sulfoxide: From Fisher Scientific Co., was dried over calcium hydride and distilled at reduced pressure. Bp 72°C/14 mm [Lit. 51-52°C/1 mm[10]].

Ethylmethyl Sulfoxide: Prepared by *N*-bromosuccinimide (NBS) oxidation[10] of ethylmethyl sulfide, was dried over calcium hydride and distilled under vacuum. Bp 75°C/14 mm [Lit. 72-74°C/11 mm[11]].

Trimethylene Sulfoxide: Prepared by H_2O_2 oxidation[12] of trimethylene sulfide, was dried over calcium hydride and distilled under reduced pressure. Bp 91.0°C/14 mm [Lit. 91.2°C/14 mm[12]].

Diethyl Sulfoxide: Prepared by NBS oxidation[10] of diethyl sulfide, was dried over calcium hydride and distilled under reduced pressure. Bp 88°C/14 mm [Lit. 88-90°C/15 mm[13]].

Tetramethylene Sulfoxide: From Aldrich Chemical Co., was dried over calcium hydride and distilled at reduced pressure. Bp 110°C/14 mm [Lit. 105-107°C/12 mm[14]].

N-Bromosuccinimide: From Matheson, Coleman and Bell, mp 181-183°C, used without further purification.

Hydrogen Peroxide: From J. T. Baker Chemical Co., 30% "Baker Analyzed" grade, was used as such.

Hydrogen Sulfide: C.P. grade from Matheson of Canada Ltd., was passed from the steel cylinder through columns containing $CaCl_2$ and a tube of P_2O_5 before use.

Sulfur: From The British Drug Houses Ltd., sublimed product of high purity, *i.e.*, better than 99.9%S, was used without further purification.

Hydrogen Polysulfide (H_2S_x): Prepared by the method described in Reference 15 from Na_2S_x.

Instrumentation

The kinetic studies were performed by following sulfur production (λ = 320 nm) with a Beckman ACTA V uv-Visible recording spectrophotometer capable of either single beam or double beam operation. Matched 10 mm silica cells, housed in temperature controlled rectangular cell holders were used for the sample and solvent reference. The desired temperatures were maintained within ± 0.2°.

An automatic balancing a.c. conductance bridge with digital print-out (General Radio Type 1680A) was used for conductance measurements. The cells were of 8 ml capacity with platinum bead electrodes and were thermostatted in an oil bath at 25° during the measurements.

The rate data were analyzed on an EAI-TR20 analogue computer. Nmr spectra were obtained with a Varian A-60 spectrometer.

Kinetic Procedure

For each kinetic run about 20 ml of each sulfoxide was used. Prior to each run, the sulfoxide samples were brought to the temperature of that run and the H_2S gas passed through. In view of the low solubility of sulfur in the sulfoxides, initial H_2S concentrations were chosen so that the final sulfur concentration would be less than saturation. The concentration of the H_2S was determined by weight difference before and after passage of the gas. Normally the gas flow was so adjusted that the desired concentrations were reached within about one minute; 3 ml samples of H_2S/sulfoxide solution were withdrawn from the stock solution and placed in 1 cm uv cells which were then immediately sealed and placed in the thermostatted cell compartment of the spectrophotometer. The reactions were conveniently followed by continuous recording of the rise in product sulfur absorption at or near 320 nm. Calibration plots of absorbance *versus* concentration of sulfur were constructed for each sulfoxide at each required temperature and used throughout the kinetic studies for conversion of observed absorbances into concentrations. The overall accuracy in concentration measurements was 0.5%. The sulfur concentration-time data yielded rate constants and activation parameters by use of analog computer analysis.

In those solutions of H_2S where the concentration was 0.05 M or more, formation of yellow colors was observed. These colors became more intense with time, reached a maximum and faded. Spectrophotometrically they displayed a broad absorption band in the visible around 420 nm; one example is given in Figure I. The color production is considered to be due to the intermediates involved in the reactions and will be discussed in a later section.

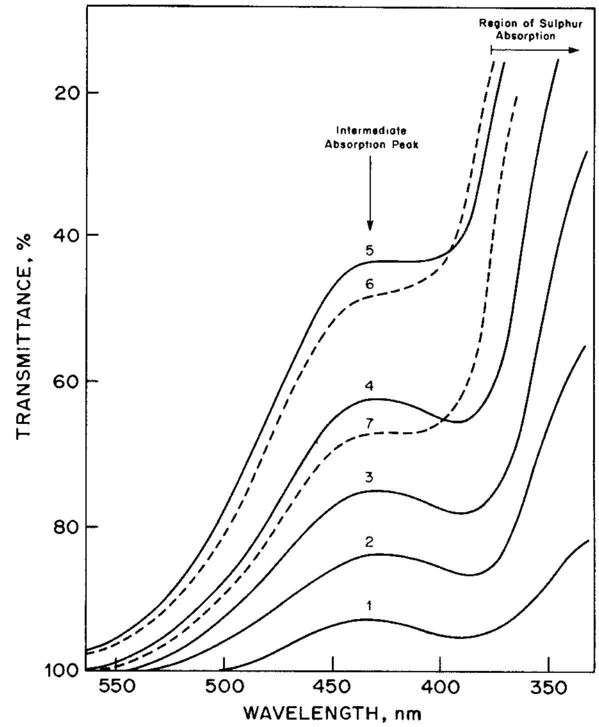


FIGURE I

UV-Visible Spectra of Dimethyl Sulfoxide/H_2S Reaction Mixture at Various Times

Results

Kinetic

Tests of the concentration-time data for simple first and second order kinetic behavior failed. This observation coupled with the clear spectroscopic evidence in Figure I of the growth and disappearance of a uv absorption at 420 nm suggested a more complex mechanism involving a relatively long lived intermediate. The irreversibility of the overall reaction was established by failure to observe the formation of any of the starting materials on bringing the products together under reaction conditions. Thus, consecutive type reactions with a simplified molecular scheme as shown below were postulated,

$$RSOR'\text{ (excess)} + H_2S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

$$\text{Intermediate species} \xrightarrow[\text{nonreversible}]{k_2} RSR' + 1/8S_8 + H_2O$$

It should be noted that the k_1 forward step is pseudo first order due to the relative excess of sulfoxide reactant over H_2S. The intermediate species involve tetravalent sulfur complexes in equilibrium with their ionic counterparts and will be discussed in detail later. Treatment of the rate equations for the above scheme is best accomplished by analog methods. Computer parameters representing k_1, k_{-1}, and k_2 were varied to yield a best fit of sulfur concentration *versus* time curves to those obtained experimentally. In general computer-generated curves could be well matched with the experimental ones. In addition to sulfur concentration curves the computer program generated the concentration of H_2S and the intermediates with respect to time. A typical computer output showing simultaneous behavior of the concentrations of the three species with time is shown in Figure II. The good fit of experimental and fitted sulfur concentrations are demonstrated.

The extracted rate constants for the various steps in the proposed mechanism at the several temperatures examined for each of the reactant sulfoxides used are reported in Table I. While k_1 and k_2 vary over a range of about 1000 and 400 times respectively, k_{-1} is of the same order of magnitude for all the sulfoxides with the exception of trimethylene sulfoxide. Figure III, based on kinetic data at 30° gives the plots of concentrations of elemental sulfur produced against time for the five reactions studied. In terms of the

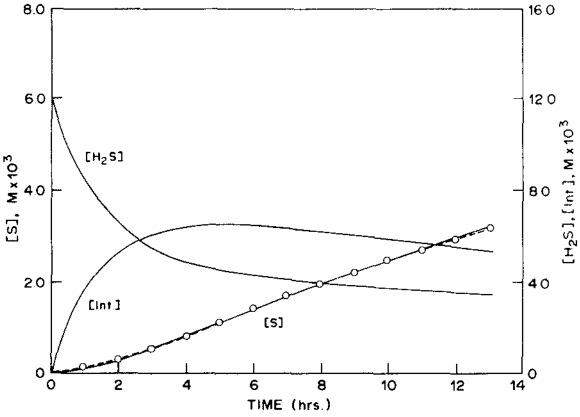


FIGURE II

Experimental (- - -) and Computer Generated (——) Curves for Dimethyl Sulfoxide/H_2S Reaction at 50°C

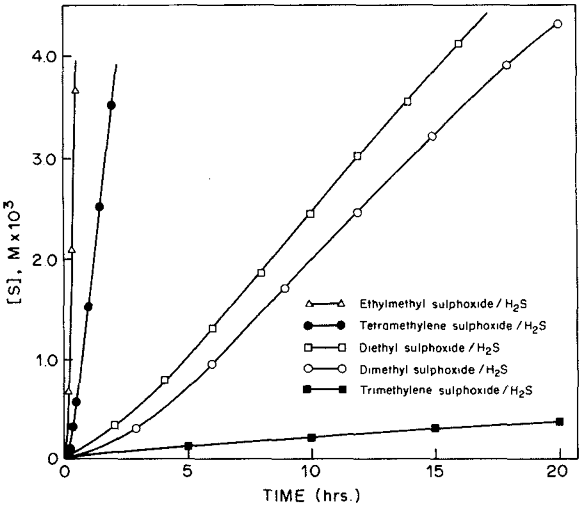


FIGURE III

The Production of Elemental Sulfur with Time in Five Sulfoxide/Hydrogen Sulfide Reactions at 30°C

TABLE I

The Rate Constants of the Reactions of Sulfoxides with Hydrogen Sulfide

	k_1 (sec^{-1}) x 10^{-5}				k_{-1} (sec^{-1}) x 10^{-5}				k_2 (sec^{-1}) x 10^{-5}			
Sulfoxide	25°	30°	40°	50°	25°	30°	40°	50°	25°	30°	40°	50°
Trimethylene	–	0.19	0.40	0.92	–	0.55	1.11	2.23	–	0.04	0.08	0.17
Diethyl	5.30	8.10	16.40	36.00	3.90	5.80	11.90	22.7	0.36	0.52	1.03	2.12
Dimethyl	3.87	5.75	11.70	23.20	2.28	3.42	6.95	13.90	0.41	0.60	1.27	2.50
Tetramethylene	58.40	83.60	164.0	334.0	4.50	7.70	18.70	37.3	4.20	5.60	11.70	26.7
Ethylmethyl	111.0	167.0	334.0	672.0	3.00	5.00	10.0	21.7	9.30	14.60	28.3	60.0

TABLE II

Enthalpies and Entropies of Activation for Various Steps in Reactions of Sulfoxides with Hydrogen Sulfide

	Step 1 (k_1)		Step 2 (k_{-1})		Step 3 (k_2)	
Sulfoxide	ΔH* (kcals/mole)	ΔS* (EU)	ΔH* (kcals/mole)	ΔS* (EU)	ΔH* (kcals/mole)	ΔS* (EU)
Trimethylene	12.4	–37	13.1	–39	13.4	–43
Diethyl	13.8	–32	12.6	–36	13.2	–39
Dimethyl	13.0	–35	13.2	–36	13.3	–38
Tetramethylene	13.8	–30	14.1	–29	14.0	–33
Ethylmethyl	13.2	–29	12.8	–32	13.5	–32

overall production of sulfur, the order of sulfoxide reactivity was:

Ethylmethyl > Tetramethylene > Diethyl > Dimethyl
> Trimethylene

The dependence of the rate constants on temperature was used to calculate enthalpies and entropies of activation (Table II) for the three important steps in the reactions.

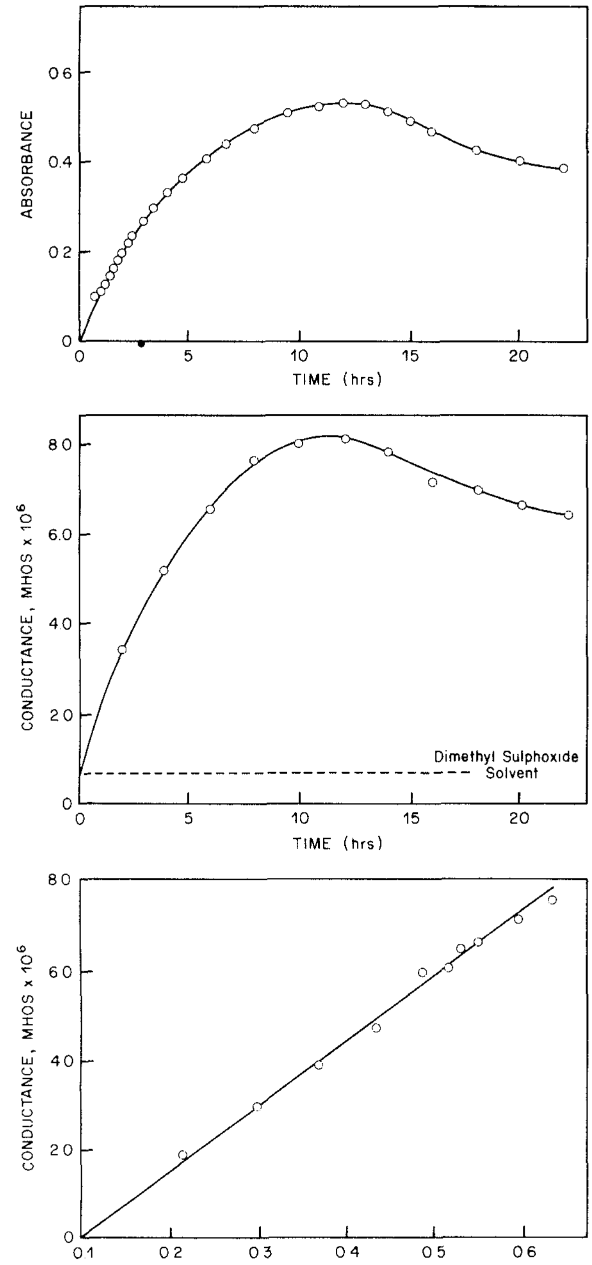


FIGURE IV

The Absorbance and Conductance Behavior with Time of a Dimethyl Sulfoxide/H_2S Reaction Mixture at 25°C

Spectroscopic and Conductimetric

As was mentioned earlier the reaction observed in more concentrated H_2S solutions in sulfoxides leads to the formation of transient yellow colors with λ_{max} around 420 nm. The lower limit of H_2S concentration for the spectrophotometric detection of the colors is about 0.05 M. Figure I illustrates the uv-visible spectra of the reaction mixtures as a function of time. While the absorption band near 420 nm increases and then decreases in intensity, suggesting intermediate species, the intensity in the sulfur (*i.e.*, reaction product) absorption region continuously increases with time. It may therefore be deduced from this experimental observation that in the sulfoxide/H_2S reactions the concentrations of the intermediate species build up, reach a maximum and then decrease due to subsequent reaction to yield sulfur, the concentration of which increases continuously. This is in accordance with the proposed reaction scheme. In Figure IV there is a sample plot of the absorbance of the suspected intermediate versus time for the reaction of dimethyl sulfoxide with H_2S.

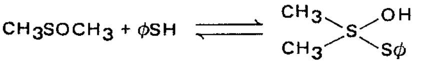
The conductance behavior of the reaction mixtures as a function of time showed a remarkable parallelism to the increasing and decreasing spectrophotometric absorption behavior. Figure IV also illustrates the conductance versus time for the same reaction of dimethyl sulfoxide with H_2S. The parallelism becomes more evident when absorbance data is plotted against the corresponding (same time points) conductance data both of which are for dimethyl sulfoxide/H_2S run under the same reaction conditions, yielding a straight line. It is also seen from Figure IV that for the dimethyl sulfoxide/H_2S reaction mixture, the times of maximum absorbance and conductance are, within experimental error, the same. The conclusion is therefore justified that the intermediate species in sulfoxide/H_2S reactions that give rise to absorption in the visible spectrum are also responsible for the observed conductance behavior.

Discussion

Proposed Mechanism

The experimental results observed leave little doubt about the involvement of intermediate species. The essential feature of the proposed mechanism (Figure V) is the initial reversible formation of the intermediate tetracovalent species, RR'S(OH)(SH), which in turn is in fast equilibrium with its ionic counterparts; the tetracovalent species, together with the participation of more sulfoxide molecules leads to products in a sequence of steps at least one of which is relatively slow.

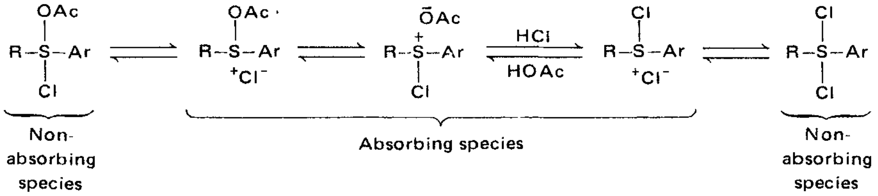
The proposed initial slow and reversible interaction of a sulfoxide molecule with H_2S is analogous to the reaction of sulfoxides with thiols. Wallace and coworkers[4,6,7] reported the formation of sulfur intermediates similar to I, *e.g.*,



$$CH_3SOCH_3 + \phi SH \rightleftharpoons \underset{CH_3}{\overset{CH_3}{}}\!>S<\!\underset{S\phi}{\overset{OH}{}}$$

They were however unable to isolate or even detect the tetracovalent species by nmr or chromatographic analysis. Further support for the formation of intermediates of this type is to be found in the reactions of sulfoxides with hydrogen iodide[11,16,19] and the actual isolation and characterization of Ar_2SCl_2.[20] The tetracovalent SF_4 molecule also has a trigonal bypyramidal structure.

The existence of equilibria between **1** and the ionic counterparts **2** and **3** is analogous to those observed in the chlorinolysis of sulfides in acetic acid,[21] and the HCl-catalyzed stereomutation reactions of sulfoxides in aqueous acetic acid,[22] *e.g.*



On mixing Cl_2 and RSAr in glacial acetic acid for example, there appeared strong uv absorbance at 390 nm (orange-yellow color) which was not characteristic of either the reactants or the products. The absorbing species have been suggested to be ionic.[21] The transient absorption maximum in sulfoxide/H_2S reactions at about 420 nm may well be due to the ionic species **2** and **3** in Figure V.

Further support for both the presence of ionic intermediary species and their time dependent concentrations comes from the conductance studies. While electrical conductivity necessarily implies the presence of ions, the possibility that this may be caused by small amounts of impurities cannot be ruled out. This, however, is unlikely in view of the fact that the conductance behavior of the reaction mixtures with time parallels their increasing and decreasing spectrophotometric absorption behavior as demonstrated in Figure IV.

Failure to observe an nmr signal for the proposed long lived species **1**, **2** and **3** requires explanation. Although specific nmr responses for terminal –SH protons in hydrogen polysulfide mixtures are observed in non-basic solvents such as CCl_4 and CS_2, in sulfoxide solvents the exchange rate between –SH protons is almost certainly much faster and could well be fast enough to yield a single time averaged –SH signal close to the H_2S proton position. Indeed, in the nmr examination of the reaction, the observed position of the H_2S signal was 8.2τ, somewhat lower than the normal position in CS_2 (9.1τ) and *furthermore* as the reaction proceeded this peak became broader and less well defined. Both the lower field position and the line broadening are in keeping with time averaging of signals from protons in different chemical environments.

The fact that the combined ionic and non-ionic intermediate concentrations reach levels comparable to the initial H_2S concentration (see Figure II) is explained by the consumption of these species in a reaction sequence involving at least one slow step. It is proposed that the reaction of I with a sulfoxide molecule to give 4 is the rate determining component of the overall reaction sequence (Figure V). This is a reasonable assumption since again an –SH entity is reacting with the sulfoxide S=O as in the initial reaction step. Subsequent reaction of **4**. involving as it does highly reactive polysulfides, will be fast. Hydrogen polysulfides have been observed to decompose rapidly into H_2S and sulfur in several organic and inorganic media.[23] Likewise we have also shown that they are very unstable in the presence of sulfoxides, decomposing to H_2S and sulfur, and also reducing the latter to the corresponding sulfides. The reason for this must lie partly in the acidity of H_2S_x species which were shown[24] to be much more acidic than H_2S.

Little attention appears to have been given in previous publications to the problem of how the individual sulfur atoms from the reactant molecules are built into the final cyclooctasulfur species S_8.

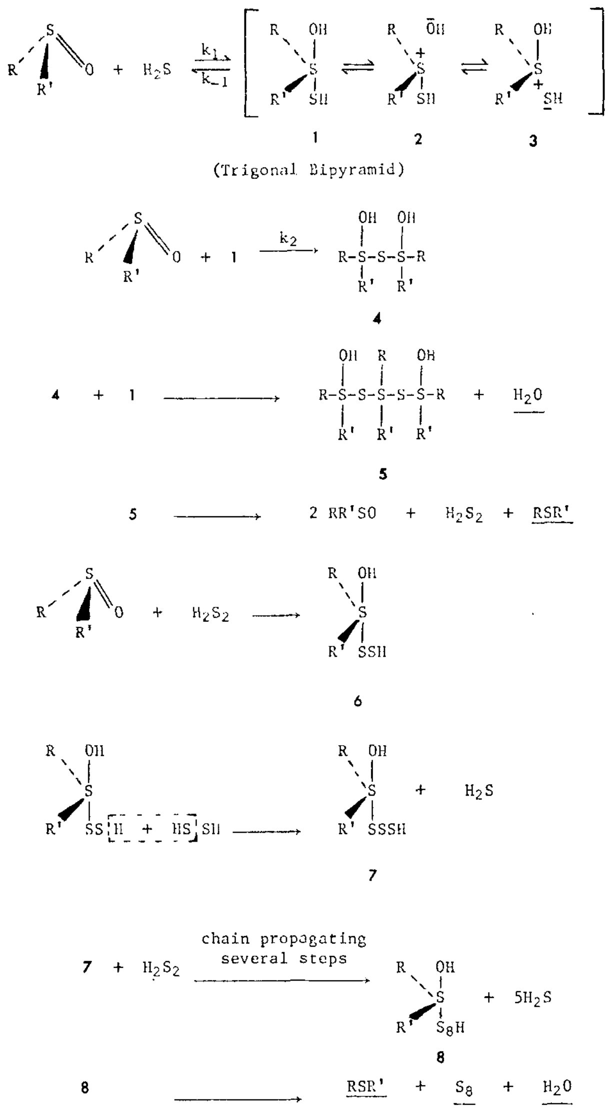
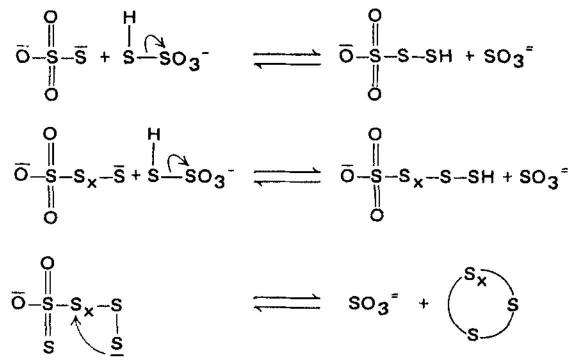


FIGURE V

Proposed Mechanism for the Reaction of Sulfoxides with H_2S

The mechanism proposed in Figure V is analogous to the sulfur chain propagation and cyclization pathway suggested[25] for the decomposition of thiosulfuric acid to give sulfur and sulfite. These reactions are *fast* compared with the initial reaction of H_2S with sulfoxide. We have shown by nmr that H_2S_x species are unstable in the presence of sulfoxide, and there is little or no discrimination between the H_2S_x species as far as reactivity is concerned. While the intermediate species (*e.g.*, 7) shown in Figure V are non-ionic it is possible that the ionized form of the polysulfane chain $RSSS^-H^+$ could be involved in the chain propagation as in the thiosulfuric acid case.



Kinetic Evidence

The rate data presented in Table I provide further support for the mechanism outlined in Figure V. The order of reactivity, as illustrated by the various forward rate constants at 30°, is summarized in Table III together with the infrared stretching frequencies of the sulfoxide S=O bond. As the stretching frequency increases and the S=O bond becomes stronger the rate of reaction with the –SH function decreases as reflected in both forward rate determining steps k_1 *and* k_2. Both of these steps involve –SH attack on the sulfoxide S=O group, H–SH in the case of k_1 and the –SH functional group of the intermediate species in the case of k_2. The variation in reactivity of the sulfoxides can also be viewed from an acid-base point of view with the acidic H_2S reacting more readily with increasingly basic sulfoxides. A

TABLE III

Variation of Rate Constants (30°C) with ν(SO) and Basicity of Sulfoxides

	Sulfoxide	ν(S=O), cm^{-1}	Rate Constants for RSOR′ + H_2S reaction k_1	k_{-1}	k_2
increasing basicity (11)	Ethylmethyl	1018 (1050)*	167.0×10^{-5}	5.00×10^{-5}	14.60×10^{-5}
	Tetramethylene	1033	83.6×10^{-5}	7.70×10^{-5}	5.60×10^{-5}
	Diethyl	1055	8.10×10^{-5}	5.80×10^{-5}	0.52×10^{-5}
	Dimethyl	1068	5.75×10^{-5}	3.42×10^{-5}	0.60×10^{-5}
	Trimethylene	1092	0.19×10^{-5}	0.55×10^{-5}	0.04×10^{-5}

* The S=O stretch in this sulfoxide is a doublet (this work).

similar dependence of rates on sulfoxide basicity[11] has been observed in the reaction with thiols.[12] Although ethylmethyl sulfoxide proved to be the fastest reacting sulfoxide, in the absence of additional information, we are not in a position to claim it to be the most basic.

The expected presence of substantial ring strain (~15 kcal/mol) in 4 membered cyclic trimethylene sulfoxide does not make it more reactive than the 5 membered cyclic tetramethylene sulfoxide which probably has very little strain (~1 kcal/mol). On the contrary, the effect of the ring strain is to strengthen the SO bond, making it less reactive.

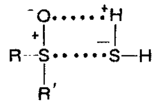
A further rationalization for the observed order of reactivities for some of the sulfoxides may be made through the use of Internal Strain Hypothesis.[26] In cyclic systems where reaction at a ring atom involves no ring opening, striking changes in reactivity are observed with variation in ring size. These differences in chemical behavior have been attributed to the changes in internal strain which accompany changes in coordination number of the ring atom undergoing reaction. In the case of 3- and 4-membered ring sulfoxides, the application of the Hypothesis is relatively simple and straightforward; generally for these systems a chemical change involving a change in coordination number of one of the ring atoms from 3 or 4 to 5, for example, a change in structure from tetrahedral to trigonal bipyramidal, will result in an increase in internal strain which will be unfavorable for the chemical change. Thus ethylene and trimethylene sulfoxides are not expected to be as reactive as the open chain ones.

All of the foregoing argues in favor of the proposed initial slow formation of an intermediate or intermediates which then react further in a second relatively slow step to initiate a sequence of fast reactions yielding product. However, we have not as yet considered the relative insensitivity of k_{-1} to sulfoxide structure. It might be expected that the trigonal bipyramidal structure of the initial intermediate would lead to less sensitivity of reactivity to structure variation than was the case in the sulfoxide. Steric strain resulting from cyclization or substituent group repulsions will be more influential in determining S=O double bond activity than in determining the stability of a tetracoordinate type structure, such as **1**. The small variation of k_{-1} with structure is therefore not surprising. Even the relatively strain free trigonal bipyramid intermediate, however, will eventually respond to steric factors, and this may well be the explanation for the noticeably different k_{-1} value in the trimethylene case.

Activation Parameters

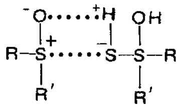
The activation parameters are assembled in Table II. The ΔH* values vary less than ±0.9 kcal/mol for all the reaction steps. Since the uncertainty is ±1.1 kcal/mol, the differences in the reported values are not significant. The similarity in the values of $\Delta H^*_{(k_1)}$ and $\Delta H^*_{(k_2)}$ is not unexpected since in terms of the proposed mechanism both steps (corresponding to k_1 and k_2) involve the interaction of an S=O group with an –SH entity.

While ΔH* variation is not greater than the experimental uncertainty as the sulfoxide reactant is changed, the corresponding ΔS* variation is clearly significant (–29 to –43 EU with an uncertainty of ±2.5 EU). In other words the rate of sulfoxide/H_2S reactions may be said to be entropy controlled. This is a situation which is not uncommon in reactions which require very specific geometry in the transition state.[27] In view of the large negative entropies of activation, it is reasonable to postulate the following four center transition states for steps corresponding to k_1 and k_2:



(a)

Transition state for k_1



(b)

Transition state for k_2

The significance, if any, of the slightly greater negative ΔS* values for step 3 (k_2) compared with step 1 (k_1) (see Table II) may be in the somewhat greater loss in internal degrees of freedom in transition state (b) which has a more complex structure than the transition state (a). However, caution should be exercised in interpreting the effect of structure on entropy since this is by no means a well understood concept.[27]

The similarity of both the enthalpy and entropy of the reverse reaction (k_{-1}) to those for both forward steps places some important restraints on the details of the mechanistic interpretation. Clearly the simple reverse decomposition of the intermediate **1** to initial reactants would not be expected to have an associated negative entropy change comparable to the forward formation step. The large negative entropy associated with the reverse (k_{-1}) step therefore suggests that an equally specific geometry must be generated in this decomposition.

References

1. T. Durst in "Advances in Organic Chemistry," Vol. 6, E. C. Taylor, H. Wynberg, Eds., Interscience, New York, 1969.
2. W. W. Epstein and F. W. Sweat, *Chem. Rev.*, **67**, 247 (1967).
3. C. N. Yiannos and J. V. Karabinos, *J. Org. Chem.*, **28**, 3246 (1963).
4. T. J. Wallace, *J. Am. Chem. Soc.*, **86**, 2018 (1964).
5. T. J. Wallace, *Chem. Ind.* (*London*), 501 (1964).
6. T. J. Wallace and J. J. Mahon, *J. Am. Chem. Soc.*, **86**, 4099 (1964).
7. T. J. Wallace and J. J. Mahon, *J. Org. Chem.*, **30**, 1502 (1965).
8. T. J. Wallace, *Chem. Ind.*, (*London*), 1558 (1966).
9. T. J. Wallace, U.S. Patent, 3,376,313 (1968).
10. R. Harville, S. F. Reed, *J. Org. Chem.*, **33**, 3976 (1968).
11. S. Tamagaki, *et al.*, *Bull. Chem. Soc. Japan*, **44**, 2456 (1971).
12. A. Cerniani, *et al.*, *Gazz. Chim. Ital.*, **90**, 382 (1960).
13. CRC, Handbook of Chemistry and Physics, 49th Edition, 1968–1969.
14. E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. 3, Chemical Publishing Co., Inc., New York, 1960.
15. E. Muller, Ph.D. Thesis, University of Calgary, Calgary, Alberta, 1968.
16. D. Landini and F. Rolla, *Int. J. Sulfur Chem.*, *A*, **2**, 43 (1972).
17. D. Landini, *et al.*, *J. Am. Chem. Soc.*, **92**, 7168 (1970).
18. D. Landini, F. Montanari, *Chem. Commun.*, **3** (1969).
19. J. H. Krueger, *Inorg. Chem.*, **5**, 132 (1966).
20. N. C. Braeziger, *et al.*, *J. Am. Chem. Soc.*, **91**, 5749 (1969).
21. H. Kwart, *et al.*, *Chem. Commun.*, 765 (1967).
22. H. Kwart and H. Omura, *J. Am. Chem. Soc.*, **93**, 7250 (1971).
23. L. Gmelin, "Handbuch der Anorganischen Chemie," Vol. IX, Sec. 2, Verlag Chemie, 1942.
24. G. Nickless, Ed., "Inorganic Sulphur Chemistry," Elsevier, Amsterdam, 1968.
25. W. A. Pryor, "Mechanisms of Sulphur Reactions," McGraw-Hill, New York, 1962.
26. H. C. Brown, *J. Am. Chem. Soc.*, **73**, 212 (1951).
27. L. L. Schaleger and F. A. Long *in* "Advances in Physical Organic Chemistry," Vol. 1, V. Gold, Ed., Academic Press, London, 1963.