(9:1) gave a pale yellow solid which was recrystallized from ethyl acetate–hexane to give 22.1 g. (44.2%) of VII, m.p. 136.5–137°. Three recrystallizations of this material from ethyl acetate–hexane gave pure dihydroazepinethione as pale yellow needles, m.p. 136.5–137°; λ_{max}^{EtOH} 244 (8150), 310 (13,450), and 364 sh mμ (1050). The n.m.r. spectrum of VII is very similar to that of IV[10]: 3-methyl (94 c.p.s., doublet, J = 6.5 c.p.s.), 3-proton (153 c.p.s., quintuplet, J = 5.5 c.p.s.), 4-proton (294 c.p.s., doublet, J = 5.5 c.p.s.), 5-methyl (109 c.p.s., triplet, J = 1.5 c.p.s.), 6-proton (350 c.p.s., singlet), and 7-methyl (224.5 c.p.s., singlet).

Anal. Calcd. for C$_9$H$_{13}$NS: C, 64.62; H, 7.83; N, 8.37; S, 19.17. Found: C, 65.00; H, 7.79; N, 8.24; S, 19.37.

2-Ethylthio-3,5,7-trimethyl-3H-azepine (Vb).—Triethyloxonium fluoroborate, prepared in the usual manner (see above) from 11.1 g. (0.12 mole) of epichlorohydrin, 22.8 g. (0.16 mole) of boron trifluoride etherate, and 75 ml. of anhydrous ether, was dissolved in 50 ml. of dry methylene chloride. This solution was stirred while a solution of 16.7 g. (0.10 mole) of VII in 100 ml. of dry methylene chloride was added dropwise. The resulting solution was stirred at room temperature for 2 hr. and allowed to stand overnight. To the stirred solution was cautiously added 19 g. of a 50% aqueous potassium carbonate solution. The precipitated solid was removed by filtration and the filtrate was dried, filtered, and evaporated. The residual oil was distilled to give 9.2 g. (47.2%) of colorless liquid, b.p. 72–74° (0.2 mm.), n^{26}D 1.5462. A redistilled sample, b.p. 76° (0.25 mm.), n^{26}D 1.5498, was submitted for analysis; λ_{max}^{EtOH} 225 (12,900) and 284 mμ (6800).

Anal. Calcd. for C$_{11}$H$_{17}$NS: C, 67.63; H, 8.77; N, 7.17; S, 16.42. Found: C, 67.73; H, 8.66; N, 6.63; S, 16.05.

Reactions of Thiols with Sulfoxides.   II.   Kinetics and Mechanistic Implications[1]

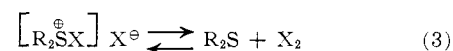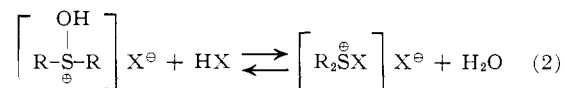BY THOMAS J. WALLACE AND JOHN J. MAHON

A detailed kinetic study on various thiol–sulfoxide reactions has been carried out. The reactions investigated gave good pseudo-first-order kinetics for thiol and sulfoxide disappearance in the presence of excess sulfoxide and thiol, respectively. When equimolar quantities of thiol and sulfoxide were employed, good second-order behavior was observed. Thus it is concluded that these reactions are over-all second order in nature. Rates of reaction were markedly dependent on the acidity of the thiol. The ease of oxidation for a series of thiols by TMSO was benzene- > 2-methylbenzene- > α-toluene- > 1-dodecanethiol. A linear relationship between the pK_a of each thiol and the activation energy for reaction with TMSO was observed. It is concluded that these reactions proceed by a rate-determining step involving formation of an unstable sulfoxide–thiol adduct which is rapidly consumed by reaction with another molecule of thiol. This conclusion was substantiated by n.m.r. studies.

Introduction

In a previous paper,[2] the scope, synthetic applications, and limitations for the oxidation of thiols and dithiols by aliphatic sulfoxides in a nitrogen atmosphere were presented. Of the sulfoxides investigated, tetramethylene sulfoxide (TMSO) and dimethyl sulfoxide (DMSO) were found to be the most efficient oxidizing agents. Stoichiometrically, it was established that 2 moles of thiol react with 1 mole of sulfoxide to produce 1 mole of disulfide (oxidized thiol), 1 mole of sulfide (reduced sulfoxide), and 1 mole of water. In these initial studies,[1,2] a variation of the reaction temperature established that the ease of thiol oxidation was markedly dependent on the acidity of the thiol. In the presence of TMSO and DMSO at room temperature the order of thiol reactivity based on the yield of disulfide was ArSH > ArCH$_2$SH >> RSH. On the basis of this finding, it was suggested that the mechanism of thiol–sulfoxide reactions was analogous to the oxidation of halogen acids by DMSO.[3] Such reactions are believed to proceed by formation of a protonated sulfoxide adduct which is formed in an equilibrium reaction (eq. 1). It has been suggested that the proto-

$$R_2SO + HX \rightleftarrows \left[\begin{array}{c} OH \\ | \\ R\text{-}\overset{\oplus}{S}\text{-}R \end{array} \right] X^{\ominus} \qquad (1)$$
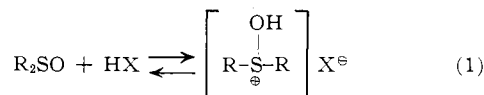
nated intermediate is then destroyed by reaction with another molecule of acid (eq. 2 and 3). The stoichiometry previously observed for the thiol–sulfoxide re-

$$\left[\begin{array}{c} OH \\ | \\ R\text{-}\overset{\oplus}{S}\text{-}R \end{array} \right] X^{\ominus} + HX \rightleftarrows \left[R_2\overset{\oplus}{S}X \right] X^{\ominus} + H_2O \quad (2)$$

$$\left[R_2\overset{\oplus}{S}X \right] X^{\ominus} \rightleftarrows R_2S + X_2 \qquad (3)$$

actions is also consistent with a reaction sequence of this general type. However, the results in the previous paper did not allow any definite conclusions on the rate-determining step and over-all reaction mechanism to be made. Conclusions of this type must be substantiated by detailed kinetic analyses. Such kinetic studies are the subject matter of the present paper.

Results

A detailed kinetic study on the oxidation of various thiols by TMSO and DMSO has been carried out. All reactions were conducted under nitrogen in sealed vials. Rate measurements were obtained by sampling the reaction mixture with a syringe and subsequently analyzing the aliquot by gas chromatography using the procedure outlined in the Experimental section. Quantitative data were obtained with the aid of an internal hydrocarbon standard. Initially, the effect of thiol acidity on the rate of oxidation was examined with four thiols and TMSO at 100°. In all cases, 6.25 mmoles of thiol was added to a four molar excess of sulfoxide which contained 6.25 mmoles of an internal standard. Pseudo-first-order rate constants for the

(1) T. J. Wallace, *Chem. Ind.* (London), 501 (1964), contains a preliminary account of a portion of this work.

(2) T. J. Wallace, *J. Am. Chem. Soc.*, **86**, 2018 (1964).

(3) For a summary see: W. O. Ranky and D. C. Nelson, "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed. Pergamon Press, Inc., New York, N. Y., 1961, Chapter 17.

Table I

Variation of Reaction Rate with Thiol Acidity at 100.0 ±0.1°

Thiol	Sulfoxide	Internal standard	k, sec.$^{-1}$	p$K_a{}^a$	E_a, kcal./mole
Benzene-	TMSO	Toluene	4.11×10^{-2}	~7	4.94 ± 0.20
			3.95×10^{-2}		
2-Methylbenzene-	TMSO	o-Xylene	6.46×10^{-3}	8	$6.22 \pm .36$
			6.80×10^{-3}		
α-Toluene-	TMSO	Diphenylmethane	1.96×10^{-4}	10.5	$13.74 \pm .01$
			1.89×10^{-4}		
1-Dodecane-	TMSO	Mesitylene	7.58×10^{-6}	~13.5	$19.36 \pm .40$
			8.00×10^{-6}		
α-Toluene-	DMSO	Diphenylmethane	4.10×10^{-5}	10.5	$14.00 \pm .10$
			4.03×10^{-5}		
1-Dodecane-	DMSO	Mesitylene	1.83×10^{-6}	~13.5	$19.42 \pm .30$
			2.03×10^{-6}		

[a] For sources see: (a) D. L. Yabroff, *Ind. Eng. Chem.*, **32**, 259 (1940); (b) M. M. Kreevoy, *et al.*, *J. Am. Chem. Soc.*, **82**, 4899 (1960); (c) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. I, Chemical Publishing Co., New York, N. Y., 1958.

disappearance of the thiols investigated are summarized in Table I along with other pertinent data. It should be emphasized that good pseudo-first-order behavior was observed in all cases. This can be clearly seen from Fig. 1 and 2. In Fig. 1, good first-order behavior was ob-
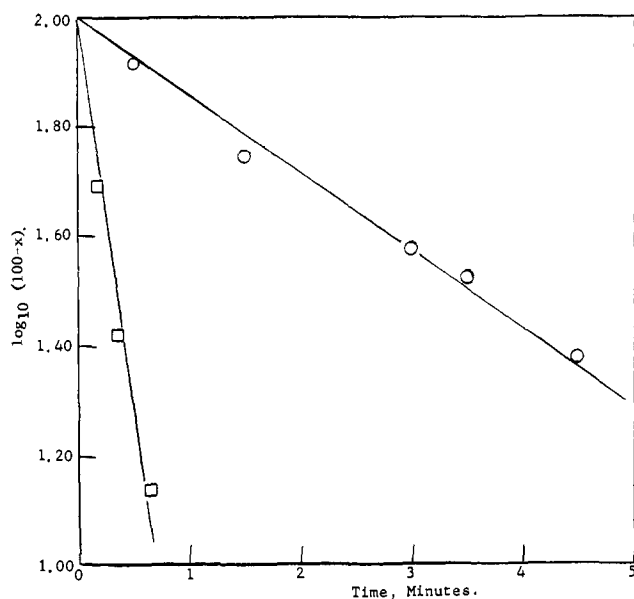

Fig. 1.—Pseudo-first-order rate plots for the oxidation of benzenethiol and 2-methylbenzenethiol by TMSO at 100°: ○, 2-methylbenzenethiol; □, benzenethiol.

served for the disappearance of benzene- and 2-methylbenzenethiol in the presence of TMSO despite the rapidity of both reactions. In Fig. 2, similar results are shown for the disappearance of α-toluenethiol in the presence of TMSO and DMSO. Further, as shown in Table I, good reproducibility of rate constants was observed. The order of thiol reactivity with TMSO was benzene- > 2-methylbenzene- > α-toluene- > 1-dodecanethiol. Based on the observed rate constants, it would appear that aromatic thiols are about 10^3 to 10^4 times more reactive than aliphatic thiols. The observed rates for the oxidation of α-toluenethiol and 1-dodecanethiol by DMSO indicate that TMSO is about five times more effective than DMSO as an oxidizing agent.

The temperature dependence of reaction rate as a function of thiol acidity has also been measured. Reaction rates for the four above thiols with TMSO were determined between 55 and 100°. At least two rate constants were measured at each of the three temperatures used. As shown in Fig. 3, good Arrhenius

plots were obtained over this temperature range. The calculated activation energies are shown in Table I. These values also reflect the importance of thiol acidity in these reactions. This fact is further emphasized in Fig. 4. As indicated, a linear correlation between the activation energy and the pK_a of each thiol was observed.[4] Thus, it would appear that thiol acidity
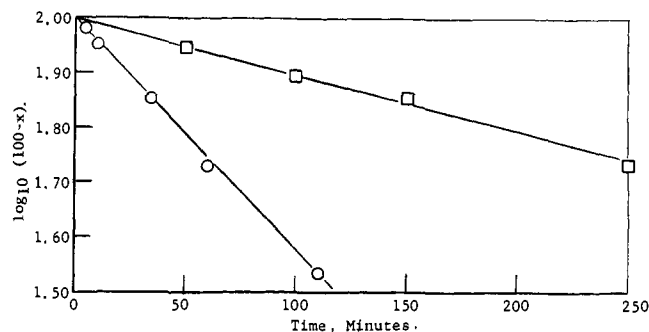

Fig. 2.—Pseudo-first-order rate plots for the oxidation of α-toluenethiol by TMSO and DMSO at 100°: □, α-toluenethiol + DMSO; ○, α-toluenethiol + TMSO.

plays a key role with respect to the rate-determining step in these reactions.

Having determined the effect of thiol acidity on the rate of reaction, we felt it desirable to ascertain how the rate varied with the structure of the sulfoxide. Thus, the oxidation of α-toluenethiol[5] by phenyl methyl sulfoxide and diphenyl sulfoxide was investigated under the previously described pseudo-first-order conditions at 100°. These results are summarized in Table II

Table II

Effect of Sulfoxide Structure on the Rate of α-Toluenethiol Oxidation at 100.0 ± 0.1°

Sulfoxide[a]	Rate of thiol disappearance, sec.$^{-1}$ [b]	Rel. rate
TMSO	1.96×10^{-4}	159
DMSO	4.10×10^{-5}	33.3
PMSO[c]	7.76×10^{-6}	6.22
DPSO[c]	1.23×10^{-6}	1.00

[a] A 4:1 M excess was employed. [b] Diphenylmethane was employed as an internal standard. [c] PMSO = phenyl methyl sulfoxide and DPSO = diphenyl sulfoxide.

along with those previously obtained with DMSO and TMSO. Based on the relative rates of thiol oxidation,

(4) The linearity of this relationship may be fortuitous because of the different methods employed for determining pK_a values for thiols.

(5) In this and subsequent kinetic studies, α-toluenethiol was employed because of its intermediate acidity. Thus, reactions were neither extremely fast nor extremely slow.

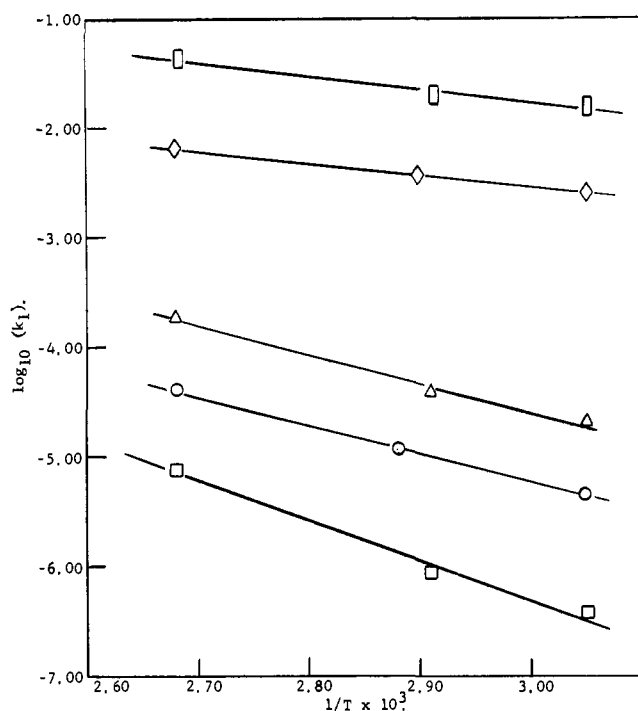Fig. 3.—Typical activation energy plots for various thiol–sulfoxide reactions between 55 and 100°: O, α-toluenethiol + DMSO; □, 1-dodecanethiol + TMSO; △, α-toluenethiol + TMSO; ◇, 2-methylbenzenethiol + TMSO; ⬓, benzenethiol + TMSO.
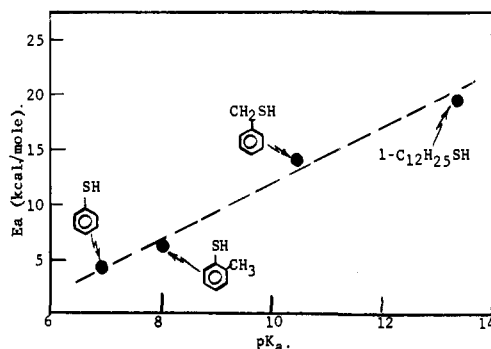

Fig. 4.—Correlation between energy of activation for the reaction of various thiols with TMSO and the acidity of the thiol.

it would appear that phenyl substitution decreases the reactivity of the sulfoxide group; e.g., TMSO was 159 times more reactive than DPSO.

Kinetic studies to determine the over-all reaction order were next undertaken. This information, in combination with the above data, would then allow some reasonable conclusions with regard to the rate-determining step and over-all mechanism of the reaction to be made. At this point it was anticipated that the over-all reaction would be first order in thiol and sulfoxide. The order for sulfoxide disappearance in the presence of excess thiol was first determined at 100° using 6.25 mmoles of TMSO and DMSO and a four molar excess of α-toluenethiol. As shown in Fig. 5, good first-order disappearance for both sulfoxides was observed. Further, the pseudo-first-order rates of thiol and sulfoxide disappearance were, for all practical purposes, identical (see Table III for a comparison). The oxidation of α-toluenethiol by TMSO and DMSO at 100° was next investigated using equimolar quantities of thiol and sulfoxide. All pertinent data
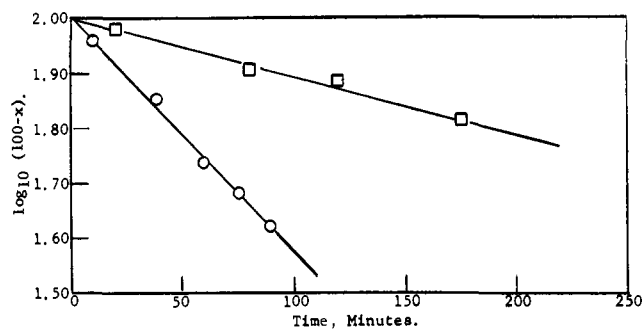

Fig. 5.—Pseudo-first-order rate plots for the disappearance of DMSO and TMSO in the presence of excess α-toluenethiol at 100°: □, DMSO + α-toluenethiol; O, TMSO + α-toluenethiol.
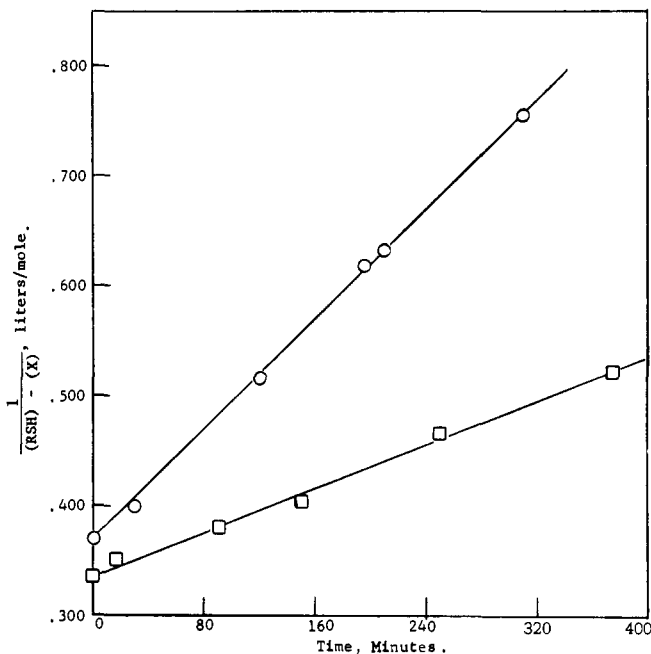

Fig. 6.—Second-order rate plots for the oxidation of α-toluene-thiol by TMSO and DMSO at 100°: O, $C_6H_5CH_2SH$ + TMSO; □ $C_6H_5CH_2SH$ + DMSO.

on these reactions are summarized in Table IV. The disappearance of α-toluenethiol under these conditions gave excellent second-order behavior when plotted according to a conventional second-order rate expression (see Fig. 6). Based on these results it was concluded that these reactions are over-all second order in nature.

TABLE III

COMPARISON OF PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THIOL AND SULFOXIDE DISAPPEARANCE AT 100°

Reactant[a] measured	Reactant[b] in excess	k, sec.$^{-1}$
α-Toluenethiol	TMSO	1.96×10^{-4}
α-Toluenethiol	DMSO	4.10×10^{-5}
TMSO	α-Toluenethiol	1.95×10^{-4}
DMSO	α-Toluenethiol	4.19×10^{-5}

[a] Diphenylmethane was employed as the internal standard. [b] A 4:1 M excess was employed.

In several large-scale experiments, attempts to isolate a sulfoxide–thiol adduct by fractional distillation were unsuccessful. The absence of a stable adduct was also confirmed by g.c. Finally, the reaction of α-toluenethiol with DMSO at 55° was examined by n.m.r. over a 28-hr. period. Samples were withdrawn periodically from the reaction mixture and immediately

TABLE IV

CONDITIONS EMPLOYED IN THE DETERMINATION OF SECOND-ORDER RATE CONSTANTS FOR THE OXIDATION OF α-TOLUENETHIOL BY DMSO AND TMSO AT 100°

| Sulfoxide, mmoles, moles/l.	α-Toluene-thiol, mmoles, moles/l.	DPM,[a] mmoles, moles/l.	Total vol., cc.	k, l./moles/sec. $\times 10^6$
DMSO, 6.25, 2.98	6.25, 2.98	6.25, 2.98	2.103	6.86
TMSO, 6.25, 2.72	6.25, 2.72	6.25, 2.72	2.303	2.22

[a] Employed as an internal standard for quantitative g.c. analysis.

injected into tetramethylsilane. The area for methylene absorption was used as an internal standard for quantitative data. All n.m.r. spectra indicated an adduct was not present. Singlets for C–H splitting in DMS and DMSO were observed at 2.00 and 2.35 τ, respectively. A triplet was observed at 1.45, 1.70, and 1.85 τ (area at 1.70 = area at (1.45 + 1.85)) for the thiol group. A doublet at 3.50 and 3.65 τ was observed for the methylene protons of the thiol. As the reaction progressed, the area decrease at 3.65 τ was accompanied by an increase at 3.50 τ as the disulfide was formed. Phenyl absorption occurred at 7.20 τ. Integration of each spectrum indicated that at least 98% of the methyl and methylene absorption could be accounted for by reactants and final products. This indicates that the half-life of the adduct is extremely short under the present reaction conditions.
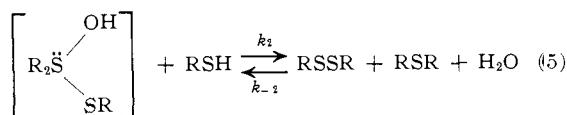
Discussion

On the basis of our kinetic studies it is obvious that any mechanism proposed must be consistent with the following facts: (a) a marked dependence of reaction rate and activation energy on the acidity of the thiol, (b) a decrease in reaction rate with increased aromaticity of the sulfoxide, (c) pseudo-first-order dependence on thiol and sulfoxide disappearance, (d) over-all second-order kinetics, and (e) a reaction stoichiometry involving 2 moles of thiol and 1 mole of sulfoxide to produce 1 mole of disulfide and 1 mole of sulfide.[2]

A sequence of reactions that is in reasonable agreement with these facts can be formulated. Initially, the thiol and sulfoxide must react to produce a sulfoxide–thiol adduct (eq. 4). The resulting adduct

$$RSH + R_2SO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \left[R_2\ddot{S} \begin{matrix} OH \\ \\ SR \end{matrix} \right] \qquad (4)$$
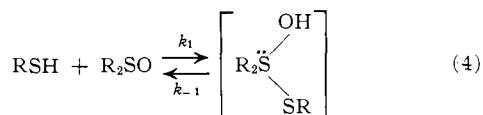
can then react further with the remaining thiol (eq. 5)

$$\left[R_2\ddot{S} \begin{matrix} OH \\ \\ SR \end{matrix} \right] + RSH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} RSSR + RSR + H_2O \quad (5)$$

to produce disulfide, sulfide, and water.[6] Based on this sequence the rate of product formation (r_p) is given by the expression

$$r_p = k_2(R_2\ddot{S}(OH)SR)(RSH) - k_{-2}(products) \qquad (6)$$

The rate of adduct formation (r_a) can be expressed as

$$r_a = k_1(RSH)(R_2SO) - k_{-1}(R_2\ddot{S}(OH)SR) - k_2(R_2\ddot{S}(OH)SR)(RSH) + k_{-2}(products) \qquad (7)$$

(6) Our results do not permit us to speculate in detail on the mode of adduct consumption. Clearly, several possibilities exist, but they have no bearing on the kinetic implications and the rate-determining step.

Assuming a steady state for the formation and disappearance of the adduct then

$$r_a = d(R_2\ddot{S}(OH)SR)/dt = 0 \qquad (8)$$

The concentration of adduct is then given by the expression

$$\left[R_2\ddot{S} \begin{matrix} OH \\ \\ SR \end{matrix} \right] = \frac{k_{-2}(products) + k_1(RSH)(R_2SO)}{k_{-1} + k_2(RSH)} \qquad (9)$$

Substituting into (eq. 6) for $\left[R_2\ddot{S} \begin{matrix} OH \\ \\ SR \end{matrix} \right]$ the rate of product formation becomes

$$r_p = \frac{k_2(k_{-2}(product) + k_1(RSH)(R_2SO))(RSH)}{k_{-1} + k_2(RSH)} - k_{-2}(products) \qquad (10)$$

If $k_1' = k_1(R_2SO)$, $k_{-2} \cong 0$, and $k_2 \gg k_{-1}$ then

$$r_p = \frac{k_2 k_1'(RSH)^2}{k_2(RSH)} = k_1'(RSH) \qquad (11)$$

These assumptions are reasonable since evidence for a stable adduct could not be obtained. The above rate expression is consistent with pseudo-first-order behavior for thiol disappearance (or sulfoxide disappearance) in the presence of excess sulfoxide (or excess thiol). For equimolar concentrations of thiol and sulfoxide the rate expression becomes

$$r_p = k_1(RSH)(R_2SO) \qquad (12)$$

which is consistent with over-all second-order behavior. Based on the above mechanism, the over-all equation for reaction is

$$2RSH + R_2SO \longrightarrow RSSR + RSR + H_2O \quad (13)$$

This is consistent with the observed stoichiometry for these reactions.

The marked dependence of rate on thiol acidity and extremely short half-life of the proposed adduct indicate that k_{-2} is negligible and that $k_2 \gg k_1$. Thus, the rate-determining step must be initial formation of the adduct (step 1). The effect of sulfoxide structure on the reaction rate is also consistent with this conclusion. As the aromaticity of the sulfoxide increases, the rate of sulfoxide reduction apparently decreases because of increased stability of these sulfoxide linkages. This could be due to resonance contributions from the phenyl group(s). It can also be
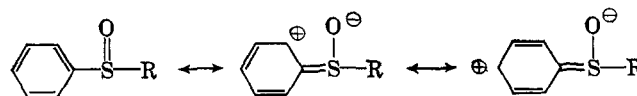
argued that the observed rate sequence parallels the expected basicity of the sulfoxides investigated. The combined rate dependence on thiol acidity and sulfoxide basicity is indicative of a highly polar transition state. Detailed kinetic studies in the presence of various catalysts are consistent with this conclusion.[7]

(7) T. J. Wallace and J. J. Mahon, J. Am. Chem. Soc., submitted for publication.

It should be noted that the proposed sulfoxide–thiol adduct is similar to those which have been postulated in the reactions of sulfoxides with halogen acids,[3] acetic anhydride,[8] methyl iodide,[9] and diazonium compounds.[10] Similarly, stable, transannular sulfoxide–ketone salts, which involve the dipolar sulfoxide group, have also been reported.[11]

Related studies on the oxidation of sulfides to sulfoxides by t-butyl hypochlorite should also be mentioned.[12] The intermediate in these reactions, which is similar to the one proposed in the present study, rapidly decomposed in the vicinity of room temperature. This is consistent with our inability to isolate a stable reaction intermediate.

Some comments on previous studies involving thiol–DMSO reactions should also be made. Yiannios and Karabinos[13] have indicated that aliphatic, aralkyl, and aromatic thiols are oxidized by DMSO at 90° at the same rate. This conclusion was based on the yield of disulfide obtained after 8 hr. of oxidation in the presence of air. Based on the present results, it would seem that the high yield of disulfide obtained from the aliphatic and aralkyl thiols investigated by these authors could be due to a co-oxidation of the thiols by oxygen.

Experimental

Reagents.—All thiols and sulfoxides employed in the present study were purified according to the methods described in the previous paper.[2] In the present study, several additional reagents were utilized: Diphenyl sulfoxide was obtained from the Eastman Organic Chemical Co. as the reagent grade material (m.p. 71°). Phenyl methyl sulfoxide was synthesized by oxidation of the corresponding sulfide in a hydrogen peroxide–acetic acid medium.

General Procedure for Kinetic Studies.—A general procedure was employed in all kinetic studies. The sulfoxide, internal hydrocarbon standard, and catalyst (when used) were weighed into a vial in a nitrogen drybox with the aid of an analytical balance. The vial was capped (under nitrogen) with a self-sealing neoprene diaphragm. The stopper extended down from the mouth of the vial and further sealing was accomplished by wrapping a piece of heavy copper wire around this portion of the diaphragm. Thus, the contents of the vial were doubly protected against moisture and oxygen. Upon sealing, the vial was placed in a Primoil-D constant temperature bath (±0.1°). After the vial had reached thermal equilibrium, the desired quantity of prethermostated thiol was then injected into the vial by a syringe. When perfected, this operation can be performed in about 3 sec. Sampling during each reaction was also accomplished with a syringe. The total volume of each reaction ranged from 2 to about 5 ml. The aliquots that were withdrawn ranged from 5

to 10 μl. Each aliquot was immediately injected into a sealed vial containing a small quantity (0.25 to 0.50 ml.) of cold acetone (0° or below). The last step stopped the reaction. A portion of the acetone solution was withdrawn by a syringe and subsequently analyzed by gas–liquid chromatography. Quantitative data were obtained from the areas of the internal standard and reactant in question using predetermined molar response factors.

Gas–Liquid Chromatographic Techniques.—The g.l.c. unit employed was an F and M Model #609 flame ionization gas chromatography equipped with a Minneapolis Honeywell recorder and a disk integrator (Model #201). The injection port of the unit was maintained at 305° and the inlet pressure of helium was 36 p.s.i.g. The block of the detector was maintained at a constant temperature of 245°. The helium flow through the column was 100 ml./min. when measured at room temperature with a flow meter. Quantitative data for all thiols, DMSO, and TMSO were obtained on a 3-ft. 20% Carbowax (20MM) on Chromosorb-W column (0.25-in. stainless steel tubing). This column is a slight modification of one which has been employed by Cates and Meloan[14,15] for the separation of mixtures of sulfoxides. Details on the application of the present technique to the separation of sulfide–sulfoxide–sulfone mixtures can be found elsewhere.[16] In the present study, this column gave excellent separation of all the thiol–hydrocarbon–sulfoxide mixtures investigated. No interference by sulfide or disulfide was encountered. A list of molar response factors between each reactant whose disappearance was measured and its corresponding internal standard are shown in Table V. Usually, the sulfoxide was eluted from the column before the thiol and its internal standard. Disulfide elution required a temperature of 250° or above.[16] Each thiol–hydrocarbon combination could be used in the presence of the four sulfoxides studied. The lower column temperature (140–165°) employed for sulfoxide disappearance gave greater resolution in the initial stage of the chromatographs.

TABLE V

SUMMARY OF GAS CHROMATOGRAPHIC CONDITIONS

Reactant measured	Internal standard	Response factor	Preferred column temp., °C.
Benzenethiol	Toluene	1.15	200
α-Toluenethiol	Diphenylmethane	1.87	210
2-Methylbenzene	o-Xylene	1.24	210
1-Dodecanethiol	Mesitylene	1.54	225
TMSO	Diphenylmethane	2.15	165
DMSO	Diphenylmethane	4.00	140

N.m.r. Study.—The α-toluenethiol–DMSO reaction was carried out at 55° under nitrogen in a manner analogous to the kinetic studies. Aliquots were withdrawn after 2.5, 6, 23, and 28 hr. of reaction and injected into TMS (equal volume). Analyses were performed on a Varian n.m.r. spectrometer (Model A-60).

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