AN ABSTRACT OF THE THESIS OF

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Title MECHANISMS OF REACTIONS OF SULFINIC ACIDS
I. THE SULFIDE - SULFINIC ACID REACTION
II. THE DISULFIDE - SULFINIC ACID REACTION

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(Major professor)

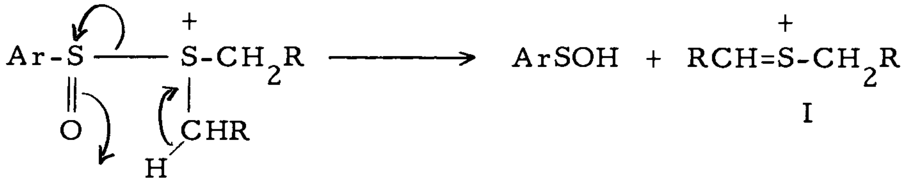
I

The detailed mechanism of the recently discovered alkyl sulfide - p-toluenesulfinic acid reaction:

$$5\,ArSO_2H + (RCH_2)_2S \rightarrow 2\,ArSO_2SAr + ArSO_2SCH_2R + RCHO + 3\,H_2O$$

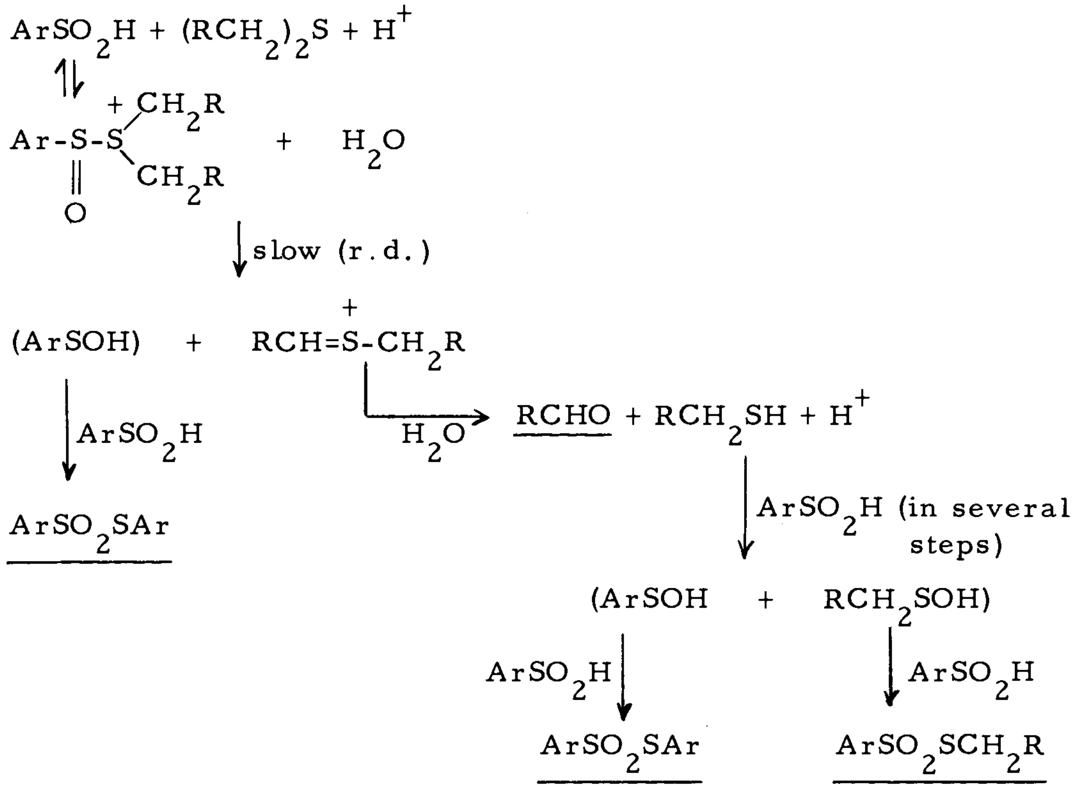
has been determined.

Comparison of the rate constants for α, α-dideuteriobenzyl sulfide and benzyl sulfide showed a large primary isotope effect for the reaction. The variation with sulfide structure of the rate constants for a series of primary alkyl sulfides, $(RCH_2)_2S$, the observed isotope effect, and other previously known features of the reaction indicate the rate-determining step to be:



(Eq. 1)

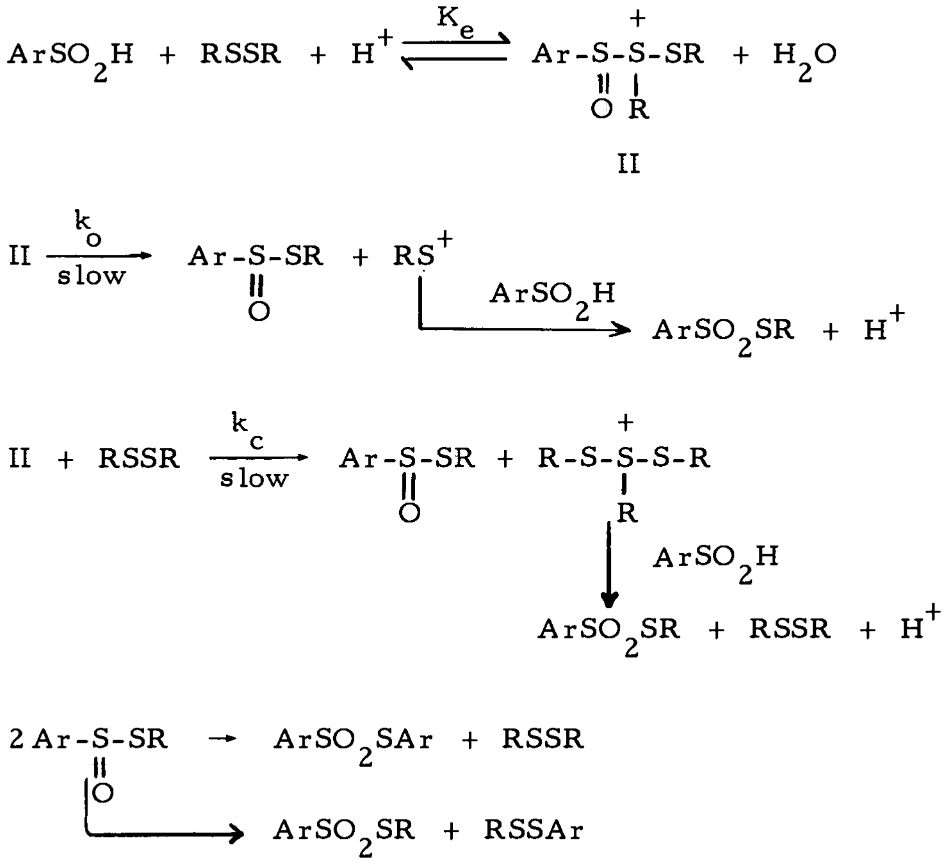
Experiments with *n*-butyl α-acetoxybutyl sulfide and *n*-butyl mercaptan showed that under the reaction conditions used the ion I will undergo almost instantaneous hydrolysis to aldehyde and mercaptan. Additional experiments with mercaptan and sulfinic acid indicate this hydrolysis will be followed by a very rapid reaction between mercaptan and sulfinic acid, with the formation of the two thiolsulfonates $ArSO_2SAr$ and $ArSO_2SCH_2R$. The detailed course of the over-all reaction is thus as shown below.



The recently discovered reaction between p-tolyl disulfide and p-toluenesulfinic acid:

$$4\,ArSO_2H + ArSSAr \rightarrow 3\,ArSO_2SAr + 2\,H_2O$$

has now been extended to a wide variety of alkyl and aryl disulfides. These studies have allowed the mechanism previously suggested for this reaction to be established with certainty. This mechanism can be illustrated generally as:



$$ArSO_2H + RSSR + H^+ \overset{K_e}{\rightleftharpoons} Ar{-}\underset{\underset{\displaystyle O}{\|}}{S}{-}\underset{\underset{\displaystyle R}{|}}{\overset{+}{S}}{-}SR + H_2O$$

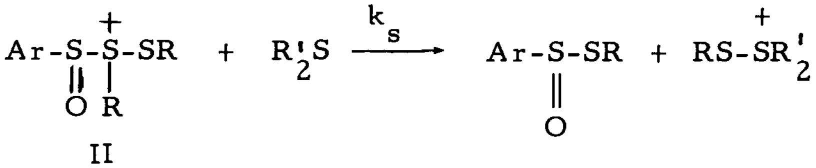
II

$$II \xrightarrow[\text{slow}]{k_o} Ar{-}\underset{\underset{\displaystyle O}{\|}}{S}{-}SR + RS^+ \qquad RS^+ \xrightarrow{ArSO_2H} ArSO_2SR + H^+$$

$$II + RSSR \xrightarrow[\text{slow}]{k_c} Ar{-}\underset{\underset{\displaystyle O}{\|}}{S}{-}SR + R{-}S{-}\underset{\underset{\displaystyle R}{|}}{\overset{+}{S}}{-}S{-}R \qquad R{-}S{-}\underset{\underset{\displaystyle R}{|}}{\overset{+}{S}}{-}S{-}R \xrightarrow{ArSO_2H} ArSO_2SR + RSSR + H^+$$

$$2\,Ar{-}\underset{\underset{\displaystyle O}{\|}}{S}{-}SR \rightarrow ArSO_2SAr + RSSR \qquad 2\,Ar{-}\underset{\underset{\displaystyle O}{\|}}{S}{-}SR \rightarrow ArSO_2SR + RSSAr$$

The reaction is subject to powerful catalysis by small amounts of sulfide, through the intervention of the following reaction:



$$\mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}\overset{+}{\underset{\underset{R}{|}}{S}}{-}SR} + \mathrm{R'_2S} \xrightarrow{k_s} \mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}SR} + \mathrm{RS{-}\overset{+}{S}R'_2}$$

II

There are two important features of the disulfide - sulfinic acid reaction; the first being conversion of the poor leaving group RS- of the disulfide to the good leaving group $\mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}\overset{+}{\underset{\underset{R}{|}}{S}}{-}}$ of intermediate II, through electrophilic attack on the disulfide by $\mathrm{ArSO^+}$. The second feature is nucleophilic assistance of the decomposition of II by sulfur nucleophiles, such as sulfides and disulfides.

The catalysis by sulfur nucleophiles is probably the most important feature of this reaction and its potential as a general method for cleavage of sulfur - sulfur bonds is discussed.

MECHANISMS OF REACTIONS OF SULFINIC ACIDS
I. THE SULFIDE - SULFINIC ACID REACTION
II. THE DISULFIDE - SULFINIC ACID REACTION

by

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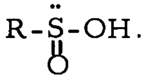
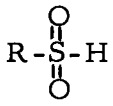
MECHANISMS OF REACTIONS OF SULFINIC ACIDS

PART I: THE SULFIDE - SULFINIC ACID REACTION

PART II: THE DISULFIDE - SULFINIC ACID REACTION

MECHANISMS OF REACTIONS OF SULFINIC ACIDS
I: THE SULFIDE - SULFINIC ACID REACTION
II: THE DISULFIDE - SULFINIC ACID REACTION

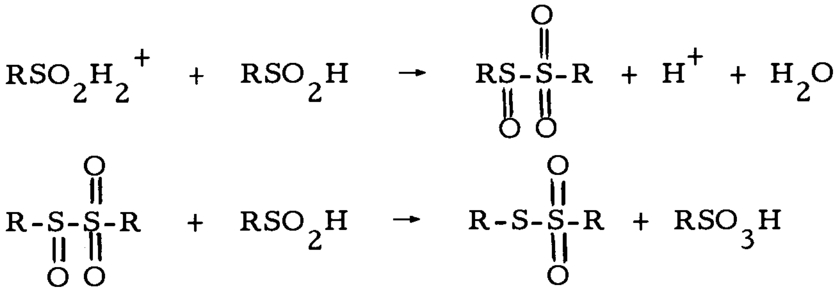
GENERAL INTRODUCTION

The first preparation of a sulfinic acid was in 1868 when Otto (49, p. 11) described the synthesis of p-toluenesulfinic acid. The structure of sulfinic acids has been studied by Bredereck and co-workers (9). They used the ultraviolet spectra of the acids to decide if there were any unshared electrons present on the sulfur atom. In very dilute solutions, in both polar and non-polar media, they found only the ester form to be present:  $R\text{-}\underset{\underset{O}{\|}}{\overset{\cdot\cdot}{S}}\text{-}OH$. They also noted that both in the solid state and in carbon tetrachloride solution, the infrared spectrum of the sulfinic acid showed a band at 3.9-4.0 μ. This is usually a band characteristic of an S-H group, but apparently not in this case. (This evidence had led some Russian workers (28) to assume  $R\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}H$ as the structure of the acid in the solid state.)

One of the interesting reactions of sulfinic acids is their disproportionation, first discovered by Otto and Pauly (50, p. 319; 53; 54). They heated p-toluenesulfinic acid with water under pressure and found the acid to disproportionate according to the equation:

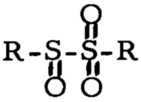
$$3\,ArSO_2H \longrightarrow ArSO_2SAr + ArSO_3H + H_2O \qquad \text{(Eq. 1)}$$

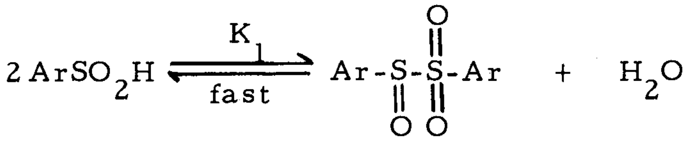
They considered the reaction to be an equilibrium since the disproportionation could be suppressed by increasing the amount of water present (54). Bredereck and coworkers (10) found the disproportionation of p-toluenesulfinic acid will also take place in non-aqueous media such as dioxane. They found the reaction to be acid-catalyzed, and assumed the starting material to be partly protonated. The following reaction sequence was suggested:



$$RSO_2H_2^+ + RSO_2H \rightarrow R\underset{\underset{O}{\|}}{S}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-R + H^+ + H_2O$$

$$R-\underset{\underset{O}{\|}}{S}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-R + RSO_2H \rightarrow R-S-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-R + RSO_3H$$

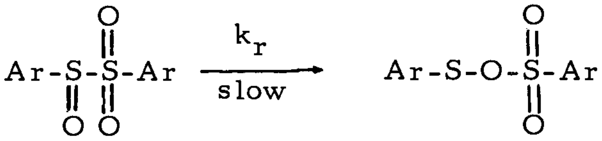
In 1962 Kice and Bowers (33) studied the disproportionation of p-toluenesulfinic acid, but in acetic acid containing limited amounts of water and sulfuric acid. The reaction was found to be second-order in sulfinic acid, strongly retarded by added water, and only slightly enhanced by added sulfuric acid. In addition, they observed a small negative salt effect. In this system the hydrolysis of p-toluenesulfinyl p-tolyl sulfone,  $R-\underset{\underset{O}{\|}}{S}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-R$, was found to be much more rapid than any reaction of this compound with sulfinic acid. Thus, in view of the observed kinetics, a direct reaction between the sulfinyl sulfone and sulfinic acid did not seem possible as the rate-determining step for the disproportionation of p-toluenesulfinic acid in this medium. Later, Kice and Pawlowski (36) studied the decomposition of p-toluenesulfinyl p-tolyl sulfone in anhydrous dioxane at 50°. Kinetic experiments showed the rate of this decomposition to be the same whether or not p-toluenesulfinic acid was present. The reaction was always first-order in sulfinyl sulfone, although the product composition did vary with the presence of sulfinic acid. All of these experiments are best explained by assuming that the disproportionation of the sulfinic acid does involve the sulfinyl sulfone, but that the rate-determining step is the unimolecular decomposition of this compound, rather than its direct reaction with sulfinic acid, as postulated by Bredereck (10). One plausible path for the unimolecular decomposition of the sulfinyl sulfone is rearrangement to a sulfenyl sulfonate II, which would then react rapidly with sulfinic acid as shown in Eq. 1 c. The overall mechanism for the disproportionation would then be as in Eq. 1.



$$2\,ArSO_2H \underset{fast}{\overset{K_1}{\rightleftharpoons}} Ar\text{-}\underset{\underset{O}{\|}}{S}\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}Ar + H_2O$$

(Eq. 1 a)

I



$$Ar\text{-}\underset{\underset{O}{\|}}{S}\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}Ar \xrightarrow[slow]{k_r} Ar\text{-}S\text{-}O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}Ar$$

(Eq. 1 b)

II

$$\mathrm{II} + \mathrm{ArSO_2H} \xrightarrow[\text{fast}]{} \mathrm{ArSO_2SAr} + \mathrm{ArSO_3H} \qquad \text{(Eq. 1 c)}$$

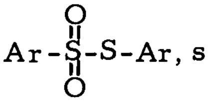
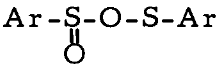
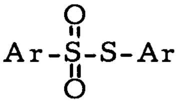
The initial equilibrium (Eq. 1 a) between two sulfinic acid molecules and the sulfinyl sulfone will greatly favour the sulfinic acid. In the last reaction (Eq. 1 c), the sulfenyl sulfonate is, analogous to sulfenyl halides, expected to react very rapidly with sulfinic acid. The products observed might also be produced from the intermediate II by two alternate reaction routes in the medium acetic acid-water-sulfuric acid:

$$\mathrm{II} + \mathrm{H_2O} \rightarrow \mathrm{ArSO_3H} + [\mathrm{ArSOH}] \qquad \text{(Eq. 1 d)}$$

$$\xrightarrow{\mathrm{ArSO_2H}} \mathrm{ArSO_2SAr} + \mathrm{H_2O}$$

$$\mathrm{II} \rightarrow \mathrm{ArSO_3^-} + \mathrm{ArS^+} \xrightarrow[\mathrm{HSO_2Ar}]{} \mathrm{ArSO_3H} + \mathrm{ArSO_2SAr} \qquad \text{(Eq. 1 e)}$$

The iodide-catalyzed disproportionation of p-toluenesulfinic acid has been investigated by Allen and Reich (1). However, from the rather confused character of their results, no definite conclusions can be drawn about the mechanism or its relation to the normal disproportionation.

One of the products from the normal disproportionation of the sulfinic acid, the thiolsulfonate, deserves some further comment. Although Otto (50, p. 319) considered the thiolsulfonate to have the structure  $Ar-\overset{O}{\underset{O}{S}}-S-Ar$, serious consideration has also been given at times to two other structures for this compound. The mixed sulfinic-sulfenic anhydride  $Ar-\underset{O}{S}-O-S-Ar$ was ruled out by Smiles and Gibson (60) since the properties of the thiolsulfonate did not correlate with those of sulfenic and sulfinic anhydrides. It is much more difficult to decide between the disulfoxide  $Ar-\underset{O}{S}-\underset{O}{S}-Ar$ and the thiolsulfonate  $Ar-\overset{O}{\underset{O}{S}}-S-Ar$ structures. Having ruled out the sulfinic-sulfenic anhydride structure, Smiles and Gibson (60) summed up the facts for and against the other two structures. They also included an additional experiment: a symmetrical thiolsulfonate was reacted with a mercaptan, and an unsymmetrical disulfide was found among the products:

$$RSO_2SR + H\text{-}SR' \rightarrow RSO_2H + RSSR'$$

This result, together with earlier evidence, caused the authors to favour the thiolsulfonate as the correct structure. From an analysis of infrared spectra, Bredereck and coworkers were able to present (11) unambiguous evidence in 1960 for the thiolsulfonate structure.

Sulfinic acids react very easily with mercaptans to form thiolsulfonate, disulfide and water. The reaction, as first observed by von Braun (8, p. 2838), showed the stoichiometry:

$$2\,RSO_2H + 2\,HSR' \rightarrow RSO_2SR' + R'SSR + 2\,H_2O$$

Marvel and Johnson (42) suggested an initial disproportionation between one molecule each of sulfinic acid and mercaptan to form two sulfenic acid molecules (RSOH). Each of these would further react with sulfinic acid or mercaptan, respectively, to form thiolsulfonate or disulfide.

Horner and Basedow (29, p. 109) have observed that benzenesulfinic acid undergoes autoxidation, apparently through a radical reaction.

In 1962 a reaction between p-toluenesulfinic acid and p-tolyl disulfide was observed for the first time by Kice and Bowers (34). The overall stoichiometry of the reaction was:

$$4\,ArSO_2H + ArSSAr \rightarrow 3\,ArSO_2SAr + 2\,H_2O \qquad \text{(Eq. 2)}$$

$$(Ar = \underline{p}\text{-}CH_3\text{-}C_6H_4\text{-})$$

Detailed discussion of this reaction will be deferred until later (Part II). However, certain features of its apparent mechanism led Kice and Bowers (34) to suspect that a reaction between the same sulfinic acid and certain alkyl sulfides might also be possible. Such a reaction was indeed found to occur (35). Benzyl and n-butyl sulfide reacted rapidly with p-toluenesulfinic acid under the same conditions that were used for the disulfide - sulfinic acid reaction: limited amounts of sulfuric acid and water in acetic acid at 70°.

Benzyl sulfide reacted with p-toluenesulfinic acid according to the stoichiometric equation:

$$5\ ArSO_2H + (PhCH_2)_2S \rightarrow$$

$$2\ ArSO_2SAr + ArSO_2SCH_2Ph + PhCHO + 3\,H_2O \quad \text{(Eq. 3)}$$

Some information about the mechanism of the sulfide - sulfinic acid reaction was obtained by the same authors (35). The details will be presented in Part I (page 9).

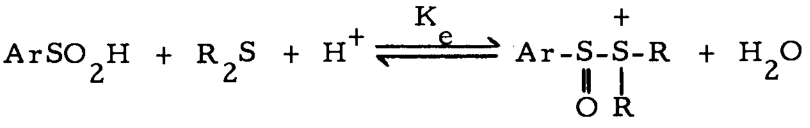
Although some features of the mechanisms of both the disulfide - sulfinic acid reaction and the sulfide - sulfinic acid reaction were known, there were many unanswered questions left in both cases. The purpose of the present work was therefore to obtain information that would enable the detailed mechanisms of these two reactions to be established with certainty. Part I of this thesis describes the studies of the alkyl sulfide - sulfinic acid reaction, Part II the investigation of the disulfide - sulfinic acid reaction.

PART I

THE SULFIDE - SULFINIC ACID REACTION

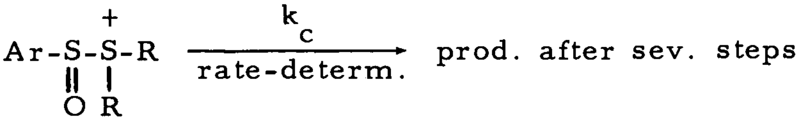
INTRODUCTION

As was briefly mentioned before, Kice and Bowers (35) found a rapid reaction to occur at 70° between p-toluenesulfinic acid and both benzyl and n-butyl sulfide in acetic acid containing 1-5% water and 0.3 to 0.7 M sulfuric acid. The reaction between benzyl sulfide and p-toluenesulfinic acid produced p-tolyl p-toluenethiolsulfonate, benzyl p-toluenethiolsulfonate and benzaldehyde in the amounts shown in Eq. 3. Kinetic experiments showed the reaction to be first-order both in sulfide and sulfinic acid. A large excess of sulfide was used, so that its concentration was essentially constant during a given experiment. When the disappearance of sulfinic acid was measured (by titration of aliquots with nitrite), a plot of log $(ArSO_2H)$ versus time gave a straight line. To show that the reaction was also first-order in sulfide, a series of runs at different initial sulfide concentrations was carried out, and the variation of the observed rate constant, k_1, with initial sulfide concentration, (R_2S), was determined. The ratio $k_1/(R_2S)$ was found to be independent of sulfide concentration. The rate was also found to depend strongly on the acidity of the medium. A plot of log k_s versus $-H_o$ was linear with a slope of 1.48, the same as for the p-tolyl disulfide - p-toluenesulfinic acid reaction (34). The rate was also found to be markedly retarded by an increase in the stoichiometric concentration of water. Since the reaction was first-order in both sulfide and sulfinic acid, the transition state of the rate-determining step would have to be derived from one molecule each of sulfide and sulfinic acid. Since the reaction is also strongly acid-catalyzed and strongly retarded by added water, a mechanism involving the formation of ion III in an initial equilibrium, followed by its rate-determining breakdown, was suggested.



$$\mathrm{ArSO_2H} + \mathrm{R_2S} + \mathrm{H^+} \overset{K_e}{\rightleftharpoons} \mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}\overset{+}{\underset{\underset{R}{|}}{S}}{-}R} + \mathrm{H_2O} \qquad \text{(Eq. 4a)}$$

III



$$\mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}\overset{+}{\underset{\underset{R}{|}}{S}}{-}R} \xrightarrow[\text{rate-determ.}]{k_c} \text{prod. after sev. steps} \qquad \text{(Eq. 4b)}$$

Such a mechanism would give the rate expression:

$$-\frac{d(\mathrm{ArSO_2H})}{dt} = k_cK_e(\mathrm{ArSO_2H})(\mathrm{R_2S})\left[\frac{a_{H^+}}{a_{H_2O}}\right]\frac{f_{R_2S}\cdot f_{ArSO_2H}}{f^*_c}$$

where f^*_c is the activity coefficient for the transition state of the slow step. The expression for the rate constant is accordingly:

$$k_s = \text{const.}\left[\frac{a_{H^+}}{a_{H_2O}}\right]\frac{f_{R_2S}\cdot f_{ArSO_2H}}{f^*_c}$$

The exact way in which the intermediate III decomposed was not determined. As will be discussed later (page 20), there were two possibilities for this decomposition that seemed equally reasonable from the data originally obtained. Also, these data gave no information about the reactions after the rate-determining step. Thus, the purpose of the first part of this work was to determine the rate-determining step of the alkyl sulfide - p-toluenesulfinic acid reaction, and also to clarify, if possible, the nature of the subsequent reactions leading to the final products observed.

RESULTS AND DISCUSSION

1. Stoichiometry of the Reaction between Alkyl Sulfides and p-Toluenesulfinic Acid

Kice and Bowers' original studies (35) left some uncertainty about the stoichiometry of the reaction between alkyl sulfides and p-toluenesulfinic acid. Although the stoichiometry shown in Eq. 3 was established for the benzyl sulfide - sulfinic acid reaction, in the reaction of n-butyl sulfide with the same sulfinic acid no n-butyl p-toluenethiolsulfonate seemed to be formed. In the present work this matter has been clarified both by a reinvestigation of the products of the n-butyl sulfide - sulfinic acid reaction and by study of the products of the reaction of ethyl sulfide with p-toluenesulfinic acid. Investigation of reaction stoichiometry has also been extended to include two secondary alkyl sulfides (isopropyl and 2-octyl). The results of all these product studies are shown in Table 1.

In the reaction between n-butyl sulfide and the sulfinic acid we found that, contrary to the original report (35), n-butyl p-toluenethiolsulfonate was indeed formed; the mole ratio of the p-tolyl ester to the alkyl p-toluenethiolsulfonate was 2.24. This is reasonably close to the 2:1 ratio of aryl to alkyl thiolsulfonate required by Eq. 6 (page 19). In the earlier studies (35) the formation of n-butyraldehyde was demonstrated, although unfortunately the

TABLE 1

PRODUCTS FROM THE REACTION BETWEEN ALKYL SULFIDES AND p-TOLUENESULFINIC ACID

Solvent: 0.6 M sulfuric acid - 0.56 M water - acetic acid. Temperature: 70°.

Run:	P 1	P 2	P 3	P 4	P 5
Sulfide used:	n-$(Bu)_2S$	EtSEt	$(Me_2CH)_2S$	$(C_6H_{13}\underset{Me}{C}H)_2S$	
Reaction time	1 hr.	1.5 hr.	2 hrs.	2 hrs.	2 hrs.
Reactants (mmoles)					
$ArSO_2H$	5	5	4.75[1]	4.75[1]	4.75[1]
RSR	10	10	14.25	14.25	14.25
Products (mmoles)					
RSR recovered	7.75 (86%)	--	10.9 (82%)	12.9 (96%)	12.5 (94%)
$ArSO_2SAr$	1.52 (76%)	2.16 (108%)	1.28 (72%)	1.29 (75%)	1.26 (73%)
$ArSO_2SR$	0.68 (68%)	1.11 (111%)	0.70 (79%)	0.75 (87%)	0.685 (79%)
$\frac{ArSO_2SAr}{ArSO_2SR}$	2.24	1.95	1.83	1.72	1.84
Aldehyde or ketone:	Butyraldeh.[a]	Acetaldeh.[b]	Acetone[c]	2-Octanone	2-Octanone[d]

1) In each case a sample was titrated before the reaction mixture was worked up. The titrations showed reaction P 3 to be 94% completed, P 4 and P 5 91% completed. This was taken into account when the yields (in %) were calculated.

a), b), c) and d). Isolation of these compounds is described in the Experimental section, 10 a) - d).

amount could not be determined quantitatively with any accuracy.

The ethyl sulfide - sulfinic acid reaction gave p-tolyl p-toluenethiolsulfonate and ethyl p-toluenethiolsulfonate in a mole ratio of 1.95, in excellent agreement with the 2:1 mole ratio expected from Eq. 6. Although not determined quantitatively, acetaldehyde was shown to be one of the products of this reaction by its isolation as its 2,4-dinitrophenylhydrazone.

The first secondary sulfide, isopropyl sulfide, was reacted with p-toluenesulfinic acid to give a mole ratio of 1.83 between the products, p-tolyl p-toluenethiolsulfonate and isopropyl p-toluenethiolsulfonate. Acetone was also isolated as a product from this reaction. Similar to acetaldehyde and n-butyraldehyde, acetone has a low enough boiling point to make a quantitative isolation (from the present reaction mixtures) very difficult.

Two experiments with the secondary sulfide 2-octyl sulfide (P 4 and P 5) showed mole ratios of 1.72 and 1.84 between produced p-tolyl p-toluenethiolsulfonate and 2-octyl p-toluenethiolsulfonate. In the last experiment (P 5), attempts were made to isolate the 2-octanone produced quantitatively. Only 48% of the amount calculated from Eq. 6 could, however, be isolated. In addition to the products listed in Table 1, we also isolated some 2-octyl sulfoxide in experiments P 4 and P 5, about 0.5 mmoles in each experiment. One possible way in which 2-octyl sulfoxide can be formed, is through the intermediate $\mathrm{Ar{-}S{-}O{-}\overset{+}{S}{<}^{R}_{R}}$ (IV) which can decompose to the sulfoxide and the sulfenium ion $\mathrm{ArS^{+}}$. Formation of such an intermediate should be subject to less steric hindrance from the two sec-octyl groups than the formation of the usual ion $\mathrm{Ar{-}\underset{\underset{O}{\|}}{\overset{+}{S}}{-}SR_2}$. However, if IV were formed and decomposed in the manner indicated below, the overall stoichiometry of the sulfide - sulfinic acid reaction should be altered in such a way that the mole ratio of p-tolyl to alkyl p-toluenethiolsulfonate would be larger than normal.

$$\mathrm{ArSO_2H + H^+ + R_2S \rightleftharpoons \underset{IV}{ArS{-}O{-}\overset{+}{S}{<}^{R}_{R}} + H_2O} \qquad \text{(Eq. 5 a)}$$

$$\mathrm{IV \rightarrow ArS^+ + R{-}\underset{\underset{O}{\|}}{S}{-}R} \qquad \text{(Eq. 5 b)}$$

$$\mathrm{ArS^+ + ArSO_2H \rightarrow ArSO_2SAr + H^+} \qquad \text{(Eq. 5 c)}$$

Summation of equations 5a - 5c gives:

$$\mathrm{2\,ArSO_2H + R_2S \rightarrow ArSO_2SAr + R{-}\underset{\underset{O}{\|}}{S}{-}R + H_2O} \qquad \text{(Eq. 5 d)}$$

This ratio was, however, slightly lower than normal. Because of this discrepancy, the above explanation for the formation of the sulfoxide in the sec-alkyl sulfide reactions is less attractive than would otherwise be the case. We also might mention that no _n_-butyl sulfoxide was found from earlier experiments with _n_-butyl sulfide, in spite of an extensive search for this sulfoxide* among the products.

The reaction with 2-octyl sulfide is obviously not as clear cut as the reactions with the primary sulfides. In order to get some more information about the additional facet of the 2-octyl sulfide - sulfinic acid reaction, the following experiments (P 9 - P 12) were made: When 2-octyl sulfide was heated alone in 0.6 _M_ sulfuric acid - 0.56 _M_ water - acetic acid for two hours, no sulfoxide was formed (P 12). Neither did 2-octanone give any reaction upon heating in the same solvent for two hours (P 10). When 2-octyl sulfide and 2-octanone were heated together under the same conditions as before, some 2-octyl sulfoxide was formed (P 9), but in a smaller amount than from the original reaction. The presence of _p_-toluenesulfinic acid might promote this reaction - but in a way we do not yet understand. Such a reaction would also explain the observed low yield of 2-octanone. A possible consumption of _p_-tolyl _p_-toluenethiolsulfonate by some of the other products was ruled out since no increased amount of 2-octyl sulfoxide was observed when 2-octyl sulfide, 2-octanone and _p_-tolyl _p_-toluenethiolsulfonate were subjected to the usual reaction conditions (P 11).

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* Unpublished observations by John L. Kice and Kerry W. Bowers.

The formation of 2-octyl sulfoxide might also be explained by an alternate reaction route subsequent to reaction 5 b, and which would lead to about the same ratio between p-tolyl p-toluenethiolsulfonate and 2-octyl p-toluenethiolsulfonate formed. The sulfenium ions ArS^+ formed in reaction 5b, might react with excess sulfide present instead of with sulfinic acid:

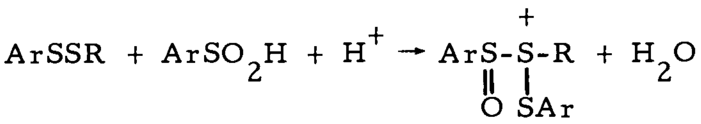
$$ArS^+ + R_2S \rightarrow \underset{V}{Ar\text{-}\overset{+}{S}\text{-}SR_2} \qquad \text{(Eq. 5 e)}$$

Intermediate V might then either react further with sulfinic acid (Eq. 5 f), or it might decompose unimolecularly to form an olefin, disulfide and a proton (Eq. 5 g):

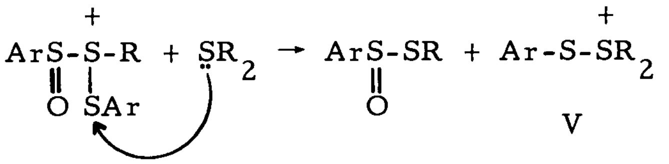
$$\underset{V}{Ar\text{-}\overset{+}{S}\text{-}SR_2} + ArSO_2H \rightarrow ArSO_2SAr + R_2S + H^+ \qquad \text{(Eq. 5 f)}$$

$$Ar\overset{+}{S}SR_2 \rightarrow \text{olefin} + ArSSR + H^+ \qquad \text{(Eq. 5 g)}$$

Any disulfide formed in reaction 5 g will certainly react through the following two reactions:

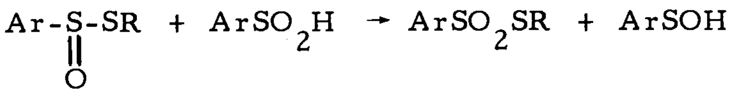


$$ArSSR + ArSO_2H + H^+ \rightarrow Ar\underset{\underset{O}{\|}}{S}\text{-}\underset{\underset{SAr}{|}}{\overset{+}{S}}\text{-}R + H_2O \qquad \text{(Eq. 5 h)}$$



$$Ar\underset{\underset{O}{\|}}{S}\text{-}\underset{\underset{SAr}{|}}{\overset{+}{S}}\text{-}R + \ddot{S}R_2 \rightarrow Ar\underset{\underset{O}{\|}}{S}\text{-}SR + \underset{V}{Ar\text{-}\overset{+}{S}\text{-}SR_2} \qquad \text{(Eq. 5 i)}$$

Intermediate V, formed in reaction 5 i might again react through either equation 5 f or 5 g, whereas the thiolsulfinate, $Ar\text{-}\underset{\overset{\|}{O}}{S}\text{-}SR$ will react with sulfinic acid to form thiolsulfonate and the unstable sulfenic acid:



$$Ar\text{-}\underset{\overset{\|}{O}}{S}\text{-}SR + ArSO_2H \rightarrow ArSO_2SR + ArSOH \qquad \text{(Eq. 5 j)}$$

The sulfenic acid, ArSOH might react with excess sulfide present to form intermediate V, which again has the two possibilities 5 f or 5 g for further reaction:

$$ArSOH + R_2S \xrightarrow{H^+} \underset{V}{ArS\text{-}\overset{+}{S}R_2} + H_2O \qquad \text{(Eq. 5 k)}$$

Since p-tolyl p-toluenethiolsulfonate is formed when intermediate V reacts through reaction 5 f, whereas alkyl p-toluenethiolsulfonate is formed in steps subsequent to reaction 5 g, a proper balance between the two reaction paths 5 f and 5 g for the further reaction of intermediate V, could lead to the ratio observed between the two thiolsulfonates.

An indication of the reaction sequence 5 a, 5 b, 5 e, 5 f or 5 g, the latter followed by reactions 5 h - k, was found in the peculiar behaviour of the isopropyl sulfide catalyzed reactions between phenyl disulfide and sulfinic acid (Runs 69 and 70, Table 27, Appendix 2).

Run 69, which was followed for 55 minutes, showed a decreasing rate constant k_1 with time (upwards curvature of the plot log $(ArSO_2H)$ versus time). This suggests that the catalyst, isopropyl sulfide, was gradually destroyed during the reaction. Isopropyl sulfide, being a secondary sulfide, could therefore form intermediate V, $Ar\text{-}\overset{+}{S}\text{-}SR_2$, which presumably reacted mostly through reaction sequence 5 g - k, thereby decomposing the sulfide.

According to our present knowledge about the stoichiometry of the reaction between alkyl sulfides and p-toluenesulfinic acid, the stoichiometry:

$$5\,ArSO_2H \quad + \quad (RCH_2)_2S \quad \rightarrow$$

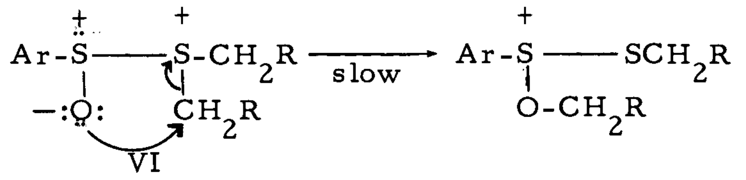
$$2\,ArSO_2SAr \quad + \quad ArSO_2SCH_2R \quad + \quad RCHO \quad + \quad 3\,H_2O \qquad \text{(Eq. 6)}$$

seems to be general for all primary alkyl sulfides.

The two secondary sulfides that were studied, show a somewhat lower ratio between symmetrical and mixed thiolsulfonate than expected from Eq. 6. Isolation of small amounts of sulfoxide from one of these reactions, demonstrates a less clear cut reaction pattern than for the primary sulfides. Although the main paths of these reactions are suspected to follow Eq. 6, additional reactions make these systems more complex than the primary cases.

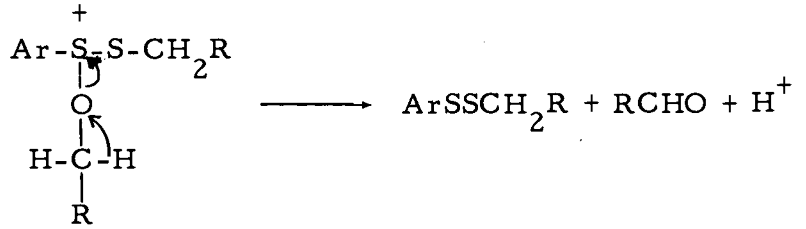
2. The Rate-Determining Step

The exact nature of the rate-determining step for the alkyl sulfide - p-toluenesulfinic acid reaction had not been determined by the previous studies of Kice and Bowers (35). There were two plausible possibilities for the rate-determining decomposition of the intermediate $Ar\text{-}\underset{O}{\overset{+}{S}}\text{-}S(CH_2R)_2$. One possibility was an S_Ni displacement, analogous to the mechanism for the acid-catalyzed rearrangement of sulfoxides, suggested by Kenney and coworkers (32):



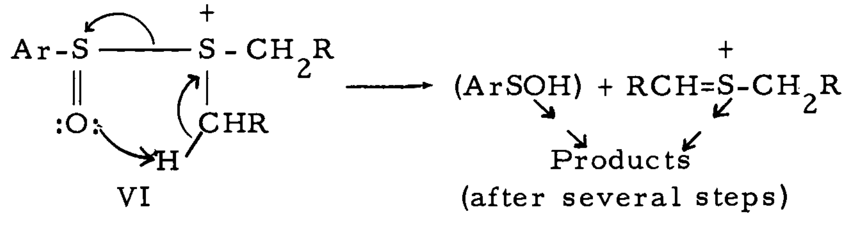
(Eq. 7 a)

followed by:



An analogy for this last step would be the oxidation - reduction between alkyl halides and dimethyl sulfoxide (30), (32).

The other possibility for the rate-determining step was an abstraction of an α-proton from one of the alkyl groups by the oxygen:



(Eq. 7b)

Substitution of deuterium for all four α-hydrogens in the sulfide would lead to the breakage of a carbon-deuterium bond in the rate-determining step shown in Eq. 7b. Since a carbon-deuterium bond is stronger than that between carbon and hydrogen, the activation energy is higher for breakage of a C - D bond, and the observed reaction rate should be slower if this were the rate-determining step. On the other hand, if the reaction went by route 7a, a comparison of the rates for α-deuterated and normal sulfide should show no primary isotope effect. α-Deuterium should not in any case have any significant effect on the initial equilibrium (Eq. 4a).

The sulfides chosen for these experiments were benzyl sulfide and α,α-dideuteriobenzyl sulfide. The latter, when prepared from α,α-dideuteriobenzyl alcohol, contained 3.82 deuterium atoms per molecule. When the reactions were carried out in 0.6 $\underline{M}$ sulfuric acid - 0.56 $\underline{M}$ water - acetic acid at 70°, the rate constants k_s were found as:

$$\begin{array}{ll} \text{Benzyl sulfide:} & k_s = 3.6 \times 10^{-3}\ \underline{M}^{-1}\ \text{sec.}^{-1} \\ \alpha,\alpha\text{-Dideuteriobenzyl sulfide:} & k_s = \underline{0.8 \times 10^{-3}\ \underline{M}^{-1}\ \text{sec.}^{-1}} \\ & \Delta = 2.8 \times 10^{-3}\ \underline{M}^{-1}\ \text{sec.}^{-1} \end{array}$$

Since the deuterium sulfide was only 95.5% deuterated in the α-position, the corrected value of Δ is $2.9 \times 10^{-3}\ \underline{M}^{-1}\ \text{sec.}^{-1}$, and the ratio between the rate constants for normal and deuterated sulfide accordingly:

$$\frac{k_H}{k_D} = \frac{3.6 \pm 0.05}{0.7 \pm 0.05} = 5.2 \pm 0.4 \text{ (8\% accuracy)}$$

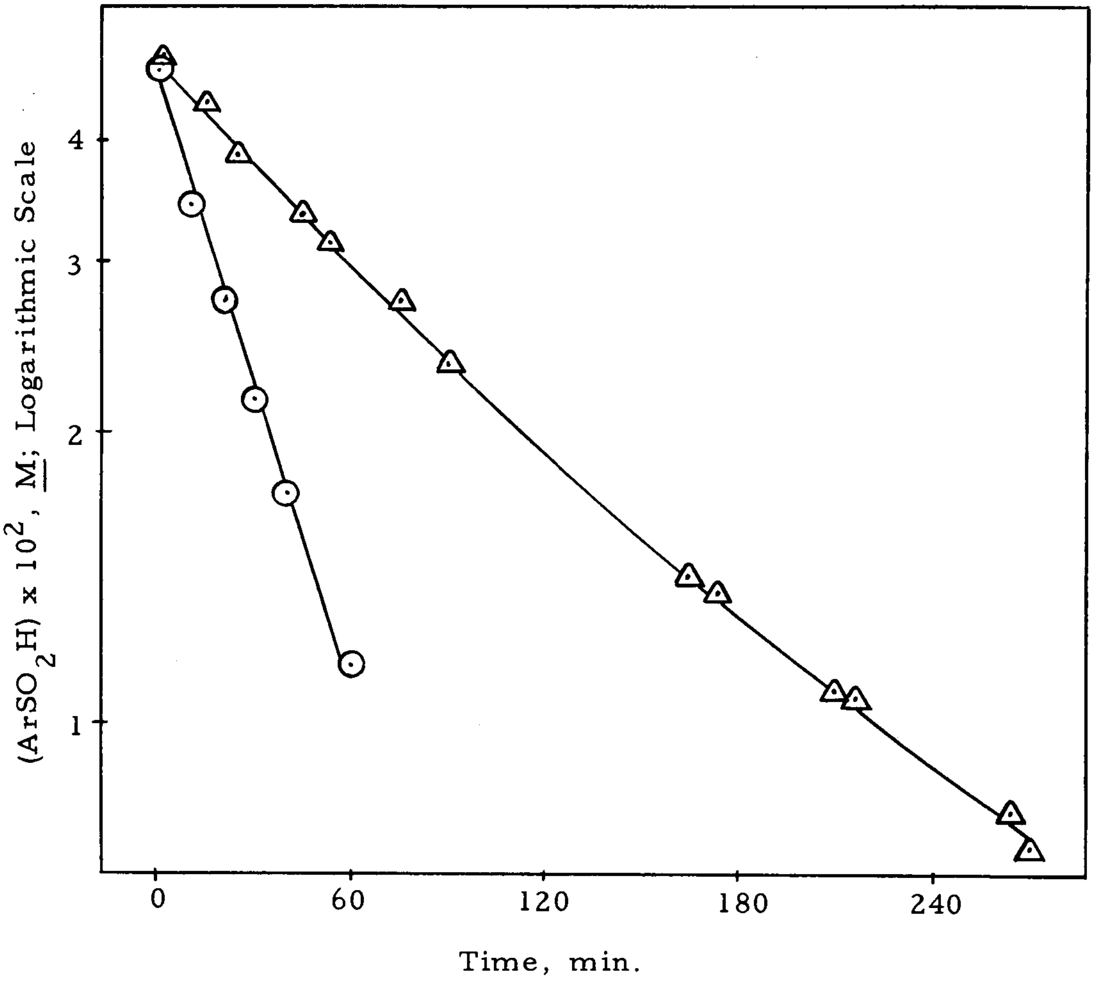
This large primary isotope effect thus rules out reaction 7 a (page 20) as the rate-determining step, and indicates strongly reaction 7 b (page 20) as the slow step. Curves 1 and 2, Figure 1, where log $(ArSO_2H)$ is plotted versus time for the reactions of normal and α-deuterated benzyl sulfide, respectively, illustrate the large primary isotope effect.

3. Effect of Sulfide Structure on the Reaction Rate

Reaction rates were measured for primary, secondary and tertiary alkyl sulfides, and also for one cyclic sulfide, (thioxane).

For all these experiments the solvent used was 0.6 M sulfuric acid - 0.56 M water - acetic acid at 70°. The initial sulfide concentration was varied for most of the sulfides studied, in order to establish that the reaction was first-order in sulfide. However, under all our reaction conditions some of the normal disproportionation, which is second-order in sulfinic acid (33), also occurred. In most cases this reaction was so slow compared to the sulfide - sulfinic acid reaction, that good first-order kinetics were observed. (A large stoichiometric excess of the sulfide was always used). From the observed rate constant, k_{exp}, the product $k_2(ArSO_2H)_{av.}$ of the second-order rate constant k_2 for the disproportionation (33) and the average value of the sulfinic acid concentration during the experiment, was subtracted. The pseudo first-order rate constant

Figure 1. Plot of log ($ArSO_2H$) versus Time for Benzyl and α, α-Dideuteriobenzyl Sulfide when reacted with p-Toluenesulfinic Acid.



○ Curve 1, Run 1, benzyl sulfide;

△ Curve 2, Runs 3 and 4, α, α-dideuteriobenzyl sulfide.

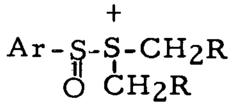
obtained, k_1, was converted to the actual rate constant k_s by dividing by the sulfide concentration (R_2S). This can be shown by the following equations:

$$\text{Rate} = -\frac{d(ArSO_2H)}{dt} = k_s(R_2S)(ArSO_2H) + k_2(ArSO_2H)^2$$

$$k_{exp} = k_s(R_2S) + k_2(ArSO_2H)_{av.} = k_1 + k_2(ArSO_2H)_{av.}$$

$$k_s = \frac{k_{exp} - k_2(ArSO_2H)_{av.}}{(R_2S)}$$

For some of the less reactive sulfides, however, the second-order disproportionation of sulfinic acid was no longer negligible compared to the sulfide - sulfinic acid reaction. This was apparent since a plot of $\log(ArSO_2H)$ versus time would show an upward curvature towards the end of a run. In such cases the data were treated as for parallel first- and second-order reactions, using the method outlined by Frost and Pearson (21, p. 165). The sulfinic acid concentration was plotted versus time, and a smooth curve was drawn through the points. At different points on the curve the value $-d(ArSO_2H)/dt = \lambda$ was found at the tangent to the curve. A plot of $\lambda/(ArSO_2H)$ versus the sulfinic acid concentration, gave k_1 as the intercept at $(ArSO_2H) = 0$, and k_2 as the slope of the line. The constant k_2 was of course known from earlier experiments (33).

The structure of the intermediate  $\mathrm{Ar{-}\underset{\overset{\|}{O}}{S}{-}\overset{+}{\underset{\overset{|}{CH_2R}}{S}}{-}CH_2R}$ and the nature of the rate-determining step (Eq. 7b) suggest that the sulfide sulfur will possess a large amount of positive charge in transition state for the rate-determining step. This large positive charge on the sulfide sulfur in transition state should be stabilized by electron-donating alkyl groups in the sulfide. Such a stabilization of the positive charge would lower the difference between the energy of the starting sulfide and the transition state of the rate-determining step and accordingly would increase the overall reaction rate. Electron-withdrawing alkyl groups would, on the other hand, be expected to give less reactive sulfides. Steric effects might also influence the reactivity of the sulfides, i.e. bulky alkyl groups might inhibit the formation of ion III from the sulfide and $ArSO^+$.

The results of the kinetic studies with the different alkyl sulfides are summarized in Tables 2, 3, and 4.

Table 2 lists k_s values for the primary alkyl sulfides of the general formula $(RCH_2)_2S$, and also the corresponding σ^* values for the alkyl groups R (47, p. 619). In cases where purely inductive effects influence the reactivity of aliphatic compounds, the Taft relation, $\log k/k_o = \sigma^* \rho^*$ is valid, σ^* being the polar substituent constant and ρ^* the reaction constant. Thus, the Taft relationship gives a quantitative relationship between reactivity and

TABLE 2

RATE CONSTANTS OF PRIMARY ALKYL SULFIDE - SULFINIC ACID REACTIONS, AND σ* VALUES

The reactions were carried out in 0.6 M sulfuric acid - 0.56 M water - acetic acid solutions at 70°. The sulfides were of the general formula $(RCH_2)_2S$, σ* values are taken from (47, p. 619).

Sulfide	$k_s \times 10^3$, M^{-1} sec.$^{-1}$	$3 + \log k_s$	Alkyl group R	σ*
Benzyl	3.58	0.555	C_6H_5-	+0.60
β-Phenylethyl	3.55	0.551	C_6H_5-CH_2-	+0.215
Carboxymethyl	a)	a)	HOOC-	
Carboxyethyl	0.12	-0.920	$HOOCCH_2$-	+1.05
Ethyl	10.2	1.009	CH_3-	0.00
n-Amyl	15.1	1.179	$CH_3(CH_2)_3$-	-0.13
β-Phenoxyethyl	0.30	-0.523	C_6H_5O-CH_2-	+0.85
iso-Butyl	9.03	0.956	$(CH_3)_2CH$-	-0.19
n-Butyl (35)	17.5	1.244	CH_3-CH_2CH_2-	-0.115

a) Too small to measure.

TABLE 3

RATE CONSTANTS OF REACTIONS BETWEEN SECONDARY ALKYL SULFIDES AND SULFINIC ACID

The reactions were carried out in 0.6 M sulfuric acid - 0.56 M water - acetic acid solutions at 70°.

Sulfide	$k_s \times 10^3$, $\underline{M}^{-1}$ sec.$^{-1}$
Isopropyl	2.57
sec-Butyl	2.88
sec-Octyl	2.42

TABLE 4

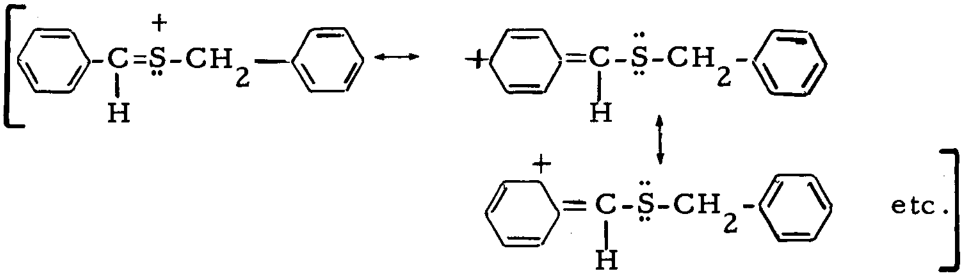
RATE CONSTANTS OF REACTIONS BETWEEN OTHER ALKYL SULFIDES AND SULFINIC ACID

The reactions were carried out in 0.6 M sulfuric acid - 0.56 M water - acetic acid solutions at 70°.

Sulfide	$k_s \times 10^3$, $\underline{M}^{-1}$ sec.$^{-1}$
Benzyl phenyl	0.288
1,4-Thioxane	0.086
2-Butoxyethyl	too slow to measure
3-keto *n*-butyl	23.1
t-Butyl	21.9

structure of the alkyl group. Curve 3 (Figure 2) shows a plot of $\log k_s$ for the primary sulfides versus their respective σ^* values.

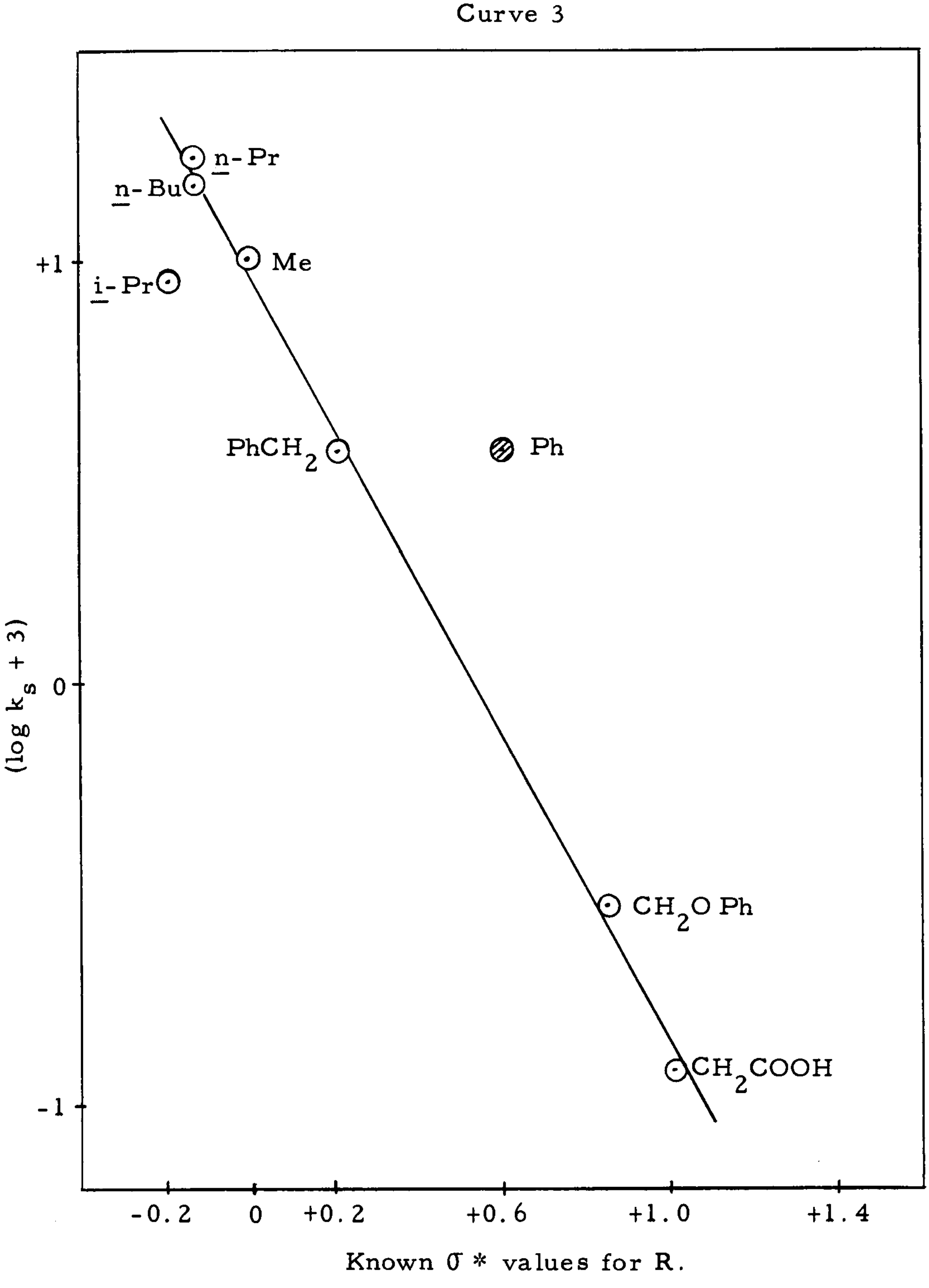
The data are in very good agreement with the Taft relationship ($\rho^* = -1.8$) with the exception of benzyl and isobutyl sulfide. Benzyl sulfide shows about five times higher reactivity than expected. This can in fact be taken as additional evidence for the postulated rate-determining step. Since the developing carbon-sulfur double bond in the transition state for the slow step is conjugated with the benzyl-benzene ring, resonance forms with the positive charge in the benzene ring are possible:



Such resonance forms will lower the energy of the transition state for the rate-determining step and thereby increase the over-all rate of the reaction. Benzyl sulfide is the only sulfide of those studied that has the possibility for resonance structures of this type.

Curve 3 shows the reactivity of isobutyl sulfide to be somewhat less than half of what we would expect from the Taft relationship (k_s found: 9×10^{-3} $\underline{M}^{-1}$ sec.$^{-1}$, k_s expected: 21.4×10^{-3} $\underline{M}^{-1}$ sec.$^{-1}$). This lower reactivity is evidently caused by the larger

Figure 2. Plot of log k_s for Primary Alkyl Sulfides $(RCH_2)_2S$, versus known σ^* Values for R.

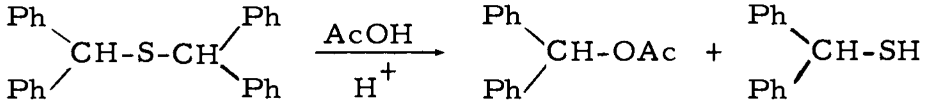


steric requirements of the branched alkyl groups. Thus, branching on the β-carbon seems to lower the reactivity of the sulfide. Since benzyl sulfide, which also has branching at this carbon atom, shows increased reactivity, we might assume that the actual rate-enhancing resonance effect is somewhat masked by this retarding effect.

n-Amyl sulfide is slightly less reactive than n-butyl sulfide (35). Thus, we might suggest that even unbranched aliphatic chains can cause steric hindrance. This effect is, however, so small that it should not be regarded as conclusive evidence.

If we look at the rate constants for the three secondary sulfides, which have branched α-carbons, we notice remarkably similar rate constants. Moreover, sec-butyl sulfide shows about one-sixth the reactivity of n-butyl sulfide. In other words, there seems to be no doubt as to the rate retarding effect of alkyl groups with large steric requirements near the sulfur atom. Isopropyl sulfide is, as expected from inductive effects, slightly less reactive than sec-butyl sulfide. sec-Octyl sulfide is, however, less reactive than both of the other secondary sulfides. This might again indicate that long unbranched aliphatic chains are able to shield the sulfur atom to some degree.

Although no actual rate constant was measured for benzhydryl sulfide, the reaction was found to be very fast (Run 21). The sulfinic acid was completely consumed in less than 20 minutes. This indicates a rate constant comparable to that for n-butyl sulfide. The high reactivity of benzhydryl sulfide, compared to the other secondary sulfides, seems at first somewhat surprising. One attractive explanation is that some of the sulfide undergoes hydrolysis:



$$\mathrm{Ph_2CH\text{-}S\text{-}CHPh_2} \xrightarrow[H^+]{AcOH} \mathrm{Ph_2CH\text{-}OAc} + \mathrm{Ph_2CH\text{-}SH}$$

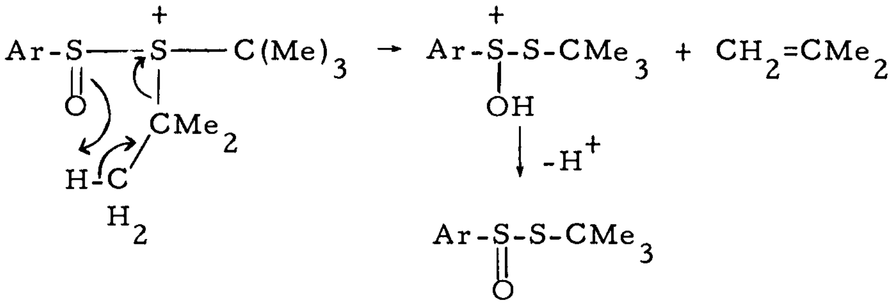
The mercaptan produced would then react very rapidly with the sulfinic acid. Details of the reaction between mercaptans and sulfinic acid will be described later (page 37), but anticipating slightly, the initial step of this reaction is a rapid disproportionation to the two sulfenic acids ArSOH and RSOH. The sulfenic acids will react rapidly with more sulfinic acid (or mercaptan) to form the products.

t-Butyl sulfide also shows an unexpectedly large rate constant, which is somewhat greater than that for n-butyl sulfide. Hydrolysis of the t-butyl sulfide seems again to be the simplest explanation:

$$\mathrm{(CH_3)_3C\text{-}S\text{-}C(CH_3)_3} \xrightarrow[H^+]{AcOH} \mathrm{(CH_3)_3COAc} + \mathrm{(CH_3)_3C\text{-}SH}$$

Both benzhydryl and t-butyl sulfide are likely to undergo hydrolysis in strongly acidic media since cleavage of the C-S bond following electrophilic attack on the sulfur atom, will give the relatively stable carbonium ions, $Ph_2\overset{+}{C}H$ and $(CH_3)C^+$. These then rapidly solvolyse.

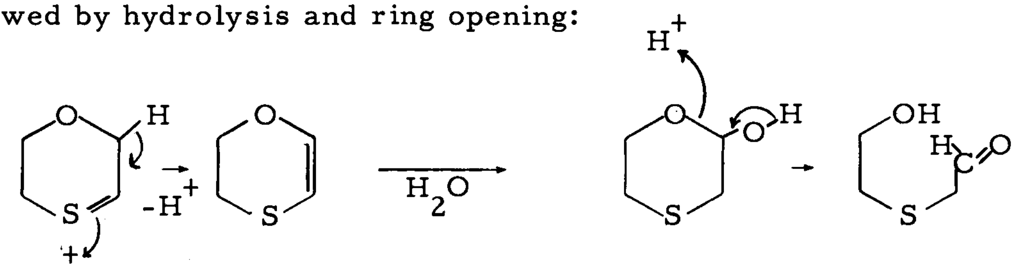
If t-butyl sulfide were to react in a similar way to reaction 7b (page 20), it would have to lose a β-hydrogen since there are no α-hydrogens present:



Perhaps such an elimination might proceed with a faster rate than when α-hydrogens are eliminated as in reaction 7b, although there is no particular reason that we can see why it should do so.

The primary sulfide, β-n-butoxyethyl sulfide (Run 25) seemed to undergo hydrolysis to the free diol, thiodiethanol. Under the present reaction conditions the hydroxyl groups could easily be esterified by some of the acetic acid, producing thiodiethyl acetate and water. Since water has a large retarding effect on the alkyl sulfide - sulfinic acid reaction, the observed low rate constant is not surprising.

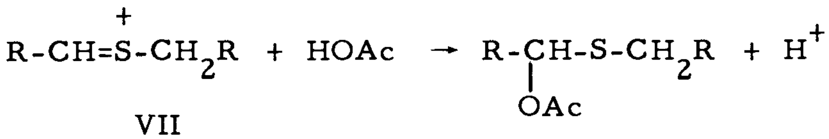
The only cyclic sulfide that was studied, thioxane, shows far less reactivity than expected from inductive effects. Its rate constant is about one twelfth of that expected for β-methoxyethyl sulfide (R = CH_3OCH_2-, $\sigma^* = +0.52$) which is the sulfide it should resemble most closely. As we shall see later, the intermediate $R\text{-}CH{=}\overset{+}{S}\text{-}CH_2R$ usually hydrolysed very rapidly to aldehyde and mercaptan and the latter will react very rapidly with sulfinic acid. The intermediate from thioxane might instead undergo isomerization, followed by hydrolysis and ring opening:



The occurrence of such an isomerization and hydrolysis would lead to the sulfide - sulfinic acid reaction consuming only 40% of the usual amount of the sulfinic acid per mole of sulfide reacting. This is most easily seen from Chart 2 (page 48) which shows that three sulfinic acid molecules are consumed after formation of the intermediate $RCH{=}\overset{+}{S}CH_2R$. This explanation could, however only account for part of the retardation observed. The low reactivity of thioxane might possibly also be caused by steric factors, i.e. the required geometry of the transition state for the elimination reaction might be difficult to achieve. Other cyclic sulfides should be studied, however, before we make any further conclusions.

4. Reaction Sequence After the Rate-Determining Step

Having determined the exact nature of the rate-determining step, we can now turn our attention to the further reactions of the intermediate $RCH=\overset{+}{S}-CH_2R$ (VII) formed in this slow step. This intermediate might be solvolysed by acetic acid to the α-acetoxy sulfide, the reaction being:



$$R-CH=\overset{+}{S}-CH_2R + HOAc \rightarrow R-\underset{OAc}{\underset{|}{C}}H-S-CH_2R + H^+$$

VII

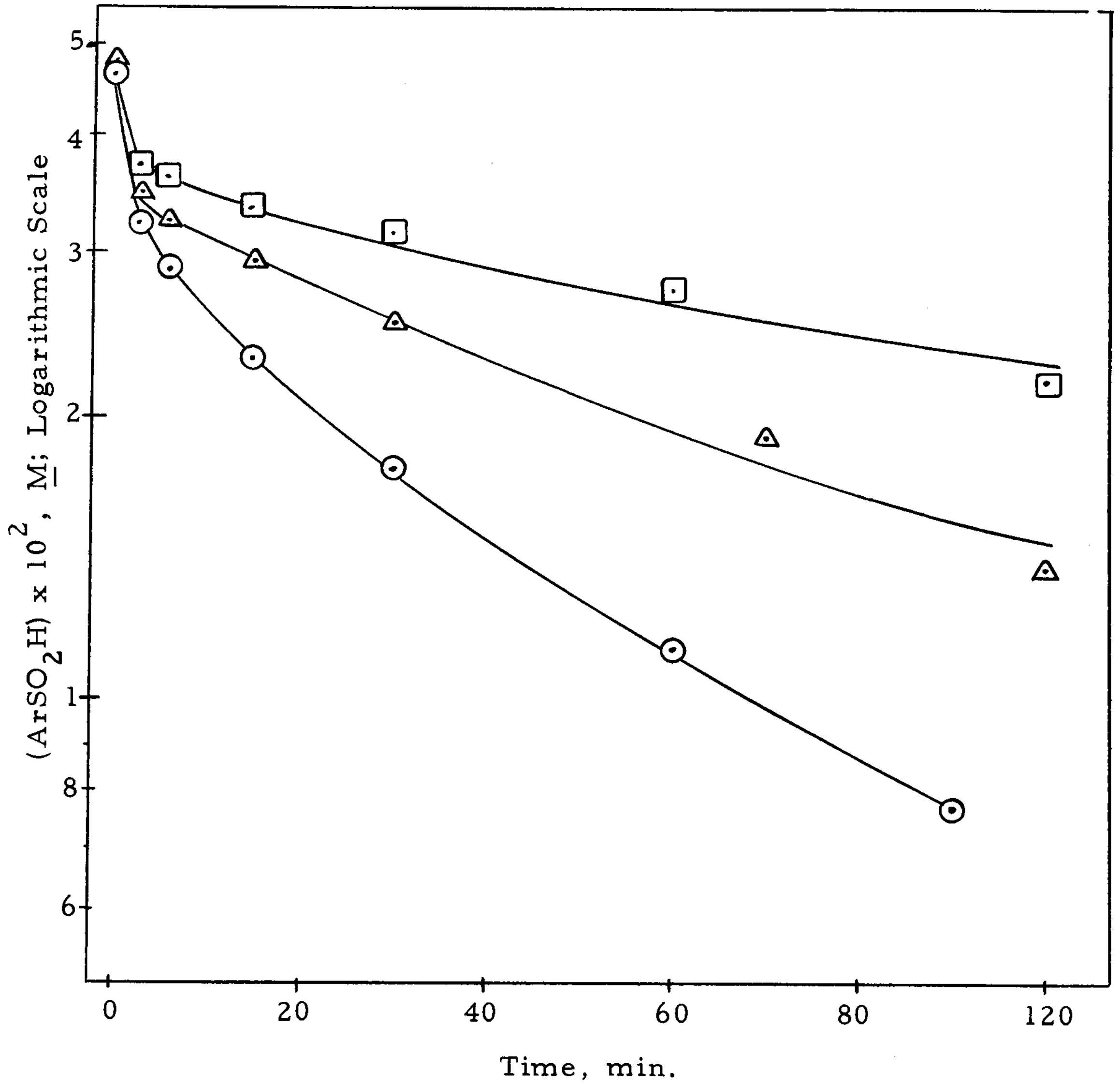
We would expect the α-acetoxy sulfide to hydrolyse rapidly to mercaptan and aldehyde. The intermediate VII might, as another possibility, hydrolyse directly to mercaptan and aldehyde. Sosnovsky (61) has actually made α-acetoxy sulfides by reacting sulfides with t-butyl peracetate in the presence of cuprous ions. This permits one to test the behaviour of the α-acetoxy sulfide directly under the conditions used for the sulfide - sulfinic acid reaction. n-Butyl α-acetoxybutyl sulfide was synthesized and used in Experiments 28-30 (Table 24). Additional experiments that are not listed, showed that on storage, even at -20°, the n-butyl α-acetoxybutyl sulfide underwent slow decomposition. The sulfide was therefore always distilled immediately before each kinetic experiment. In Experiments 28 and 29 0.8 mmole of n-butyl α-acetoxybutyl sulfide was added to a solution (45 ml.) of sulfinic acid with vigorous stirring. (The solution turned dark yellow immediately after the addition; such a colour change was not observed in ordinary kinetic runs.)

Curve 4 in Figure 3 (Run 29) shows a large initial consumption of sulfinic acid, 0.60 mmole during the first three minutes after the addition of n-butyl α-acetoxybutyl sulfide. If we also look at Curve 6 in Figure 3 (Run 31), we see the same initial consumption of sulfinic acid when 0.8 mmole of n-butyl mercaptan is added under the same reaction conditions. In another identical experiment with the α-acetoxy sulfide, the formation of n-butyraldehyde was demonstrated by sweeping it out of the reaction solution and through a trap containing 2,4-dinitrophenylhydrazine. The n-butyraldehyde 2,4-dinitrophenylhydrazone which precipitated was recrystallized and identified.

We have in other words shown that under the conditions used for the sulfide - sulfinic acid reaction the intermediate $RCH{=}\overset{+}{S}{-}CH_2R$ will be converted almost instantaneously to mercaptan and aldehyde, and that the mercaptan formed will react very rapidly with some of the sulfinic acid present.

Curves 4 and 6 in Figure 3 (Runs 29 and 31) show a much slower disappearance of sulfinic acid after the initial fast disappearance. This slower reaction is markedly accelerated when phenyl

Figure 3. Plot of log ($ArSO_2H$) versus Time for Reactions of p-Toluenesulfinic Acid with n-Butyl α-Acetoxybutyl Sulfide, n-Butyl Mercaptan, and the first Reaction Catalyzed by Phenyl Sulfide.



△ Curve 4, Run 29, n-butyl α-acetoxybutyl sulfide;

○ Curve 5, Run 30, α-acetoxy sulfide and phenyl sulfide;

□ Curve 6, Run 31, n-butyl mercaptan.

sulfide is present, as can be seen from Curve 5 (Run 30) which shows a run, otherwise identical to Run 29, where 0.1 M phenyl sulfide was present.

These experiments strongly indicate that the initially formed mercaptan reacts very rapidly with some sulfinic acid to form at least some disulfide. The much slower reaction of disulfides with sulfinic acids is known from earlier work (34) to be subject to catalysis by phenyl sulfide.

5. Reaction between Mercaptans and p-Toluenesulfinic Acid

The stoichiometry of the reaction between p-toluenesulfinic acid and n-butyl mercaptan was studied in several experiments. Table 5 shows the results from four of these experiments.

In the experiments on the following page (S 1 to S 4) a certain amount (0.4 mmole) of n-butyl mercaptan was added to the sulfinic acid (1.25 mmoles) with vigorous stirring. The mercaptan was dissolved in various amounts of the usual acid mixture, but the final volume of the mercaptan - sulfinic acid mixture was always the same (25 ml.). The time for the addition of mercaptan was also varied. Samples were titrated exactly five minutes after the start of the addition of mercaptan. These experiments show the stoichiometry of the reaction between sulfinic acid and mercaptan to vary

TABLE 5

STOICHIOMETRY OF THE n-BUTYL MERCAPTAN-p-TOLUENESULFINIC ACID REACTION

The reactions were carried out in 0.6 M sulfuric acid - 0.56 M water - acetic acid at 70°.

Run	S 1	S 2	S 3	S 4
$ArSO_2H$, mmoles	1.25	1.25	1.25	1.25
Solvent, ml.	10.00	15.00	20.00	24.00
n-BuSH, mmoles	0.4	0.4	0.4	0.4
Solvent, ml.	15.0	10.0	5.0	1.0
Addition time,* min.	5.17	3.5	2.5	0.67
Remaining $ArSO_2H$ (mmoles) after 5 min.	0.653 (after 6 min.)	0.745	0.755	0.845
Reacted $ArSO_2H$/ n-BuSH	1.49	1.26	1.24	1.01

* n-butyl mercaptan was added to the solution of sulfinic acid with very efficient stirring.

with the reaction conditions. The highest ratio of reacted sulfinic acid (mmoles) to mercaptan is found for experiment S 1, where the initial concentration of mercaptan is lowest, and the time for its addition is maximum. This, and the other experiments (S 2 to S 4) show that reaction mixtures with low mercaptan concentration give higher ratios of reacted sulfinic acid to reacted mercaptan. The ratio varies between 1.49 and 1.01 in these experiments.

In experiments S 5 to S 11 (Table 6 below), various amounts of n-butyl mercaptan in 5 ml. of acid solution were added at various rates to a solution of 1.2 mmoles of sulfinic acid in 20 ml. of the same acid solution. These experiments also show that the lower the average mercaptan concentration during the reaction, the higher the ratio of reacted sulfinic acid to reacted mercaptan. This ratio varies between 1.77 and 0.80.

The products from the reaction between n-butyl mercaptan and p-toluenesulfinic acid were studied in three similar experiments (P 6 to P 8). From all these reactions, four different products were formed; n-butyl disulfide, n-butyl p-tolyl disulfide, p-tolyl p-toluenethiolsulfonate and n-butyl p-toluenethiolsulfonate. The results of experiments P 6 to P 8 are shown in Table 7.

In all these experiments the sulfinic acid is always present in excess. Therefore the fact that the stoichiometry of the reaction

TABLE 6

STOICHIOMETRY OF THE n-BUTYL MERCAPTAN - p-TOLUENESULFINIC ACID REACTION

The reactions were carried out in 0.6 M sulfuric acid - 0.56 M water - acetic acid at 70°. The n-butyl mercaptan was dissolved in 5 ml. of the solvent and added to the sulfinic acid (1.20 mmoles) in 20 ml. of the solvent with vigorous stirring.

Run	n-BuSH added (mmoles)	Addition time (min.)	Unreacted $ArSO_2H$ (mmoles) at 5 min.	Reacted $ArSO_2H$/ n-BuSH
S 5	0.4	0.67	0.88	0.80
S 6	0.4	1.5	0.81	0.98
S 7	0.4	3.3	0.695	1.26
S 8	0.4	5.0	0.645	1.39
S 9	0.2	4.0	0.845	1.77
S 10	0.6	4.67	0.56	1.07
S 11	0.8	4.5	0.465	0.92

TABLE 7

PRODUCTS FROM n-BUTYL MERCAPTAN AND p-TOLUENESULFINIC ACID

The reactions were carried out in 0.6 M sulfuric acid - 0.56 M water - acetic acid at 70°. The mercaptan was dissolved in a part of the solvent and added to the sulfinic acid in the rest of the solvent with vigorous stirring.

Run	Rx. ratio (moles) $ArSO_2H$/BuSH	Reactants (mmoles)		Products (mmoles)			
		$ArSO_2H$	BuSH	BuSSBu	BuSSAr	$ArSO_2SAr$	$ArSO_2SBu$
P 6	1.72	9.5	3.04	0.20	0.41	1.20	1.40
P 7	1.50	9.0	2.88	0.31	0.53	0.99	1.17
P 8	0.97	7.0	4.48	0.78	0.97	0.93	1.055

Products (mole fraction)

Run	BuSSBu	BuSSAr	$ArSO_2SAr$	$ArSO_2SBu$	$\frac{\Sigma \text{ Thiolsulfonates}}{\Sigma \text{ Disulfides}}$
P 6	0.06	0.13	0.37	0.44	4.26
P 7	0.10	0.18	0.33	0.39	2.58
P 8	0.21	0.26	0.25	0.28	1.13

varies with average mercaptan concentration suggests that in the course of the mercaptan - sulfinic acid reaction some intermediate must be formed which has the properties outlined in the following paragraph.

This intermediate must react further through two competing reactions, both of which are faster than the initial reaction between sulfinic acid and mercaptan. In one of these reactions, the intermediate reacts with mercaptan, and at a higher rate than the initial reaction of mercaptan with sulfinic acid. Otherwise the mercaptan would be completely consumed by sulfinic acid, and a constant stoichiometry should be observed. Because of the variable stoichiometry of the reaction with varying average mercaptan concentration, the mercaptan must compete for the intermediate either with sulfinic acid, or with a unimolecular decomposition of the intermediate. Thus, at relatively high average mercaptan concentration, the mercaptan competes favourably for the intermediate and more disulfide is formed. Although not the only possible intermediate, a sulfenic acid, RSOH, is an attractive one, and emphasizing that this is only one possibility, we suggest the following scheme for the reaction between mercaptan and sulfinic acid:

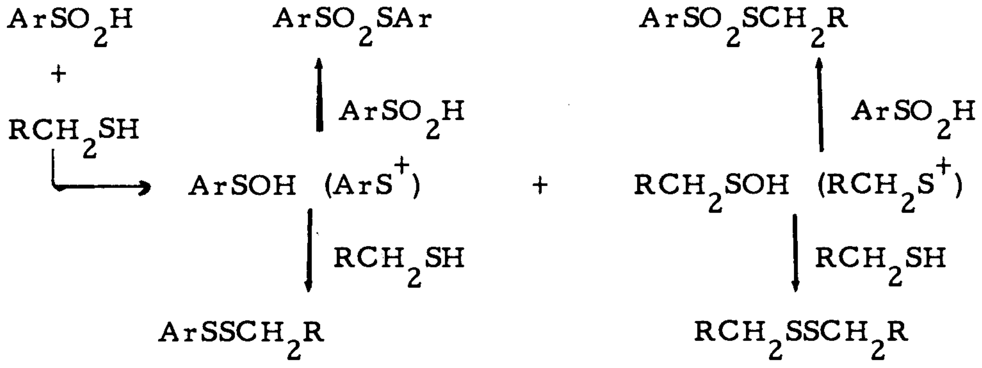


Chart 1

As a possible complication of this scheme, some of the thiolsulfonate formed might react further with mercaptan, since such a reaction has been observed (4):

$$ArSO_2SCH_2R + RCH_2SH \rightarrow ArSO_2H + RCH_2SSCH_2R$$

This reaction is, however, rather unlikely under the strongly acid conditions used for these experiments. The mercaptide ion, RCH_2S^-, is assumed to be the reacting species, and its concentration must be extremely low in the acetic acid - sulfuric acid system being used. Besides, such a competition for the mercaptan between sulfinic acid and thiolsulfonate would presumably occur in the manner shown below:

$$RSSR + ArSO_2H \xleftarrow[ArSO_2SR]{k_b} RSH \xrightarrow[ArSO_2H]{k_a} ArSO_2SR + ArSO_2SAr$$

In this scheme the rate of formation of disulfide from reaction of thiolsulfonate with mercaptan, relative to the overall rate of consumption of mercaptan would be:

$$\frac{\frac{d(\mathrm{RSSR})}{dt}}{-\frac{d(\mathrm{RSH})}{dt}} = \frac{k_b(\mathrm{RSH})(\mathrm{T.S.})}{(\mathrm{RSH})\,[k_a(\mathrm{ArSO_2H}) + k_b(\mathrm{T.S.})]}$$

$$= \frac{k_b(\mathrm{T.S.})}{k_a(\mathrm{ArSO_2H}) + k_b(\mathrm{T.S.})}$$

(T.S.) = (thiolsulfonate)

Formation of any disulfide by this reaction would therefore occur at a rate which was independent of the average concentration of mercaptan present. Thus, even if this reaction between mercaptan and thiolsulfonate were to occur, it could not be responsible for the variation of reaction stoichiometry with average mercaptan concentration.

The reaction between isopropyl mercaptan and p-toluenesulfinic acid was also studied briefly, and the results are shown in Table 8 below.

In both experiments (P 9 and P 10) the sulfinic acid was present in large excess compared to mercaptan. Also here the stoichiometry varies with the concentration of mercaptan. The ratio of reacted sulfinic acid to mercaptan was larger when the

TABLE 8

PRODUCTS FROM ISOPROPYL MERCAPTAN AND p-TOLUENESULFINIC ACID

The mercaptan was dissolved in some of the 0.6 M sulfuric acid - 0.56 M water - acetic acid solution (amount indicated below) and then added to the solution of sulfinic acid with vigorous stirring.

Run	Rx. ratio (moles) $ArSO_2H/RSH$	Addn. time, min.	Reactants, mmoles $ArSO_2H$	Reactants, mmoles Me_2CHSH	Products, mmoles [a)] $ArSO_2SCHMe_2$	Products, mmoles [a)] $ArSO_2SAr$
P 9	1.15	10	9 in 80 ml.	2.88 in 20 ml.	0.55	1.18
P 10	0.71	3.6	7.0 in 60 ml.	4.48 in 15 ml.	0.31	0.98

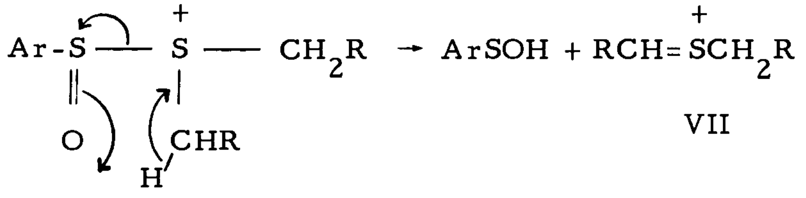
a) The amounts of disulfides, $ArSSCHMe_2$ and $Me_2CHSSCHMe_2$ were not determined.

latter was present in low concentration. Only the total amounts of disulfides produced were determined, but the amounts of both thiolsulfonates were determined separately.

6. Conclusions about the Alkyl Sulfide - p-Toluenesulfinic Acid Reaction

Our findings about the mechanism of the alkyl sulfide - sulfinic acid reaction can be summed up in three main points:

1. Nature of the rate-determining step. Kinetic experiments with α,α-dideuteriobenzyl sulfide and benzyl sulfide revealed a large primary isotope effect for the alkyl sulfide - sulfinic acid reaction. This isotope effect, together with the variation of the reactivity of alkyl sulfides with their structure, allowed us to decide between the two possibilities for the rate-determining step that Kice and Bowers (35) previously had considered (Eq. 7 a and Eq. 7 b). The rate-determining step involves abstraction of an α-hydrogen by the oxygen in intermediate VI, shown as:



$$\mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}\overset{+}{\underset{\underset{CHR{-}H}{|}}{S}}{-}CH_2R \rightarrow ArSOH + RCH{=}\overset{+}{S}CH_2R} \qquad \text{(Eq. 7 b)}$$

VI

VII

2. Further reactions of the intermediate $\mathrm{RCH{=}\overset{+}{S}{-}CH_2R}$ (VII) formed in the rate-determining step. When n-butyl α-acetoxybutyl sulfide or n-butyl mercaptan was reacted with p-toluenesulfinic acid, the same rapid initial consumption of sulfinic acid took place in both cases. This fact plus the isolation of n-butyraldehyde from the α-acetoxy sulfide demonstrate that VII once formed will undergo a very rapid hydrolysis to aldehyde, RCHO and mercaptan, $\mathrm{RCH_2SH}$.

3. *Further reactions of the mercaptan produced from the hydrolysis of the intermediate* $RCH=\overset{+}{S}CH_2R$. The mercaptan RCH_2SH, formed in the hydrolysis of VII, reacts rapidly with *p*-toluenesulfinic acid. The final products of this reaction can be understood in terms of an initial reaction to give the two sulfenic acids ArSOH and RCH_2SOH. Each of these will then react rapidly either with sulfinic acid or mercaptan, as shown in Chart 1 (page 43). The relative amounts of sulfenic acid reacting with mercaptan or sulfinic acid are dependent on the average mercaptan concentration present.

Under the conditions used for the alkyl sulfide - sulfinic acid reaction, the average concentration of mercaptan present will be very low. The reaction between sulfenic acid and sulfinic acid is therefore the major reaction. This gives thiolsulfonates as products.

The over-all course of the main reaction between alkyl sulfides and *p*-toluenesulfinic acid can therefore be illustrated as shown in Chart 2:

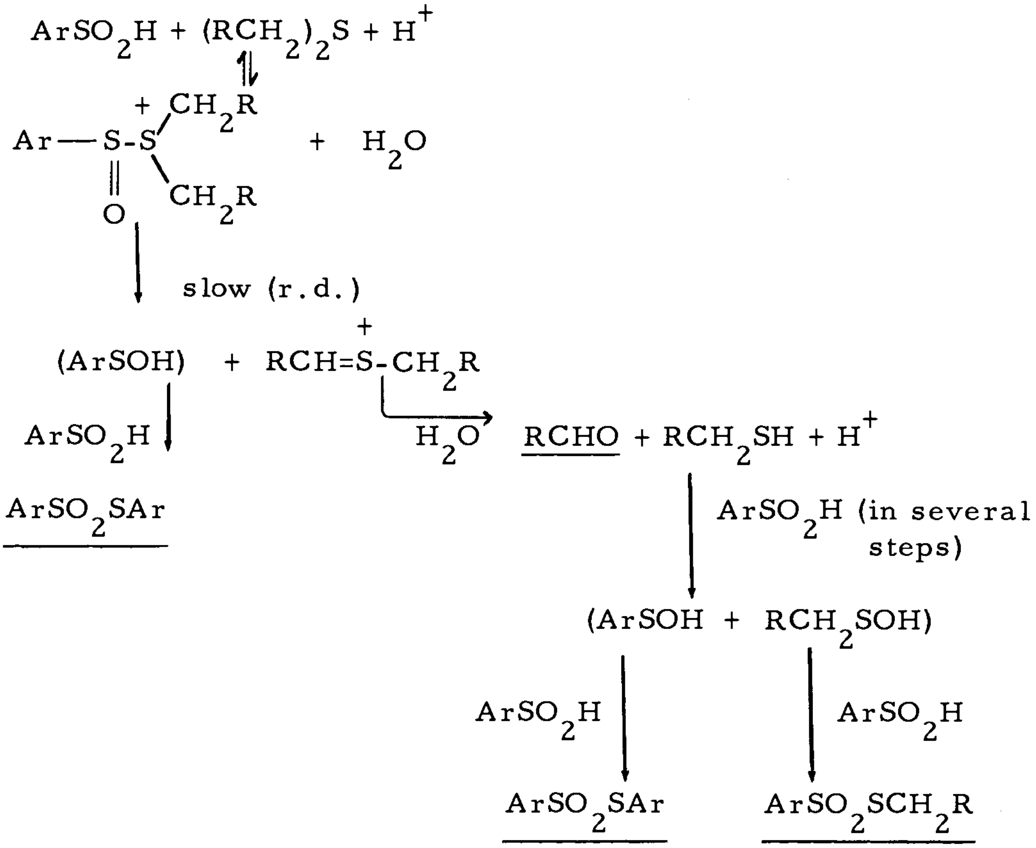


Chart 2

Even if the average concentration of mercaptan is quite low during the alkyl sulfide - sulfinic acid reaction, a small amount of sulfenic acid will react with mercaptan instead of with sulfinic acid to form disulfides (Chart 1, page 43). The extremely effective catalysis by alkyl sulfides of the disulfide - sulfinic acid reaction will be discussed in detail later (Part II) but has already been demonstrated in reactions 33 and 34 (see also Curves 11 and 12, Figure 11, Appendix 1). In our experiments the alkyl sulfides were always present in large stoichiometric excess. We would therefore expect a rapid consumption of the disulfides once they had been formed. We can also show through calculations that the disulfides (formed from the two sulfenic acids and mercaptan) will react further with sulfinic acid to maintain the stoichiometry of equation 6 (page 19). This circulation of disulfides is therefore of no consequence for the main reaction between alkyl sulfides and p-toluenesulfinic acid, and can thus be disregarded.

EXPERIMENTAL

1. Purification of Commercial Sulfides

The liquid sulfides were fractionally distilled through a vacuum-jacketed Vigreux column (length 20 cm.) using a variable take-off still head which allowed control of the reflux ratio. The distillation apparatus could be used for normal or reduced pressure. The solid sulfides were recrystallized; the solvents used are indicated below.

<u>β-Phenylethyl Sulfide</u> (Wateree Chemical Company Inc.). The sulfide seemed to be contaminated with some β-phenylethyl disulfide, and was therefore refluxed with lithium aluminum hydride in ether for one hour. After hydrolysis of the excess hydride, the ether layer was washed three times with water and dried over anhydrous sodium sulfate. The residue was fractionally distilled under reduced pressure. The fraction with b.p. 150-151° (0.25 mm.), was used for kinetic experiments. Literature value (17, p. 92), b.p. 190-192° (8 mm.).

<u>Carboxymethyl Sulfide</u> (British Drug Houses, reagent grade), was recrystallized once from hot water, then heated with water and activated charcoal. The hot solution was filtered through Celite.

The acid which separated upon cooling, was recrystallized from ethyl acetate/benzene and melted at 129°. Literature value (39, p. 2818), m.p. 129°.

2-Carboxyethyl Sulfide (Matheson Coleman and Bell, reagent grade), was recrystallized twice from hot water. The acid melted at 130-131°. Literature value (40), m.p. 128°.

Ethyl Sulfide (Matheson Coleman and Bell, reagent grade). B.p. 92° (760 mm.). Literature value (65), b.p. 92° (761 mm.).

n-Butyl Sulfide (Eastman Organic Chemicals, reagent grade). B.p. 69° (12 mm.). Literature value (65), b.p. 187° (765 mm.).

n-Amyl Sulfide (Aldrich Chemical Co., Inc., reagent grade). B.p. 44-46° (0.1 mm.). Literature value (65), b.p. 84.5° (4 mm.).

Isobutyl Sulfide (Wateree Chemical Company, Inc.). B.p. 53-53.5° (10 mm.). Literature value (65), b.p. 169° (772 mm.).

Isopropyl Sulfide (Aldrich Chemical Company). B.p. 118-118.5° (760 mm.). Literature value (65), b.p. 119° (761 mm.).

sec-Butyl Sulfide (Aldrich Chemical Company, Inc.). B.p. 165-166° (760 mm.). Literature value (65), b.p. 164.5° (739 mm.).

Benzyl Phenyl Sulfide. The crude sulfide was chromatographed on alumina (Merck, acid washed), and eluted with petroleum ether. After recrystallization from hot 95% ethanol it melted at 42-43°. Literature value (20), m.p. 42°.

1,4-Thioxane (Wateree Chemical Company Inc., reagent grade). B.p. 147-147.5° (760 mm.). Literature value (13, p. 1806), b.p. 147° (755 mm.).

t-Butyl Sulfide (Aldrich Chemical Company Inc., reagent grade). B.p. 150° (760 mm.). Literature value (17), b.p. 148-149° (760 mm.).

Phenyl Sulfide (Wateree Chemical Company Inc.). B.p. 146° (12 mm.). Literature value (65), b.p. 145° (8 mm.).

n-Butyl Mercaptan (Wateree Chemical Company Inc.). B.p. 97° (760 mm.). Literature value (66), b.p. 98.1° (765.5 mm.).

n-Butyl Disulfide (Eastman Organic Chemicals, reagent grade). B.p. 110° (14 mm.). Literature value (65), b.p. 84° (3 mm.).

Isopropyl Mercaptan (Wateree Chemical Company, Inc.). B.p. 53° (760 mm.). Literature value (66), b.p. 50.6° (753 mm.).

2. Preparation of Sulfides

a) Synthesis of α, α-Dideuteriobenzyl Sulfide

i. α, α-Dideuteriobenzyl Alcohol. Lithium aluminum deuteride (2 g., 0.0476 mole) in 85 ml. of dry ether was stirred for 40 minutes. Methyl benzoate (13.58 g., 0.0998 mole) in 34 ml. of dry ether was added during 40 minutes, and the solution was stirred for another three hours. Methanol (25 ml.) was added, then water (25 ml.), and finally 6 N hydrochloric acid (about 50 ml.). Stirring was continued until the solution became clear. The ether layer was separated and washed with water (3 x 20 ml.), then dried over anhydrous sodium sulfate. Distillation of the residue after removal of the ether, gave 8.43 g. (76%) of the alcohol, b.p. 101° (20 mm.).

ii. α, α-Dideuteriobenzyl Chloride (25). α, α-Dideuteriobenzyl alcohol (4.78 ml., 0.046 mole) in 5 ml. of benzene was added to thionyl chloride (4.35 ml., 0.06 mole). The mixture was refluxed for six-and-a-half hours, then cooled. After removal of the benzene, the residue was distilled, giving 3.80 g. (65%) of chloride, b.p. 70° (16 mm.).

iii. α, α-Dideuteriobenzyl Sulfide (51). α, α-Dideuteriobenzyl chloride (3.80 g., 0.0297 mole) in 8 ml. of ethanol was added to sodium sulfide nonahydrate (3.56 g., 0.0149 mole) in 3 ml. of water. The mixture was refluxed for 14 hours. After cooling, the solution was poured into 100 ml. of water, then extracted with ether (3 x 75 ml.). The combined ether extracts were washed twice with water, then dried over anhydrous sodium sulfate. The crude product of m.p. 50-51°, was recrystallized from 10 ml. of 100% ethanol. The product, 2.66 g. (41%), melted at 50-50.5°. An infrared spectrum of the sulfide showed C-D (stretch) absorptions at 2080 cm.^{-1} (w), 2120 cm.^{-1} (m) and 2180 cm.^{-1} (w). The product was analysed for its deuterium content.* Calculated percent excess deuterium for four deuterium atoms per molecule: (4/14) 100% = 28.6%. Found: 27.6% excess deuterium, i.e. the actual deuterium content was:

$$\frac{27.6}{28.6} \times 4 \text{ D-atoms/molecule} = \underline{3.82 \text{ D-atoms/molecule}}.$$

b) Synthesis of Benzyl Sulfide

Benzyl sulfide was prepared in the same way as its deuterium analog except for the use of lithium aluminum hydride in the first reaction. M.p. 49-49.5°.

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* Deuterium analysis by Mr. Josef Nemeth, Urbana, Ill.

c) Synthesis of β-Phenoxyethyl Sulfide (56).

Thiodiglycol (73.2 g., 0.6 mole), phenol (226.2 g., 2.4 mole), p-toluenesulfonic acid (7.2 g., 0.042 mole) and xylene (20 ml.) were mixed together, stirred and refluxed under a Dean & Stark reflux condenser for four-and-a-half hours. Nineteen milliliters of water were produced during the reaction. The solution was cooled and ether (450 ml.) was added. After extraction with 6 N sodium hydroxide (330 ml.), the ether solution was washed three times with water, filtered and dried over anhydrous sodium sulfate. The ether was removed at about 20 mm. pressure, the excess phenol and xylene at 1.5 mm. The residue was distilled at 0.1 mm. pressure. The second fraction (9.88 g.) boiled at 158-175° (0.1 mm.). Recrystallized from 100% ethanol, the product melted at 54-55°. Literature value (56), m.p. 54.3-54.4°.

d) Synthesis of 2-Octyl Sulfide

i. 2-Octyl Mercaptan (19). A mixture of 2-octyl bromide (19.3 g., 0.1 mole), and thiourea (7.6 g., 0.1 mole) in 95% ethanol (50 ml.) was refluxed for 24 hours. Sodium hydroxide (6 g., 0.15 mole) in water (60 ml.) was added to the solution, which was kept under N_2 atmosphere. The reaction mixture was refluxed for two more hours, cooled, and the two layers were separated. The aqueous layer was acidified with dilute sulfuric acid, then extracted with benzene (15 ml.). The benzene extract was added to the main portion of mercaptan, the whole was washed twice with water and dried over anhydrous sodium sulfate. The residue, after removal of the benzene, yielded 10.4 g., b.p. 87-89° (28 mm.). Literature value (14), b.p. 88.9° (30 mm.). Iodine titration showed the product to be pure mercaptan.

ii. 2-Octyl Sulfide. 2-Octyl mercaptan (10.4 g., 0.071 mole) was dissolved in methanol (32 ml.) under N_2 atmosphere. Potassium hydroxide (4 g., 0.071 mole) dissolved in methanol (24 ml.) was added, and 2-octyl bromide (13.7 g., 0.071 mole) was then added dropwise with stirring of the solution. The reaction mixture was refluxed (N_2 atmosphere, stirring), for ten hours. After cooling, the precipitated potassium bromide was filtered off. The filtrate was poured into water (900 ml.), and extracted with ether. The combined ether extracts were washed twice with water, then dried over anhydrous sodium sulfate. After removal of the ether, the residue yielded 11.2 g. (61%) of 2-octyl sulfide, b.p. 129-130.5° (2 mm.). Literature value (31), b.p. 175° (20 mm.).

e) Synthesis of Benzhydryl Sulfide

i. Benzhydryl Chloride (25). Thionyl chloride (20 g., 0.168 mole) was slowly added to a suspension of benzhydrol (30 g., 0.163 mole) in toluene (75 ml.). The mixture was refluxed for two-and-a-half hours (until no more SO_2 or HCl was evolved). After removal of the toluene, the residue gave 31.3 g. (94%) benzhydryl chloride, b.p. 157° (16 mm.). Literature value (25), b.p. 161-162° (13 mm.).

ii. Benzhydryl Mercaptan (22). Benzhydryl chloride (16.8 g., 0.083 mole) was slowly added to thiourea (6.48 g., 0.085 mole) in 32 ml. of 95% ethanol. The mixture was refluxed for two-and-a-half hours. Sodium hydroxide (6.4 g., 0.16 mole) in 40 ml. of water was added, and reflux was continued for two more hours. The solution was cooled and acidified, then extracted with 2 x 50 ml. of ether. The combined ether extracts were washed with water and dried over anhydrous sodium sulfate. After removal of the ether, the residue was distilled, giving 10.5 g. (63%) of benzhydryl mercaptan b.p. 105-108° (0.2 mm.).

iii. Benzhydryl Sulfide (58). Benzhydryl mercaptan (10 g., 0.05 mole) and benzhydryl chloride (14 g., 0.069 mole) were refluxed in 60 ml. of dry benzene for 28 hours (N_2 atmosphere). Most of the benzene was then removed, and the mixture was heated at

110° for another three hours. The residue was treated with about 5 ml. of 95% ethanol to react with the excess benzhydryl chloride (or $(Ph_2CH)_3S^+Cl^-$). The solvent was removed under reduced pressure (0.5 mm.) at room temperature. The residue was treated with ether, then filtered. The filtrate gave an oil after removal of the ether. The crude product was chromatographed on 80 g. of alumina (Merck, acid washed) and eluted with 400 ml. of petroleum ether. The oily product gave 8.4 g. of crystalline material from petroleum ether. Recrystallization from n-hexane gave 6.7 g. (36%) of benzhydryl sulfide, m.p. 66.5°. Literature value (58), m.p. 66.5°.

f) Synthesis of β-n-Butoxyethyl Sulfide (56)

Thiodiethanol (36.6 g., 0.3 mole), n-butanol (89 g., 1.2 moles) and p-toluenesulfonic acid (3.7 g., 0.0215 mole) were refluxed under a Dean & Stark column for five hours. Ten-and-a-half milliliters of water were separated from the reaction mixture. After cooling, the product was washed with 5% sodium carbonate (50 ml.), then three times with water. The product was filtered through cotton and the butanol was removed under reduced pressure (20 mm.). The residue gave 53 g. (66%) of β-n-butoxyethyl sulfide b.p. 151-152° (11 mm.). Literature value (56), b.p. 162-164° (20 mm.).

g) Synthesis of γ-Keto-n-Butyl Sulfide

Methyl vinyl ketone (27 g., 0.386 mole) was cooled in an ice-bath. Hydrogen sulfide was led through the liquid for five minutes; piperidine (three drops) in benzene (4 ml.) was then added, and hydrogen sulfide was led through the solution for three more hours. The reaction mixture was washed with dilute hydrochloric acid and water. It was then filtered and the solvent removed at 45° and 15 mm. pressure. The residue was distilled, giving 13.7 g. (41%) of γ-keto-n-butyl sulfide, b.p. 121° (1.5 mm.). The sulfide was heated at 70° and 15 mm. pressure for one hour (to get rid of any mercaptan present) and then redistilled, b.p. 122° (1.6 mm.).

h) Synthesis of n-Butyl α-Acetoxybutyl Sulfide (61)

A mixture of n-butyl sulfide (32.7 ml., 0.192 mole) and cuprous bromide (33.3 mg., 0.117 mmole) in dry benzene (17 ml.) was heated to 75° under a nitrogen atmosphere. t-Butyl peracetate (19 ml., 0.1 mole) was added during four hours with stirring. The reaction mixture was kept at 75-80° for 79 hours. Seventeen milliliters of ether were added after cooling. The solution was extracted with 2 N sodium carbonate, then washed three times with water, filtered and dried over anhydrous sodium sulfate. After removal of the benzene and ether under reduced pressure, the residue was fractionally distilled at 0.9 mm. pressure. The distillate, (9.4 g.), boiled at 68-72° (0.9 mm.). An infrared spectrum of the product showed strong absorptions at 1725 cm.$^{-1}$ and 1225 cm.$^{-1}$, indicating the presence of an acetate group. A nuclear magnetic resonance spectrum of the product showed a triplet centered at 4.08τ (the proton on the carbon attached to the acetoxy group). The spectrum also showed a strong singlet at 7.98τ (the three methyl protons of the acetoxy group) and a complex pattern caused by the other methyl and methylene protons. Separate integrations of the area under the triplet at 4.08τ, and under all the remaining resonance peaks, showed a ratio between the two areas of 1/22. From the number of protons in n-butyl α-acetoxybutyl sulfide, this ratio was expected to be 1/19.

3. Synthesis of p-Toluenesulfinic Acid

Sodium p-toluenesulfinate was prepared (26, p. 492) by reduction of p-toluenesulfonyl chloride with zinc. The sodium salt was recrystallized from water and dried. Only small portions of this salt were hydrolysed at a time, because of the low stability of the sulfinic acid. The sodium salt was dissolved in water, filtered, and 6 N hydrochloric acid was added until the sulfinic acid precipitated. The dried sulfinic acid was dissolved in ether, the ether solution was filtered, and an equal volume of n-hexane was added. After cooling in an ice bath, the crystalline sulfinic acid was filtered off and dried in vacuum. One more crystallization from the same solvents gave pure p-toluenesulfinic acid, m.p. 85°. The acid was stored at -20° in the dark.

4. Preparation of Stock Solutions

Glacial acetic acid (Baker and Adamson, reagent grade) was refluxed with 10% of its volume of acetic anhydride for 24 hours, then slowly distilled through an Oldershaw column (20 theoretical plates). The reflux ratio was kept 6:1.

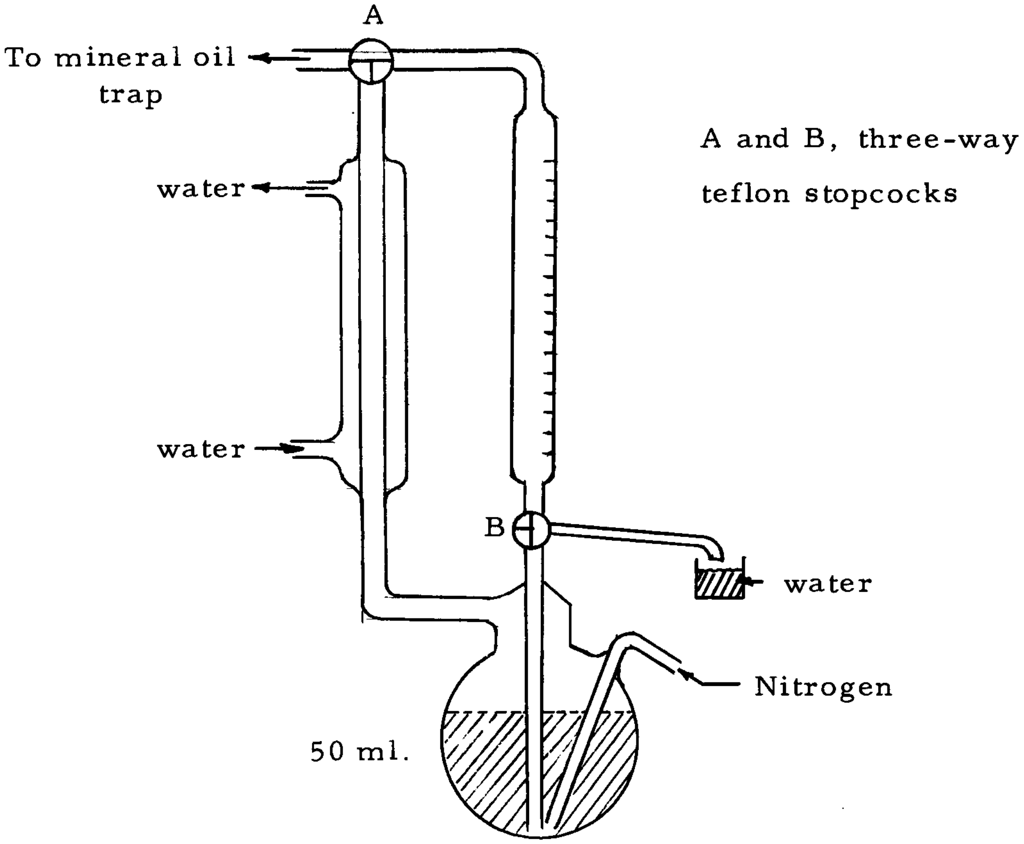
A solution of 0.56 M water in acetic acid was prepared by pipetting 10 ml. of distilled water into a 1 l. volumetric flask, which was then filled up to volume with the purified acetic acid. The water content of the solution was checked by a Karl Fisher titration (43, p. 105 ff.).

Reagent grade sulfuric acid (Baker and Adamson) was used for the sulfuric acid - water - acetic acid solutions. Titration of the sulfuric acid with 0.1 N sodium hydroxide showed 96.5% purity of the acid. We assumed the remaining 3.5% to be water. Stock solutions of sulfuric acid - 0.56 M water - acetic acid were always made with five or ten times the sulfuric acid concentration wanted for the kinetic runs. In preparing these solutions, we added acetic anhydride in an amount corresponding to the water content of the sulfuric acid used. Some of the previously prepared solution of 0.56 M water - acetic acid was mixed with the weighed amounts of sulfuric acid and acetic anhydride. The two solutions were combined in a volumetric flask which then was filled up to volume with the same 0.56 M water - acetic acid solution.

5. General Procedure for the Kinetic Experiments with Alkyl Sulfides and p-Toluenesulfinic Acid

The sulfide and the sulfinic acid were weighed out separately and dissolved in the acetic acid - water stock solution. The appropriate amount of the sulfuric acid solution was added to the sulfide solution. The sulfinic acid solution was then added, and the mixture was made up to volume and transferred to the reaction flask. After deaerating the system for five to ten minutes at room temperature, the reaction vessel was transferred to the constant temperature bath, where it was allowed to equilibrate for three minutes before the first sample (at zero time) was withdrawn. The sample (5 ml.) was poured directly into a beaker containing an equal volume of water. The technique used for withdrawing samples is described, referring to Figure 4 of the reaction vessel.

Figure 4.



A and B, three-way teflon stopcocks

Nitrogen was bubbled quite rapidly through the solution and stopcock A was turned 180° from the position shown in Figure 4. Some of the reaction mixture was thus forced up into the burette, and trapped by turning stopcock B 45° clockwise. The pressure in the flask was released by returning A to its original position and closing the nitrogen flow. The sample was transferred to the beaker containing water by turning B another 45° clockwise. When the desired amount had been taken out, the rest of the solution was returned to the reaction vessel by turning B counterclockwise to its original position.

The sulfinic acid content of the samples was determined by titration with 0.2 N sodium nitrite solution (42). Two moles of sulfinic acid react with one mole of nitrous acid to form N,N-di (p-tolylsulfonyl) hydroxylamine:

$$2\,ArSO_2H + HNO_2 \rightarrow (ArSO_2)_2NOH + H_2O$$

The tip of the burette containing the sodium nitrite solution, was immersed into the sample, which was stirred with a magnetic stirrer. The titration was followed by taking out one drop of the solution (with a glass rod) and placing it on a small strip of potassium-iodide starch paper placed on a white porcelain plate. The end point was indicated by a purple spot on the potassium-iodide starch paper.

6. General Procedure for the Kinetic Experiments with *n*-Butyl α-Acetoxybutyl Sulfide

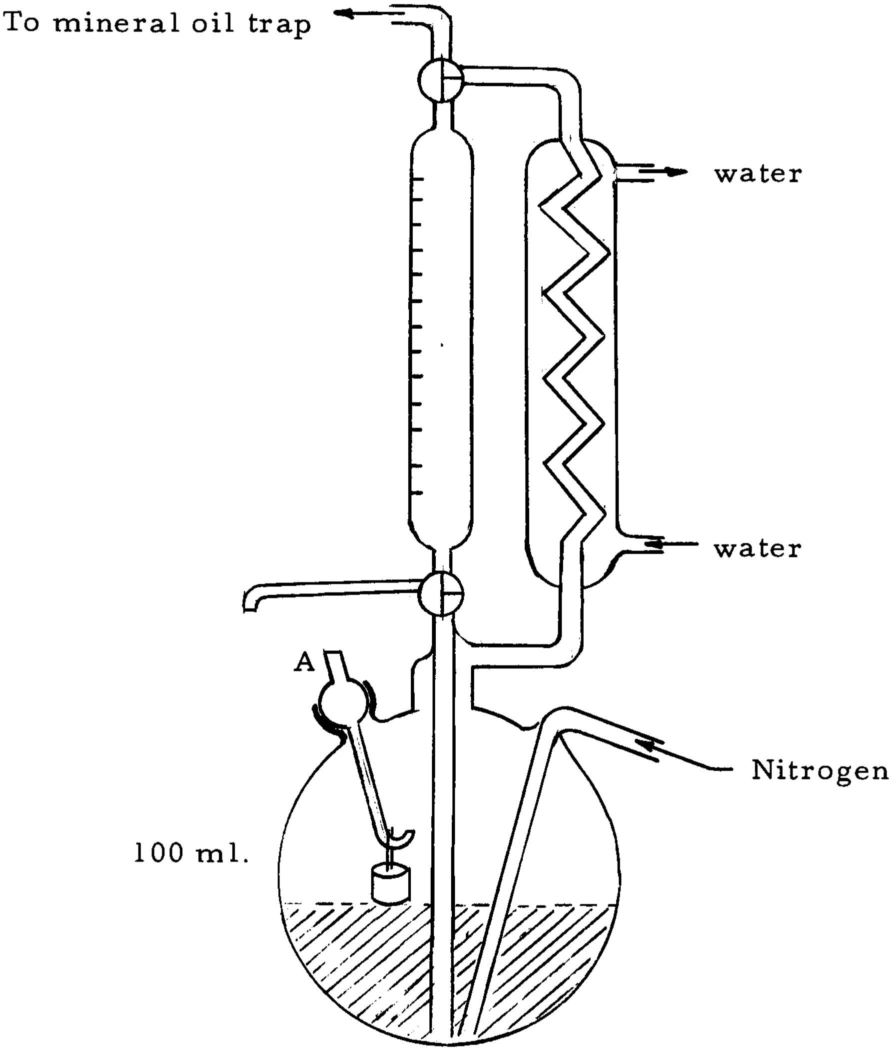
A slightly modified reaction vessel, shown in Figure 5, was used for these experiments.

The glass bucket containing the *n*-butyl α-acetoxybutyl sulfide, could be dropped into the solution by turning the joint A.

The sulfinic acid was dissolved in the acetic acid - water solution and transferred to a volumetric flask which was filled up to volume with the same solvent and the appropriate amount of sulfuric acid. This solution was then transferred to the reaction vessel. The *n*-butyl α-acetoxybutyl sulfide was weighed directly into a small glass bucket, which was placed on the glass rod connected to joint A, and transferred to the reaction vessel. The glass bucket containing the sulfide was thus suspended above the solution of sulfinic acid. The whole system was deaerated for five to ten minutes, transferred to the constant temperature bath and heated for three minutes. At that time the first sample was taken out. The *n*-butyl α-acetoxybutyl sulfide was dropped into the solution immediately afterwards, and the solution was swirled vigourously for about one minute. The next sample was taken out three minutes after the addition of the sulfide.

The same procedure was used for the kinetic experiments with *n*-butyl mercaptan, *n*-butyl disulfide and *n*-butyl sulfide (Runs 31-34).

Figure 5.



7. General Procedure for the Stoichiometry Experiments with *n*-Butyl Mercaptan

The apparatus shown in Figure 5 was modified so that a separatory funnel could be fitted on joint A instead of the glass rod.

The desired sulfuric acid - water - acetic acid solution was first made up. The sulfinic acid was weighed out, dissolved in a measured volume of the solvent and transferred to the reaction vessel. The mercaptan, dissolved in a certain amount of the same sulfuric acid - water - acetic acid solution, was transferred to a pressure equalizing dropping funnel which was fitted on to the reaction vessel. The system was deaerated for five to ten minutes and heated in the constant temperature bath for three minutes before the addition of mercaptan was started. The time for the addition was measured exactly, and the solution was swirled vigourously during the addition. A sample was taken out at a measured time after the addition was completed.

8. General Procedure for the Product Studies

a) Products from Mercaptan and *p*-Toluenesulfinic Acid

The solutions of sulfinic acid and mercaptan were prepared separately and transferred to the reaction vessel and the separatory funnel, respectively. After complete addition of mercaptan, a sample was taken out for titration, and the rest of the reaction mixture was poured into ten times its volume of distilled water. The water suspension was extracted three times with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution until neutral, then twice with distilled water and finally dried over anhydrous sodium sulfate. The ether was carefully removed through a Vigreux column. The residue was chromatographed on about 30 times its weight of alumina (Merck, acid washed). The eluting solvents were gradually varied from pure n-hexane to pure benzene and finally to ethyl ether.

b) Products from Alkyl Sulfides and p-Toluenesulfinic Acid

The reaction mixture was made up exactly as for the kinetic runs. At the end of the reaction, the product was poured into ten times its volume of distilled water. The product was worked up in the same way as described for the reaction of mercaptans with sulfinic acid.

9. Analysis of the Products by means of Nuclear Magnetic Resonance Spetra

The product compositions of Runs P 1 - P 10(Tables 1, 7 and 8) were determined with the help of nuclear magnetic resonance spectra. The products from an experiment were chromatographically separated into two main fractions: (1) sulfides (or disulfides) eluted with n-hexane, and (2) a mixture of thiolsulfonates eluted with 25-50% benzene in n-hexane (varying with the sulfide). The n.m.r. spectra were run on these separate fractions (of known weight) and analysis of the integral was based on the chemical shift for characteristic protons in the different compounds, as shown in Table 25. The areas under the indicated peaks were measured and the composition of the different compound mixtures could thus be calculated.

To illustrate the technique used, the product composition from experiment P 7 is calculated below.

Fraction 1 was a mixture of disulfides, ArSSBu-n (M = 212) and n-BuSSBu-n, (M = 178). Total weight: 167 mg. (Ar = p-CH_3-C_6H_4-).

The area under the singlet at τ = 7.68 (for $C\underline{H}_3$-C_6H_4-) was 5.78, and the area under the triplet at τ = 7.34 (for all the -$C\underline{H}_2$-S) was 8.4. Since there are three hydrogens in ArSSBu-n contributing to the singlet, the amount of unsymmetric disulfide present is n'_{Ar} = 5.78/3 = 1.93. Contributing to the triplet are four hydrogens in n-butyl disulfide and two hydrogens in n-butyl p-tolyl disulfide. Thus, calling the amount of n-butyl disulfide present for n'_R:

$$4\,n'_R + 2\,n'_{Ar} = 8.4$$

$$n'_R = \frac{8.4 - 2(1.93)}{4} = \underline{1.14}$$

The two disulfides are thus present in the (mole) ratio:

$$\frac{n_{Ar}}{n_R} = \frac{1.93}{1.14} = 1.69$$

The total amount of the two disulfides (in mmoles) is found from the equation:

$$M_{Ar}(n_{Ar}) + M_R(n_R) = \text{Total weight of sample (mg.)}$$

$$212\,n_{Ar} + 178\,n_R = 167$$

$$n_{Ar}\,[\,212 + 178/1.69\,] = 167,\ \underline{n_{ArSSBu\text{-}n} = 0.53 \text{ mmole}}$$

$$\underline{n_{n\text{-}BuSSBu\text{-}n} = 0.31 \text{ mmole}}$$

The thiolsulfonates were divided into fractions 2 and 3. Both fractions were a mixture of $ArSO_2SAr$ (M = 278) and $ArSO_2SBu$-*n* (M = 244).

Fraction 2, total weight, 414 mg.

The area under the two singlets at τ = 7.62 and 7.58 (for the methyl protons, $C\underline{H}_3$-C_6H_4-S- and $C\underline{H}_3$-C_6H_4-SO_2-, respectively) was 10.05. Contributing to these singlets are three hydrogens in $ArSO_2SR$ and six hydrogens in $ArSO_2SAr$, i.e.

$$3\,n'_R \;+\; 6\,n'_{Ar} \;=\; 10.05$$

The area under the triplet at τ = 7.05 (for -S-$C\underline{H}_2$-) was 3.3. There are only two hydrogens in $ArSO_2SBu$-$\underline{n}$ contributing to this absorption, i.e.

$$2\,n'_R \;=\; 3.3, \quad \underline{n'_R \;=\; 1.65}$$

The mole ratio of the two thiolsulfonates is therefore:

$$\frac{n_{ArSO_2SAr}}{n_{ArSO_2SR}} = \frac{0.85}{1.65} = \underline{0.515}$$

Total amounts of thiolsulfonate (mmoles):

$$278\,n_{Ar} + 244\,n_R = 414$$

$$n_{Ar}\,[278 + 244/0.515] = 414, \quad \underline{n_{ArSO_2SAr} = 0.55 \text{ mmole}}$$

$$\underline{n_{ArSO_2SBu\text{-}\underline{n}} = 1.07 \text{ mmoles}}$$

Fraction 3, total weight, 146 mg.

Area at τ = 7.05 was 0.95, i.e. $n'_R = (0.95/2) = \underline{0.475}$

Area at τ = 7.62 and 7.58 was 13.4.

$$3\,n'_R + 6\,n'_{Ar} = 13.4$$

$$\frac{n_{ArSO_2SAr}}{n_{ArSO_2SBu\text{-}\underline{n}}} = \frac{2}{0.475} = \underline{4.2}$$

The amounts present of the two thiolsulfonates:

$$278\,n_{Ar} + 244\,n_R = 146$$

$$\underline{n_{ArSO_2SAr} = 0.44 \text{ mmole}} \qquad \underline{n_{ArSO_2SBu\text{-}\underline{n}} = 0.104 \text{ mmole}}$$

10. Ketonic Products from the Alkyl Sulfide - Sulfinic Acid Reactions

Table 1 lists among the products from experiments P 1 to P 5, aldehydes from the primary sulfides, and ketones from the secondary sulfides. These compounds were isolated as follows:

a) n-Butyraldehyde (Experiment P 1)

In a separate experiment, 6.5 mmoles of n-butyl α-acetoxybutyl sulfide were added to 5 mmoles of p-toluenesulfinic acid in 50 ml. of 0.3 M sulfuric acid - 0.56 M water - acetic acid during about two minutes. Nitrogen was swept through the solution, which was kept at 70° for one hour. Before the experiment was started, the reaction vessel was connected to a gas trap containing 195 mg. of 2,4-dinitrophenylhydrazine in 10 ml. of sulfuric acid and 90 ml. of water. The n-butyraldehyde produced, precipitated as its 2,4-dinitrophenylhydrazone. This was crystallized once from methanol and then once from ethanol, raising the melting point from 108° of the crude product to 121-122°. Literature value (59, p. 283), m.p. 122°.

b) Acetaldehyde (Experiment P 2)

The reaction vessel was connected to a gas trap containing 195 mg. of 2,4-dinitrophenylhydrazine dissolved in 10 ml. of sulfuric acid and 90 ml. of water Nitrogen was swept through the reaction mixture during the reaction. The crude 2,4-dinitrophenylhydrazone which precipitated (16 mg.), was filtered off and recrystallized twice from methanol. The pure acetaldehyde 2,4-dinitrophenylhydrazone melted at 155-156° and showed no depression of melting point in admixture with an authentic sample, m.p. 160-162°. Literature value (59, p. 283), m.p. 147° or 168°.

c) Acetone (Experiment P 3)

In an identical experiment the reaction vessel was connected to a gas trap containing 200 mg. of 2,4-dinitrophenylhydrazine in

10 ml. of sulfuric acid and 90 ml. of water. Nitrogen was swept through the reaction mixture. At the end of the reaction, there had been formed only very small amounts of a precipitate in the gas trap. The reaction mixture was therefore transferred to another flask and distilled through a Vigreux column into a solution of 198 mg. of 2,4-dinitrophenylhydrazine in 10 ml. of methanol and 2 ml. of concentrated hydrochloric acid. Four milliliters of distillate were collected. The precipitated 2,4-dinitrophenylhydrazone (50 mg.) was filtered off and recrystallized from ethanol/water. The yellow, crystalline product melted at 125-127°. It showed no depression of melting point in admixture with an authentic sample of 2-propanone 2,4-dinitrophenylhydrazone. Literature value (59, p. 316), m.p. 126°.

d) 2-Octanone (Experiment P 5)

2-Octanone was separated from the other products by chromatography on alumina (Merck, acid washed), after the usual work-up of the products. The ketone was eluted from the column with 25 (vol)% benzene in *n*-hexane, and the solvent was distilled off carefully through a Vigreux column. The residue was dissolved in 0.9 ml. of 95% ethanol, water was then added until the solution became turbid, and finally a few drops of ethanol were added to obtain a clear solution. After addition of semicarbazide hydrochloride (94 mg., 0.81 mmole) and sodium acetate (136 mg., 1.66 mmoles) in a few drops of water, the mixture was heated on a water-bath until all material was dissolved. The crude product which separated out after cooling, was filtered off and recrystallized from ethanol/water, giving 77 mg. (0.42 mmoles, 48%), m.p. 125-126°. Literature value (59, p. 316), m.p. 122°.

11. Products from 2-Octyl Sulfide and *p*-Toluenesulfinic Acid

In addition to the products listed for experiments P 4 and P 5 (Table 1) there was obtained in both cases an unidentified fraction which was eluted with ether from alumina. In the first case the weight of this fraction was 214 mg., in the second, 165 mg. The combined fractions were subjected to molecular distillation in a micro Hickman still, the bath temperature being 105°, pressure 10^{-4} mm. An infrared spectrum of the distillate showed strong absorption at 1025 cm.$^{-1}$, characteristic for sulfoxides. In addition the spectrum showed absorptions at 1385 cm.$^{-1}$ and 1465 cm.$^{-1}$ indicating an octyl group. No other functional groups were apparently present.

Analysis: Calculated for $C_{16}H_{34}OS$: C, 70.01; H, 12.48; S, 11.68. Found: C, 70.12; H, 12.65; S, 11.78. A nuclear magnetic resonance spectrum of the purified product showed a rather complex, but quite characteristic pattern for the methyl and methylene protons. The identity of the product was definitely established by the additional experiments outlined below.

a) Oxidation of 2-Octyl Sulfide to 2-Octyl Sulfoxide (23)

2-Octyl sulfide (516 mg., 2 mmoles) was dissolved in acetone (5 ml.), and 30% hydrogen peroxide (2.2 mmoles, 0.25 ml.) was added. The reaction mixture was left for seven days at room temperature. Titration of a small sample of the reaction mixture (with thiosulfate after addition of excess sodium iodide) showed the reaction to be essentially complete. The product was poured into water (75 ml.), extracted with ether (3 x 25 ml.) and finally dried over anhydrous sodium sulfate. The 2-octyl sulfoxide was separated from unreacted sulfide by chromatography on alumina (15 g.). The sulfide (111 mg.) was eluted with *n*-hexane, the sulfoxide, 441 mg., 1.61 mmoles (80.5%), with benzene. The sulfoxide was subjected to molecular distillation in a micro Hickman still at 10^{-4} mm., bath temperature 110°. An infrared spectrum of the pure 2-octyl sulfoxide showed a strong absorption band at 1025 cm.$^{-1}$, characteristic of the $S \rightarrow O$ group, but no bands for a sulfone group (at about 1125 and 1300 cm.$^{-1}$). The spectrum was identical with that of the isolated ether fractions (Runs P 4 and P 5, Table 1). The nuclear magnetic resonance spectra of the two compounds were also identical.

b) Oxidation of 2-Octyl Sulfide to 2-Octyl Sulfone (55)

2-Octyl sulfide (1.03 g., 4 mmoles) was dissolved in glacial acetic acid (20 ml.) and 30% hydrogen peroxide (8.8 mmoles, 0.88 ml.) was added. The mixture was then heated at 90° for two hours. The product was poured into water (200 ml.) and extracted with ether (3 x 60 ml.). The combined ether extracts were washed with saturated sodium bicarbonate solution until neutral, then with water (2 x 15 ml.) and finally dried over anhydrous sodium sulfate. After removal of the ether under reduced pressure, the crude product was chromatographed on alumina (35 g.). The 2-octyl sulfone, 1.14 g., (98%) was eluted with benzene. The chromatographed product was distilled in a micro Hickman still at 10^{-4} mm. pressure and bath temperature 125°. An infrared spectrum of the pure 2-octyl sulfone showed strong absorption bands at 1125 cm.$^{-1}$ and 1300 cm.$^{-1}$, characteristic for a sulfone group. The spectrum showed in addition the two peaks at 1385 cm.$^{-1}$ and 1465 cm.$^{-1}$ for the 2-octyl group.

Analysis: Calculated for $C_{16}H_{34}O_2S$: C, 66.15; H, 11.80; S, 11.04. Found: C, 66.28; H, 12.04; S, 11.30.

c) Oxidation of 2-Octyl Sulfoxide to 2-Octyl Sulfone (55)

Some of the purified ether fractions from experiments P 4 and P 5, Table 1, (155 mg., 0.56 mmole) was dissolved in glacial acetic acid (2 ml.). To this solution was added 30% hydrogen peroxide (0.07 ml., 0.7 mmole) and the mixture was heated at 90° for two hours. It was then poured into water (25 ml.) and extracted with ether (3 x 12 ml.). The combined ether extracts were washed with saturated sodium bicarbonate solution until neutral, washed with water (2 x 7 ml.) and finally dried over anhydrous sodium sulfate. After removal of the ether under reduced pressure, the residue, 130 mg., (80%) was dried in a desiccator at 0.1 mm. pressure for one hour. The infrared spectrum was identical with that of authentic 2-octyl sulfone, as were the nuclear magnetic resonance spectra of the two compounds.

Having shown the ether fractions from experiments P 4 and P 5 to be 2-octyl sulfoxide, the following experiments were done to get information about the reaction through which the sulfoxide was formed.

d) Experiments P 9 - P 12

Experiment P 9. 2-Octyl sulfide (3.87 g., 15 mmoles) and

2-octanone (1.284 g., 10 mmoles) were heated in 100 ml. of 0.6 M sulfuric acid - 0.56 M water - acetic acid at 70° for two hours. The product was worked up as usual. Chromatography on alumina (Merck, acid washed, 80 g.) gave in addition to unreacted sulfide and octanone, an ether fraction of weight 120 mg. An infrared spectrum indicated that the fraction contained some 2-octyl sulfoxide. There was, however, also some unidentified material present.

Experiment P 10. 2-Octanone (1.284 g., 10 mmoles) was heated at 70° for two hours in 100 ml. of 0.6 M sulfuric acid - 0.56 M water - acetic acid. The reaction mixture was worked up as usual. Chromatography on alumina gave essentially no material (8 mg.) eluted with ether.

Experiment P 11. 2-Octyl sulfide (3.87 g., 15 mmoles), 2-octanone (642 mg., 5 mmoles) and p-tolyl p-toluenethiolsulfonate (556 mg., 2 mmoles) were heated at 70° for two hours in 100 ml. of 0.6 M sulfuric acid - 0.56 M water - acetic acid. The product was worked up in the usual way. Chromatography on alumina gave an ether fraction of weight 24.3 mg. An infrared spectrum of this material indicated it consisted mainly of 2-octyl sulfoxide.

Experiment P 12. 2-Octyl sulfide (1.935 g., 7.5 mmoles) was heated at 70° for two hours in 50 ml. of 0.6 M sulfuric acid -

0.56 M water - acetic acid. The product was worked up as usual, the ether fraction contained 4 mg. of unidentified material. Unreacted sulfide was recovered in 95% yield (1.853 g.).

12. Preparation of Compounds used as Authentic Specimens

a) Synthesis of n-Butyl p-Toluenethiolsulfonate

i. Potassium p-Toluenethiolsulfonate (18). A solution of potassium hydroxide (22.4 g., 0.4 mole) in water (32 ml.) was saturated with hydrogen sulfide under cooling. The solution was then heated to 70° and p-toluenesulfonyl chloride (32 g., 0.168 mole) was added in portions. After cooling in ice-water, the crude product (48 g.) was filtered off, then heated with water (48 ml.) until the supernatant became clear. Warm water (57 ml.) was added, the mixture was filtered into a warm Erlenmeyer flask, and then allowed to cool slowly to room temperature. After cooling in ice-water, the crystalline product, 22.5 g. (58%) was filtered off and dried.

ii. n-Butyl p-Toluenethiolsulfonate (6, 7). Potassium p-toluenethiolsulfonate (11.3 g., 0.05 mole) was dissolved in acetone (45 ml.) and water (6 ml.). n-Butyl bromide (6.9 g., 0.05 mole) was added, and the mixture was stirred at room temperature for six days. Potassium bromide was filtered off, and the acetone was removed under reduced pressure. The water solution was extracted with ether (2 x 35 ml.). The combined ether extracts were washed with water (2 x 5 ml.), then dried over anhydrous sodium sulfate. After removal of the ether, the residue, 7.5 g. (61%), was distilled in a Hickman still, with bath temperature 110°, pressure 10^{-4} mm.

Analysis: Calculated for $C_{11}H_{16}O_2S_2$: C, 54.06; H, 6.60. Found: C, 54.13; H, 6.74.

A nuclear magnetic resonance spectrum of n-butyl p-toluenethiolsulfonate showed a triplet centered at 7.05τ (methylene protons next to the sulfide sulfur). The spectrum also showed a singlet at 7.58 τ (methyl protons of the tolyl group) and a more complex pattern at higher field (remaining protons of the butyl group). At very low field two doublets appeared (protons on the benzene ring).

b) Synthesis of Ethyl p-Toluenethiolsulfonate (6, 7)

Potassium p-toluenethiolsulfonate (6.8 g., 0.03 mole) was dissolved in acetone (27 ml.) and water (3.6 ml.). Ethyl bromide (3.3 g., 0.03 mole) was added, and the mixture was stirred at room temperature for seven days. The reaction mixture was worked up in the same way as for n-butyl p-toluenethiolsulfonate. The crude product, 5.77 g. (89%), was distilled in a Hickman still, bath temperature 100°, pressure 10^{-4} mm.

Analysis: Calculated for $C_9H_{12}O_2S_2$: C, 49.95; H, 5.59. Found: C, 50.12; H, 5.63.

A nuclear magnetic resonance spectrum showed a quartet centered at 7.04 τ (methylene protons), a singlet at 7.62 τ (methyl protons of the tolyl group) and a triplet centered at 8.78 τ (methyl protons of the ethyl group).

c) Synthesis of Isopropyl *p*-Toluenethiolsulfonate

Isopropyl disulfide (2.26 g., 15 mmoles) and *p*-toluenesulfinic acid (0.78 g., 5 mmoles) were heated at 70° for three-and-a-half hours in 100 ml. of 0.6 *M* sulfuric acid - 0.56 *M* water - acetic acid. The product was poured into water (800 ml.) and extracted with ether (3 x 200 ml.). The combined ether extracts were washed with sodium bicarbonate solution until neutral, then washed with water (2 x 25 ml.) and dried over anhydrous sodium sulfate. After removal of the ether under reduced pressure, the residue was chromatographed on alumina (50 g.). Isopropyl disulfide was eluted with *n*-hexane, the isopropyl *p*-toluenethiolsulfonate (324 mg.) with 25% benzene in *n*-hexane. The thiolsulfonate was distilled in a micro Hickman still at 5×10^{-5} mm. pressure and bath temperature 90-95°.

Analysis: Calculated for $C_{10}H_{14}O_2S_2$: C, 52.14; H, 6.13.
Found: C, 52.10; H, 6.17.

A nuclear magnetic resonance spectrum showed a septet centered at 6.52 τ (single proton on carbon attached to the sulfide sulfur), a singlet at 7.60 τ (methyl protons of tolyl group) and a doublet centered at 8.70 τ (six methyl protons of the isopropyl group).

d) Synthesis of 2-Octyl p-Toluenethiolsulfonate

The thiolsulfonate fractions from experiments P 4 and P 5 (Table 1) were combined and carefully rechromatographed. The alkyl p-toluenethiolsulfonate was eluted with 10% benzene in n-hexane, whereas the p-tolyl p-toluenethiolsulfonate was eluted with 25% benzene in n-hexane. Some of the pure 2-octyl p-toluenethiolsulfonate was analysed.

Analysis: Calculated for $C_{15}H_{24}O_2S_2$: C, 59.95; H, 8.05.
Found: C, 60.16; H, 7.94.

A nuclear magnetic resonance spectrum of the product showed a slightly deformed quartet centered at 6.71 τ (single proton on carbon attached to the sulfide-sulfur), a singlet at 7.57 τ (methyl protons of tolyl group) and a more complex pattern at higher field (remaining protons of the 2-octyl group).

e) Synthesis of n-Butyl p-Tolyl Disulfide

A solution of p-toluenesulfinic acid (4.67 g., 30 mmoles) in 0.6 M sulfuric acid - 0.56 M water - acetic acid (300 ml.) was deaerated for ten minutes and then heated at 70° for seven minutes. A solution of n-butyl mercaptan (8.1 g., 90 mmoles) in 0.56 M water - acetic acid (8 ml.) was added during 20 seconds while the flask was shaken vigourously. The solution was left for three more minutes at 70°, then poured into 1.5 liters of distilled water. The water suspension was extracted with ether (3 x 400 ml.). The combined ether extracts were washed with sodium carbonate until neutral, then with water (2 x 40 ml.) and finally dried over anhydrous sodium sulfate. The ether was removed under reduced pressure, and the residue (10.8 g.) was chromatographed on alumina (95 g., Merck, acid washed). The mixture of disulfides was eluted with n-hexane. After removal of the hexane, the residue (10.3 g.) was distilled under reduced pressure. Two main fractions were obtained: n-Butyl disulfide b.p. 72° (1.6 mm.) and n-butyl p-tolyl disulfide (4.7 g.) b.p. 120-120.5° (1.6 mm.).

Analysis:* Calculated for $C_{11}H_{16}S_2$: C, 62.30; H, 7.59; mol. wt., 212. Found: C, 62.20; H, 7.72; mol.wt. (osmometric in $CHCl_3$), 210.

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* Sample prepared by Mr. G. Bray, the same procedure for preparation of the disulfide was used.

PART II

THE DISULFIDE - SULFINIC ACID REACTION

INTRODUCTION

During their studies of the disproportionation of p-toluenesulfinic acid, Kice and Bowers (33) observed a slight increase of the second-order rate constant towards the end of runs at high sulfuric acid concentration and high water concentration. Having ruled out any effect by the sulfonic acid or p-tolyl p-toluenethiolsulfonate that were produced from the disproportionation:

$$3\,ArSO_2H \rightarrow ArSO_2SAr + ArSO_3H + H_2O \qquad \text{(Eq. 8)}$$

$(Ar = \underline{p}\text{-}CH_3\text{-}C_6H_4\text{-})$,

the authors suggested a reaction between p-toluenesulfinic acid and p-tolyl disulfide. Disulfides were previously known hydrolysis products from thiolsulfonates. A recation between a disulfide and a sulfinic acid, however, had not been observed before. Kice and Bowers (34) showed that such a reaction does occur readily, and they undertook a detailed study of this reaction between p-tolyl disulfide and p-toluenesulfinic acid. Only two compounds, p-tolyl p-toluenethiolsulfonate and unreacted p-tolyl disulfide, were found when the above mentioned disulfide and sulfinic acid were reacted in 0.5 M sulfuric acid - 0.56 M water - acetic acid. The amounts were found to be in agreement with the stoichiometric equation:

$$4\,ArSO_2H + ArSSAr \rightarrow 3\,ArSO_2SAr + 2\,H_2O \qquad \text{(Eq. 9)}$$

(Ar = $\underline{p}$-CH_3-C_6H_4-).

A detailed study of the kinetics of the reaction was also carried out. The kinetic experiments were always made in the presence of a large stoichiometric excess of disulfide, so that the disulfide concentration was nearly constant during each experiment. At high sulfuric acid concentrations, the reaction was found to be first-order in sulfinic acid, i.e. a plot of log ($ArSO_2H$) versus time gave a straight line. It could be shown, however, that the normal disproportionation of the sulfinic acid must make a small contribution to the experimental first-order rate constant, and consequently, the product of the second-order rate constant for the disproportionation, k_2 (33) and the average concentration of sulfinic acid during an experiment, was subtracted from the experimental first-order rate constant, k_{exp}, in order to obtain k_1, the rate constant for the disulfide - sulfinic acid reaction. At constant disulfide concentration the rate of the disappearance of sulfinic acid can thus be expressed as:

$$-\frac{d(ArSO_2H)}{dt} = \underset{\substack{\text{rate const. for}\\ \text{disulfide - sulfinic}\\ \text{acid reaction.}}}{\underset{\uparrow}{k_1}(ArSO_2H)} + \underset{\substack{\text{contribution from}\\ \text{normal dispropor-}\\ \text{tionation of ArSO}_2\text{H.}}}{k_2(ArSO_2H)^2}$$

In experiments where the sulfuric acid concentration was low, both reactions had rates of comparable magnitude, and a plot of log $(ArSO_2H)$ versus time showed upwards curvature towards the end of an experiment. These reactions were treated as parallel first and second-order reactions (21, p. 165).

A series of runs, at a given sulfuric acid concentration, and with different initial concentrations of disulfide, showed an increase of the ratio $k_1/(ArSSAr)$ with increasing initial disulfide concentration. When $k_1/(ArSSAr)$ was plotted versus $(ArSSAr)$ a straight line was observed, suggesting that k_1 was given by an expression of the type:

$$k_1 = K_e[k_o + k_c(ArSSAr)]\ (ArSSAr) \qquad \text{(Eq. 10a)}$$

This expression for k_1 would be consistent with the following kinetic form for the reaction:

$$ArSO_2H + ArSSAr \underset{\text{fast}}{\overset{K_e}{\rightleftharpoons}} \text{Intermediate}$$

$$\text{Intermediate} \xrightarrow[\text{slow}]{k_o} \text{Products}$$

$$\text{Intermediate} + ArSSAr \xrightarrow[\text{slow}]{k_c} \text{Products} + (ArSSAr)$$

One way in which the disulfide could facilitate the decomposition of the intermediate would be by nucleophilic attack on it. If so, other sulfur nucleophiles, such as sulfides, should also be able to increase the decomposition rate of the intermediate. Experiments where phenyl sulfide was added to the reaction mixture, showed a large increase of the reaction rate, and in a control experiment the same sulfide was shown to have no effect on the disproportionation of sulfinic acid. In the presence of phenyl sulfide the following reaction therefore occurs:

$$\text{Intermediate} + Ph_2S \xrightarrow{k_s} \text{Products} + Ph_2S$$

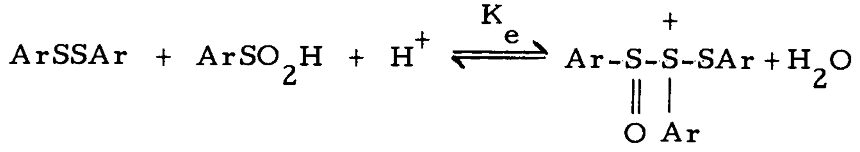
and the expression for the first-order rate constant becomes, accordingly:

$$k_1 = K_e\,[k_o + k_c\,(ArSSAr) + k_s(Ph_2S)]\,(ArSSAr) \qquad \text{(Eq. 10b)}$$

From the two expressions for k_1, in the presence or in absence of phenyl sulfide, we can calculate the two ratios k_o/k_c and k_s/k_c. The reactivity of phenyl sulfide was found to be nine times that of p-tolyl disulfide. This is in reasonable agreement with what might be expected regarding the relative nucleophilicity of these two compounds from studies such as the oxidation of sulfides and disulfides by perbenzoic acid.

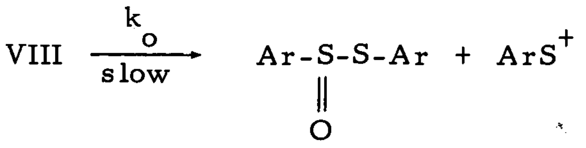
Experiments at several sulfuric acid concentrations showed that the ratio k_o/k_c was not influenced by the acidity of the medium. The overall rate did, however, depend greatly on the concentration of strong acid, and much more so than the normal disproportionation of sulfinic acid. A plot of log k_1 versus H_o (34) gave a straight line of slope -1.48. Because of the independence of k_o/k_c, at a given disulfide concentration the variation of log k_1 with the sulfuric acid concentration should be independent of the disulfide concentration chosen, as seen from Eq. 10a.

The rate of the disulfide - sulfinic acid reaction also showed a somewhat larger dependence on the stoichiometric water concentration than the normal disproportionation. For instance, by increasing the stoichiometric water concentration from 0.56 to 2.22 M, the rate of the normal disproportionation (Eq. 8) was decreased by a factor of seven (33), whereas the rate of the disulfide - sulfinic acid reaction (Eq. 9) was decreased by a factor of 16 (34). This larger dependence on water concentration seems reasonable since an increase in the stoichiometric water concentration will decrease the acidity of the medium, and as shown above, the reaction is very sensitive to the acidity of the medium. Based on these experiments, Kice and Bowers suggested the following mechanism for the reaction between p-tolyl disulfide and p-toluenesulfinic acid:



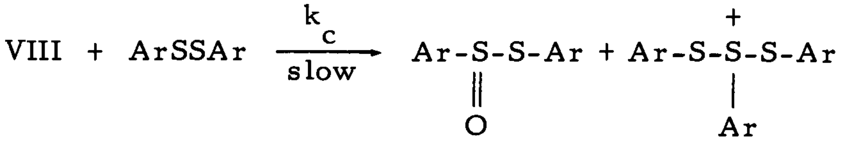
$$\mathrm{ArSSAr} + \mathrm{ArSO_2H} + \mathrm{H^+} \overset{K_e}{\rightleftharpoons} \mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}\overset{+}{\underset{\underset{Ar}{|}}{S}}{-}SAr} + \mathrm{H_2O} \quad \text{(Eq. 11a)}$$

VIII



$$\text{VIII} \xrightarrow[\text{slow}]{k_o} \text{Ar-}\underset{\substack{\| \\ \text{O}}}{\text{S}}\text{-S-Ar} + \text{ArS}^{+}$$

(Eq. 11b)



$$\text{VIII} + \text{ArSSAr} \xrightarrow[\text{slow}]{k_c} \text{Ar-}\underset{\substack{\| \\ \text{O}}}{\text{S}}\text{-S-Ar} + \text{Ar-S-}\overset{+}{\underset{\substack{| \\ \text{Ar}}}{\text{S}}}\text{-S-Ar}$$

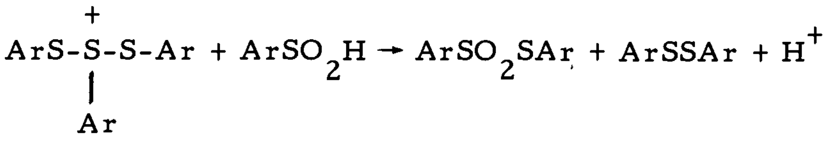
(Eq. 11c)

(Ar = $\underline{p}$-CH_3-C_6H_4-)

The three unstable intermediates that were formed in the two slow steps, would most likely react further according to the following equations:

$$\text{ArS}^{+} + \text{ArSO}_2\text{H} \rightarrow \text{ArSO}_2\text{SAr} + \text{H}^{+}$$

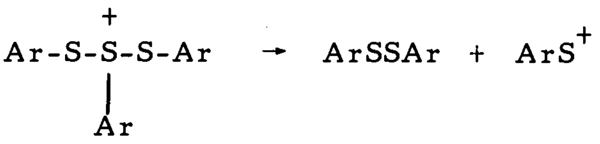
(Eq. 11d)



$$\text{ArS-}\overset{+}{\underset{\substack{| \\ \text{Ar}}}{\text{S}}}\text{-S-Ar} + \text{ArSO}_2\text{H} \rightarrow \text{ArSO}_2\text{SAr} + \text{ArSSAr} + \text{H}^{+}$$

(Eq. 11e)

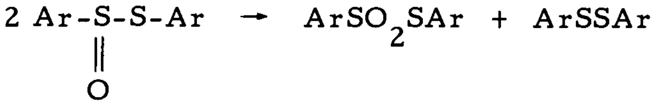
or, alternatively to equation 11 e,



$$\text{Ar-S-}\overset{+}{\underset{\substack{| \\ \text{Ar}}}{\text{S}}}\text{-S-Ar} \rightarrow \text{ArSSAr} + \text{ArS}^{+}$$

(Eq. 11f)

where ArS^{+} would react further according to equation 11 d.



$$2\ \text{Ar-}\underset{\substack{\| \\ \text{O}}}{\text{S}}\text{-S-Ar} \rightarrow \text{ArSO}_2\text{SAr} + \text{ArSSAr}$$

(Eq. 11g)

If we assume this reaction to be general for all disulfides, RSSR, then the reactions can be illustrated as follows:

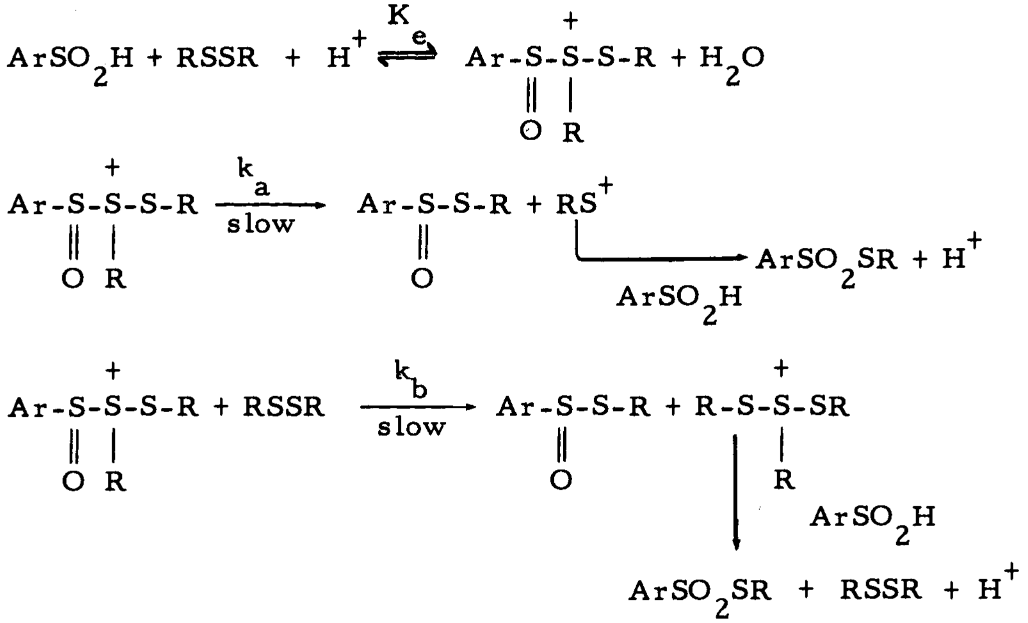


Chart 3

In the present work we were interested in attempting to establish whether in fact the reactions shown in Chart 3 are general for all disulfides when reacted with p-toluenesulfinic acid. We were also interested in seeing if the rate dependence on sulfuric acid concentration, which was found for p-tolyl disulfide, is the same when other disulfides are reacted with p-toluenesulfinic acid. The third point, and one of particular interest, was a more detailed study of the catalysis of the disulfide - sulfinic acid reaction by sulfides. We were interested in the dependence of the catalyzing power of a sulfide on its nucleophilicity, and in the manner in which inductive effects, and the steric effects of the alkyl groups of the disulfides might influence the rates of the reactions in question.

RESULTS

1. Products of the Disulfide - Sulfinic Acid Reaction

The products of the reaction of a variety of alkyl disulfides with p-toluenesulfinic acid in acetic acid - water - sulfuric acid solvent were determined. The disulfides used were: Methyl, benzyl, n-butyl and isopropyl disulfide. The results are given below in Table 9.

Alkyl p-toluenethiolsulfonate is the main product regardless of which disulfide is used. This result is in agreement with what we would expect from Chart 3 (page 92). When methyl disulfide was reacted, there was formed almost 30 times more methyl p-toluenethiolsulfonate than p-tolyl p-toluenethiolsulfonate, whereas the ratio between isopropyl p-toluenethiolsulfonate and p-tolyl p-toluenethiolsulfonate (Experiment P 14) was only about five. The corresponding ratios for Experiments P 12 and P 13 are eight and about seven.

Another product of the alkyl disulfide - sulfinic acid reactions is the unsymmetrical alkyl aryl disulfide ArSSR. With n-butyl and benzyl disulfide the unsymmetrical disulfide is formed in an amount equal to about three tenths the amount of alkyl p-toluenethiolsulfonate formed. When isopropyl disulfide was reacted, the amount of isopropyl p-tolyl disulfide was about two tenths of the isopropyl p-toluenethiolsulfonate isolated.

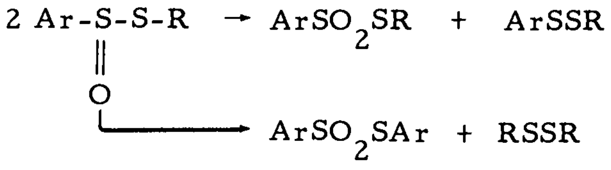
TABLE 9

PRODUCTS FROM THE DISULFIDE - p-TOLUENESULFINIC ACID REACTIONS

In experiments P 11 - P 13 the reactants were dissolved in 100 ml. of the solvent, in P 14, in 50 ml. of the solvent. The solvent used was 0.56 M water - acetic acid with sulfuric acid concentration as indicated in each case. Temperature: 70°.

Run:	P 11	P 12	P 13	P 14
Disulfide	MeSSMe	$(\underline{n}\text{-BuS-})_2$	$(\text{PhCH}_2\text{S-})_2$	$(\text{Me}_2\text{CHS-})_2$
Reaction time, hrs.	0.67	0.75	2.5	3.5
(H_2SO_4), M	0.2	0.4	0.6	0.6
Reactants, mmoles:				
$ArSO_2H$	7.5	7.5	4.75	2.25
RSSR	15.0	15.0	14.25	6.75
Products, mmoles:				
RSSR	--	11.80	11.80	3.56
RSSAr	--	1.28	0.83	0.18
$ArSO_2SAr$	0.14	0.55	0.41	0.26
$ArSO_2SR$	4.17	4.32	2.66	1.13
$\frac{RSSAr}{ArSO_2H_{\text{reacted}}}$	--	0.17	0.175	0.08
$\frac{ArSO_2SAr}{ArSO_2H_{\text{reacted}}}$	0.02	0.073	0.086	0.116
$\frac{ArSO_2SR}{ArSO_2H_{\text{reacted}}}$	0.56	0.58	0.56	0.50

The presence of p-tolyl p-toluenethiolsulfonate and mixed disulfide among the products from all these reactions, can be explained by the disproportionation of mixed thiolsulfinates which has been observed by Barnard (3) to occur according to both the paths below:



$$2\ \mathrm{Ar\text{-}}\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{S}}\mathrm{\text{-}S\text{-}R} \rightarrow \mathrm{ArSO_2SR} + \mathrm{ArSSR}$$

$$\rightarrow \mathrm{ArSO_2SAr} + \mathrm{RSSR}$$

From the mechanism suggested (Chart 3, p. 92) for the alkyl disulfide - sulfinic acid reaction, the mixed thiolsulfinate ArS(O)SR should be formed in the two slow steps of the reaction.

Unpublished observations have also shown another possibility for the further reaction of the mixed thiolsulfinates. Discussion of this reaction will be deferred until later (page 134).

Grishko and Gur'yanova (27) have observed exchange between alkyl disulfides and thiolsulfonates. When doubly S^{35} labelled ethyl disulfide was heated at 162° for three-and-a-half hours with p-tolyl p-toluenethiolsulfonate, a considerable amount of exchange was found, the reaction being:

$$\mathrm{ArSO_2SAr} + \mathrm{C_2H_5\text{-}S^{*}\text{-}S^{*}\text{-}C_2H_5} \rightarrow \mathrm{ArSO_2S^{*}C_2H_5} + \mathrm{ArS\text{-}S^{*}C_2H_5}$$

(Ar = p-$\mathrm{CH_3\text{-}C_6H_4\text{-}}$, $S^{*} = S^{35}$).

Since such an exchange reaction has been observed, it might also be responsible for some of the mixed disulfides and thiolsulfonates found from reactions P 11 - P 14. To check this possibility, we heated each of the three disulfides, methyl, n-butyl and benzyl disulfide with p-tolyl p-toluenethiolsulfonate, using exactly the same reaction conditions as in experiments P 11 - P 13. The results from these exchange experiments are given in Table 10.

The products from p-tolyl p-toluenethiolsulfonate and methyl and benzyl disulfide showed very small amounts of exchange, 2.0% and less than 5%, respectively. The reaction of n-butyl disulfide with p-tolyl p-toluenethiolsulfonate showed 20% exchange. There is no obvious reason for this somewhat higher value. Since these three exchange experiments (P 15 - P 17) show at most only modest amounts of exchange between disulfides and thiolsulfonates under the present reaction conditions, the mixed disulfides and thiolsulfonates must be primary products from the disulfide - sulfinic acid reaction.

2. Kinetics of the Disulfide - Sulfinic Acid Reaction

For all the kinetic experiments we used a large stoichiometric excess of disulfide to keep the disulfide concentration essentially constant during the course of an experiment. The experimental pseudo first-order rate constant, k_{exp}, was determined in most

TABLE 10

EXCHANGE REACTIONS BETWEEN DISULFIDES AND *p*-TOLYL *p*-TOLUENETHIOLSULFONATE

The reactions were carried out in 0.56 *M* water - acetic acid with sulfuric acid concentration as indicated in each case. Temperature: 70°. Total volume of the reaction mixture in each experiment: 50 ml.

Run	P 15	P 16	P 17
Disulfide used:	MeSSMe	$(n\text{-BuS-})_2$	$(\mathrm{PhCH_2S}\text{-})_2$
Reaction time, hrs.	0.67	0.75	2.5
(H_2SO_4), *M*	0.2	0.4	0.6
Reactants, mmoles:			
$ArSO_2SAr$	1.5	1.5	1.5
RSSR	7.5	7.5	7.5
Products, mmoles:			
$ArSO_2SAr$	1.35	1.09	1.13
$ArSO_2SR$	0.03	0.30	<0.05
% Exchange	2.0	20	<5

cases as the slope of the straight line obtained by plotting log $(ArSO_2H)$ versus time. As in the sulfide - sulfinic acid reactions, the contribution to k_{exp} from the normal disproportionation of sulfinic acid, $k_2(ArSO_2H)_{av.}$, was subtracted from k_{exp} to obtain k_1, the pseudo first-order rate constant for the disulfide - sulfinic acid reaction.

Some of the less reactive disulfides reacted with sulfinic acid with a rate comparable to that of the disproportionation of sulfinic acid. The plot of log $(ArSO_2H)$ versus time was no longer a straight line; so these reactions were treated as parallel first- and second-order reactions (21, p. 165). This method is illustrated for dithiodipropionic acid in the Experimental section (page 149). All the kinetic experiments with disulfides and sulfinic acid are listed in Table 26, Appendix 2.

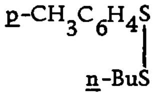
a) Rate Dependence on Disulfide

The initial concentration of disulfide, although in large stoichiometric excess, was varied for each disulfide from run to run in order to find the order of the reaction in disulfide. A reaction first-order in disulfide would show a constant value of $k_1/(RSSR)$, whereas $k_1/(RSSR)^2$ would be constant for a reaction second-order in disulfide. Both these ratios are listed for the various runs with the different disulfides in Table 11.

TABLE 11

KINETICS OF THE DISULFIDE - SULFINIC ACID REACTIONS

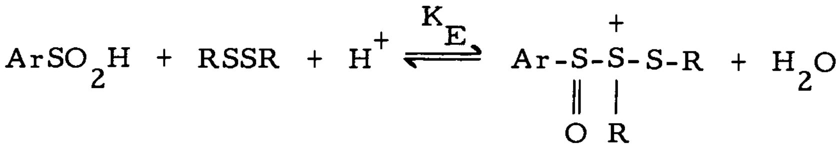
The reactions were carried out at 70° in 0.56 M water - acetic acid with sulfuric acid concentration as indicated in each case. $(ArSO_2H)_o$, 0.05 M unless otherwise indicated. (Ar = p-CH_3-C_6H_4-).

Disulfide	(H_2SO_4), M	(RSSR) M	$k_1 x 10^4$ sec.$^{-1}$	$\left[\frac{k_1 x 10^3}{(RSSR)}\right]$	$\left[\frac{k_1 x 10^2}{(RSSR)^2}\right]$
MeSSMe	0.2	0.20	20.80	10.40	5.2
		0.15	11.70	7.80	5.2
		0.10	5.20	5.20	5.2
		0.051 *	1.46	2.86	5.6
EtSSEt	0.2	0.20	5.22	2.61	1.31
		0.15	3.15	2.10	1.40
		0.10	1.45	1.45	1.45
n-BuSSBu-n	0.26	0.20	9.80	4.90	2.45
		0.15	5.60	3.74	2.50
		0.10	2.55	2.55	2.55
		0.05 *	0.75	1.50	3.00
$(PhCH_2S\text{-})_2$	0.4	0.20	2.20	1.10	0.55
		0.15	1.39	0.93	0.62
		0.10	0.68	0.68	0.68
$(Me_2CHS\text{-})_2$	0.4	0.20	1.16	0.58	0.29
		0.15	0.76	0.51	0.34
		0.10	0.38	0.38	0.38
 $p\text{-}CH_3C_6H_4S$ n-BuS	0.3	0.15	5.61	3.74	2.50
		0.12	3.60	3.00	2.50
		0.10	2.55	2.55	2.55
		0.05 *	0.79	1.58	3.16
PhSSPh	0.6	0.30 **	1.70	0.57	0.19
		0.20 **	0.83	0.42	0.21
		0.10	0.22	0.22	0.22
$(HOOCCH_2CH_2S)_2$	0.6	0.10	0.23	0.23	0.23
		0.07	0.13	0.186	0.27

* $(ArSO_2H)_o$: 0.03 M

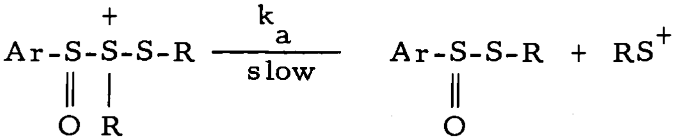
** Experiments by Mr. C. G. Venier.

The ratio $k_1/(RSSR)$ is clearly not a constant for any of the disulfides listed in Table 11. The ratio $k_1/(RSSR)^2$ is much closer to being a constant. This is particularly true for methyl disulfide. In that case $k_1/(RSSR)^2$ varies by only 7.7%. A maximum variation of 26% is found for n-butyl p-tolyl disulfide. For further interpretation of the data in Table 11, we recall that the p-tolyl disulfide reaction indicated the kinetically important steps in the alkyl disulfide - sulfinic acid reaction should be:



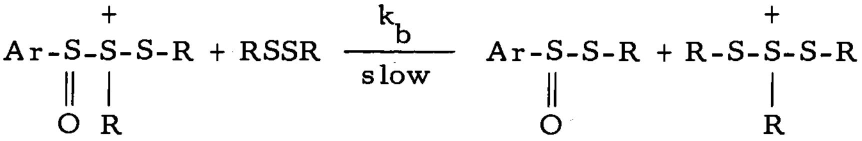
$$ArSO_2H + RSSR + H^+ \overset{K_E}{\rightleftharpoons} Ar{-}\underset{\underset{O}{\|}}{S}{-}\overset{+}{\underset{\underset{R}{|}}{S}}{-}S{-}R + H_2O \qquad (Eq.\ 12a)$$

IX



$$Ar{-}\underset{\underset{O}{\|}}{S}{-}\overset{+}{\underset{\underset{R}{|}}{S}}{-}S{-}R \xrightarrow[slow]{k_a} Ar{-}\underset{\underset{O}{\|}}{S}{-}S{-}R + RS^+ \qquad (Eq.\ 12b)$$

IX



$$Ar{-}\underset{\underset{O}{\|}}{S}{-}\overset{+}{\underset{\underset{R}{|}}{S}}{-}S{-}R + RSSR \xrightarrow[slow]{k_b} Ar{-}\underset{\underset{O}{\|}}{S}{-}S{-}R + R{-}S{-}\overset{+}{\underset{\underset{R}{|}}{S}}{-}S{-}R \qquad (Eq.\ 12c)$$

IX

The rate of the reaction should therefore be given by:

$$\text{Rate} = k_a(IX)f_{IX}/f^*_a + k_b(IX)(RSSR)\,\frac{f_{IX}\,f_{RSSR}}{f^*_b}$$

where f^*_a is the activity coefficient of transition state for reaction 12b, and f^*_b the activity coefficient for transition state of reaction 12 c. An expression for IX is obtained from:

$$K_E = \frac{(IX)\, f_{IX}\, a_{H_2O}}{a_{H^+}\, (RSSR)\, f_{RSSR}\, (ArSO_2H)\, f_{ArSO_2H}}$$

If we define a new equilibrium constant:

$$K_e = K_E \frac{a_{H^+}\, f_{RSSR}\, f_{ArSO_2H}}{f_{IX}\, a_{H_2O}} = \frac{(IX)}{(RSSR)(ArSO_2H)}$$

and the two rate constants:

$$k_o = k_a \frac{f_{IX}}{f_a^*} \quad ; \qquad k_c = k_b \frac{f_{IX}\, f_{RSSR}}{f_b^*}$$

The expression for intermediate IX is:

$$(IX) = K_e\, (RSSR)(ArSO_2H)$$

and the rate expression converts to:

$$\underline{\text{Rate} = K_e(RSSR)(ArSO_2H)\,[k_o + k_c(RSSR)]}$$

The expression for the rate constant k_1 is therefore:

$$k_1 = K_e(RSSR)\,[k_o + k_c(RSSR)]$$

For fixed sulfuric acid and water concentrations, a plot of $k_1/(RSSR)$ versus (RSSR) should give a straight line with slope k_cK_e and intercept k_oK_e. Thus, the ratio of the intercept and the slope will give k_o/k_c, which expresses the relative rate of unimolecular decomposition of intermediate IX to the rate of nucleophilic attack on IX by disulfide.

Curve 7 (Figure 6) is a plot of $k_1/(RSSR)$ versus (RSSR) for methyl disulfide at 0.2 M sulfuric acid concentration.

The ratio k_o/k_c for methyl disulfide at 0.2 M sulfuric acid concentration is found from Curve 7 as 0.004. Thus, at 0.1 M methyl disulfide concentration only about 4% of the intermediate IX decomposes unimolecularly (0.4/0.104%), whereas 96% of IX yields products through reaction with the disulfide in a bimolecular reaction. Table 15 (page 113) shows the ratio k_o/k_c at 0.3 M sulfuric acid concentration to be about the same for the two alkyl disulfides, ethyl and n-butyl disulfide, indicating again almost exclusive bimolecular decomposition of intermediate IX. The highest value of k_o/k_c is found for isopropyl disulfide Thus, at 0.1 M concentration of this disulfide, the amounts of IX converted to products by the unimolecular and bimolecular routes are about equal.

Similar plots of $k_1/(RSSR)$ versus (RSSR) for the other disulfides listed in Table 11, give the value of k_oK_e and k_cK_e for each of these at the particular sulfuric acid concentration used. The curves 8 - 14 are shown in Figures 7 and 8, and the k_oK_e and k_cK_e values obtained from these curves are listed in Table 12.

Figure 6. Plot of k_1/(MeSSMe) versus (MeSSMe) for the Disulfide-Sulfinic Acid Reaction at 0.2 M H_2SO_4, and 70°.

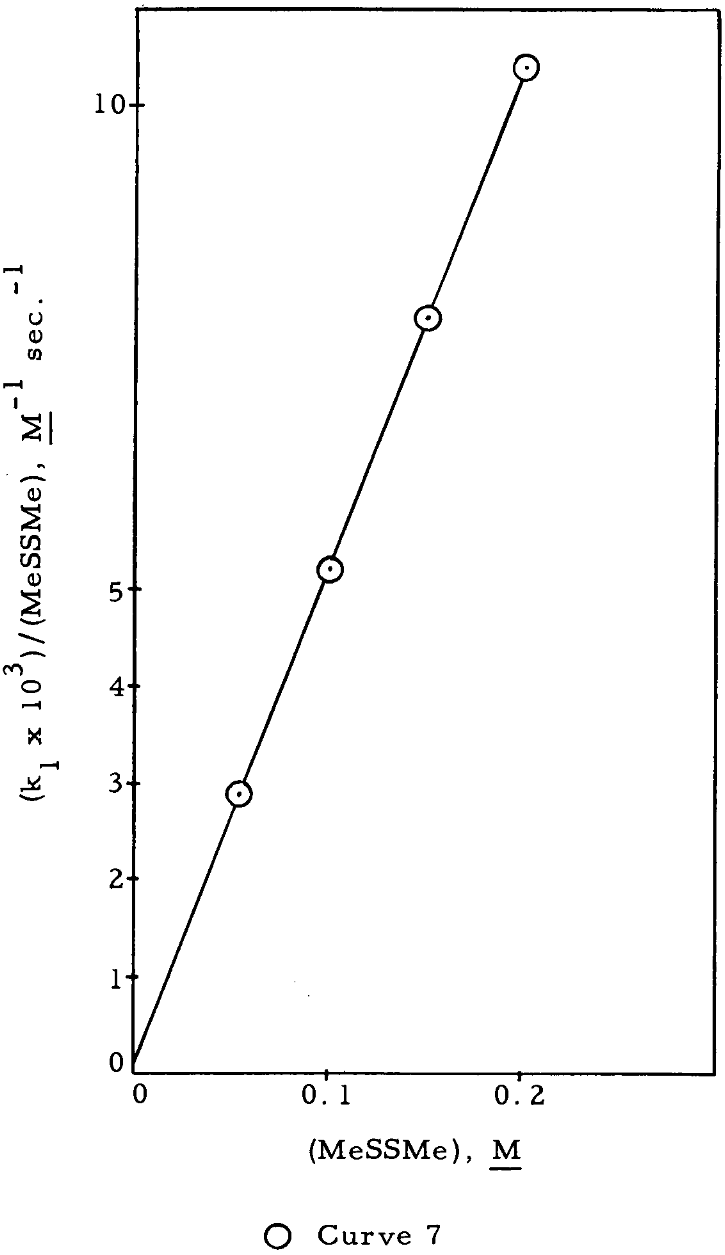


Figure 7. Plot of $k_1/(RSSR)$ versus (RSSR) for Ethyl, n-Butyl, Benzyl and Isopropyl Disulfide at 70° and (H_2SO_4) as shown in Table 12.

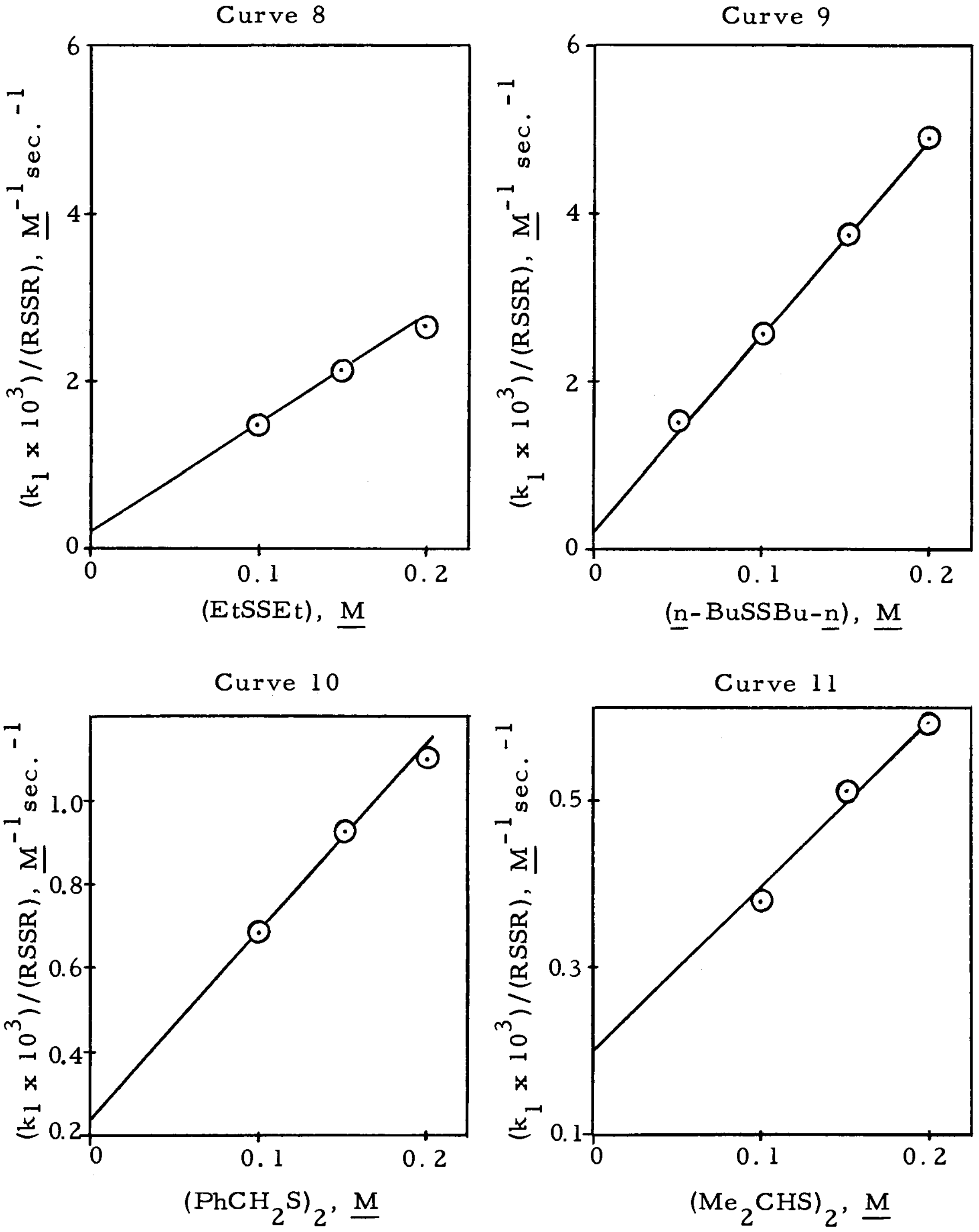


Figure 8. Plot of k_1/(RSSR) versus (RSSR) for p-Tolyl n-Butyl Disulfide, Phenyl Disulfide and Dithiodipropionic Acid at 70° and (H_2SO_4) as shown in Table 12.

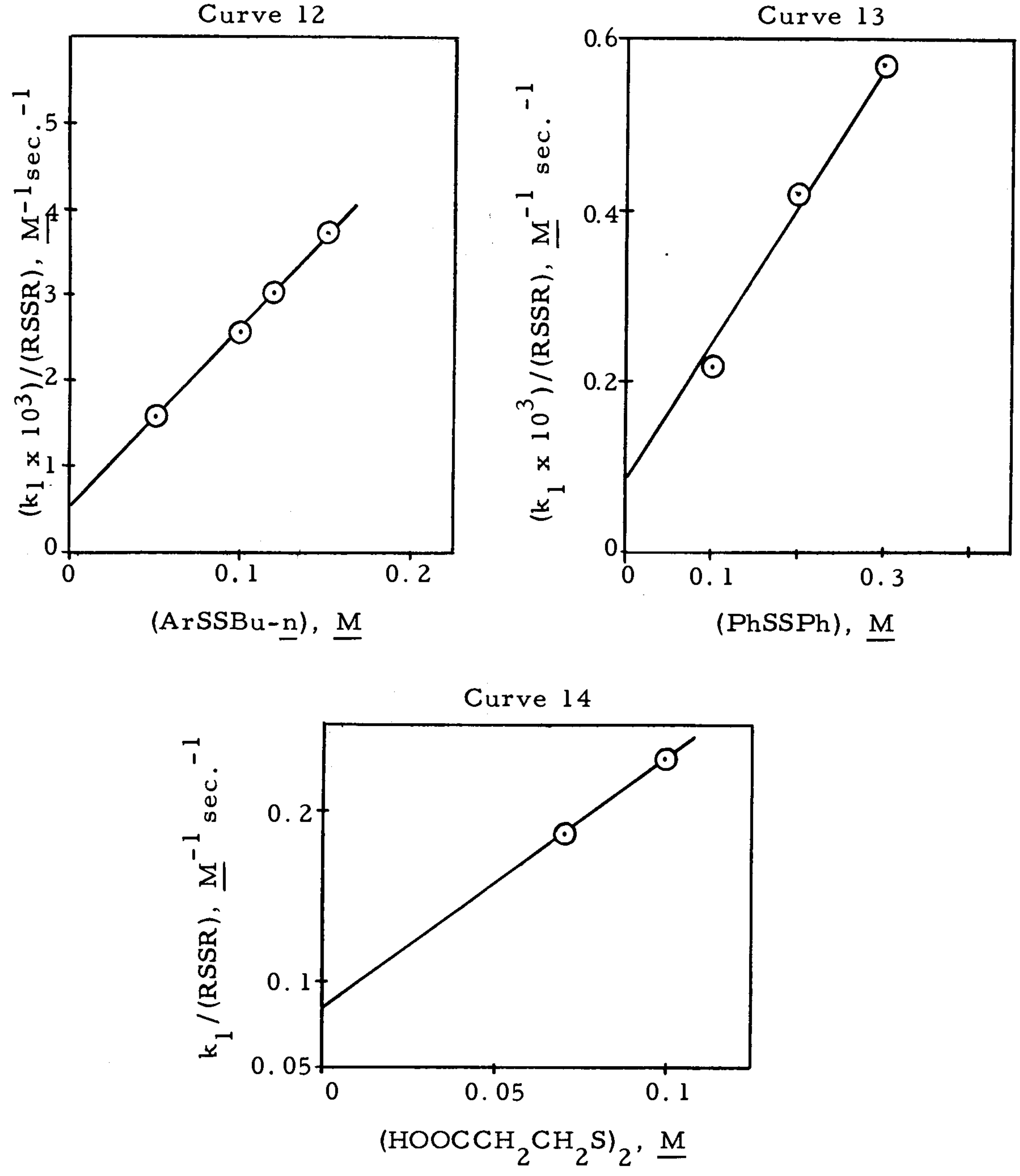


TABLE 12

RELATIVE REACTIVITIES OF DISULFIDES AS NUCLEOPHILES

The reactions were carried out at 70° in 0.56 M water - acetic acid with sulfuric acid concentration as indicated in each case.

k_oK_e: Rate constant for unimolecular decomposition of the intermediate Ar-S(O)-$\overset{+}{\mathrm{S}}$(R)-S-R, times the equilibrium constant for reaction 12a.

k_cK_e: Rate constant for disulfide-catalyzed decomposition of the intermediate ArS(O)-$\overset{+}{\mathrm{S}}$(R)-S-R, times the equilibrium constant for reaction 12 a.

Disulfide	(H_2SO_4), M	$k_oK_e \times 10^3$	$k_cK_e \times 10^3$	Curve no.
MeSSMe	0.2	0.20	51	7
EtSSEt	0.2	0.20	13	8
n-BuSSBu-n	0.26	0.2	23	9
$PhCH_2SSCH_2Ph$	0.4	0.23	4.6	10
$(Me_2CHS\text{-})_2$	0.4	0.21	1.9	11
p-$CH_3C_6H_4SSBu$-n	0.3	0.50	21.3	12
PhSSPh	0.6	0.075	1.6	13
$(HOOCCH_2CH_2S\text{-})_2$	0.6	0.085	1.46	14

b) Rate Dependence on Sulfuric Acid

The ratio k_o/k_c for p-tolyl disulfide was previously found to be independent of the concentration of sulfuric acid present (34), and this is presumably also true for all disulfides. The reaction rates will, however, change with sulfuric acid concentration, since the equilibrium preceding the two rate-determining steps is acid dependent, thus making k_oK_e and k_cK_e acid dependent. As was mentioned before, (page 90) we can find the variation of k_1 with sulfuric acid concentration by plotting log k_1 versus $-H_o$, using a fixed initial disulfide concentration, which may be chosen arbitrarily. Noyce and Snyder (48) have given H_o values at different sulfuric acid concentrations in 0.96% water - acetic acid. This water concentration is close enough to 0.56 M for our purpose, so that the data, which are listed below in Table 13, can be used directly.

TABLE 13

ACIDITY CONSTANTS OF SULFURIC ACID IN
0.96% WATER - ACETIC ACID (48)

(H_2SO_4), M	H_o
0.2	-1.58
0.4	-2.07
0.6	-2.38
0.8	-2.61
1.0	-2.79

When the sulfuric acid concentration is plotted versus H_o and a smooth curve is drawn through the points, we find the values of H_o at 0.26 M and 0.3 M sulfuric acid concentration to be -1.76 and -1.86, respectively.

The dependence of k_1 on sulfuric acid concentration was studied most extensively for n-butyl disulfide. Values of k_1 (Table 26, Appendix 2), are listed in Table 14 with the corresponding H_o values from Table 13. Table 14 also gives corresponding values for benzyl disulfide at two different sulfuric acid concentrations.

TABLE 14

RATE CONSTANTS OF n-BUTYL AND BENZYL DISULFIDE AT DIFFERENT SULFURIC ACID CONCENTRATIONS

Initial concentrations of $(n\text{-BuS-})_2$ and $(PhCH_2S\text{-})_2$: 0.15 M. The reactions were carried out at 70° in 0.56 M water - acetic acid with sulfuric acid concentration as indicated in each case.

Disulfide	(H_2SO_4), M	$k_1 \times 10^4$	$\log k_1 + 4$	$-H_o$	Run no.
$(n\text{-BuS-})_2$	0.20	3.07	0.487	1.58	46
	0.26	5.60	0.748	1.76	43
	0.30	7.30	0.863	1.86	47
	0.40	15.10	1.179	2.07	48
$(PhCH_2S\text{-})_2$	0.30	0.69	-0.161	1.86	52
	0.40	1.39	0.143	2.07	50

A plot of log k_1 versus H_o (Curve 15, Figure 9) shows a linear relationship, the slope of the line being -1.43 for n-butyl disulfide. The two points for benzyl disulfide can also accommodate a line with the same slope (Curve 16).

The slope of the linear plot of log k_1 versus H_o was previously found to be -1.48 for p-tolyl disulfide. This value seems to be close enough to those presently obtained for n-butyl disulfide and benzyl disulfide (-1.43), to assume this dependence of rate on sulfuric acid concentration to be a general one for the disulfide - p-toluenesulfinic acid reaction. Since the ratio k_o/k_c is independent of H_o at a fixed disulfide concentration, we can extrapolate k_cK_e at one sulfuric acid concentration to another, using the equations:

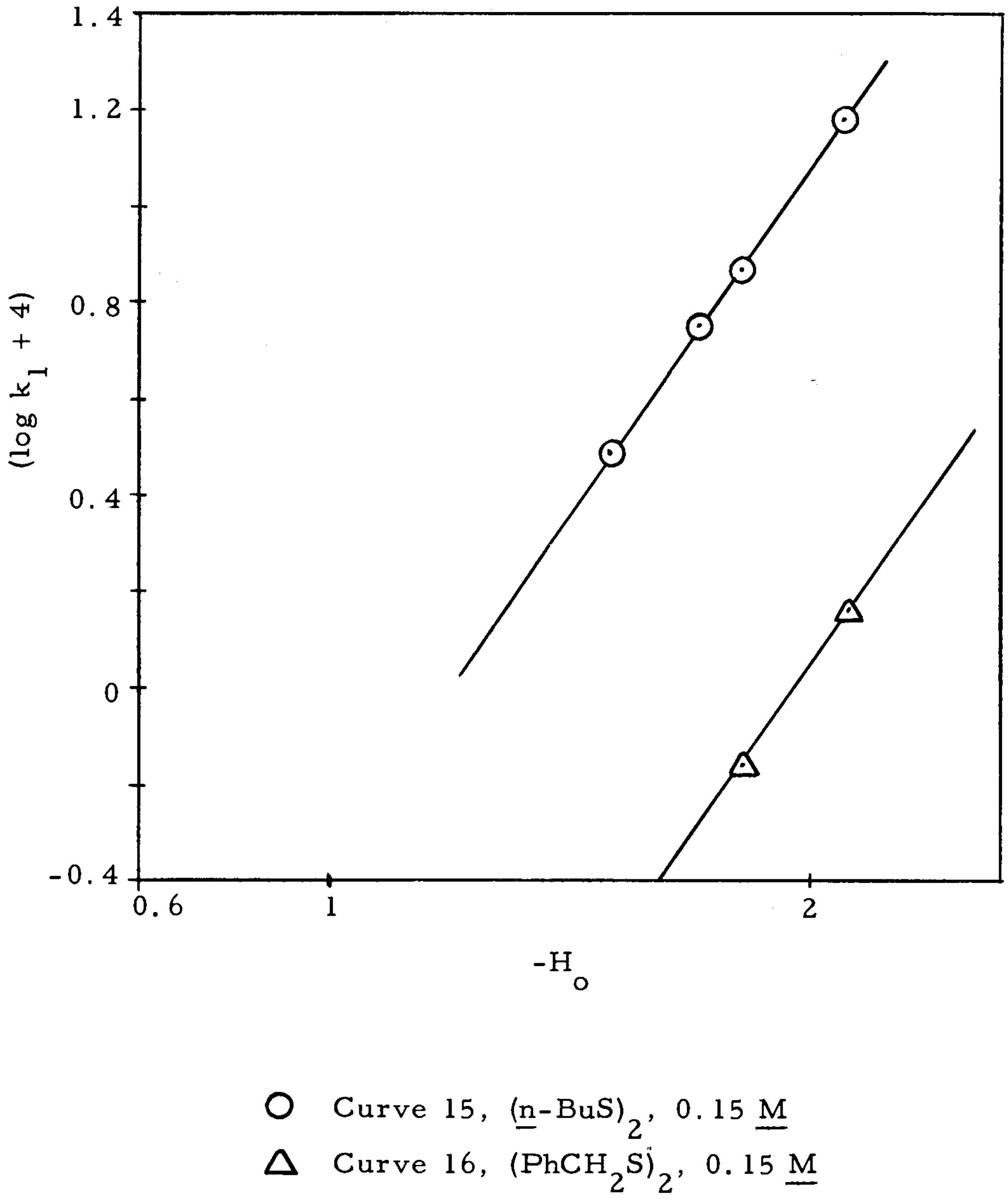
$$k_1 = k_cK_e(\mathrm{RSSR})\,[k_o/k_c + (\mathrm{RSSR})]$$

$$\frac{d \log k_1}{dH_o} = \frac{d \log k_cK_e}{dH_o} \qquad \text{(Eq. 13a)}$$

Taking the value of d log k_1/dH_o as -1.45, Eq. 13a converts to:

$$\underline{\Delta \log k_cK_e = -1.45\, \Delta H_o} \qquad \text{(Eq. 13b)}$$

Figure 9. Plot of the Acidity Constant H_o versus log k_1 for the Reaction of p-Toluenesulfinic Acid with (n-BuS)$_2$ or (PhCH$_2$S)$_2$.



c) Relative Reactivity of Disulfides in their Reaction with p-Toluenesulfinic Acid

To compare the reactivities of the various disulfides, expressed by the value of k_cK_e, we must extrapolate k_cK_e to a common sulfuric acid concentration. The value of sulfuric acid concentration was chosen as 0.3 M, and the rate constants for the different disulfides were converted, using Eq. 13b. The results are given in Table 15.

As an example, the conversion of k_cK_e for methyl disulfide from 0.2 M H_2SO_4 (Table 12), to 0.3 M H_2SO_4 (Table 15), is shown:

The acidity constant H_o decreases with 0.28 units from 0.2 M to 0.3 M H_2SO_4, and the increase in log k_cK_e and k_oK_e is therefore:

$$\Delta \log k_cK_e = \Delta \log k_oK_e = -1.45(-0.28) = \underline{0.406}$$

$$\log k_cK_e = \log 0.05 + 0.406 = 0.105 - 1$$

$$\underline{k_cK_e = 0.127} \quad \text{at} \quad 0.3\ \underline{M}\ H_2SO_4$$

$$\log k_oK_e = \log 0.0002 + 0.406 = 0.707 - 4$$

$$\underline{k_oK_e = 0.51 \times 10^{-3}} \quad \text{at} \quad 0.3\ \underline{M}\ H_2SO_4$$

TABLE 15

REACTIVITIES OF DISULFIDES IN THEIR REACTION WITH *p*-TOLUENESULFINIC ACID

Solvent : 0.3 *M* sulfuric acid - 0.56 *M* water - acetic acid.

Temperature : 70°.

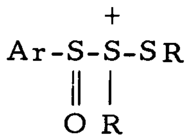
Disulfide	$k_cK_e \times 10^2$	$k_oK_e \times 10^3$	k_o/k_c
MeSSMe	12.7	0.51	0.004
EtSSEt	3.3	0.51	0.015
$(n\text{-BuS-})_2$	3.2	0.28	0.009
$(PhCH_2S\text{-})_2$	0.23	0.12	0.05
$(Me_2CHS\text{-})_2$	0.09	0.10	0.11
$(HOOCCH_2CH_2S\text{-})_2$	0.026 [1]		
$(HOOCCH_2S\text{-})_2$	[2]		
$p\text{-}CH_3C_6H_4SSBu\text{-}n$	2.1		0.024
$(p\text{-}CH_3C_6H_4S\text{-})_2$	0.29 [3]		0.076 [3]
PhSSPh	0.028	0.013	0.05

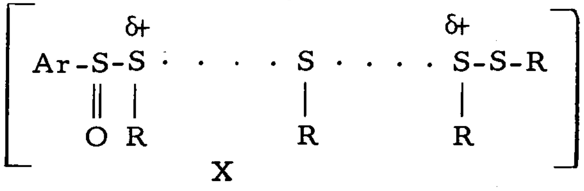
[1] Less accurate than other values; based on only two runs at 0.6 *M* H_2SO_4.

[2] Too small to measure at 0.6 *M* H_2SO_4.

[3] Data of (34).

Table 15 shows a very low value of k_cK_e for dithiodipropionic acid, and for dithiodiacetic acid k_cK_e was even lower (no exact value could be obtained).

The transition state for the nucleophilic attack by the disulfide on the intermediate  $\mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}\overset{+}{\underset{\underset{R}{|}}{S}}{-}SR}$ (Eq. 12c), can be illustrated as:



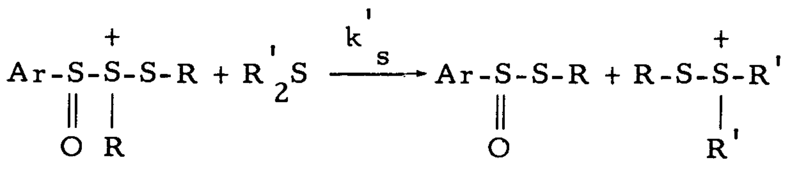
$$\underset{X}{\left[\mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}\overset{\delta+}{\underset{\underset{R}{|}}{S}}\cdots\cdots\underset{\underset{R}{|}}{S}\cdots\cdots\overset{\delta+}{\underset{\underset{R}{|}}{S}}{-}S{-}R}\right]}$$

Here two of the disulfide sulfur atoms have a partial positive charge, in contrast to the disulfide itself which is uncharged. Since the reaction rate increases with decreasing energy difference between reactants and transition state, we would expect a higher reaction rate of reaction 12c for disulfides with alkyl groups capable of stabilizing the positive charge on the sulfur atom. On the other hand, disulfides with electron withdrawing alkyl groups would increase the energy difference between transition state and disulfide, and therefore lower the reaction rate. The low k_cK_e values observed for dithiodiacetic and dithiodipropionic acid are therefore in accord with the electron withdrawing effect of the carboxyl groups.

Reaction 12c also seems to be subject to steric effects, since ethyl and n-butyl disulfide show about the same value of k_cK_e, whereas isopropyl disulfide, which has alkyl groups that are inductively quite similar, shows a k_cK_e value about 35 times smaller. Also, methyl disulfide shows a k_cK_e value about four times larger than for ethyl and n-butyl disulfide, a much larger reactivity difference than expected from inductive effects.

3. Sulfide Catalysis of the Disulfide - Sulfinic Acid Reaction

Earlier experiments have already demonstrated the catalysis by phenyl sulfide of the reaction between p-tolyl disulfide and p-toluenesulfinic acid (34). Sulfides are generally better nucleophiles than disulfides, and they should therefore promote the decomposition of the intermediate $Ar\text{-}\underset{\underset{O}{\|}}{S}\text{-}\overset{+}{\underset{\underset{R}{|}}{S}}\text{-}S\text{-}R$ by nucleophilic attack, leading to a higher overall rate of the reaction. We therefore would expect sulfide catalysis to be general for all disulfide - sulfinic acid reactions. Also, the more nucleophilic a sulfide is, the better it should catalyze the reaction between a certain disulfide and the sulfinic acid. Finally, since we believe that for sulfide catalyzed reactions between disulfide and sulfinic acid, the following step, in addition to steps 12b and 12c (page 101), becomes kinetically important:



$$Ar\text{-}\underset{\underset{O}{\|}}{S}\text{-}\overset{+}{\underset{\underset{R}{|}}{S}}\text{-}S\text{-}R + R'_2S \xrightarrow{k'_s} Ar\text{-}\underset{\underset{O}{\|}}{S}\text{-}S\text{-}R + R\text{-}S\text{-}\overset{+}{\underset{\underset{R'}{|}}{S}}\text{-}R' \qquad \text{(Eq. 12d)}$$

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and since the expression for the over-all rate constant is:

$$k_1 = k_oK_e(RSSR) + k_cK_e(RSSR)^2 + k_sK_e(R'_2S)(RSSR) \quad \text{(Eq. 14)}$$

$$k_s = k'_s\,[f_{R'_2S}\,f_{IX}/f^*_s] \;;\quad f^*_s = \text{activity coefficient for transition state of Eq. 12d.}$$

the rate of the catalyzed reaction should be proportional to the amount of sulfide added.

The contribution of added sulfide to the first-order rate constant k_1 is:

$$k_sK_e(R'_2S)(RSSR) = k_1 - k_oK_e(RSSR) - k_cK_e(RSSR)^2$$

The right hand side of this equation can be expressed as $k_1 - k^o_1$, k^o_1 being the rate constant when no sulfide is present.

The various expected features of sulfide catalysis of the disulfide - sulfinic acid reaction have all been tested, and the results are given below.

a) Influence of Sulfide Concentration on the Catalysis

The product k_sK_e is given by the equation:

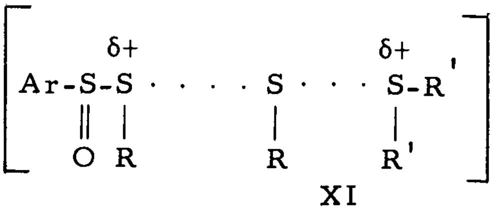
$$k_sK_e = \frac{k_1 - k^o_1}{(R'_2S)(RSSR)}$$

At a fixed sulfuric acid concentration, the value of k_sK_e should be a constant, for a given disulfide and sulfide. By varying the initial concentration of sulfide and keeping all the other variables constant, the predicted first-order dependence on sulfide concentration can be checked. A series of runs was made for each of the three systems: phenyl disulfide - phenyl sulfide, n-butyl disulfide - n-butyl sulfide and methyl disulfide - phenyl sulfide. These systems ought to be sufficiently different to give information about the influence of sulfide concentration on this reaction in general. The results are given in Table 16.

The value of $k_s K_e$ is a constant for each of the three systems, and the sulfide-catalyzed reaction is therefore first-order in sulfide.

b) Influence of Sulfide Structure on its Catalyzing Power

Analogous to the disulfides, we also expect electron releasing alkyl groups on the sulfide to increase its nucleophilicity and thereby increase its catalyzing power. The transition state for the sulfide catalyzed decomposition of the intermediate $\text{Ar-}\underset{\underset{O}{\|}}{S}\text{-}\overset{+}{\underset{\underset{R}{|}}{S}}\text{-S-R}$ can be shown as:



$$\left[\text{Ar-}\underset{\underset{O}{\|}}{S}\text{-}\overset{\delta+}{\underset{\underset{R}{|}}{S}}\cdots\cdots\underset{\underset{R}{|}}{S}\cdots\overset{\delta+}{\underset{\underset{R'}{|}}{S}}\text{-R}'\right]$$

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where electron releasing alkyl groups on the sulfide will stabilize the

TABLE 16

EFFECT OF SULFIDE CONCENTRATION ON THE SULFIDE CATALYZED DISULFIDE - SULFINIC ACID REACTION

The reactions were carried out at 70° in 0.56 M water - acetic acid with sulfuric acid concentration as indicated in each case. $(ArSO_2H)_o$: 0.05 M, (Ar = p-$CH_3C_6H_4$-).

Disulfide	Sulfide	(H_2SO_4), M	(RSSR), M	(R'_2S), M	$k_1 \times 10^4$ sec.$^{-1}$	$\frac{k_1 - k_1^{\circ}}{(RSSR)(R'_2S)} = k_sK_e$
PhSSPh	Ph_2S	0.60	0.10	0.00	0.22	
				0.05	2.24	0.040
				0.10	4.21	0.040
				0.15	6.01	0.039
(n-BuS-)$_2$	n-Bu$_2$S	0.20	0.10	0.0000	1.24	
				0.0025	9.35	3.2
				0.0050	17.1	3.2
MeSSMe	Ph_2S	0.20	0.10	0.00	5.2	
				0.10	6.5	0.013
				0.15	7.3	0.014

partial positive charge on the sulfide sulfur.

The catalyzing effect of phenyl, benzyl and n-butyl sulfide was studied in the reaction between phenyl disulfide and sulfinic acid. The catalyzing effect of phenyl and n-butyl sulfide was also studied with four other disulfides, namely, n-butyl, isopropyl, methyl and benzyl disulfide. Table 17 shows the results.

For each of the five disulfides used, the catalytic power of n-butyl sulfide is seen, from the value of k_sK_e, to be much larger than that of phenyl sulfide. This is exactly what we would expect from consideration of inductive effects. Benzyl sulfide catalyzes the phenyl disulfide - sulfinic acid reaction to a degree intermediate between phenyl and n-butyl sulfide, which also is in accord with our expectations.

c) Dependence of Sulfide Catalysis on Sulfuric Acid Concentration

Experiments with two different systems of sulfide - disulfide - sulfinic acid were made to check the dependence of k_sK_e on the sulfuric acid concentration. Previous experiments with p-tolyl disulfide and p-toluenesulfinic acid had indicated the same relationship between k_sK_e and H_o as between k_cK_e and H_o.

The rate for the phenyl sulfide catalyzed reaction between n-butyl disulfide and p-toluenesulfinic acid was measured at 0.2 and

TABLE 17

EFFECT OF SULFIDE STRUCTURE ON ITS CATALYSIS OF THE DISULFIDE - SULFINIC ACID REACTION

The reactions were carried out at 70° in 0.56 M water - acetic acid with sulfuric acid concentration as indicated in each case. $(ArSO_2H)_o$: 0.05 M, (Ar = p-CH_3-C_6H_4-).

Disulfide	Sulfide	(H_2SO_4), M	(RSSR), M	(R'_2S), M	$k_1 \times 10^4$ sec.$^{-1}$	k_sK_e
PhSSPh	Ph_2S	0.60	*	*	*	0.040
	$(PhCH_2)_2S$	0.60	0.10	0.005	4.11	0.78
	n-Bu_2S	0.60	0.10	0.005	9.19	1.80
(n-BuS-$)_2$	n-Bu_2S	0.20	*	*	*	3.2
	Ph_2S	0.20	0.10	0.10	2.49	0.013
$(Me_2CHS-)_2$	none	0.40	0.10	0.00	0.38	
	Ph_2S	0.40	0.10	0.10	0.80	0.004
	n-Bu_2S	0.40	0.10	0.005	4.25	0.78
MeSSMe	Ph_2S	0.20	*	*	*	0.014
	n-Bu_2S	0.20	0.10	0.0025	29.6	9.8
$(PhCH_2S)_2$	none	0.40	0.10	0.00	0.68	
	Ph_2S	0.40	0.10	0.10	1.60	0.0092
	n-Bu_2S	0.40	0.10	0.005	13.30	2.5

* Experimental data from which k_sK_e was calculated are given in Table 16.

0.3 M sulfuric acid concentration. The rate of the system: Benzyl disulfide - n-butyl sulfide - p-toluenesulfinic acid was measured at 0.3 and 0.4 M sulfuric acid concentration. The values of $k_1/(RSSR)$ obtained in each case, together with k_cK_e, k_sK_e and the ratio k_s/k_c are listed for the two systems in Table 18.

TABLE 18

DEPENDENCE OF SULFIDE CATALYSIS ON SULFURIC ACID CONCENTRATION

The reactions were carried out in 0.56 M water - acetic acid with sulfuric acid concentration as indicated in each case. Temperature: 70°. $(ArSO_2H)_o$: 0.05 M, (Ar = p-CH_3-C_6H_4-).

Disulfide	Sulfide	(H_2SO_4), M	$\frac{k_1 x10^3}{(RSSR)}$	$(k_cK_e x10^2)$ for RSSR	k_sK_e for R'_2S	k_s/k_c	Run
(n-BuS-$)_2$	Ph_2S	0.2	2.49	1.26	0.0125	0.99	76
		0.3	5.76	3.2	0.030	0.94	77
$(PhCH_2S)_2$	(n-Bu$)_2$S	0.3	6.69	0.23	1.27	$5.52x10^2$	83
		0.4	13.30	0.46	2.52	$5.48x10^2$	84

Table 18 shows the values 0.99 and 0.94 for k_s/k_c in the system (n-BuS-$)_2$ - Ph_2S - sulfinic acid, and 5.52×10^2 and 5.48×10^2 for k_s/k_c in the second system; $(PhCH_2S-)_2$ - n-Bu_2S -

sulfinic acid. Therefore, since the ratio k_s/k_c has approximately the same value at both sulfuric acid concentrations in each system, k_sK_e clearly shows the same acid dependence as k_cK_e. We can therefore extrapolate all k_sK_e values for the sulfides in their reaction with different disulfides and sulfinic acid, to a common sulfuric acid concentration, using Eq. 13b. The values of k_sK_e for n-butyl and phenyl sulfide were calculated at 0.3 M sulfuric acid concentration in their reactions with five different disulfides, and are shown in Table 19. Also the ratio between the reactivities of the two sulfides with these same disulfides are given in Table 19.

TABLE 19

RELATIVE REACTIVITY OF SULFIDES AS CATALYSTS IN VARIOUS DISULFIDE - p-TOLUENESULFINIC ACID REACTIONS

Solvent: 0.3 M sulfuric acid - 0.56 M water - acetic acid.
Temperature: 70°.

	Disulfide, RSSR				
	R = Me	n-Bu	i-Pr	$PhCH_2$	Ph
k_sK_e for n-Bu_2S	25.00	8.15	0.39	1.27	0.32
$k_sK_e \times 10^2$ for Ph_2S	3.56	3.0	0.20	0.46	0.71
$(k_s^{Bu}/k_s^{Ph}) \times 10^{-2}$	7.00	2.7	2.0	2.8	0.45

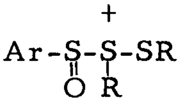
DISCUSSION

The first point we wanted to clarify was whether the mechanism outlined in Chart 3 was general for all disulfides when reacted with p-toluenesulfinic acid. The general features of this mechanism can be summed up in four points:

1. The predicted kinetic form for the reaction.
2. The prediction of general catalysis of the reaction by sulfur nucleophiles.
3. The expected change in the catalytic effectiveness of a sulfur nucleophile with changes in the inductive effects of the alkyl groups of the sulfur nucleophile.
4. The effect on the rate of changes in the steric requirements of the alkyl groups of the disulfide.

We will now look at each of these features in detail, and compare the results with what we would expect from the suggested mechanism in Chart 3.

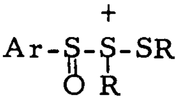
1. Kinetic form of the disulfide - sulfinic acid reaction

The unstable intermediate  $\mathrm{Ar{-}\underset{\overset{\|}{O}}{S}{-}\underset{\overset{|}{R}}{\overset{+}{S}}{-}SR}$ (IX) is formed from one mole each of sulfinic acid, disulfide and a proton in a fast equilibrium (Eq. 12a). There are two possible routes for the further reaction of intermediate IX, both of which are of consequence for the rate expression. The unimolecular decomposition of IX to thiolsulfinate ArS(O)SR and the ion RS^+ (Eq. 12b) will contribute a term first-order in disulfide and sulfinic acid to the rate expression. The nucleophilic attack by disulfide on intermediate IX (Eq. 12c) will contribute to the rate expression with a term first-order in sulfinic acid and second-order in disulfide. The rate expression we would expect for the disulfide - sulfinic acid reaction is therefore:

$$-\frac{d(ArSO_2H)}{dt} = K_e(RSSR)(ArSO_2H)[k_o + k_c(RSSR)]$$

Table 11 shows the results from kinetic experiments with eight different disulfides and p-toluenesulfinic acid. Several runs were made with each disulfide, and each run with a different initial disulfide concentration. The disulfide was, however, always kept in stoichiometric excess. As seen from Table 11, all the reactions are closer to second- than first-order, but neither of the ratios, $k_1/(RSSR)$ and $k_1/(RSSR)^2$, are a constant for any of the disulfides. This is in agreement with what we would expect from the suggested mechanism, where the rate expression has both a first- and a second-order term in disulfide.

2. General catalysis of the disulfide - sulfinic acid reaction by sulfur nucleophiles

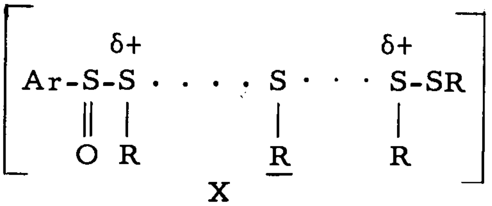
We would also expect other sulfur nucleophiles to be active in a displacement reaction on the divalent sulfur of the intermediate  $\mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}\overset{+}{\underset{\underset{R}{|}}{S}}{-}SR}$. Sulfides, being stronger nucleophiles than disulfides, should increase the over-all rate, contributing reaction 12d (page 115), and the term $k_sK_e(R'_2S)(RSSR)$ to the rate constant k_1 for the sulfide catalyzed reaction (Eq. 14). The catalysis by sulfides should therefore be proportional to the concentration of sulfide present, and the product k_sK_e should be a constant for a given disulfide - sulfide - sulfinic acid system at a given sulfuric acid concentration. When the initial sulfide concentration was varied for three such systems (Table 16), the value of k_sK_e was found to be constant in each of the three systems. This indicates that the catalysis by sulfides of the disulfide - sulfinic acid reaction through reaction 12d exhibits the proper dependence on sulfide concentration. These results and the experiment with benzyl sulfide as a catalyst also suggest that, as expected, such catalysis is general for sufficiently nucleophilic sulfides.

3. Inductive effects of the alkyl groups of the sulfur nucleophile

The rate of reaction 12c (page 101) is expected to be strongly influenced by the nature of the alkyl groups of the disulfide.

Similarly, the rate of reaction 12d (page 115) is expected to be influenced by the nature of the alkyl groups of both the sulfide and the disulfide.

The alkyl groups of the disulfide will, however, also influence the initial equilibrium 12a, and this effect can unfortunately not be separated from that on the rate-determining step 12c. The product k_cK_e which we have measured, expresses the relative stability of the transition state of reaction 12c:

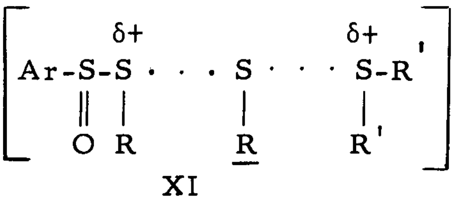


$$\left[\mathrm{Ar{-}\underset{\| \atop O}{S}{-}\overset{\delta+}{\underset{| \atop R}{S}}\cdots\underset{| \atop \underline{R}}{S}\cdots\overset{\delta+}{\underset{| \atop R}{S}}{-}SR}\right]$$

X

to that of the disulfide, RSSR. This is partly determined by the ability of the sulfur atoms of the disulfide to accommodate a positive charge. Electron donating alkyl groups will stabilize such a positive charge, whereas electron withdrawing alkyl groups are expected to destabilize a positive charge on the sulfur atoms. This effect is indicated by the very low k_cK_e values for dithiodipropionic acid and dithiodiacetic acid (Table 15). The higher value of k_cK_e for p-tolyl disulfide than for phenyl disulfide also indicates the importance of inductive effects.

The product k_sK_e, of the rate constant for the sulfide catalyzed decomposition of intermediate IX (Eq. 12d, page 115) and the equilibrium constant for reaction 12a (page 101) is influenced by the nature of the alkyl groups of both sulfide and disulfide. In this case we can eliminate the effect of the disulfide structure on the initial equilibrium by measuring k_sK_e for different sulfides but using the same disulfide. In such a case the k_sK_e values will be a measure of the nucleophilicity of the sulfides. The transition state for reaction 12d can be illustrated as:



$$\left[\mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}\overset{\delta+}{\underset{\underset{R}{|}}{S}}\cdots\underset{\underset{\underline{R}}{|}}{S}\cdots\overset{\delta+}{\underset{\underset{R'}{|}}{S}}{-}R'}\right]$$

XI

For a given disulfide the energy difference between transition state XI and the sulfide R'_2S will determine the rate of the sulfide catalyzed reaction. Sulfides with electron-donating alkyl groups, should be more reactive because they will be better able to stabilize the partial positive charge which develops on the sulfide sulfur in the transition state of 12d. In agreement with this, Table 17 shows that n-butyl sulfide has a much higher k_sK_e value than phenyl sulfide for each of the five disulfides studied, and also in the one case where its behaviour was examined, benzyl sulfide has, as expected, a k_sK_e value intermediate between the other two sulfides.

4. Steric effects of the alkyl groups of the disulfide

Experiments by Fava and Iliceto (16) with exchange reactions between alkyl thiosulfates and isotope-labelled sulfite:

$$R\text{-}S\text{-}SO_3^- + \overset{*}{S}O_3^= \rightarrow R\text{-}S\text{-}\overset{*}{S}O_3^- + SO_3^= \qquad (S^* = S^{35})$$

have shown the importance of the steric requirements of the alkyl groups R- in determining the rates of nucleophilic displacement on the divalent sulfur. Thus the relative rates of the exchange reaction for different alkyl groups are: Me, 100; Et, 50; i-Pr, 0.7; t-Bu, 0.0006. This series shows a remarkable similarity to the relative rates for S_N2 substitutions in the series RCH_2X; increased steric requirements of the substituents R cause a drastic decrease in the reaction rate. We would expect that the rates of reactions 12c and 12d would be similarly sensitive to the steric requirements of the alkyl group of the disulfide.

Whereas the influence of the steric requirements of the different alkyl groups of the thiosulfates could be measured directly, this is unfortunately not the case either for the disulfide catalyzed reaction 12c, or for the sulfide catalyzed reaction 12d.

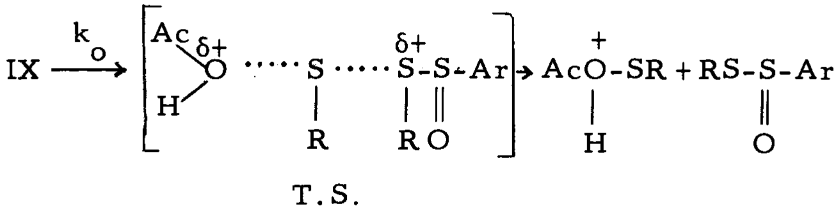
If we first consider the sulfide catalyzed reaction, we may vary the R groups of the disulfide without changing the attacking nucleophile. Thus, except for the fact that in XI the R group in the leaving group $\mathrm{ArS(O)}\overset{+}{\underset{\substack{| \\ \mathrm{R}}}{\mathrm{S}}}\text{-}$ is also going to vary as we vary disulfide, we have otherwise a system in which the variation of k_sK_e with disulfide for a given sulfide would measure the steric effect of changing R on the rate of 12d. Provided we confine ourselves to a series of disulfides in which the inductive effect of R remains fairly constant, we can hope that the influence of the R fragment in the leaving group will be relatively small, and in such a series the value of k_sK_e for a given sulfide with the different disulfides would presumably give a good indication of the steric influence of the disulfide R group on the rate of reaction 12d. Table 19 shows that the rate pattern expected from Fava and Iliceto's work (16), methyl > ethyl $\cong$ *n*-butyl $\gg$ isopropyl, is indeed observed for the k_sK_e values for both *n*-butyl and phenyl sulfide reacting with the series, methyl, *n*-butyl and isopropyl disulfide. The variation in k_sK_e with disulfide is somewhat larger for *n*-butyl sulfide than for phenyl sulfide. This might indicate a larger sensitivity to steric effects of disulfide R groups for *n*-butyl sulfide than for phenyl sulfide.

The situation in reaction 12c is much more complicated, since the attacking nucleophile is the disulfide, RSSR, itself. In transition state X, all the four R groups are therefore changed when one changes disulfide. The variation in the k_cK_e values for the same set of disulfides (Table 15) is therefore only indicative of such steric requirements of the disulfide R groups. The k_cK_e value for methyl disulfide is about four times larger than those for ethyl and n-butyl disulfide, and about 100 times larger than the k_cK_e value for isopropyl disulfide. In this series it must be remembered that the steric requirements of the attacking nucleophile are also changing as the disulfide is changed and this will have an effect on the relative energies of transition state X and the disulfide RSSR. The results are, however, also in accord with what we would expect from Fava and Iliceto's work (16) on the steric influence of alkyl groups on displacement rates at an adjacent divalent sulfur.

The four expected features of the mechanism of the disulfide - sulfinic acid reaction thus appear to be substantiated by our experiments, and the mechanism in Chart 3 can be considered general for all disulfides.

5. Other features of the disulfide - sulfinic acid reaction shown by the kinetic experiments

Table 15 gives the ratio k_o/k_c, between the rate constant for unimolecular decomposition of intermediate IX (Eq. 12b) and the rate constant for nucleophilic attack by disulfide on intermediate IX, (Eq. 12c). In the unimolecular decomposition for n-butyl disulfide the ion n-BuS$^+$ would be formed, whereas for n-butyl p-tolyl disulfide the ion ArS$^+$ would be formed. The p-tolyl sulfenium ion, ArS$^+$, has several possibilities for resonance stabilization which are not available for the ion n-BuS$^+$. We would therefore expect the unimolecular decomposition of intermediate IX to be much more important for n-butyl p-tolyl disulfide than for n-butyl disulfide. Table 15 shows, however, not too dissimilar k_o/k_c values for the two disulfides, 0.009 for n-butyl disulfide and 0.024 for n-butyl p-tolyl disulfide. This small a difference suggests that formation of a free sulfenium ion need not be involved in reaction 12b. Instead one may have a solvolysis of ion IX in which a solvent molecule interacts strongly as a nucleophile with the sulfur atom in question in the transition state (see Eq. 15) and thereby bears most of the positive charge.

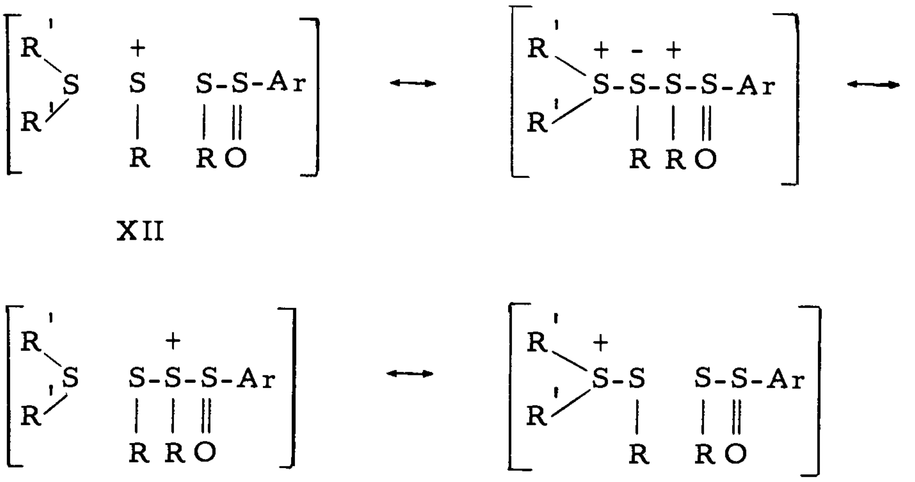


(Eq. 15)

Previous study of solvolysis reactions has revealed a large number of examples of such nucleophilic assistance by solvent (12). The solvolysis of benzylic and primary alkyl tosylates (63, p. 647) seems to be a particularly relevant example since the steric shielding of the reaction site should be similar to that in the present reaction.

Contrary to what one might first think, such nucleophilic assistance by solvent in transition state for the rate-determining step need not lead to any noticeable dependence of k_o/k_c on the acidity of the medium, even though one solvent molecule is involved in transition state of reaction 15. From what is known from Bunnett's work k_oK_e could easily show a very similar dependence on acidity to k_cK_e (12, p. 4970).

Although n-butyl sulfide is always a much more powerful catalyst for the disulfide - sulfinic acid reaction than phenyl sulfide, the ratio (k_s^{Bu}/k_s^{Ph}) shows a distinct variation with disulfide (Table 19). The ratio between the catalytic effect of n-butyl sulfide and phenyl sulfide (k_s^{Bu}/k_s^{Ph}) is 700 for methyl disulfide, about 250 for n-butyl and benzyl disulfide, 200 for isopropyl disulfide and only 45 for phenyl disulfide. Perhaps part of the explanation for these results might reside in steric effects, since the ratio (k_s^{Bu}/k_s^{Ph}) is largest for methyl disulfide, about half that value for n-butyl and benzyl disulfide and somewhat smaller for isopropyl disulfide. However, the much lower value of 45 for (k_s^{Bu}/k_s^{Ph}) which is found for phenyl disulfide, could hardly be explained by steric effects alone. We therefore suggest, that while there might be some steric hindrance by bulky alkyl groups on the disulfide to the approach of the sulfide (reaction 12d), and that this might be more serious for the n-butyl sulfide-catalyzed reaction than for the phenyl sulfide-catalyzed one, another important factor may be that the amount of positive charge on the sulfide-sulfur in transition state of reaction 12d varies somewhat with the disulfide involved. The various resonance structures of this transition state can be shown as:



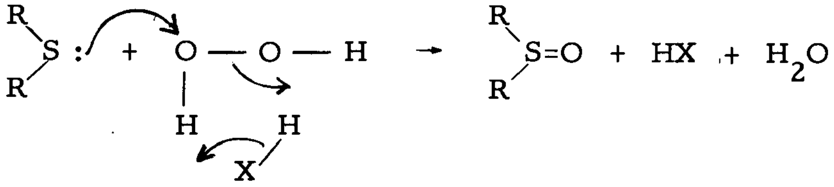
XII

We would certainly expect structure XII to be a more important contributor for aryl disulfides, since the positive charge of the sulfenium ion RS^+ can be delocalized into the aromatic ring. If so, there will be less total positive charge on the sulfur of R'_2S in the transition state for the phenyl disulfide reactions than for those cases involving alkyl disulfides, and k_s will be less sensitive to sulfide nucleophilicity.

As an analogy we might mention bimolecular nucleophilic displacements on benzyl chloride where the resonance structure $(N^- \; PhCH_2^+ \; Cl^-)$ is relatively important, since the positive charge can be delocalized into the benzene ring, whereas for S_N2

displacements on n-alkyl chlorides similar resonance structures are of very little importance. Until more experimental data are available, further speculation about this point seems premature.

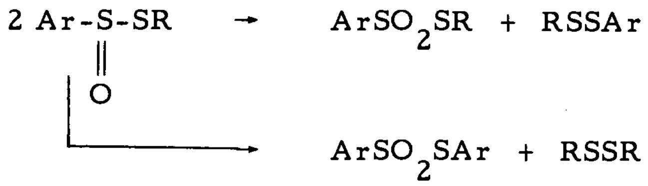
The relatively high value of (k_s^{Bu}/k_s^{Ph}), above 200 for three of the disulfides, suggests a very high sensitivity of reaction 12d to the nucleophilicity of the sulfide. For example, this value may be compared with the ratio of the oxidation rates of the two sulfides by aqueous hydrogen peroxide, the reaction being:



The ratio between the oxidation rate of n-butyl sulfide and phenyl sulfide was found to be only 50 (44, p. 1310).

6. Further reactions of the thiolsulfinate ArS(O)SR

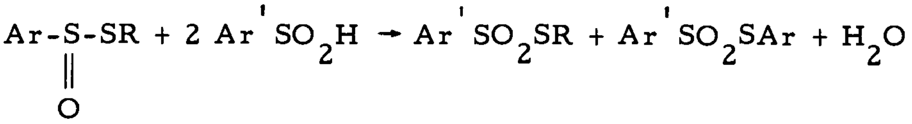
In the various disulfide - sulfinic acid reactions, there are thus three kinetically important steps from which thiolsulfinates are produced (Eq. 12b, 12c, and 12d). As we mentioned before (page 96) thiolsulfinates have been observed to disproportionate in two ways (3):



$$2\ \text{Ar-}\underset{\underset{\text{O}}{\|}}{\text{S}}\text{-SR} \rightarrow \text{ArSO}_2\text{SR} + \text{RSSAr}$$

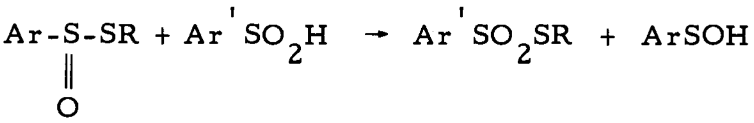
$$\rightarrow \text{ArSO}_2\text{SAr} + \text{RSSR}$$

We originally assumed these reactions to be dominant in our system, and indeed, the final reaction products can all be explained perfectly well on this basis. However, some recent experiments by Venier* have shown that an acid-catalyzed reaction between p-toluenesulfinic acid and thiolsulfinates is actually much faster than the disproportionation of the latter in our sulfuric acid - water - acetic acid system. This reaction can be shown as:



$$\text{Ar-}\underset{\underset{\text{O}}{\|}}{\text{S}}\text{-SR} + 2\ \text{Ar}'\text{SO}_2\text{H} \rightarrow \text{Ar}'\text{SO}_2\text{SR} + \text{Ar}'\text{SO}_2\text{SAr} + \text{H}_2\text{O}$$

Further studies of this reaction* have indicated initial formation of sulfenic acid, according to the equation:



$$\text{Ar-}\underset{\underset{\text{O}}{\|}}{\text{S}}\text{-SR} + \text{Ar}'\text{SO}_2\text{H} \rightarrow \text{Ar}'\text{SO}_2\text{SR} + \text{ArSOH}$$

The sulfenic acid will usually react further with sulfinic acid to form thiolsulfonate and water, but in presence of disulfide, the following acid catalyzed reaction could take place:

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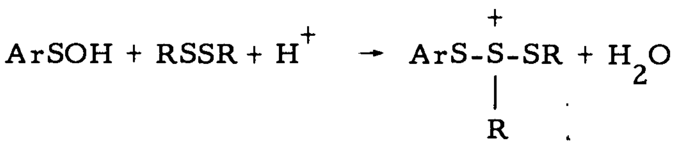
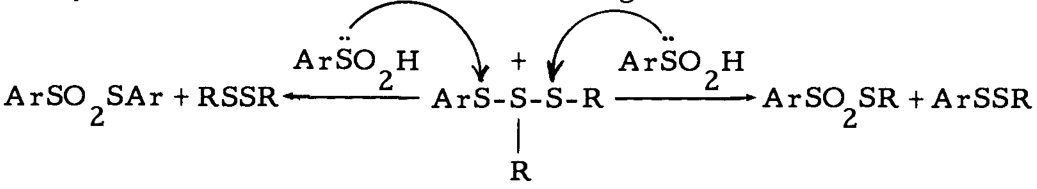
* Unpublished observations by Mr. C. G. Venier.



$$\mathrm{ArSOH + RSSR + H^+ \rightarrow ArS\text{-}\underset{\substack{|\\ R}}{\overset{+}{S}}\text{-}SR + H_2O}$$

XIII

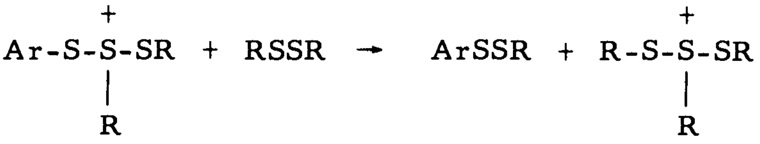
Either of the divalent sulfur atoms in intermediate XIII can be further attacked by sulfinic acid, the reactions being:



$$\mathrm{ArSO_2SAr + RSSR \xleftarrow{Ar\ddot{S}O_2H} ArS\text{-}\underset{\substack{|\\ R}}{\overset{+}{S}}\text{-}S\text{-}R \xrightarrow{Ar\ddot{S}O_2H} ArSO_2SR + ArSSR}$$

XIII

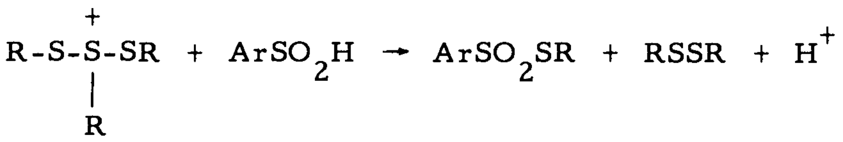
Or, the intermediate XIII may undergo exchange with disulfide:



$$\mathrm{Ar\text{-}S\text{-}\underset{\substack{|\\ R}}{\overset{+}{S}}\text{-}SR + RSSR \rightarrow ArSSR + R\text{-}S\text{-}\underset{\substack{|\\ R}}{\overset{+}{S}}\text{-}SR}$$

XIII XIV

Reaction of intermediate XIV with sulfinic acid will produce mixed thiolsulfonate and reform the original symmetric disulfide:



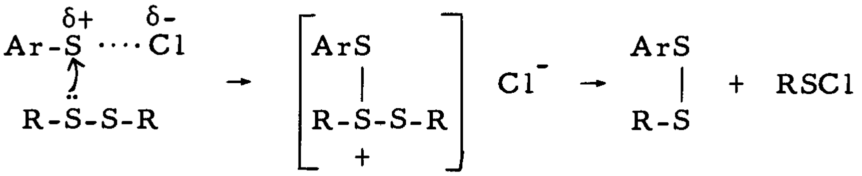
$$\mathrm{R\text{-}S\text{-}\underset{\substack{|\\ R}}{\overset{+}{S}}\text{-}SR + ArSO_2H \rightarrow ArSO_2SR + RSSR + H^+}$$

XIV

7. General importance of the disulfide - sulfinic acid reaction

The disulfide - sulfinic acid reaction is of importance for our general understanding of disulfide reactions. Although divalent sulfur atoms are very easily subject to nucleophilic attack, disulfides are generally quite stable compounds, since simple nucleophilic cleavage of the disulfide bond would involve RS- as a leaving group, and in the absence of special stabilizing features in R this is a quite poor leaving group.

The first important feature of the disulfide - sulfinic acid reaction is conversion of the poor leaving group RS- in the disulfide to a good leaving group $\text{Ar-}\underset{O}{\overset{\|}{S}}\text{-}\overset{+}{\underset{R}{S}}\text{-}$ through electrophilic attack on the disulfide by the sulfinium ion, $\overset{+}{ArSO}$. There are other known examples of such electrophilic catalysis of cleavage of disulfides. For instance, Moore and Porter (45) have reported exchange of arenesulfenyl halides with disulfides, the latter being attacked by the polarized arenesulfenyl halide:

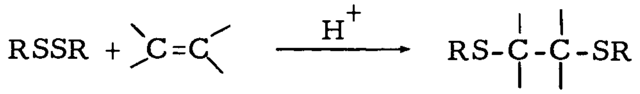


$$\begin{array}{c}\overset{\delta+}{\text{Ar-S}}\cdots\overset{\delta-}{\text{Cl}}\\ \uparrow\\ \text{R-}\ddot{\text{S}}\text{-S-R}\end{array} \rightarrow \left[\begin{array}{c}\text{ArS}\\ |\\ \text{R-S-S-R}\\ +\end{array}\right]\text{Cl}^- \rightarrow \begin{array}{c}\text{ArS}\\ |\\ \text{R-S}\end{array} + \text{RSCl}$$

The observed disulfide exchange in hydrochloric or sulfuric acid (52, p. 591) is an example of proton catalysis of the heterolytic cleavage of disulfides:

$$2\ RSSR' \overset{H^+}{\rightleftharpoons} RSSR + R'SSR'$$

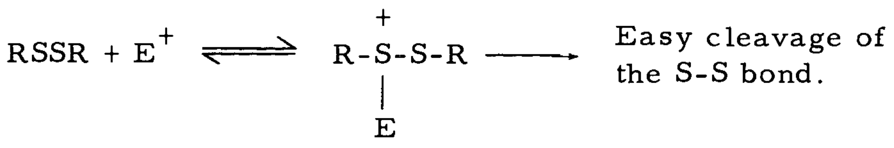
Parker and Kharasch (52, p. 590) have also described an acid catalyzed reaction between olefins and disulfides:



$$\mathrm{RSSR} + \mathrm{{>}C{=}C{<}} \xrightarrow{H^+} \mathrm{RS{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}SR}$$

In this case the catalyzing electrophile is the carbonium ion formed by protonation of the olefin.

From these examples we might expect the heterolytic cleavage of disulfides to be catalyzed generally by electrophiles, E^+, the reaction being:



$$\mathrm{RSSR} + E^+ \rightleftharpoons \mathrm{R{-}\overset{+}{\underset{\underset{E}{|}}{S}}{-}S{-}R} \longrightarrow \text{Easy cleavage of the S-S bond.}$$

XV

The truly important new feature of the disulfide - sulfinic acid reaction is the following: The disulfide, activated by addition of an electrophile, has previously always been considered to decompose unimolecularly into RSE and the sulfenium ion, RS^+. For the disulfide - sulfinic acid reaction, however, we observed nucleophilic attack on the intermediate $\mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}\overset{+}{\underset{\underset{R}{|}}{S}}{-}SR}$ (IX) by sulfur nucleophiles (sulfides and disulfides) leading to the displacement of the group $\mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}\overset{+}{\underset{\underset{R}{|}}{S}}{-}}$. Moreover, for almost all the disulfides this bimolecular decomposition of intermediate IX was found to be the main reaction route of the intermediate, and its unimolecular decomposition was of minor importance. This result also implies that other sulfur - sulfur bond cleavage reactions which are catalyzed by electrophiles E^+ are not unimolecular decompositions as previously assumed. Careful kinetic studies of reactions involving disulfide cleavage could establish such catalysis by nucleophiles.

We also think the nucleophilic catalysis of the further reaction of intermediate IX as observed in the disulfide - sulfinic acid reaction has considerable potential practical value for other reactions involving sulfur - sulfur bond cleavage. Thus, sulfides, being stronger nucleophiles than disulfides, accelerated the reaction rate greatly when added in small amounts to the reaction mixture. This feature suggests therefore that strong nucleophiles in general should be active as catalysts for this and other reactions of this type, promising great synthetic possibilities of reactions involving cleavage of disulfides.

EXPERIMENTAL

1. Purification of Commercial Disulfides

The liquid disulfides were fractionally distilled, and the same apparatus as described earlier (Part I, page 50) was used. The crystalline disulfides were recrystallized as indicated in each case.

Methyl Disulfide (Eastman Organic Chemicals, reagent grade). B.p. 109° (760 mm.). Literature value (65), b.p 109.5° (774 mm.).

Ethyl Disulfide (Eastman Organic Chemicals, reagent grade). B p. 152° (760 mm.). Literature value (65), B.p. 152° (754 mm.).

n-Butyl Disulfide (Eastman Organic Chemicals, reagent grade). B.p. 110° (14 mm.). Literature value (65), b.p. 84° (3 mm.).

Benzyl Disulfide (Aldrich Chemical Co., Inc., reagent grade), was recrystallized three times from 100% ethanol, m.p. 71-72°. Literature value (5, p. 914), m.p. 74°.

Dithiodiacetic Acid was prepared by acid hydrolysis of the diethyl ester. The diethyl ester (12.67 g., 0.053 mole) was dissolved in 3 N hydrochloric acid (127 ml.) and refluxed for 30 minutes. After cooling, the product was extracted with ether (3 x 60 ml.). The combined ether extracts were washed with water (2 x 15 ml.) and dried over anhydrous sodium sulfate. The residue was recrystallized once from ether/benzene giving 3.2 g. (33%) of dithiodiacetic acid, m.p. 108-109°. Literature value (46), m.p. 106-107°.

Dithiodipropionic Acid (Wateree Chemical Company) was recrystallized from hot water, m.p. 155-156°. Literature value (57, p. 125), m.p. 157.5°.

Isopropyl Disulfide (Aldrich Chemical Company, Inc., reagent grade). The disulfide was contaminated with an impurity which could not be removed by the usual fractional distillation. The distillate, b.p. 174-174.5° (760 mm.), (literature value (65), b.p. 176° (767 mm.)), was therefore subjected to preparative gas liquid chromatography.

n-Butyl p-Tolyl Disulfide was prepared as previously described (Part I, page 84).

Phenyl Disulfide (Aldrich Chemical Company, Inc., reagent grade) was recrystallized from 100% ethanol. M.p. 61-61.5°. Literature value (62), m.p. 61.5°.

The procedures for purification of the four sulfides _n_-butyl sulfide, benzyl sulfide, isopropyl sulfide and phenyl sulfide, have been described previously (Part I, pp. 51, 52).

2. _p_-Toluenesulfinic Acid

The preparation of this acid is described in Part I, page 60 .

3. Stock Solutions

The solutions used for the kinetic experiments and the product studies were 0.56 _M_ water - acetic acid with various amounts of sulfuric acid added. The purification of glacial acetic acid is described in Part I, page 61, and the preparation of stock solutions in Part I, page 61.

4. Preparations of Disulfides

a) _n_-Butyl _p_-Tolyl Disulfide

This disulfide was prepared from _n_-butyl mercaptan and _p_-toluenesulfinic acid as described in Part I, page 84.

b) Preparation of Isopropyl _p_-Tolyl Disulfide*

Isopropyl mercaptan (6.8 g., 90 mmoles) was dissolved in an

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* This preparation was carried out by Mr. Gary Bray.

equal volume of acetic acid and added rapidly to a well-stirred solution of p-toluenesulfinic acid (4.67 g., 30 mmoles) in 300 ml. of 0.56 M water - acetic acid - 0.6 M sulfuric acid at 60°. The solution was poured into water after three minutes and extracted with ether. The ether extract was washed with aqueous bicarbonate until neutral and dried over sodium sulfate. The residue, after removal of the ether, was fractionally distilled. The first fraction (3.5 g.) boiled at 23° (0.6 mm.) and was shown to be isopropyl disulfide. The second main fraction (4.1 g.), b.p. 93-94° (0.1 mm.), n_D^{25}: 1.5738, was shown by nuclear magnetic resonance and infrared spectra to be isopropyl p-tolyl disulfide.

Analysis: Calculated for $C_{10}H_{14}S_2$: C, 60.50; H, 7.12; Mol. wt., 198. Found: C, 60.60; H, 7.12; Mol. wt. (osmometric in $CHCl_3$), 195.

c) Preparation of Benzyl p-Tolyl Disulfide *

Benzyl mercaptan was reacted with p-toluenesulfinic acid using exactly the same procedure as described for isopropyl p-tolyl disulfide, but at 70°. The product was poured into water and was worked up in the same way as before. Fractional crystallization of the residue gave two main fractions, benzyl disulfide, m.p. 72°, and

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* This preparation was carried out by Mr. Gary Bray.

benzyl p-tolyl disulfide (30% yield), m.p. 34-35°. The latter had infrared and nuclear magnetic resonance spectra consistent with the assigned structure.

Analysis: Calculated for $C_{14}H_{14}S_2$: C, 68.24; H, 5.72; Mol. wt., 246. Found: C, 68.68; H, 5.77; Mol. wt. (osmometric in $CHCl_3$), 248.

5. Preparations of Thiolsulfonates

a) n-Butyl p-Toluenethiolsulfonate

Preparation of this compound is described in Part I, page 80.

b) Isopropyl p-Toluenethiolsulfonate

This compound was prepared from p-tolyl disulfide and p-toluenesulfinic acid as described in Part I, page 82.

c) Methyl p-Toluenethiolsulfonate

A method for preparation of this compound has been described by Gibson (24).

d) Benzyl p-Toluenethiolsulfonate

Loudon and Livingston (38) have described a method for preparation of this compound.

e) Preparation of *p*-Tolyl *p*-Toluenethiolsulfonate

p-Toluenesulfinic acid (2.34 g., 15 mmoles) was dissolved in 75 ml. of glacial acetic acid and heated at 70° (nitrogen atmosphere) for one-and-a-half hours. The product was poured into one liter of water and extracted with ether (3 x 250 ml.). The combined ether extracts were washed with saturated sodium bicarbonate solution until neutral, with water (2 x 35 ml.), and were finally dried over anhydrous sodium sulfate. The residue after evaporation of the ether, was recrystallized from ethanol-water, giving 940 mg. (3.38 mmoles, 68%) of *p*-tolyl *p*-toluenethiolsulfonate, m.p. 76-77°. Literature value (33), m.p. 76°.

6. Procedures for the Product Studies

a) The Disulfide - Sulfinic Acid Reactions

The disulfide and the sulfinic acid were dissolved separately in some of the acetic acid - water - sulfuric acid solution (Table 9). The two solutions were combined in a volumetric flask, made up to volume with the same solvent and rapidly transferred to the reaction vessel. This apparatus has been described previously (Part I, page 64, and Figure 4). After deaeration at room temperature for five minutes, the reaction vessel was placed in the constant temperature bath. At the end of the reaction time, the product was poured into ten times its volume of water and extracted three times with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution until neutral, twice with water and then dried over anhydrous sodium sulfate. The ether was carefully distilled off through a Vigreux column. The residue was chromatographed on about 30 times its weight of alumina (Merck, acid washed) and separated into two main fractions. The disulfides were eluted with *n*-hexane, and the thiolsulfonates with 25 - 50 (vol)% benzene in *n*-hexane, the solvent depending on the alkyl group of the mixed thiolsulfonate, $ArSO_2SR$. The two fractions were analysed by measuring the areas under certain peaks of the nuclear magnetic resonance spectra. Details of this technique are described in Part I, page 69. Table 28 (Appendix 2) lists the τ-values of the characteristic peaks that were used for analysing the products from benzyl disulfide and *p*-toluenesulfinic acid. The mixture of benzyl disulfide and *p*-tolyl disulfide shows a singlet at 6.17 τ (methylene protons in benzyl *p*-tolyl disulfide), another singlet at 6.52 τ (methylene protons in benzyl disulfide), and finally a singlet at 7.68 τ (methyl protons of benzyl *p*-tolyl disulfide). Comparison of the areas at 6.52 τ and 7.68 τ will thus give the relative amounts of benzyl disulfide and benzyl *p*-tolyl disulfide.

The mixture of benzyl *p*-toluenethiolsulfonate and *p*-tolyl p-toluenethiolsulfonate was analysed by comparing the combined areas of the two singlets at 7.58 and 7.62 τ (methyl protons of the p-tolyl sulfone group and methyl protons of the p-tolyl sulfide group, respectively), and the area of the singlet at 5.76 τ (methylene protons of the benzyl group).

The mixture of isopropyl disulfide and p-tolyl isopropyl disulfide was analysed using the relative areas of the doublet at 8.72 τ (methyl protons of the isopropyl group) and the singlet at 7.68 τ (methyl protons of the p-tolyl group).

The selected peaks used in the analysis of the three mixtures: Isopropyl p-toluenethiolsulfonate and p-tolyl p-toluenethiolsulfonate; n-butyl p-toluenethiolsulfonate and p-tolyl p-toluenethiolsulfonate; and n-butyl p-tolyl disulfide and n-butyl disulfide are listed in Table 25, Appendix 1.

The mixture of methyl p-toluenethiolsulfonate and p-tolyl p-toluenethiolsulfonate could not be analysed by the same method because of overlap of all the methyl proton absorptions. The mixture could, however, be separated by careful chromatography on alumina. The p-tolyl p-toluenethiolsulfonate, m.p. 76-77°, was eluted with 25(vol)% of benzene in n-hexane whereas the methyl p-toluenethiolsulfonate, m.p. 58°, was somewhat more strongly adsorbed to the column and was eluted with 50 (vol) % of benzene in n-hexane. Fractions of ten milliliters were collected, evaporated, and a melting point was taken of each of the fractions. Fractions with identical melting points were combined, and the two products were weighed.

b) Reactions between Disulfides and p-Tolyl p-Toluenethiolsulfonate

For these experiments, P 15 - P 17 (Table 10), exactly the same procedure was used as for the product studies of the disulfide - sulfinic acid reactions. For each disulfide the same reaction conditions, and reaction time, were used as before, only substituting p-tolyl p-toluenethiolsulfonate for the sulfinic acid. The products were also worked up in the usual way, separating the methyl p-toluenethiolsulfonate and p-tolyl p-toluenethiolsulfonate by careful chromatography, but analysing the other thiolsulfonate mixtures by their nuclear magnetic resonance spectra.

7. Procedures for the Kinetic Experiments

a) The Disulfide - Sulfinic Acid Reactions

The procedure for these experiments was exactly the same as for the sulfide - sulfinic acid reactions (Part I, page 62). The reaction vessel is shown in Figure 4, page 63, and the operation of it is described on page 64. The samples were analysed for their sulfinic acid content by titration with 0.2 N sodium nitrite as previously described. The results from these experiments are listed in Table 26, Appendix 2.

In most of the experiments the disulfide - sulfinic acid reaction was much faster than the disproportionation of p-toluenesulfinic acid. Thus, by plotting log $(ArSO_2H)$ versus time, the first-order rate constant, k_{exp}, was found as the slope of the line. Subtraction from k_{exp} of the small contribution from the disproportionation of the sulfinic acid, $k_2(ArSO_2H)_{average}$, gave k_1, the pseudo first-order rate constant for the disulfide - sulfinic acid reaction.

In some cases, however, the rates of the two reactions were of the same order of magnitude, and the method outlined by Frost and Pearson (21, p. 165) was used for calculating k_1. This method is illustrated for experiment 56, the reaction of dithiodipropionic acid with p-toluenesulfinic acid. The sulfinic acid concentration is plotted versus time (Curve 23 in Figure 12, Appendix 2), and the tangent to the curve is found at different points along the curve, giving the values of $-(d\,(ArSO_2H)/dt) = \lambda$ at known times and sulfinic acid concentrations. Table 29 shows the data obtained. When $\lambda/(ArSO_2H)$ is plotted versus $(ArSO_2H)$, (Curve 24 in Figure 13, Appendix 2) a straight line is obtained, giving the first-order rate constant k_1 as the intercept with the ordinate axis at $(ArSO_2H) = 0$, and k_2 as the slope of the curve. The observed value of $k_2 = 1.3 \times 10^{-3}\ \underline{M}^{-1}\,\text{sec.}^{-1}$ is in agreement with previous results (33).

b) The Sulfide Catalyzed Reactions between Disulfides and p-Toluenesulfinic Acid

When phenyl and benzyl sulfide were used as catalysts, the disulfide, sulfinic acid and the sulfide were dissolved separately in some of the solvent (Table 27). The disulfide and sulfinic acid were combined in a volumetric flask, the sulfide was added, and the solution was rapidly made up to volume. The solution was transferred to the reaction vessel (Figure 4, page 63) and from here on the procedure was the same as described for the sulfide - sulfinic acid reactions.

In the experiments where n-butyl and isopropyl sulfide were used as catalysts, the disulfide and sulfinic acid were dissolved and transferred to the modified reaction vessel (Figure 5, page 66). The sulfide was weighed into a small glass bucket and suspended above the solution in the reaction vessel. After deaeration at room temperature, and heating at 70° for three minutes, the glass bucket was dropped into the solution which was shaken vigourously. The further procedure was the same as usual. The calculations of the first-order rate constants have also been described (page 149).

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APPENDICES

APPENDIX 1

TABLE 20

DISPROPORTIONATION OF p-TOLUENESULFINIC ACID

Temperature: 70°.

Solvent: 0.6 M sulfuric acid - 0.56 M water - acetic acid.

$(ArSO_2H)_o$: 0.05 M (Ar = p-CH_3-C_6H_4-).

Time, min.	$(ArSO_2H)$, M	$1/(ArSO_2H)$, M^{-1}
0	0.0478	20.9
30	0.0421	23.8
60	0.0390	25.6
180	0.0310	32.3
240	0.0255	39.2
330	0.0216	46.3
420	0.0185_5	54.0

$k_2 = 1.31 \times 10^{-3}\ M^{-1}\ sec.^{-1}$

TABLE 21

RATES OF REACTIONS BETWEEN PRIMARY ALKYL SULFIDES AND p-TOLUENESULFINIC ACID

Temperature: 70°. Solvent: 0.6 M sulfuric acid - 0.56 M water - acetic acid. $(ArSO_2H)_o$ = 0.05 M (Ar = p-CH_3-C_6H_4-).

Run 1		Run 2	
0.1 M $PhCH_2SCH_2Ph$		0.1 M $PhCH_2SCH_2Ph$	
Time, min.	$(ArSO_2H)$, M	Time, min.	$(ArSO_2H)$, M
0	0.0471	0	0.0464
10	0.0344	10	0.0375
20	0.0272	20	0.0291
30	0.0216	30	0.0229
40	0.0172	45	0.0159
60	0.0115	60	0.0117
		210	0.0010

k_{exp} = 3.88 x 10^{-4} $sec.^{-1}$

k_1 = 3.58 x 10^{-4} $sec.^{-1}$

k_s = 3.58 x 10^{-3} M^{-1} $sec.^{-1}$

Run 3

0.1 M $PhCD_2SCD_2Ph$

Time, min.	$(ArSO_2H)$, M
0	0.0487
15	0.0436
45	0.0337
75	0.0272
120	0.0190
165	0.0143
210	0.0108
270	0.0074

Run 4

0.1 M $PhCD_2SCD_2Ph$

Time, min.	$(ArSO_2H)$, M
0	0.0470
24	0.0389
54	0.0314
90	0.0234
132	0.0178
174	0.0137
216	0.0106
264	0.0081

$k_1^* = 0.836 \times 10^{-4}$ sec.$^{-1}$

$k_s = 0.836 \times 10^{-3}$ M^{-1} sec.$^{-1}$

* Determined by the method outlined in (21, p. 165).

Run 5

0.1 M $(PhCH_2CH_2)_2S$

Time, min.	$(ArSO_2H)$, M
0	0.0456
10	0.0357
25	0.0250
35	0.0198
45	0.0155
55	0.0127
65	0.0103

$k_{exp} = 3.86 \times 10^{-4}$ sec.$^{-1}$

$k_1 = 3.54 \times 10^{-4}$ sec.$^{-1}$

$k_s = 3.54 \times 10^{-3}$ M^{-1} sec.$^{-1}$

Run 6

0.15 M $(PhCH_2CH_2)_2S$

Time, min.	$(ArSO_2H)$, M
0	0.0437
5	0.0371
10	0.0308
15	0.0264
20	0.0216
25	0.0183
30	0.0153

$k_{exp} = 5.79 \times 10^{-4}$ sec.$^{-1}$

$k_1 = 5.36 \times 10^{-4}$ sec.$^{-1}$

$k_s = 3.57 \times 10^{-3}$ M^{-1} sec.$^{-1}$

Run 7

0.1 $\underline{M}$ $(HOOC\text{-}CH_2)_2S$

Time, min.	$(ArSO_2H)$, $\underline{M}$	$1/(ArSO_2H)$ $\underline{M}^{-1}$
0	0.0476	21.00
15	0.0460	21.75
30	0.0438	22.85
90	0.0367	27.25
180	0.0291	34.50
300	0.0226	44.30
420	0.0178	56.10

k_1 too small to measure

k_2 1.35×10^{-3} $\underline{M}^{-1}$ sec.$^{-1}$

Run 8

0.1 $\underline{M}$ $(HOOC\text{-}CH_2CH_2)_2S$

Time, min.	$(ArSO_2H)$, $\underline{M}$	$1/(ArSO_2H)$ $\underline{M}^{-1}$
0	0.0476	21.00
20	0.0430	23.25
60	0.0375	26.60
150	0.0282	35.40
240	0.0220	45.50
330	0.0173	57.60
420	0.0139	72.00

$k_1^* = 0.12 \times 10^{-4}$ sec.$^{-1}$

$k_s = 0.12 \times 10^{-3}$ $\underline{M}^{-1}$ sec.$^{-1}$

Run 9

0.1 $\underline{M}$ EtSEt

Time, min.	$(ArSO_2H)$, $\underline{M}$
0	0.0416
5	0.0325
10	0.0238
15	0.0171
20	0.0121
25	0.0093
30	0.0069

$k_{exp} = 1.04 \times 10^{-3}$ sec.$^{-1}$

$k_1 = 1.01 \times 10^{-3}$ sec.$^{-1}$

$k_s = 1.01 \times 10^{-2}$ $\underline{M}^{-1}$ sec.$^{-1}$

Run 10

0.15 $\underline{M}$ EtSEt

Time, min.	$(ArSO_2H)$, $\underline{M}$
0	0.0395
3	0.0314
6	0.0238
9	0.0181
12	0.0133
15	0.0097
18	0.0076

$k_{exp} = 1.57 \times 10^{-3}$ sec.$^{-1}$

$k_1 = 1.54 \times 10^{-3}$ sec.$^{-1}$

$k_s = 1.025 \times 10^{-2}$ $\underline{M}^{-1}$ sec.$^{-1}$

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* Determined by the method outlined in (21, p. 165).

Run 11

0.1 $\underline{M}$ $(CH_3(CH_2)_4)_2S$

Time, min.	$(ArSO_2H)$, $\underline{M}$
0	0.03915
5	0.02745
10	0.01735
15	0.01050
20	0.00666
25	0.00505
30	0.00282

$k_{exp} = 1.44 \times 10^{-3}$ sec.$^{-1}$

$k_1 = 1.42 \times 10^{-3}$ sec.$^{-1}$

$k_s = 1.42 \times 10^{-2}$ $\underline{M}^{-1}$ sec.$^{-1}$

Run 12

0.076 $\underline{M}$ $(CH_3(CH_2)_4)_2S$

Time, min.	$(ArSO_2H)$, $\underline{M}$
0	0.0418
5	0.0318
10	0.0222
15	0.0149
20	0.0101
25	0.0073
30	0.0052

$k_{exp} = 1.17 \times 10^{-3}$ sec.$^{-1}$

$k_1 = 1.15 \times 10^{-3}$ sec.$^{-1}$

$k_s = 1.51 \times 10^{-2}$ $\underline{M}^{-1}$ sec.$^{-1}$

Run 13

0.15 $\underline{M}$ $(PhOCH_2CH_2)_2S$

Time, min.	$(ArSO_2H)$, $\underline{M}$
0	0.0472
15	0.0430
60	0.0294
90	0.0214
120	0.0153
150	0.0109
180	0.0073

$k_{exp} = 1.15 \times 10^{-4}$ sec.$^{-1}$

$k_1 = 0.42 \times 10^{-4}$ sec.$^{-1}$

$k_s = 2.8 \times 10^{-4}$ $\underline{M}^{-1}$ sec.$^{-1}$

Run 14

0.15 $\underline{M}$ $(PhOCH_2CH_2)_2S$

Time, min.	$(ArSO_2H)$, $\underline{M}$
0	0.0472
10	0.0444
20	0.0420
30	0.0387
40	0.0351
50	0.0321
60	0.0296

$k_{exp(initial)} = 1.06 \times 10^{-4}$ sec.$^{-1}$

$k_1 = 0.47 \times 10^{-4}$ sec.$^{-1}$

$k_s = 0.3 \times 10^{-3}$ $\underline{M}^{-1}$ sec.$^{-1}$

Run 15

0.22 M $(PhOCH_2CH_2)_2S$

Time, min.	$(ArSO_2H)$, M
0	0.0469
10	0.0436
20	0.0412
30	0.0367
40	0.0335
50	0.0302
60	0.0270

$k_{exp(initial)} = 1.32 \times 10^{-4} sec.^{-1}$
$k_1 = 0.74 \times 10^{-4} sec.^{-1}$
$k_s = 0.33 \times 10^{-3} \underline{M}^{-1} sec.^{-1}$

Run 16

0.1 M $(Me_2CHCH_2)_2S$

Time, min.	$(ArSO_2H)$, M
0	0.0416
5	0.0322
10	0.0230
15	0.0179
20	0.0135
25	0.0104
30	0.0082

$k_{exp} = 9.26 \times 10^{-4} sec.^{-1}$
$k_1 = 9.03 \times 10^{-4} sec.^{-1}$
$k_s = 9.03 \times 10^{-3} \underline{M}^{-1} sec.^{-1}$

TABLE 22

RATES OF REACTIONS BETWEEN SECONDARY ALKYL SULFIDES AND p-TOLUENESULFINIC ACID

Temperature: 70°. Solvent: 0.6 M sulfuric acid - 0.56 M water - acetic acid. $(ArSO_2H)_o$: 0.05 M (Ar = p-CH_3-C_6H_4-).

Run 17

0.1 M $(Me_2CH)_2S$

Time, min.	$(ArSO_2H)$, M
0	0.0476
10	0.0404
20	0.0334
35	0.0254
50	0.0194
65	0.0147
85	0.0108

$k_{exp} = 2.93 \times 10^{-4}$ sec.$^{-1}$

$k_1 = 2.54 \times 10^{-4}$ sec.$^{-1}$

$k_s = 2.54 \times 10^{-3}$ $\underline{M}^{-1}$ sec.$^{-1}$

Run 18

0.15 M $(Me_2CH)_2S$

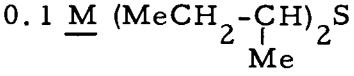
Time, min.	$(ArSO_2H)$, M
0	0.0452
10	0.0356
20	0.0272
30	0.0208
45	0.0140
60	0.0096
75	0.0067

$k_{exp} = 4.30 \times 10^{-4}$ sec.$^{-1}$

$k_1 = 3.90 \times 10^{-4}$ sec.$^{-1}$

$k_s = 2.60 \times 10^{-3}$ $\underline{M}^{-1}$ sec.$^{-1}$

Run 19


$0.1\ \underline{M}\ (\text{MeCH}_2\text{-}\underset{\text{Me}}{\underset{|}{\text{C}}}\text{H})_2\text{S}$

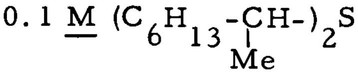
Time, min.	(ArSO_2H), $\underline{M}$
0	0.0452
10	0.0378
20	0.0308
35	0.0234
50	0.0176
65	0.0131
85	0.0101

$k_{exp} = 3.22 \times 10^{-4}\ \text{sec.}^{-1}$

$k_1 = 2.88 \times 10^{-4}\ \text{sec.}^{-1}$

$k_s = 2.88 \times 10^{-3}\ \underline{M}^{-1}\ \text{sec.}^{-1}$

Run 20


$0.1\ \underline{M}\ (\text{C}_6\text{H}_{13}\text{-}\underset{\text{Me}}{\underset{|}{\text{C}}}\text{H-})_2\text{S}$

Time, min.	(ArSO_2H), $\underline{M}$
0	0.0470
10	0.0398
25	0.0312
45	0.0220
60	0.0179
75	0.0139
90	0.0114

$k_{exp} = 2.72 \times 10^{-4}\ \text{sec.}^{-1}$

$k_1 = 2.42 \times 10^{-4}\ \text{sec.}^{-1}$

$k_s = 2.42 \times 10^{-3}\ \underline{M}^{-1}\ \text{sec.}^{-1}$

Run 21

$0.1\ \underline{M}\ (\text{Ph}_2\text{CH})_2\text{S}$

The reaction was complete in less than 20 minutes.

TABLE 23

RATES OF REACTIONS BETWEEN OTHER ALKYL SULFIDES AND p-TOLUENESULFINIC ACID

Temperature: 70°. Solvent: 0.6 M sulfuric acid - 0.56 M water - acetic acid. $(ArSO_2H)_o$: 0.05 M (Ar = p-CH_3-C_6H_4-).

Run 22

0.2 M $PhCH_2SPh$

Time, min.	$(ArSO_2H)$, M
0	0.0480
15	0.0432
45	0.0356
90	0.0291
140	0.0226
190	0.0186
260	0.0141

$k_{exp} = 0.85 \times 10^{-4}$ sec.$^{-1}$
$k_1 = 0.575 \times 10^{-4}$ sec.$^{-1}$
$k_s = 2.88 \times 10^{-4} M^{-1}$ sec.$^{-1}$

Run 23

0.1 M 1,4-Thioxane

Time, min.	$(ArSO_2H)$, M
0	0.0460
20	0.0430
60	0.0377
150	0.0298
240	0.0238
330	0.0192
420	0.0159

$k_1^* = 0.86 \times 10^{-5}$ sec.$^{-1}$
$k_s = 8.6 \times 10^{-5} M^{-1}$ sec.$^{-1}$

Run 24

0.25 M 1,4-Thioxane

Time, min.	$(ArSO_2H)$, M
0	0.0464
15	0.0434
60	0.0359
135	0.0278
210	0.0218
285	0.0174
330	0.0155

$k_1^* = 2.15 \times 10^{-5}$ sec.$^{-1}$
$k_s = 8.6 \times 10^{-5} M^{-1}$ sec.$^{-1}$

* Determined by the method outlined in (21, p. 165).

Run 25

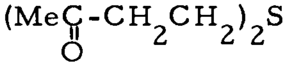
0.15 *M* $(\textit{n}\text{-BuO-CH}_2\text{CH}_2\text{-})_2\text{S}$

Time, min.	(ArSO_2H), *M*
0	0.0458
10	0.0456
20	0.0442
35	0.0424
75	0.0387
160	0.0333
240	0.0291

$k_{exp} = 3.38 \times 10^{-5}\ \text{sec.}^{-1}$

The reaction is slower than the disproportionation of *p*-toluenesulfinic acid.

Run 26

0.2 *M* 
$(\text{Me}\overset{}{\underset{\text{O}}{\underset{\|}{\text{C}}}}\text{-CH}_2\text{CH}_2)_2\text{S}$

Time, min.	(ArSO_2H), *M*
0	0.0245
5	0.0061

$k_{exp} = 4.63 \times 10^{-3}\ \text{sec.}^{-1}$

$k_1 = 4.61 \times 10^{-3}\ \text{sec.}^{-1}$

$k_s = 23.05 \times 10^{-3}\ \underline{M}^{-1}\ \text{sec.}^{-1}$

Run 27

0.1 *M* $(\text{Me}_3\text{C})_2\text{S}$

Time, min.	(ArSO_2H), *M*
0	< 0.0153
5	0.0089
11	0.0032

$k_{exp} = 2.2 \times 10^{-3}\ \text{sec.}^{-1}$

$k_1 = 2.19 \times 10^{-3}\ \text{sec.}^{-1}$

$k_s = 21.9 \times 10^{-3}\ \underline{M}^{-1}\text{sec.}^{-1}$

TABLE 24

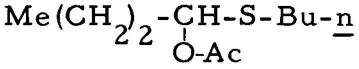
RATES OF n-BUTYL α-ACETOXYBUTYL SULFIDE, n-BUTYL MERCAPTAN AND CATALYZED n-BUTYL DISULFIDE REACTIONS WITH p-TOLUENESULFINIC ACID

Temperature: 70°. Solvent: 0.6 M sulfuric acid - 0.56 M water - acidic acid. $(ArSO_2H)_o$: 0.05 M (Ar = p-CH_3-C_6H_4-).

Run 28		Run 29	
0.0178 M $\mathrm{Me(CH_2)_2\underset{\text{O-Ac}}{CH}\text{-S-Bu-}n}$		0.0178 M $\mathrm{Me(CH_2)_2\text{-}\underset{\text{O-Ac}}{CH}\text{-S-Bu-}n}$	
Time, min.	$(ArSO_2H)$, M	Time, min.	$(ArSO_2H)$, M
(-2)	0.0478	(-2)	0.0480
0*		0*	
3	0.0355	3	0.0345
13	0.0284	6	0.0321
23	0.0243	15	0.0294
38	0.0204	30	0.0251
58	0.0171	70	0.0192
118	0.0126	120	0.0139

* The glass bucket containing the α-acetoxy sulfide was dropped into the solution of sulfinic acid.

Run 30

0.0178 $\underline{M}$

$\mathrm{Me(CH_2)_2\text{-}\underset{\text{O-Ac}}{CH}\text{-}S\text{-}Bu\text{-}\underline{n}}$

0.1 $\underline{M}$ PhSPh

Time, min.	$(ArSO_2H)$ $\underline{M}$	$1/(ArSO_2H)$ $\underline{M}^{-1}$
(-2)	0.0467	21.4
0 *		
3	0.0322	31.05
6	0.0290	34.50
15	0.0232	43.00
30	0.0177	56.40
60	0.0114	87.50
90	0.0077	129.00

$k_2 = 1.78 \times 10^{-2} \underline{M}^{-1}$ sec.$^{-1}$

Run 31

0.0178 $\underline{M}$ $\underline{n}$-BuSH

Time, min.	$(ArSO_2H)$ $\underline{M}$	$1/(ArSO_2H)$ $\underline{M}^{-1}$
(-2)	0.0478	20.90
0 **		
3	0.0375	26.60
6	0.0363	27.55
15	0.0339	29.50
30	0.0316	31.65
60	0.0275	36.30
120	0.0220	45.40

$k_2 = 2.5 \times 10^{-3} \underline{M}^{-1}$ sec.$^{-1}$

Run 32

0.0125 $\underline{M}$ $\underline{n}$-BuSSBu-$\underline{n}$

Time, min.	$(ArSO_2H)$ $\underline{M}$	$1/(ArSO_2H)$ $\underline{M}^{-1}$
0 **		
3	0.0469	21.3
6	0.0464	21.6
16	0.0431	23.2
40	0.0368	27.2
65	0.0326	30.6
100	0.0278	36.0
180	0.0208	48.1

$k_2 = 2.54 \times 10^{-3} \underline{M}^{-1}$ sec.$^{-1}$

Run 33

0.0125 $\underline{M}$ $\underline{n}$-BuSSBu-$\underline{n}$

0.1 $\underline{M}$ PhSPh

Time, min.	$(ArSO_2H)$ $\underline{M}$	$1/(ArSO_2H)$ $\underline{M}^{-1}$
0 *		
5	0.0421	23.75
15	0.0364	27.50
35	0.0294	34.00
60	0.0235	42.60
85	0.0190	52.60
105	0.0161	62.00
120	0.0149	67.10

$k_2 = 7.0 \times 10^{-3} \underline{M}^{-1}$ sec.$^{-1}$

* The glass bucket containing the α-acetoxy sulfide (Or($\underline{n}$-BuS-)$_2$) was dropped into the solution of sulfinic acid and phenyl sulfide.

** The glass bucket with $\underline{n}$-butyl mercaptan (Or($\underline{n}$-BuS-)$_2$) was dropped into the solution of sulfinic acid.

Run 34

0.01 M n-BuSBu, 0.0125 M n-BuSSBu-n

Time, min.	$(ArSO_2H)$, M	$1/(ArSO_2H)$, M^{-1}
0 *		(20.9)
5	0.0151	66.3
10	0.00898	111.0
15	0.00614	163.0
20	0.00470	213.0
25	0.00368	271.0
30	0.00306	327.0
35	0.00245	409.0

$k_2 = 0.158\ \underline{M}^{-1}\ \text{sec.}^{-1}$

* n-Butyl sulfide and n-butyl disulfide were weighed into the same glass bucket, which was dropped into the solution of sulfinic acid at zero time.

The rate constants (Runs 30 - 34) are calculated for the slow rate after the initial fast rate, see Curves 7 - 9, Figure 10.

TABLE 25

NUCLEAR MAGNETIC RESONANCE ABSORPTIONS

Compound	Solvent	τ(p.p.m.)	Characteristic Protons
n-BuSSBu-*n*	$CHCl_3$	7.34	$C_3H_7\text{-}C\underline{H}_2\text{-SS-}C\underline{H}_2\text{-}C_3H_7$ (triplet)
n-BuSS-Ar	$CHCl_3$	7.68	$C\underline{H}_3\text{-}C_6H_4\text{-}$ (singlet)
		7.34	$C_3H_7\text{-}C\underline{H}_2\text{-S}$ (triplet)
$ArSO_2SAr$	$CHCl_3$	7.62,	$C\underline{H}_3\text{-}C_6H_4\text{-}SO_2SC_6H_4\text{-}C\underline{H}_3$
		7.58	(two singlets)
$ArSO_2S\text{-Bu-}$*n*	$CHCl_3$	7.58	$C\underline{H}_3\text{-}C_6H_4\text{-}SO_2S\text{-}$ (singlet)
		7.05	$ArSO_2S\text{-}C\underline{H}_2\text{-}C_3H_7$ (triplet)
$ArSO_2S\text{-}CHMe_2$	$CDCl_3$	7.60	$C\underline{H}_3\text{-}C_6H_4\text{-}$ (singlet)
		6.52	$ArSO_2S\text{-}C\underline{H}\ Me_2$ (septet)
		8.70	$ArSO_2SCH(C\underline{H}_3)_2$ (doublet)
$ArSO_2SCH_2CH_3$	$CDCl_3$	7.62	$C\underline{H}_3\text{-}C_6H_4\text{-}$ (singlet)
		7.04	$ArSO_2S\text{-}C\underline{H}_2CH_3$ (quartet)
$ArSO_2S\underset{\substack{\vert\\ Me}}{C}H\text{-}C_6H_{13}$	$CDCl_3$	7.57	$C\underline{H}_3\text{-}C_6H_4SO_2S\text{-}$ (singlet)
		6.71	$ArSO_2S\text{-}\underset{\substack{\vert\\ Me}}{C}\underline{H}\text{-}C_6H_{13}$ (deformed quartet)

(Ar = *p*-CH_3-C_6H_4-)

Figure 10. Plot of $1/(ArSO_2H)$ versus Time for the Reaction of *p*-Toluenesulfinic Acid with *n*-BuSH; (*n*-BuS)$_2$; or (*n*-BuS)$_2$ and Ph_2S.

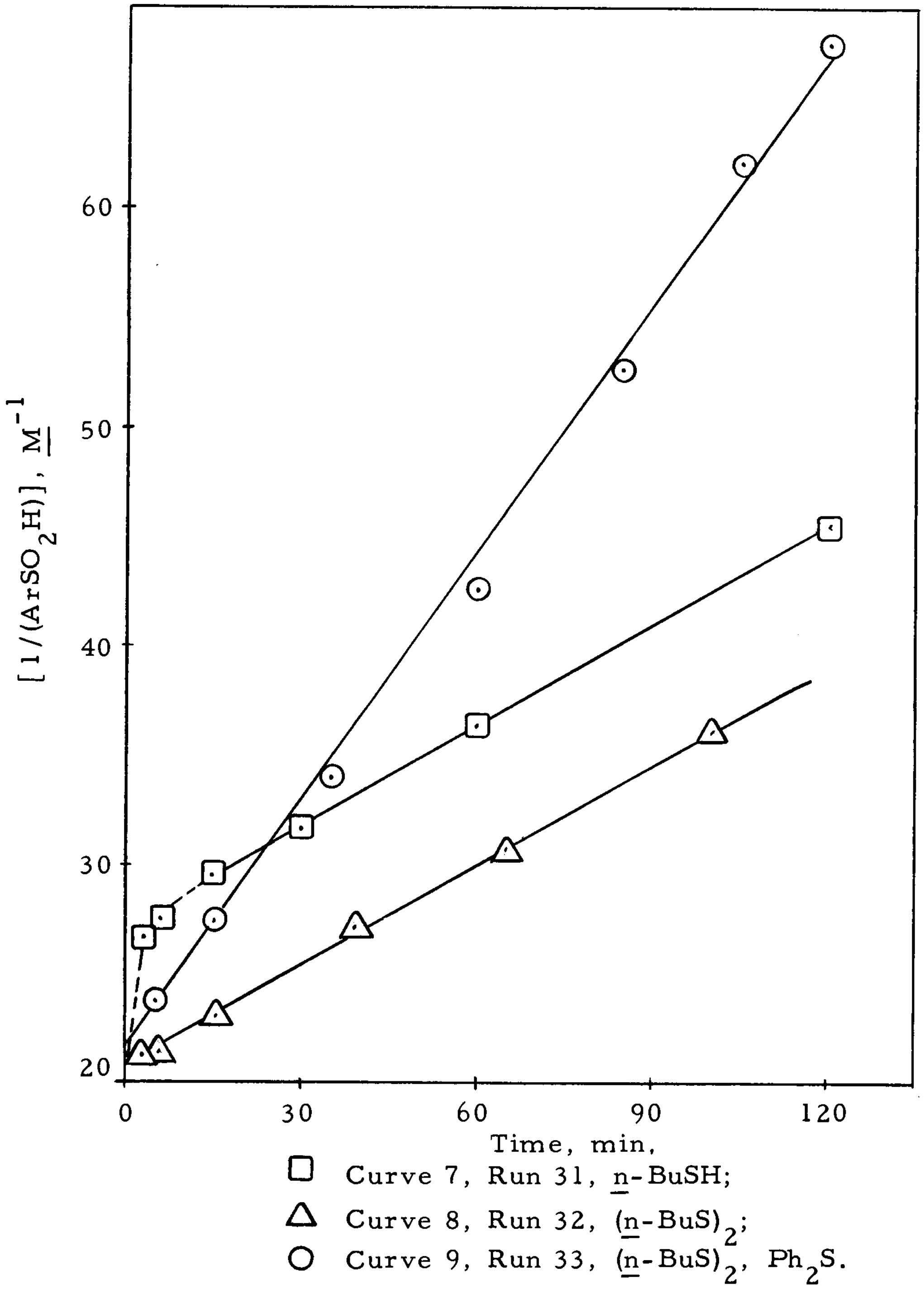
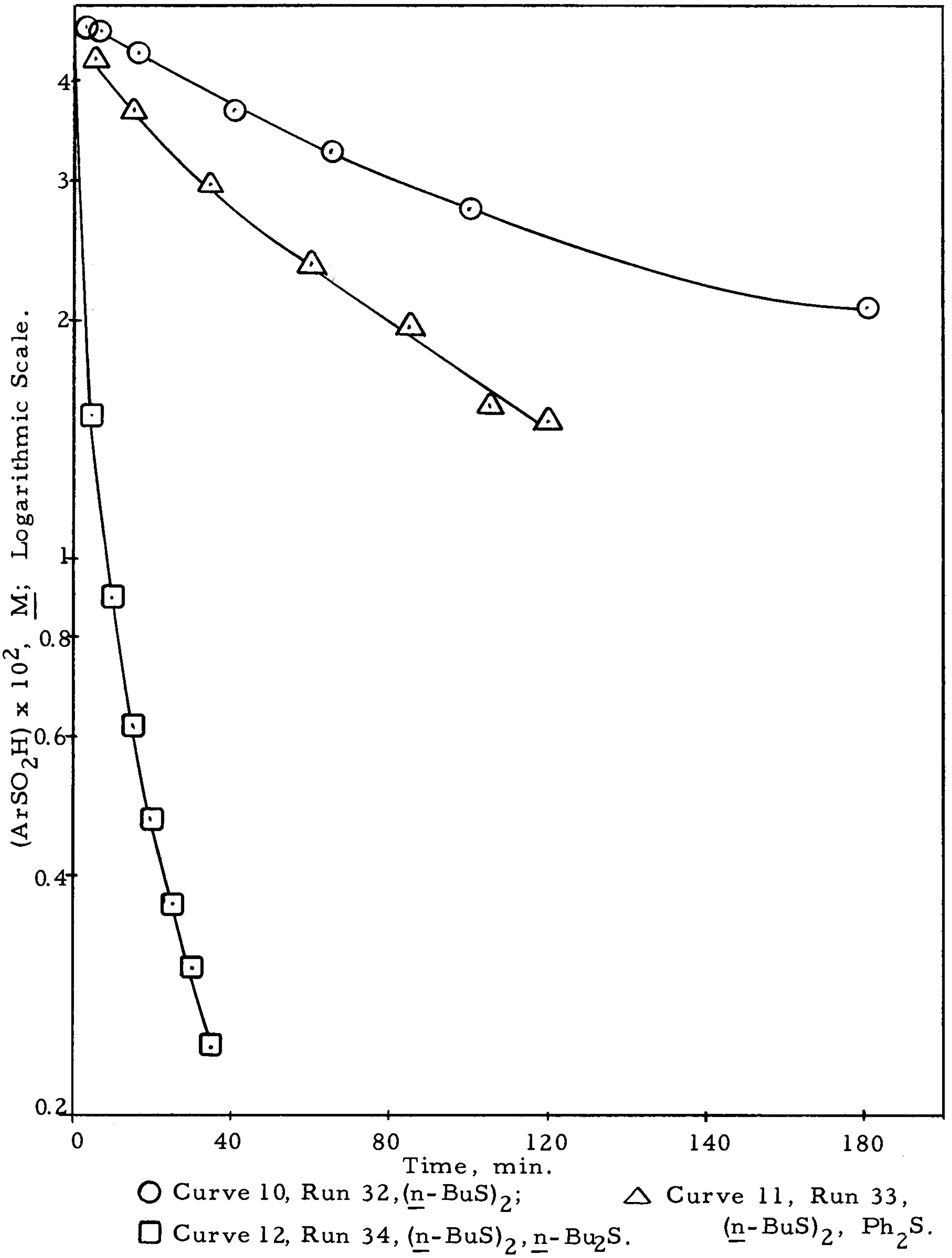


Figure 11. Plot of log (ArSO$_2$H) versus Time for the Reaction of p-Toluenesulfinic Acid with (n-BuS)$_2$; (n-BuS)$_2$ and Ph$_2$S or (n-BuS)$_2$ and n-Bu$_2$S.



APPENDIX 2

TABLE 26

RATES OF THE DISULFIDE - p-TOLUENESULFINIC ACID REACTIONS

The reactions were carried out at 70° in 0.56 M water - acetic acid with sulfuric acid concentration as indicated in each case. $(ArSO_2H)_o$: 0.05 M, unless otherwise indicated. (Ar = p-$CH_3C_6H_4$-).

Run 35

0.2 M MeSSMe,

0.2 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0389
3	0.0288
6	0.0211
9	0.0141
12	0.0099
15	0.0068
18	0.0045

k_{exp}: 20.9×10^{-4} sec.$^{-1}$,

k_1 : 20.8×10^{-4} sec.$^{-1}$

Run 36

0.15 M MeSSMe,

0.2 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0426
5	0.0318
10	0.0219
15	0.0155
20	0.0110
25	0.0074
30	0.0056

k_{exp}: 11.8×10^{-4} sec.$^{-1}$,

k_1 : 11.7×10^{-4} sec.$^{-1}$

Run 37

0.1 M MeSSMe,

0.2 M H_2SO_4

Time, min.	($ArSO_2H$), M
0	0.0452
5	0.0394
15	0.0277
25	0.0199
35	0.0141
45	0.0105
55	0.0083

k_{exp}: 5.3×10^{-4} sec.$^{-1}$,

k_1 : 5.2×10^{-4} sec.$^{-1}$

Run 38

0.051 M MeSSMe,

0.2 M H_2SO_4, 0.03 M $ArSO_2H$

Time, min.	($ArSO_2H$), M
0	
5	0.0273
20	0.0223
35	0.0186
50	0.0165
80	0.0124
110	0.0095

k_{exp}: 1.58×10^{-4} sec.$^{-1}$,

k_1 : 1.46×10^{-4} sec.$^{-1}$

Run 39

0.2 M EtSSEt,

0.2 M H_2SO_4

Time, min.	($ArSO_2H$), M
0	0.0464
5	0.0397
12	0.0313
20	0.0240
28	0.0184
35	0.0149
45	0.0107

k_{exp}: 5.38×10^{-4} sec.$^{-1}$,

k_1 : 5.22×10^{-4} sec.$^{-1}$

Run 40

0.15 M EtSSEt,

0.2 M H_2SO_4

Time, min.	($ArSO_2H$), M
0	0.0465
10	0.0380
25	0.0281
40	0.0207
55	0.0155
70	0.0116
85	0.0091

k_{exp}: 3.3×10^{-4} sec.$^{-1}$,

k_1 : 3.15×10^{-4} sec.$^{-1}$

Run 41

0.1 M EtSSEt,

0.2 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0476
15	0.0393
30	0.0331
55	0.0263
90	0.0190
130	0.0128
180	0.0083

k_{exp}: 1.59×10^{-4} sec.$^{-1}$,

k_1 : 1.45×10^{-4} sec.$^{-1}$

Run 42

0.2 M n-BuSSBu-n,

0.26 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0439
5	0.0352
10	0.0265
15	0.0199
20	0.0141
25	0.0108
30	0.0083

k_{exp}: 9.9×10^{-4} sec.$^{-1}$,

k_1 : 9.8×10^{-4} sec.$^{-1}$

Run 43

0.15 M n-BuSSBu-n,

0.26 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0464
5	0.0401
15	0.0273
25	0.0186
35	0.0137
45	0.0099
55	0.0070

k_{exp}: 5.76×10^{-4} sec.$^{-1}$,

k_1 : 5.60×10^{-4} sec.$^{-1}$

Run 44

0.1 M n-BuSSBu-n,

0.26 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0472
5	0.0444
15	0.0377
40	0.0244
60	0.0178
80	0.0128
100	0.0095

k_{exp}: 2.74×10^{-4} sec.$^{-1}$,

k_1 : 2.55×10^{-4} sec.$^{-1}$

Run 45

0.05 M n-BuSSBu-n,

0.26 M H_2SO_4, 0.03 M $ArSO_2H$

Time, min.	($ArSO_2H$), M
0	0.0282
10	0.0261
20	0.0248
40	0.0224
70	0.0186
100	0.0153
130	0.0132

k_{exp}: 0.94×10^{-4} sec.$^{-1}$,

k_1 : 0.75×10^{-4} sec.$^{-1}$

Run 46

0.15 M n-BuSSBu-n,

0.2 M H_2SO_4

Time, min.	($ArSO_2H$), M
0	0.0480
10	0.0397
25	0.0294
40	0.0211
55	0.0161
75	0.0112
95	0.0074

k_{exp}: 3.22×10^{-4} sec.$^{-1}$,

k_1 : 3.07×10^{-4} sec.$^{-1}$

Run 47

0.15 M n-BuSSBu-n,

0.3 M H_2SO_4

Time, min.	($ArSO_2H$), M
0	0.0455
5	0.0377
15	0.0232
22	0.0174
30	0.0124
40	0.0079
50	0.0054

k_{exp}: 7.4×10^{-4} sec.$^{-1}$,

k_1 : 7.3×10^{-4} sec.$^{-1}$

Run 48

0.15 M n-BuSSBu-n,

0.4 M H_2SO_4

Time, min.	($ArSO_2H$), M
0	0.0431
4	0.0319
8	0.0220
12	0.0145
16	0.0104
20	0.0075
24	0.0050

k_{exp}: 15.3×10^{-4} sec.$^{-1}$,

k_1 : 15.1×10^{-4} sec.$^{-1}$

Run 49

0.2 M $PhCH_2SSCH_2Ph$,

0.4 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0472
10	0.0405
30	0.0306
51	0.0230
75	0.0157
96	0.0120
120	0.0087

k_{exp} : 2.4×10^{-4} sec.$^{-1}$,

k_1 : 2.2×10^{-4} sec.$^{-1}$

Run 50

0.15 M $PhCH_2SSCH_2Ph$,

0.4 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0476
15	0.0410
45	0.0312
75	0.0236
105	0.0178
150	0.0122
195	0.0078

k_{exp} : 1.59×10^{-4} sec.$^{-1}$,

k_1 : 1.39×10^{-4} sec.$^{-1}$

Run 51

0.1 M $PhCH_2SSCH_2Ph$,

0.4 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0485
30	0.0402
60	0.0348
120	0.0250
180	0.0180
255	0.0124
330	0.0087

k_{exp} : 8.74×10^{-5} sec.$^{-1}$,

k_1 : 6.76×10^{-5} sec.$^{-1}$

Run 52

0.15 M $PhCH_2SSCH_2Ph$,

0.3 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0488
15	0.0451
60	0.0352
120	0.0252
180	0.0180
255	0.0124
330	0.0087

k_1^* : 6.94×10^{-5} sec.$^{-1}$

* Determined by the method outlined in (21, p. 165).

Run 53

0.18 M $(HOOCCH_2S-)_2$,

0.6 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0480
15	0.0443
60	0.0387
150	0.0302
240	0.0242
330	0.0202
420	0.0163

k_1^* : 2.2×10^{-5} sec.$^{-1}$

Run 54

0.1 M $(HOOCCH_2S-)_2$,

0.6 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0485
15	0.0447
60	0.0385
150	0.0306
240	0.0236
330	0.0190
420	0.0159

k_1^* : 0.9×10^{-5} sec.$^{-1}$

Run 55

0.1 M $(HOOCCH_2CH_2S-)_2$,

0.6 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0490
15	0.0445
60	0.0373
150	0.0275
240	0.0205
330	0.0149
420	0.0118

k_1^* : 2.3×10^{-5} sec.$^{-1}$

Run 56

0.07 M $(HOOCCH_2CH_2S-)_2$,

0.6 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0495
30	0.0430
60	0.0385
150	0.0286
240	0.0232
330	0.0184
420	0.0145

k_1^* : 1.3×10^{-5} sec.$^{-1}$

* Determined by the method outlined in (21, p. 165).

Run 57

0.2 *M* $(Me_2CHS-)_2$,

0.4 *M* H_2SO_4

Time, min.	$(ArSO_2H)$, *M*
0	0.0484
10	0.0447
30	0.0381
70	0.0273
120	0.0188
170	0.0120
210	0.0085

k_{exp}: 1.36×10^{-4} sec.$^{-1}$,

k_1 : 1.16×10^{-4} sec.$^{-1}$

Run 58

0.15 *M* $(Me_2CHS-)_2$,

0.4 *M* H_2SO_4

Time, min.	$(ArSO_2H)$, *M*
0	0.0489
10	0.0455
40	0.0376
90	0.0284
150	0.0201
210	0.0145
280	0.0095

k_{exp}: 0.96×10^{-4} sec.$^{-1}$,

k_1 : 0.76×10^{-4} sec.$^{-1}$

Run 59

0.1 *M* $(Me_2CHS-)_2$,

0.4 *M* H_2SO_4

Time, min.	$(ArSO_2H)$, *M*
0	0.0493
30	0.0423
75	0.0356
150	0.0269
225	0.0209
300	0.0159
375	0.0128

k_{exp}: 6.02×10^{-5} sec.$^{-1}$,

k_1 : 3.82×10^{-5} sec.$^{-1}$

Run 60

0.15 *M* *p*-$CH_3C_6H_4SSBu$-*n*,

0.3 *M* H_2SO_4

Time, min.	$(ArSO_2H)$, *M*
0	0.0449
10	0.0335
20	0.0244
30	0.0173
40	0.0121
50	0.0087
60	0.0062

k_{exp}: 5.78×10^{-4} sec.$^{-1}$,

k_1 : 5.61×10^{-4} sec.$^{-1}$

Run 61

0.12 M p-$CH_3C_6H_4SSBu$-n,

0.3 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0469
15	0.0340
25	0.0275
35	0.0216
50	0.0149
65	0.0109
80	0.0077

k_{exp} : 3.79×10^{-4} sec.$^{-1}$,

k_1 : 3.60×10^{-4} sec.$^{-1}$

Run 62

0.1 M p-$CH_3C_6H_4SSBu$-n,

0.3 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0460
10	0.0400
30	0.0291
50	0.0206
70	0.0147
90	0.0105
110	0.0077

k_{exp} : 2.74×10^{-4} sec.$^{-1}$,

k_1 : 2.55×10^{-4} sec.$^{-1}$

Run 63

0.05 M p-$CH_3C_6H_4SSBu$-n,

0.3 M H_2SO_4, 0.03 M $ArSO_2H$

Time, min.	$(ArSO_2H)$, M
0	0.0284
15	0.0258
45	0.0218
75	0.0182
105	0.0153
135	0.0127
165	0.0109

k_{exp} : 0.97×10^{-4} sec.$^{-1}$,

k_1 : 0.79×10^{-4} sec.$^{-1}$

Run 64

0.1 M PhSSPh,

0.6 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0464
30	0.0402
90	0.0315
150	0.0258
240	0.0194
330	0.0155
420	0.0125

k_1^* : 2.2×10^{-5} sec.$^{-1}$

* Determined by the method outlined in (21, p. 165).

TABLE 27

RATES OF THE SULFIDE CATALYZED DISULFIDE - p-TOLUENESULFINIC ACID REACTIONS

The reactions were carried out at 70°, in 0.56 M water - acetic acid with sulfuric acid as indicated for each run. $(ArSO_2H)_o$: 0.05 M, (Ar = p-$CH_3C_6H_4$-).

In experiments where phenyl and benzyl sulfide were used as catalysts, these were added before heating of the reaction mixture. n-Butyl and isopropyl sulfide were weighed out in a small glass bucket and added at a measured time, after the reaction vessel had been heated for three minutes.

Run 65

0.1 M PhSSPh, 0.15 M PhSPh,

0.6 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0448
5	0.0376
10	0.0313
15	0.0269
20	0.0218
30	0.0151
40	0.0099

k_{exp} : 6.28×10^{-4} sec.$^{-1}$,

k_1 : 6.01×10^{-4} sec.$^{-1}$

Run 66

0.1 M PhSSPh, 0.1 M PhSPh,

0.6 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0451
10	0.0356
20	0.0275
30	0.0216
40	0.0161
50	0.0125
65	0.0081

k_{exp} : 4.46×10^{-4} sec.$^{-1}$,

k_1 : 4.21×10^{-4} sec.$^{-1}$

Run 67

0.1 M PhSSPh, 0.05 M PhSPh, 0.6 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0465
15	0.0370
30	0.0299
50	0.0222
70	0.0163
90	0.0121
110	0.0091

k_{exp}: 2.5 x 10^{-4} $sec.^{-1}$,

k_1 : 2.24 x 10^{-4} $sec.^{-1}$

Run 68

0.1 M PhSSPh, 0.005 M n-Bu_2S, 0.6 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
(-1) *	
0	0.0428
5	0.0299
10	0.0222
15	0.0168
20	0.0133
24	0.0109
27	0.0093

k_{exp}: 9.45 x 10^{-4} $sec.^{-1}$,

k_1 : 9.19 x 10^{-4} $sec.^{-1}$

Run 69

0.1 M PhSSPh, 0.005 M $(Me_2CH)_2S$ 0.6 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
(-1) *	
0	0.0446
10	0.0315
18	0.0259
26	0.0226
34	0.0206
55	0.0176
80	0.0157

k_{exp}: 5.66 x 10^{-4} $sec.^{-1}$,

k_1 : 5.40 x 10^{-4} $sec.^{-1}$

Run 70

0.1 M PhSSPh, 0.005 M $(Me_2CH)_2S$, 0.6 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
(-1) *	
0	0.0444
3	0.0396
6	0.0355
9	0.0315
12	0.0290
15	0.0266
18	0.0250

k_{exp}: 5.95 x 10^{-4} $sec.^{-1}$,

k_1 : 5.53 x 10^{-4} $sec.^{-1}$

* At this time the sulfide was dropped into the reaction mixture.

Run 71

0.1 M PhSSPh, 0.005 M $(PhCH_2)_2S$,

0.6 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0459
10	0.0347
20	0.0258
30	0.0202
40	0.0157
50	0.0123
60	0.0097

k_{exp}: 4.37×10^{-4} sec.$^{-1}$,

k_1 : 4.11×10^{-4} sec.$^{-1}$

Run 72

0.1 M MeSSMe, 0.15 M PhSPh,

0.2 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0436
5	0.0360
10	0.0287
15	0.0226
20	0.0186
25	0.0145
35	0.0097

k_{exp}: 7.42×10^{-4} sec.$^{-1}$,

k_1 : 7.27×10^{-4} sec.$^{-1}$

Run 73

0.1 M MeSSMe, 0.1 M PhSPh,

0.2 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0433
5	0.0352
10	0.0287
15	0.0238
20	0.0198
25	0.0161
35	0.0117

k_{exp}: 6.30×10^{-4} sec.$^{-1}$,

k_1 : 6.14×10^{-4} sec.$^{-1}$

Run 74

0.1 M MeSSMe, 0.1 M PhSPh,

0.2 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
0	0.0448
5	0.0363
10	0.0293
16	0.0238
22	0.0182
28	0.0145
35	0.0113

k_{exp}: 6.62×10^{-4} sec.$^{-1}$,

k_1 : 6.46×10^{-4} sec.$^{-1}$

Run 75

0.1 $\underline{M}$ MeSSMe, 0.0025 $\underline{M}$ $\underline{n}$-Bu_2S,

0.2 $\underline{M}$ H_2SO_4

Time, min.	$(ArSO_2H)$, $\underline{M}$
(-1) *	
0	0.03720
3	0.02140
6	0.01190
9	0.00666
12	0.00364
15	0.00222
18	0.00121

k_{exp}: 29.7×10^{-4} sec.$^{-1}$,

k_1 : 29.65×10^{-4} sec.$^{-1}$

Run 76

0.1 $\underline{M}$ ($\underline{n}$-BuS-$)_2$, 0.1 $\underline{M}$ PhSPh,

0.2 $\underline{M}$ H_2SO_4

Time, min.	$(ArSO_2H)$, $\underline{M}$
0	0.0461
10	0.0382
25	0.0299
40	0.0230
55	0.0188
75	0.0137
95	0.0107

k_{exp}: 2.66×10^{-4} sec.$^{-1}$,

k_1 : 2.49×10^{-4} sec.$^{-1}$

Run 77

0.089 $\underline{M}$($\underline{n}$-BuS-$)_2$, 0.1 $\underline{M}$ Ph_2S,

0.3 $\underline{M}$ H_2SO_4

Time, min.	$(ArSO_2H)$, $\underline{M}$
0	0.0435
10	0.0307
17	0.0258
24	0.0206
32	0.0161
40	0.0125
50	0.0093

k_{exp}: 5.30×10^{-4} sec.$^{-1}$,

k_1 : 5.13×10^{-4} sec.$^{-1}$

Run 78

0.1 $\underline{M}$ ($\underline{n}$-BuS-$)_2$, 0.005 $\underline{M}$ $\underline{n}$-Bu_2S,

0.2 $\underline{M}$ H_2SO_4

Time, min.	$(ArSO_2H)$, $\underline{M}$
(-1) *	
0	0.0430
3	0.0321
6	0.0232
9	0.0170
12	0.0125
15	0.0089
18	0.0069

k_{exp}: 17.2×10^{-4} sec.$^{-1}$,

k_1 : 17.1×10^{-4} sec.$^{-1}$

* At this time the sulfide was dropped into the reaction mixture.

Run 79

0.1 $\underline{M}$(n-BuS-)$_2$, 0.0025 $\underline{M}$ n-Bu$_2$S,

0.2 $\underline{M}$ H_2SO_4

Time, min.	(ArSO$_2$H), $\underline{M}$
(-1) *	
0	0.04400
5	0.03235
10	0.02465
15	0.01840
20	0.01415
25	0.01050
30	0.00810

k_{exp}: 9.49 x 10^{-4} sec.$^{-1}$,

k_1 : 9.35 x 10^{-4} sec.$^{-1}$

Run 80

0.1 $\underline{M}$ (Me$_2$CHS)$_2$, 0.1 $\underline{M}$ Ph$_2$S,

0.4 $\underline{M}$ H_2SO_4

Time, min.	(ArSO$_2$H), $\underline{M}$
0	0.0465
15	0.0388
39	0.0315
72	0.0242
105	0.0198
150	0.0153
225	0.0093

k_{exp}: 1.03 x 10^{-4} sec.$^{-1}$,

k_1 : 0.80 x 10^{-4} sec.$^{-1}$

Run 81

0.1 $\underline{M}$(Me$_2$CHS)$_2$, 0.005 $\underline{M}$ n-Bu$_2$S,

0.4 $\underline{M}$ H_2SO_4

Time, min.	(ArSO$_2$H), $\underline{M}$
(-1) *	
0	0.0453
10	0.0323
18	0.0254
26	0.0206
36	0.0166
46	0.0129
56	0.0105

k_{exp}: 4.46 x 10^{-4} sec.$^{-1}$,

k_1 : 4.25 x 10^{-4} sec.$^{-1}$

Run 82

0.1 $\underline{M}$(PhCH$_2$S-)$_2$, 0.1 $\underline{M}$ Ph$_2$S,

0.4 $\underline{M}$ H_2SO_4

Time, min.	(ArSO$_2$H), $\underline{M}$
0	0.0466
10	0.0416
30	0.0325
55	0.0240
80	0.0188
110	0.0137
140	0.0105

k_{exp}: 1.81 x 10^{-4} sec.$^{-1}$,

k_1 : 1.60 x 10^{-4} sec.$^{-1}$

* At this time the sulfide was dropped into the reaction mixture.

Run 83

0.1 M $(PhCH_2S-)_2$, 0.005 M n-Bu_2S,

0.3 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
(-1) *	
0	0.0452
5	0.0359
13	0.0248
20	0.0186
26	0.0149
32	0.0119
38	0.0095

k_{exp}: 6.87×10^{-4} sec.$^{-1}$,

k_1 : 6.69×10^{-4} sec.$^{-1}$

Run 84

0.1 M $(PhCH_2S-)_2$, 0.005 M n-Bu_2S,

0.4 M H_2SO_4

Time, min.	$(ArSO_2H)$, M
(-1) *	
0	0.0433
3	0.0332
6	0.0251
9	0.0202
12	0.0157
15	0.0125
20	0.0085

k_{exp}: 13.5×10^{-4} sec.$^{-1}$,

k_1 : 13.3×10^{-4} sec.$^{-1}$

* At this time the sulfide was dropped into the reaction mixture.

TABLE 28

NUCLEAR MAGNETIC RESONANCE ABSORPTIONS

The spectra were taken of the samples dissolved in chloroform.

Compound	τ-Values	Characteristic Protons
$\underline{p}\text{-}CH_3C_6H_4SSCH_2C_6H_5$	6.17 (singlet)	$\text{-}S\text{-}C\underline{H}_2\text{-}$
	7.68 (singlet)	$C\underline{H}_3\text{-}C_6H_4\text{-}$
$(C_6H_5CH_2S\text{-})_2$	6.52 (singlet)	$\text{-}C\underline{H}_2\text{-}SS\text{-}C\underline{H}_2\text{-}$
$\underline{p}\text{-}CH_3C_6H_4SO_2SCH_2C_6H_5$	5.76 (singlet)	$\text{-}S\text{-}C\underline{H}_2\text{-}$
	7.58 (singlet)	$\underline{p}\text{-}C\underline{H}_3\text{-}C_6H_4\text{-}SO_2\text{-}$
$\underline{p}\text{-}CH_3C_6H_4SO_2SC_6H_4CH_3\text{-}\underline{p}$	7.62 (singlet)	$\text{-}S\text{-}C_6H_4\text{-}C\underline{H}_3\text{-}\underline{p}$
$(Me_2CHS\text{-})_2$	8.72 (doublet)	$(C\underline{H}_3)_2CH\text{-}SS\text{-}CH(C\underline{H}_3)_2$

TABLE 29

REACTION OF DITHIODIPROPIONIC ACID WITH p-TOLUENESULFINIC ACID

(Run 56)

Treatment of the reaction as parallel first- and second-order reactions (21, p. 165).

$\left[-\frac{d(ArSO_2H)}{dt} = \lambda\right] \times 10^6$	$\lambda/(ArSO_2H) \times 10^5$	$(ArSO_2H) \times 10$
3.26	7.05	0.461
2.78	6.60	0.421
2.08	5.66	0.368
1.61	4.74	0.304
1.135	4.45	0.255
0.845	3.91	0.216
0.715	4.15	0.172

Figure 12. Plot of ($ArSO_2H$) versus Time for the Reaction of Dithiodipropionic Acid with p-Toluenesulfinic Acid (Run 56).

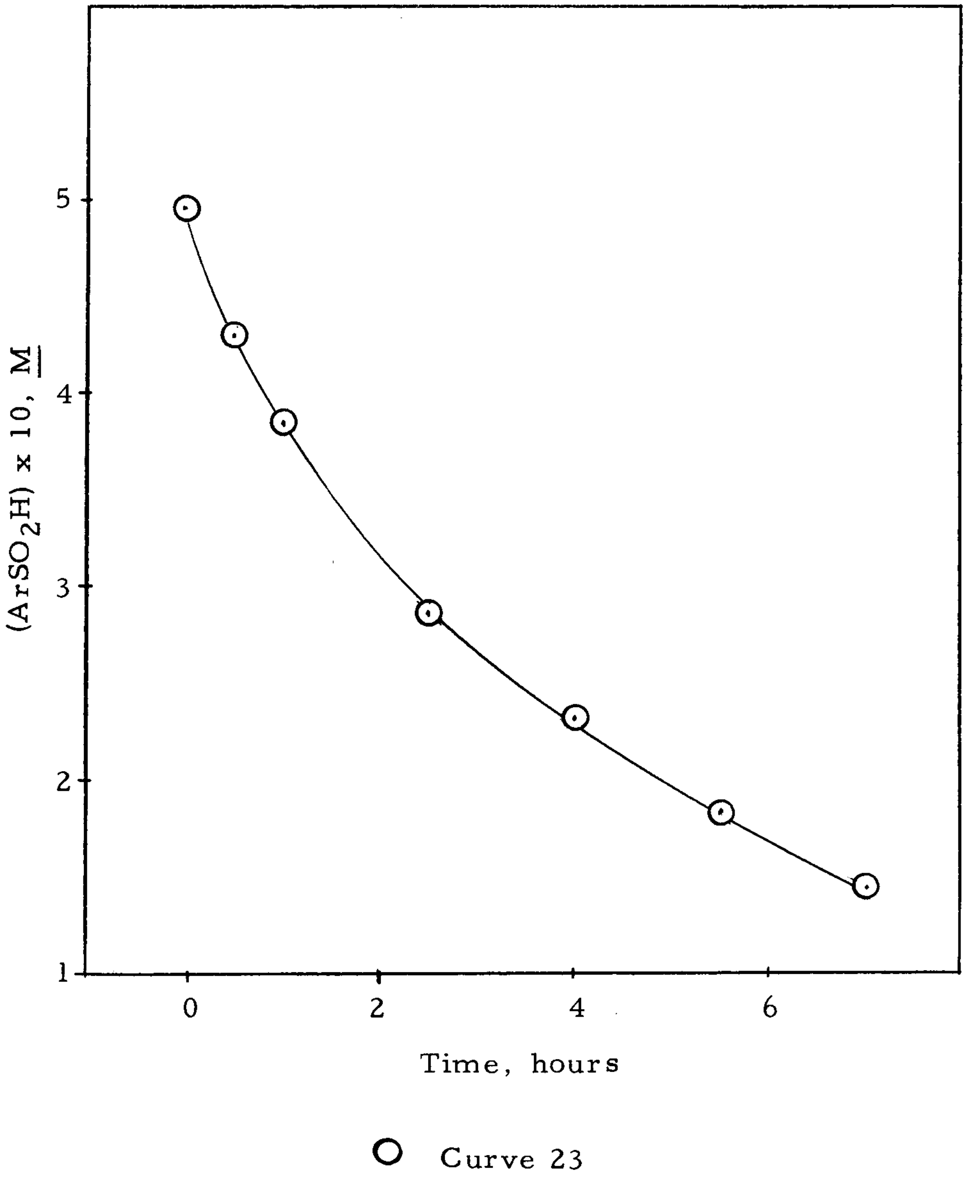


Figure 13. Plot of $(-d(ArSO_2H)/dt)/(ArSO_2H) = \lambda/(ArSO_2H)$ versus $(ArSO_2H)$ for the Reaction of Dithiodipropionic Acid with p-Toluenesulfinic Acid (Run 56).