spectrometer traces are estimated to be reliable to ±5 mμ for the TCNE spectra and to ±10–15 mμ for the broader chloranil maxima. In cases where two bands seriously overlapped, the observed maxima were corrected following the procedure described by Voigt and Reid.[33] The corrections varied from 3 to 7 mμ (Table I) and do not significantly affect the MO correlations.

Kinetic Measurements.—The kinetic procedures have been described previously[15] as has the analysis of the data to obtain the quantities k_c and K. Standard deviations reported in Table III are those obtained using the weighed least-squares procedure described by Parratt.[34]

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[33] E. M. Voigt and C. Reid, *J. Amer. Chem. Soc.*, **86**, 3931 (1964).

[34] L. G. Parratt, "Probability and Experimental Errors in Science," John Wiley and Sons, Inc., New York, N. Y., 1961.

Registry No.—**1**, 93-04-9; **2**, 2216-69-5; **3**, 10103-06-7; **4**, 3469-26-9; **5**, 5486-55-5; **6**, 3900-49-0; **7**, 5309-18-2; **8**, 10075-63-5; **9**, 10075-62-4; 2,4,7-trinitro-9-fluorenyl *p*-toluenesulfonate, 6673-16-1.

Acknowledgment.—We wish to thank the National Science Foundation (Grants GP-3350 and GP-6380) for financial support. The authors are also grateful to Mr. Kue-Hung Chau, Dr. David Beveridge, and Mr. David Buben for help with some of the computations and to Dr. Arthur Lepley for helpful discussions.

Mechanisms of Reactions of Thiolsulfinates (Sulfenic Anhydrides). II. The Thiolsulfinate–Mercaptan Reaction[1]

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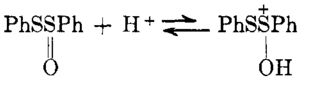
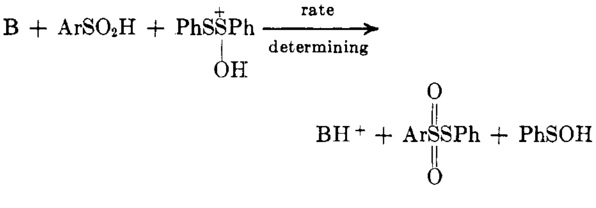
Received December 5, 1967

In acetic acid–1% water in the presence of some sulfuric acid phenyl benzenethiolsulfinate (I) reacts readily with alkanethiols to yield phenyl alkyl disulfides. Kinetic study of the reaction shows that it is first order in both mercaptan and thiolsulfinate and subject to specific H^+ catalysis. A mechanism (Chart II) is proposed which involves nucleophilic attack of the mercaptan on the sulfenyl sulfur of sulfinyl-protonated I. This mechanism differs from that for the related reaction of I with aryl sulfinic acids (eq 1 and 2) in that transfer of the proton of the thiol to a general base is *not* concerted with the formation of the new S–S bond. This finding confirms the probable correctness of an explanation advanced earlier[2] for the need for such a proton transfer in the rate-determining step of the sulfinic acid reaction. The I–mercaptan reaction can be catalyzed by the addition of small amounts of alkyl sulfides. Study of the kinetics of the sulfide-catalyzed reaction shows that it involves the same rate-determining step (eq 3) as was previously suggested[2] for sulfide catalysis of the thiolsulfinate–sulfinic acid reaction and thereby demonstrates rather unequivocally the correctness of the mechanism which has been proposed[2] for the sulfide-catalyzed I–$ArSO_2H$ reaction.

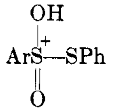
In moist acetic acid containing some sulfuric acid phenyl benzenethiolsulfinate (I), PhS(O)SPh, reacts quite readily with aryl sulfinic acids ($ArSO_2H$) to produce as the almost exclusive product the phenyl arenethiolsulfonate, $ArSO_2SPh$.[2] Kinetic studies have shown that this thiolsulfinate–sulfinic acid reaction is first order in both thiolsulfinate and sulfinic acid and that it is also apparently general acid catalyzed. On the basis of this and other evidence a mechanism involving a rate-determining general base catalyzed attack of the sulfinic acid on the protonated thiolsulfinate (eq 2) was proposed.[2] It was also suggested that the reason nucleophilic attack of the sulfinic acid on protonated I should require general base catalysis is because sulfone groups are such extremely weak basic sites[3] that II, which would result from a normal nucleophilic displacement by $ArSO_2H$, would be an extremely unstable intermediate formed only with great difficulty. By making transfer of the proton from $ArSO_2H$ concerted with the formation of the new S–S bond the need to go through II as an intermediate is avoided. However, since this is achieved only at the expense of an increase in the molecularity of the reaction, one might expect that similar displacements involving species NuH, where the intermediate HNu^+–SPh was not as energetically unfavorable as II, would not require the presence of the general base in the rate-determining step and would therefore exhibit specific oxonium ion rather than general acid catalysis.



$$\mathrm{Ph\underset{\underset{O}{\|}}{S}SPh} + H^+ \rightleftharpoons \mathrm{Ph\overset{+}{\underset{\underset{OH}{|}}{S}}SPh} \qquad (1)$$



$$B + ArSO_2H + \mathrm{Ph\overset{+}{\underset{\underset{OH}{|}}{S}}SPh} \xrightarrow[\text{determining}]{\text{rate}} BH^+ + \mathrm{Ar\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}SPh} + PhSOH \qquad (2)$$



II

$$\mathrm{Ar\overset{\overset{OH}{|}}{\underset{\underset{O}{\|}}{\overset{+}{S}}}{-}SPh}$$

Another important feature of the thiolsulfinate–sulfinic acid reaction is that the reaction can be dramatically catalyzed by the addition of small amounts of alkyl sulfides.[2] The sulfide-catalyzed process is first order in both thiolsulfinate and alkyl sulfide, but its rate is independent of sulfinic acid concentration. It exhibits specific H^+ catalysis, and the variation of its rate with sulfide structure indicates that the sulfide acts as a nucleophile. The mechanism shown in Chart I was accordingly suggested for the sulfide-catalyzed reaction. It involves rate-determining nucleophilic attack by R_2S on the protonated thiolsulfinate (eq 3). The species R_2S^+–SPh (III) so formed then

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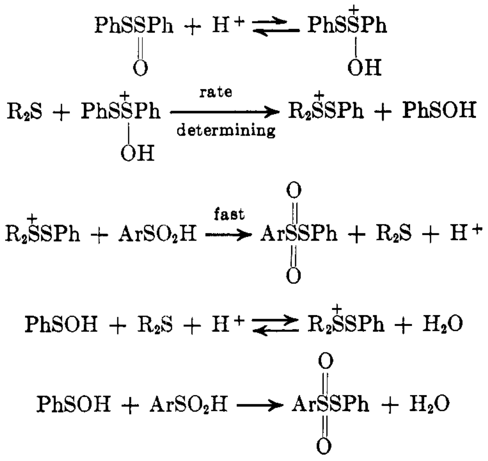
[1] This research supported by the National Science Foundation, Grant GP-6952.

[2] J. L. Kice, C. G. Venier, and L. Heasley, *J. Amer. Chem. Soc.*, **89**, 3557 (1967).

[3] S. K. Hall and E. A. Robinson, *Can. J. Chem.*, **42**, 1113 (1964), have shown that the pK_a of the conjugate acid of dimethyl sulfone is −12.3.

CHART I
MECHANISM OF THE SULFIDE-CATALYZED THIOLSULFINATE–SULFINIC ACID REACTION



$$\mathrm{Ph}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{S}}\mathrm{SPh} + \mathrm{H^+} \rightleftharpoons \mathrm{Ph}\underset{\substack{| \\ \mathrm{OH}}}{\overset{+}{\mathrm{S}}}\mathrm{SPh} \qquad (1)$$

$$\mathrm{R_2S} + \mathrm{Ph}\underset{\substack{| \\ \mathrm{OH}}}{\overset{+}{\mathrm{S}}}\mathrm{SPh} \xrightarrow[\text{determining}]{\text{rate}} \mathrm{R_2\overset{+}{S}SPh} + \mathrm{PhSOH} \qquad (3)$$

$$\mathrm{R_2\overset{+}{S}SPh} + \mathrm{ArSO_2H} \xrightarrow{\text{fast}} \mathrm{Ar}\overset{\substack{\mathrm{O} \\ \|}}{\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{S}}}\mathrm{SPh} + \mathrm{R_2S} + \mathrm{H^+} \qquad (4)$$

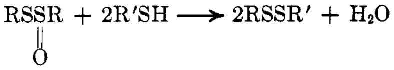
$$\mathrm{PhSOH} + \mathrm{R_2S} + \mathrm{H^+} \rightleftharpoons \mathrm{R_2\overset{+}{S}SPh} + \mathrm{H_2O} \qquad (5)$$

$$\mathrm{PhSOH} + \mathrm{ArSO_2H} \longrightarrow \mathrm{Ar}\overset{\substack{\mathrm{O} \\ \|}}{\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{S}}}\mathrm{SPh} + \mathrm{H_2O} \qquad (6)$$

reacts rapidly with $ArSO_2H$ in a subsequent step (eq 4) to yield the thiolsulfonate. The sulfenic acid (PhSOH) also produced in eq 3 yields the same product, either by first being converted into III (eq 5), or, alternatively, by direct reaction with $ArSO_2H$ (eq 6).

This mechanism predicts that alkyl sulfides should also catalyze the reaction of other reagents NuH with I *via* a mechanism analogous to that shown in Chart I. Furthermore, given the nature of this mechanism, the rate of such a sulfide-catalyzed I–NuH reaction should be the same under a given set of conditions as the rate of the sulfide-catalyzed I–sulfinic acid reaction.

Thiols have been reported[4] to react with thiolsulfinates as shown in eq 7. If this reaction also occurs



$$\mathrm{R}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{S}}\mathrm{SR} + 2\mathrm{R'SH} \longrightarrow 2\mathrm{RSSR'} + \mathrm{H_2O} \qquad (7)$$

readily between I and thiols in moist acetic acid containing some sulfuric acid, study of its kinetic behavior under the various conditions used for the I–sulfinic acid reaction should provide a meaningful test of the correctness of those aspects of the proposed mechanisms for the I–$ArSO_2H$ reactions which have just been discussed. Thus, if the previous explanation of the origin of general acid catalysis in the I–$ArSO_2H$ reaction is indeed correct, the reaction of RSH with thiolsulfinate should exhibit specific H^+, rather than general acid, catalysis, because RHS^+–SPh represents a much more favorable intermediate than II energetically. Second, the mercaptan–thiolsulfinate reaction should be susceptible to catalysis by added alkyl sulfides, and the rate of the sulfide-catalyzed reaction should be the same as the rate of the corresponding sulfide-catalyzed I–$ArSO_2H$ reaction. We have accordingly carried out a study of the reaction of I with mercaptans under these conditions in order to investigate these points.

Results

Stoichiometry of the Reaction.—That a reaction having the stoichiometry shown in eq 7 occurs between a mercaptan and I in acetic acid–0.56 *M* water–0.10 *M* H_2SO_4 was demonstrated by adding a deaerated solution containing I (2.00 mmol) to one containing thiophenol (10.0 mmol) and allowing the resulting solution to stand for 1 hr at 25°. Spectrophotometric examination at the end of this time revealed that the thiolsulfinate had completely disappeared, and iodimetric titration of a small aliquot of the solution showed that 4.00 mmol of thiophenol had been consumed in the process. Work-up of the remainder of the solution gave phenyl disulfide in a yield corresponding to 98% of that expected from the stoichiometry of eq 7 (R = R′ = Ph).

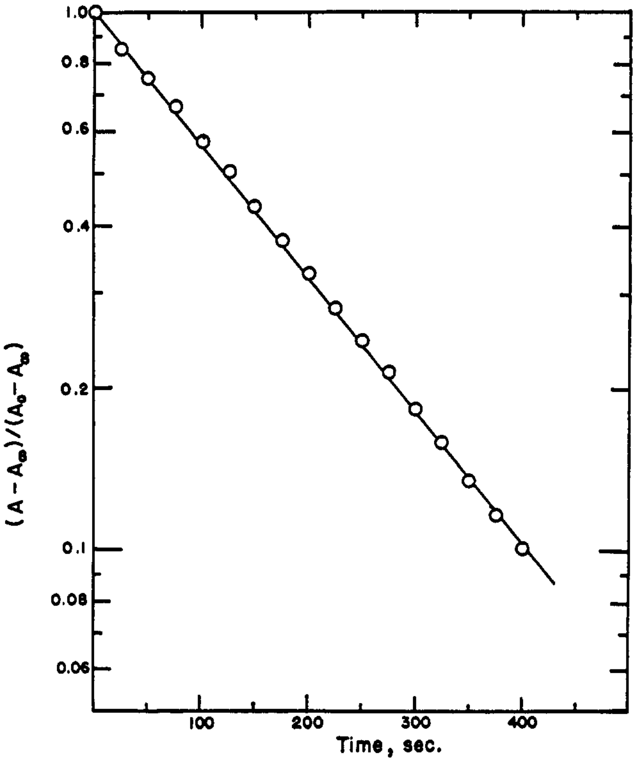


Figure 1.—Rate of disappearance of I in the presence of *n*-butyl mercaptan in acetic acid–0.56 *M* water–0.10 *M* H_2SO_4: $(I)_0$, 3.12×10^{-4} *M;* (*n*-BuSH), 3.12×10^{-3} *M*.

Kinetics of the Mercaptan–Thiolsulfinate Reaction.—The reaction between 1-butanethiol and PhS(O)SPh was the specific example of the thiolsulfinate–mercaptan reaction chosen for kinetic study. The kinetics of the reaction are most conveniently investigated by having the thiol present in considerable stoichiometric excess and following the disappearance of the thiolsulfinate spectrophotometrically. Under such conditions the disappearance of I follows good first-order kinetics, as can be seen from the plot of the data for a typical run in Figure 1.

The kinetic order in thiol can be evaluated by determining the influence of thiol concentration on k_1, the experimental first-order rate constant for disappearance of I. The relevant data are given in part A of Table I. Figure 2 shows a plot of k_1 *vs.* (RSH) for these runs; its linearity indicates the reaction is first order in thiol, as does the approximate constancy of the $k_1/(\mathrm{RSH})_{\mathrm{av}}$ values in part A of the table. In the remainder of the paper the quantity $k_1/(\mathrm{RSH})_{\mathrm{av}}$ will be denoted as k_{RSH}, the actual second-order rate constant for the mercaptan–thiolsulfinate reaction.

The dependence of k_{RSH} on the acidity of the medium was investigated both through a series of runs in acetic acid–0.56 *M* water with varying amounts of added sulfuric acid (part B of Table I) and by a pair of runs at 0.10 *M* H_2SO_4 in which the stoichiometric concentra-

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[4] A. Schoberl and H. Grafje, *Ann.*, **617**, 71 (1958).

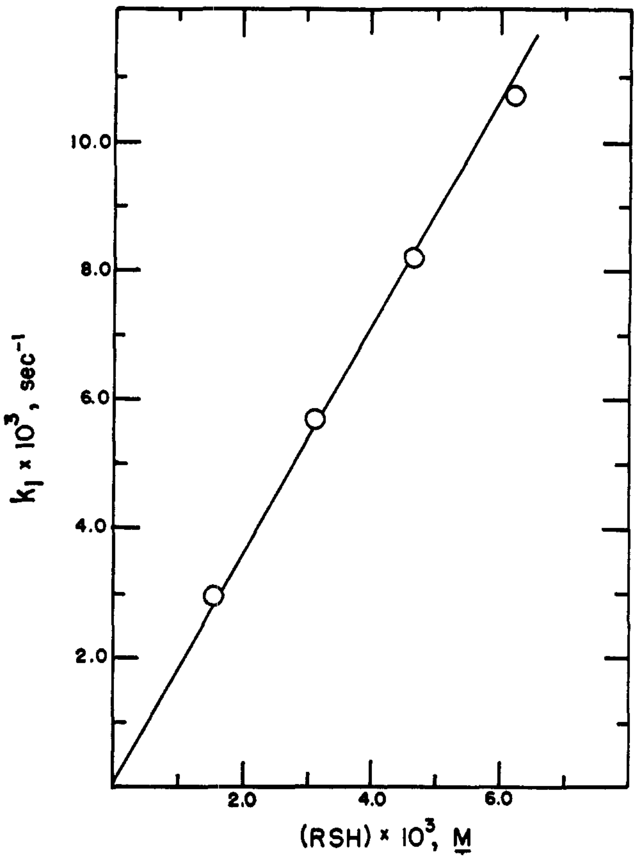

Figure 2.—Dependence of the rate of the thiolsulfinate–mercaptan reaction on mercaptan concentration. Data shown are for the reaction of I with *n*-BuSH in AcOH–0.56 *M* H_2O–0.10 *M* H_2SO_4.

tion of water in the solvent was varied (part C of Table I). Figure 3 is a plot of log k_{RSH} for these runs *vs.* the Hammett acidity function, $-H_0$, for the solutions.[5] One sees that the change in log k_{RSH} is linear with the change in H_0 for both variation in sulfuric acid concentration and water content of the medium. The slope of the plot is 1.1.

Table I

Kinetics of the Reaction of Phenyl Benzenethiolsulfinate with 1-Butanethiol[a]

C_{H_2O}, *M*	$C_{H_2SO_4}$, *M*	$(I)_0 \times 10^3$, *M*	(RSH) × 10^3, *M*	$k_1 \times 10^3$, sec^{-1}	$k_{RSH} = \left[\frac{k_1}{(RSH)_{av}}\right]^c$
	A. Dependence on Thiol Concentration				
0.56	0.10	0.16	1.6	2.95	2.0
		0.31	3.1	5.7	2.0
			4.7	8.2	1.9
			6.2	10.7	1.8
	B. Effect of Sulfuric Acid Concentration				
0.56	0.05	0.31	3.1	2.2	0.79
	0.10	*b*	*b*	*b*	2.0
	0.15	0.31	3.1	10.3	3.7
	0.20	0.31	3.1	18	6.4
	C. Effect of Stoichiometric Water Concentration				
0.56	0.10	*b*	*b*	*b*	2.0
1.12	0.10	0.31	3.1	2.9	1.04

[a] All runs at 39.6° in acetic acid solvent containing the amounts of water and sulfuric acid indicated. [b] See part A of the table for experimental data from which k_{RSH} was calculated. [c] $(RSH)_{av}$ equals the average thiol concentration during a run and is taken to be given by $(RSH)_0 - (I)_0$.

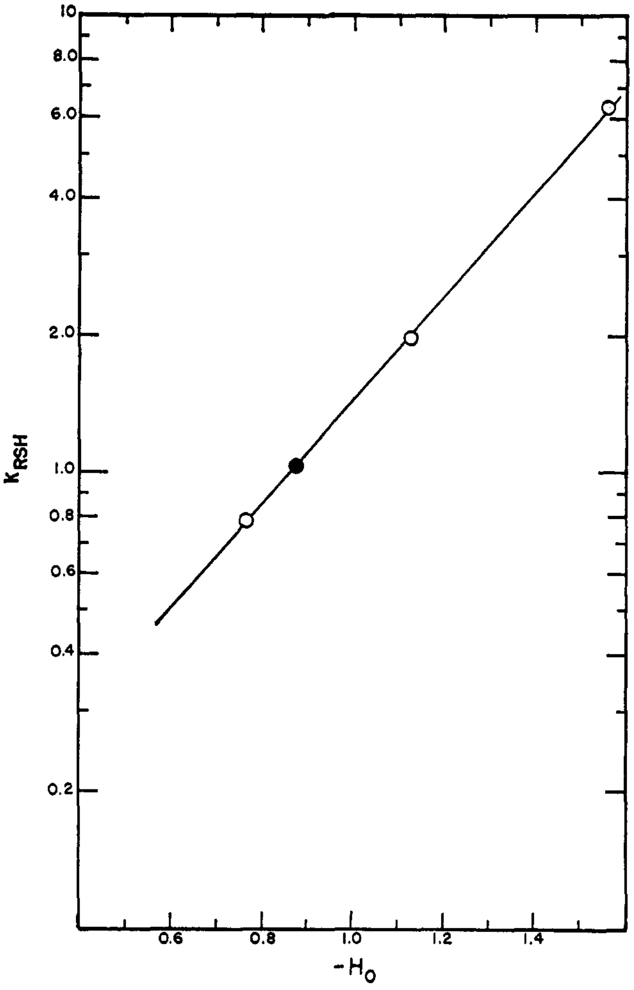

Figure 3.—Dependence of log k_{RSH} on the acidity of the medium. Open circles are for runs in AcOH–0.56 *M* H_2O with 0.05, 0.10, and 0.20 *M* H_2SO_4. Closed circle is for run in AcOH–1.12 *M* H_2O–0.10 *M* H_2SO_4.

The dependence of k_{RSH} on both sulfuric acid and water concentration is quite different from the dependence of the rate constant for the normal thiolsulfinate–sulfinic acid reaction on these same variables.[2] Thus, the rate constant for the I–$ArSO_2H$ reaction showed virtually no change upon variation of the water content of the medium, and a linear increase with (H_2SO_4), rather than a dependence of log k on $-H_0$, with variation of sulfuric acid concentration.

Sulfide Catalysis of the Thiolsulfinate–Mercaptan Reaction.—Addition of small amounts of various alkyl sulfides results in an increase in the rate of the thiolsulfinate–mercaptan reaction. Three different sulfides have been studied kinetically as catalysts for the reaction of 1-butanethiol with I. The results are summarized in Table II. The next to the last column of the table gives k_1, the experimental first-order rate constant for the disappearance of the thiolsulfinate under the various reaction conditions.

In the presence of added sulfide the rate of disappearance of I will be the sum of the rates of the normal and sulfide-catalyzed thiolsulfinate–mercaptan reactions. This means that k_1 will be given by

$$k_1 = k_{RSH}(RSH) + k_{cat} = k_1^0 + k_{cat}$$

and

$$k_{cat} = k_1 - k_1^0$$

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[5] J. Rocek, *Collect. Czech. Chem. Commun.*, **22**, 1 (1957).

Table II

Kinetics of the Sulfide-Catalyzed Reaction of Phenyl Benzenethiolsulfinate with 1-Butanethiol[a]

$C_{H_2SO_4}$, M	$(I)_0 \times 10^3$, M	(RSH) $\times 10^3$, M	$(R_2'S) \times 10^4$, M	$k_1 \times 10^3$, sec^{-1}	$k_S = \left[\frac{k_1 - k_1^0}{(R_2'S)}\right]^b$
		n-Butyl Sulfide			
0.10	0.31	3.1	0.75	21.4	2.1×10^2
			0.375	13.3	2.0×10^2
	0.16	1.6	0.20	7.4	2.2×10^2
		Benzyl Sulfide			
0.10	0.31	3.1	0.60	7.1	23
			1.2	8.6	24
			3.0	14.2	28
		4.7	3.0	16.7	28
		6.2	3.0	17.5	23
0.05	0.31	3.1	3.0	5.1	9.7
		Benzyl Phenyl Sulfide			
0.10	0.16	1.6	18.8	3.9	0.52
			37.5	4.8	0.49

[a] All runs at 39.6° in acetic acid containing 0.56 M water and the amount of sulfuric acid indicated. [b] k_1^0 equals the rate of disappearance of I in the absence of added sulfide under otherwise identical conditions. For values used see Table I.

where k_1^0 equals the rate of the normal I–mercaptan reaction under the same reaction conditions, and k_{cat} is the experimental first-order rate constant for the sulfide-catalyzed reaction; values of k_1^0 are, of course, available from Table I.

The dependence of the rate of the sulfide-catalyzed reaction on sulfide concentration can be determined from runs carried out at a constant thiol concentration but at varying sulfide concentrations. For each of the sulfides in Table II one finds that $(k_1 - k_1^0)/(R_2S)$ is independent of sulfide concentration. This demonstrates that the sulfide-catalyzed reaction is first order in sulfide.

A set of runs in Table II with benzyl sulfide as catalyst in which only the 1-butanethiol concentration was varied shows that there is no significant variation in $(k_1 - k_1^0)/(R_2S)$ with thiol concentration. This means that the rate of the sulfide-catalyzed reaction is independent of thiol concentration. This in turn means that in the sulfide-catalyzed reaction thiol does not play a role until after the rate-determining step.

Now that it is established that the sulfide-catalyzed reaction is first order in both sulfide and thiolsulfinate and independent of thiol concentration we can define k_{cat} as

$$k_{cat} = k_S(R_2S)$$

where k_S is the actual second-order rate constant for the sulfide-catalyzed thiolsulfinate–mercaptan reaction.

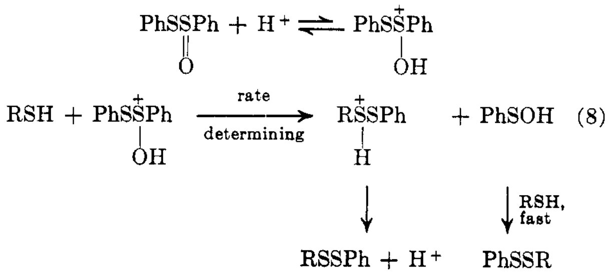
Runs at two different sulfuric acid concentrations (0.05 and 0.10 M) in acetic acid–0.56 M H_2O with benzyl sulfide as catalyst indicate that k_S shows the same dependence on acid concentration as does k_{RSH}.

Discussion

Mechanism of the Thiolsulfinate–Mercaptan Reaction.—The ordinary thiolsulfinate–mercaptan reaction is first order in both thiolsulfinate and mercaptan; it is also acid catalyzed. The dependence of its rate constant, k_{RSH}, on the acidity of the medium (Figure 3) is exactly the same as that observed[2] for the sulfide-catalyzed thiolsulfinate–sulfinic acid reaction, and quite different from that found[2] for the ordinary thiolsulfinate–sulfinic acid reaction. Since the sulfide-catalyzed I–$ArSO_2H$ reaction is known[2] to exhibit specific H^+ catalysis while the ordinary I–$ArSO_2H$ reaction exhibits general acid catalysis, the obvious inference is that the thiolsulfinate–mercaptan reaction is also specific H^+ catalyzed. The mechanism in Chart II is accordingly suggested for the reaction.

Chart II

Mechanism of the Thiolsulfinate–Mercaptan Reaction



$$\underset{\underset{O}{\|}}{PhSSPh} + H^+ \rightleftharpoons \underset{\underset{OH}{|}}{PhS\overset{+}{S}Ph}$$

$$RSH + \underset{\underset{OH}{|}}{PhS\overset{+}{S}Ph} \xrightarrow[\text{determining}]{\text{rate}} \underset{\underset{H}{|}}{R\overset{+}{S}SPh} + PhSOH \quad (8)$$

$$R\overset{+}{S}(H)SPh \longrightarrow RSSPh + H^+ \qquad PhSOH \xrightarrow{\text{RSH, fast}} PhSSR$$

The significant difference between this mechanism and the one for the thiolsulfinate–sulfinic acid reaction shown in eq 1 and 2 is the fact that in eq 8 the formation of the new S–S bond is *not* concerted with the removal of the proton of the thiol, while in eq 2 nucleophilic attack of the sulfinic acid on the protonated thiolsulfinate is accompanied by transfer of the sulfinic acid proton to a general base. As noted earlier, the hypothesis has been that it is the energetically unfavorable nature of II, the intermediate which would have to be formed if the sulfinic acid proton were not transferred, which causes the general base-catalyzed process to be preferred in that case, and the prediction was that nucleophilic attack of a reagent like RSH on the protonated thiolsulfinate would not require such general base catalysis. The present results bear out this prediction and thus provide strong evidence for the validity of the hypothesis in question.

Mechanism of the Sulfide-Catalyzed Thiolsulfinate–Mercaptan Reaction.—The mechanism (Chart I) which has been proposed[2] for the sulfide-catalyzed thiolsulfinate–sulfinic acid reaction requires that alkyl sulfides should also be able to catalyze the reaction of mercaptans with thiolsulfinates *via* an analogous mechanism. This means that the formal kinetics of such a sulfide-catalyzed I–mercaptan reaction should be the same as those for the sulfide-catalyzed I–$ArSO_2H$ reaction. Thus the reaction should be first order in both thiolsulfinate and sulfide, it should be subject to specific oxonium ion catalysis, and its rate should be independent of mercaptan concentration. This is indeed what we have found.

Since the sulfide-catalyzed reactions of mercaptans and sulfinic acids with I should both have the same rate-determining step (eq 3), the rate constants (k_S) for the two processes should be the same under a given set of reaction conditions. Table III compares the k_S values for the three sulfides used as catalysts for the I–*n*-BuSH reaction with the same quantity for these compounds as catalysts for the I–$ArSO_2H$ reaction. For each sulfide the value of k_S for the sulfide-catalyzed mercaptan reaction is within 20% of k_S for the analogous

Table III

Rate Constants for Sulfide-Catalyzed Reactions of Phenyl Benzenethiolsulfinate[a]

Sulfide	k_S, M^{-1} sec^{-1} I-n-BuSH reaction	k_S, M^{-1} sec^{-1} I-ArSO$_2$H reaction[b]
n-Bu$_2$S	2.1×10^2	1.7×10^2
$(C_6H_5CH_2)_2S$	25	21
$C_6H_5CH_2SC_6H_5$	0.50	0.42

[a] All data are for acetic acid-0.56 M water-0.10 M H_2SO_4 as solvent. The data for the sulfinic acid reaction were obtained at 39.4°, those for the mercaptan reaction at 39.6°. [b] Reference 2.

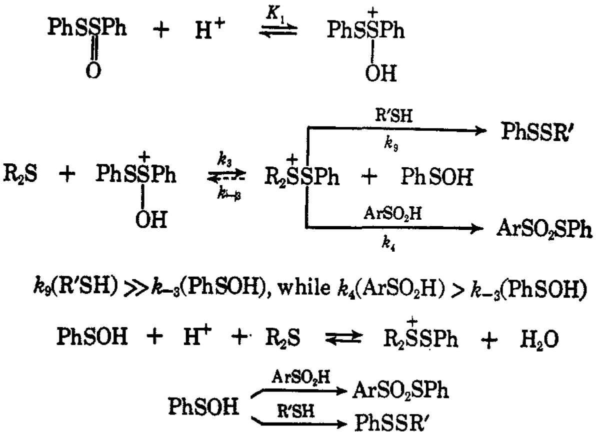
sulfide-catalyzed sulfinic acid reaction. This close correspondence in k_S values is more impressive when one notes that the three sulfides in question span a range of reactivity of a factor of about 400.

It is true, however, that instead of being exactly the same as k_S for the I-ArSO$_2$H reaction k_S for each sulfide-catalyzed mercaptan reaction is about 20% larger. Because the accuracy of measurement of k_S is probably no better than ±10% in each case, this is not actually much larger than the experimental uncertainty in k_S itself. However, we believe that the difference is probably real. Although part of it is doubtless due to the fact that the k_S values for the I-mercaptan reaction were determined at 0.2° higher temperature than those for the I-ArSO$_2$H reaction, this cannot account for all the difference. Rather we suspect that most of it results from the fact that ArSO$_2$H is not quite as efficient as the thiol in trapping R_2S^+-SPh (III), and that, in the case of the sulfide-catalyzed I-ArSO$_2$H reaction, a small percentage of the R_2S^+-SPh ions produced in eq 3 manage to return to thiolsulfinate and R$_2$S *via* reaction with PhSOH (reverse of reaction 3). The percentage of R_2S^+-SPh ions doing this is not large enough, however, to lead to any significant dependence of the rate of the sulfide-catalyzed I-ArSO$_2$H reaction on sulfinic acid concentration. In other words, since the vast majority (~85-95%) of the R_2S^+-SPh ions still disappear by reaction with ArSO$_2$H (eq 4), reaction 3 is still the rate-determining step.[6]

Chart III summarizes our present view of the mechanistic picture for the two sulfide-catalyzed reactions. The only difference between this and the scheme in Chart I is the introduction of the concept that k_4(ArSO$_2$H) is not so much larger than k_{-3}(PhSOH) that every III is scavenged by sulfinic acid. Rather a small percentage of them (between 5 and 15%, depending on sulfinic acid concentration) revert back to thiolsulfinate and R$_2$S *via* the reaction shown as having rate constant k_{-3}. In the sulfide-catalyzed I-mercaptan reaction, on the other hand, k_9(R'SH) is enough larger than k_{-3}(PhSOH) so that effectively every III is scavenged by thiol and the k_S values are uniformly a few per cent larger than those for the corresponding sulfide-catalyzed I-ArSO$_2$H reaction.

Chart III

Mechanism and Kinetic Relationships for Sulfide-Catalyzed Reactions of Phenyl Benzenethiolsulfinate



$$PhS(O)SPh + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} PhS\overset{+}{S}(OH)Ph$$

$$R_2S + PhS\overset{+}{S}(OH)Ph \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} R_2\overset{+}{S}SPh + PhSOH$$

$$R_2\overset{+}{S}SPh \xrightarrow[k_9]{R'SH} PhSSR' \qquad R_2\overset{+}{S}SPh \xrightarrow[k_4]{ArSO_2H} ArSO_2SPh$$

k_9(R'SH) >> k_{-3}(PhSOH), while k_4(ArSO$_2$H) > k_{-3}(PhSOH)

$$PhSOH + H^+ + R_2S \rightleftharpoons R_2\overset{+}{S}SPh + H_2O$$

$$PhSOH \xrightarrow{ArSO_2H} ArSO_2SPh \qquad PhSOH \xrightarrow{R'SH} PhSSR'$$

Experimental Section

Purification of Materials.—The thiols (Wateree Chemical Co.) were purified by fractional distillation under nitrogen. The preparation and purification of the remaining materials have been described previously.[2]

Procedure for Kinetic Runs.—The runs were carried out in the special spectrophotometer reaction cell described in detail in an earlier publication.[7] A measured amount of a stock solution of the thiolsulfinate was placed in chamber A of this apparatus. Measured amounts of stock solutions of the remaining reagents and any additional acetic acid-0.56 M water required for the proper final volume were placed in chamber B. The contents of the two chambers were then frozen, and the system was degassed twice using the procedure described by Kice, Guaraldi, and Venier.[7] After the second degassing, the contents of the two chambers were brought to the reaction temperature, and the two solutions were then quickly mixed. The resulting final solution was poured into the spectrophotometer cell C attached to the top of chamber B, and the apparatus was placed in the cell compartment of a Cary Model 15 spectrophotometer which was equipped to permit thermostating of cell C. The decrease in the optical density of the solution at 296 mμ was then recorded as a function of time.

Stoichiometry of the Thiolsulfinate-Mercaptan Reaction.—A deaerated solution of 2.00 mmol of I in 20 ml of acetic acid-0.56 M H$_2$O-0.10 M H$_2$SO$_4$ was added to 80 ml of the same solvent containing 10.0 mmol of thiophenol. The resulting solution was allowed to stand at 25° for 1 hr. The decrease in the optical density of the solution in the 290-310-mμ range indicated that all of the thiolsulfinate had reacted by the end of that time. A small aliquot of the solution was removed and titrated for residual thiophenol content with standard iodine solution. The remainder of the solution was then poured into ten times its volume of water in a separatory funnel. The mixture was extracted twice with a total of 400-500 ml of ether, and the combined ether extracts were then washed five times with water to remove as much acetic acid as possible. The ether extracts were then washed repeatedly with sodium bicarbonate solution until the washings remained alkaline, and, following that, were washed several more times with water. The ether solution was dried over anhydrous magnesium sulfate, and the ether was removed under reduced pressure. The residue was chromatographed on Merck acid-washed alumina. Elution with hexane gave phenyl disulfide in a yield of 98% based on the stoichiometry of eq 7 and identical in all respects with a known sample.

Registry No.—I, 1208-20-4; 1-butanethiol, 109-79-5.

Acknowledgment.—Dr. C. G. Venier assisted in carrying out several of the experiments.

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(6) Reexamination of the data (Table V of ref 2) for the sulfide-catalyzed thiolsulfinate-sulfinic acid reaction does indicate that there may be a tendency for k_S for a given sulfide to increase slightly with increasing sulfinic acid concentration, as would be required on the basis of the discussion in the preceding paragraph. Because the observed increase is, as would also be expected, quite small (~5-10%), one cannot, given the experimental uncertainty in k_S (±10%), say definitely that it is real, however.

(7) J. L. Kice, G. Guaraldi, and C. G. Venier, *J. Org. Chem.*, **31**, 3561 (1966).