Mechanisms of Reactions of Thiolsulfinates (Sulfenic Anhydrides). I. The Thiolsulfinate–Sulfinic Acid Reaction[1a]

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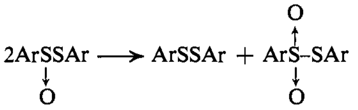
Abstract: In aqueous acetic acid containing some sulfuric acid, aryl thiolsulfinates (sulfenic anhydrides) react with aromatic sulfinic acids considerably more rapidly than they undergo disproportionation to thiolsulfonate and disulfide. The mechanism of this previously unreported thiolsulfinate–sulfinic acid reaction has been investigated. Of particular interest is the fact that the reaction is subject to rather dramatic catalysis by added alkyl or aryl sulfides. Study of the dependence of the rate of the sulfide-catalyzed reaction on various reaction variables shows that the mechanism involves a rate-determining nucleophilic attack by the sulfide on the protonated thiolsulfinate (eq 5). The catalyzed reaction is thus similar to several other recently studied S–S bond scissions in requiring both nucleophilic and electrophilic assistance. The nonsulfide-catalyzed thiolsulfinate–sulfinic acid reaction exhibits a different dependence on the acidity of the medium and a different solvent isotope effect than the sulfide-catalyzed process. This, coupled with the variation of rate with sulfinic acid structure, suggests that its mechanism involves a general base catalyzed attack of the sulfinic acid on the protonated thiolsulfinate (eq 11).

Thiolsulfinates [RS(O)SR] and those compounds designated in the earlier literature as sulfenic anhydrides (RSOSR) have been shown by Vinkler and Klivenyi[2] to be, in fact, identical and to possess the thiolsulfinate structure. This fact, and their additional observation[2b] that thiolsulfinates are invariably the initial isolable hydrolysis products of sulfenyl halides, give thiolsulfinates a position of considerable importance in organic sulfur chemistry and argue strongly for extensive study of the mechanisms of their reactions.

Although Vinkler and Klivenyi[2b] observed reaction of aryl thiolsulfinates with a variety of reagents in basic or neutral solution, the only reaction which they noted in acid medium was their disproportionation (eq 1).



$$2\mathrm{Ar}\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{S}}\mathrm{SAr} \longrightarrow \mathrm{ArSSAr} + \mathrm{Ar}\overset{\substack{\mathrm{O}\\ \uparrow}}{\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{S}}}\mathrm{-SAr} \qquad (1)$$

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This reaction, which has also been studied by Barnard,[3] seems generally in the past to have been considered the only important reaction of thiolsulfinates in acid solution.

We were therefore most interested to find that in moist acetic acid containing some sulfuric acid aryl thiolsulfinates react with arylsulfinic acids much faster than they undergo disproportionation to thiolsulfonate and disulfide, and we were led to undertake an investigation of the mechanism of this previously unreported thiolsulfinate–sulfinic acid reaction. The present paper reports the results of that investigation.

Of particular interest in these results is the marked catalysis of the thiolsulfinate–sulfinic acid reaction by small amounts of added alkyl sulfides. This represents yet another example of concomitant nucleophilic and electrophilic catalysis[4,5] of the scission of a sulfur–sulfur bond in acid solution and further indicates the potential importance of this phenomenon in organosulfur chemistry.

Results

The Thiolsulfinate–Sulfinic Acid Reaction. Stoichiometry. From Figure 1 it is evident that in acetic acid–water–sulfuric acid medium *p*-tolyl *p*-toluenethiolsulfinate (Ia, Ar = *p*-$CH_3C_6H_4$) disappears much more rapidly in the presence of added *p*-toluenesulfinic acid than it does in its absence. The principal reaction product under these conditions is *p*-tolyl *p*-toluenethiolsulfonate (IIIa, Ar = *p*-$CH_3C_6H_4$). However, some *p*-tolyl disulfide (IIa) is also formed. Results for several different initial thiolsulfinate and sulfinic acid concentrations are shown in Table I. Separate experiments in the absence of sulfinic acid showed that the rate of the usual disproportionation (eq 1) under these conditions was too slow to be responsible for more than 10% of the total disulfide formed in any of the runs in Table I. Almost all the disulfide formed must therefore arise as one of the products of the thiolsulfinate–sulfinic acid reaction.

Table I. Stoichiometry of the Reaction between *p*-Tolyl *p*-Toluenethiolsulfinate and *p*-Toluenesulfinic Acid[a]

Initial concn, *M* Thiolsulfinate	Initial concn, *M* Sulfinic acid	Products, mole/mole of thiolsulfinate $ArSO_2SAr$	Products, mole/mole of thiolsulfinate ArSSAr	$ArSO_2H$ consumed, mole/mole of thiolsulfinate
0.0038	0.0295	1.47	0.13	1.47
0.010	0.0985	1.49	0.13	1.35
0.010	0.049	1.17	0.17	1.24
0.020	0.096	1.35	0.18	1.24

[a] All runs at 39.4° in acetic acid–0.56 *M* H_2O–0.20 *M* H_2SO_4 as solvent.

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[1] (a) This research supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grants AF-AFOSR-106-63 and -65. Part of this work has appeared in preliminary form: J. L. Kice and C. G. Venier, *Tetrahedron Letters*, 3629 (1964). (b) National Science Foundation Cooperative Fellow, 1964–1966.

[2] (a) E. Vinkler and F. Klivenyi, *Acta Chim. Acad. Sci. Hung.*, **11**, 15 (1957); (b) *ibid.*, **22**, 345 (1960).

[3] D. Barnard, *J. Chem. Soc.*, 4675 (1957).

[4] J. L. Kice and E. H. Morkved, *J. Am. Chem. Soc.*, 86, 2270 (1964).

[5] J. L. Kice and G. Guaraldi, *ibid.*, **88**, 5236 (1966).

Table II. Kinetics of the Reaction of Phenyl Benzenethiolsulfinate with Sulfinic Acids[a]

Temp, °C	$ArSO_2H$, Ar	C_{H_2O}, M	$C_{H_2SO_4}$, M	$(Ib)_0 \times 10^3$, M	$(ArSO_2H)_0 \times 10^2$, M	$k_1 \times 10^4$, sec^{-1}	$\left[k_\psi = \frac{k_1}{(ArSO_2H)_{av}}\right]^b$
A. Dependence on Thiolsulfinate Concn							
49.3	p-$CH_3C_6H_4$	0.56	0.10	7.6	6.0	8.9	
				3.8	6.0	9.0	
B. Dependence on Sulfinic Acid Concn							
39.4	p-$CH_3C_6H_4$	0.56	0.10	3.8	3.0	2.5	0.0093
					6.0	5.1	0.0089
					9.0	7.9	0.0091
C. Effect of Sulfinic Acid Structure							
39.4	C_6H_5	0.56	0.10	3.8	3.0	2.6	0.0096
	p-BrC_6H_4	0.56	0.10	3.8	3.0	3.6	0.013
	p-$O_2NC_6H_4$	0.56	0.10	3.8	3.0	8.4	0.031
D. Effect of Sulfuric Acid Concn							
39.4	p-$CH_3C_6H_4$	0.56	0.10	c	c	c	0.0091
			0.20	3.8	3.0	4.6	0.017
			0.30	3.8	3.0	6.6	0.024
			0.40	3.8	3.0	8.9	0.033
E. Effect of Stoichiometric Water Concn							
39.4	p-$CH_3C_6H_4$	0.28	0.20	3.8	3.0	4.2	0.015
		0.56	0.20	3.8	3.0	4.6	0.017
		1.16	0.20	3.8	3.0	4.6	0.017
F. Solvent Isotope Effect (Solvent = DOAc)							
39.4	p-$CH_3C_6H_4$	0.56 (D_2O)	0.10	3.8	3.0	2.0	0.0073

[a] Solvent, acetic acid containing the amounts of water and sulfuric acid indicated. [b] $(ArSO_2H)_{av}$ calculated according to eq 2b using a = 1.5. [c] See part B for experimental data from which k_ψ was calculated.

The data in Table I indicate that the amount of thiolsulfonate formed and the amount of sulfinic acid consumed increase somewhat with increasing initial concentration ratio of sulfinic acid to thiolsulfinate. The stoichiometry observed here, where we have 1.25–1.50 moles of sulfinic acid consumed per mole of thiolsulfinate, is significantly different from that observed for the *sulfide-catalyzed* thiolsulfinate–sulfinic acid reaction (*vide infra*), where one has almost exactly 2 moles of sulfinic acid consumed per mole of thiolsulfinate.

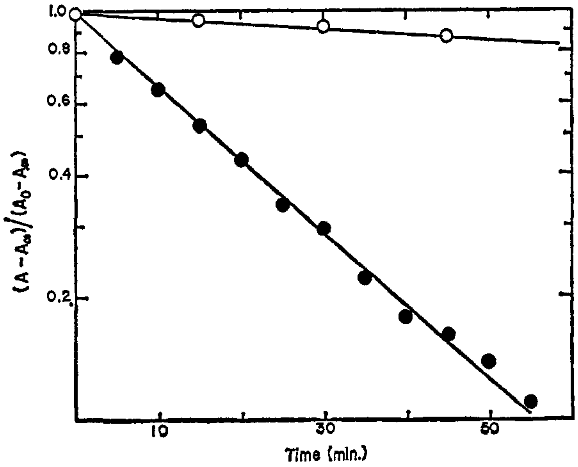

Figure 1. Rate of disappearance of Ia in the presence and absence of p-toluenesulfinic acid: ●, $(Ia)_0$, 3.8×10^{-3} M, $(ArSO_2H)_0$, 3×10^{-2} M; ○, $(Ia)_0$, 2×10^{-2} M, no sulfinic acid added. Both runs in AcOH–0.56 M H_2O–0.20 M H_2SO_4 as solvent.

We have also investigated the stoichiometry of the reaction for the system phenyl benzenethiolsulfinate (Ib, Ar = C_6H_5)-p-toluenesulfinic acid. The thiolsulfonate fraction in this case consists almost entirely of the unsymmetrical thiolsulfonate, phenyl p-toluenethiolsulfonate (p-$CH_3C_6H_4SO_2SC_6H_5$). The other product formed in measurable yield is phenyl disulfide. The yields of thiolsulfonate and disulfide per mole of thiolsulfinate reacting are similar to those for the Ia-p-toluenesulfinic acid system under the same reaction conditions.

Kinetics of the Reaction. Dependence on Thiolsulfinate Concentration. The majority of the kinetic studies of the thiolsulfinate–sulfinic acid reaction have been carried out on the two systems, Ia-p-toluenesulfinic acid (Table III) and Ib-p-toluenesulfinic acid (Table II). Limited studies have been made with Ib and several other aromatic sulfinic acids (Table II). The kinetics of the reactions are most conveniently studied by having the sulfinic acid present in considerable stoichiometric excess and following the disappearance of the thiolsulfinate spectrophotometrically (for the exact procedure see Experimental Section). As Figure 1 shows, under such conditions the disappearance of the thiolsulfinate follows good first-order kinetics. That the reaction is definitely first order in thiolsulfinate is evident from the runs in part A of Table II which show that the experimental first-order rate constant, k_1, for the Ib-p-toluenesulfinic acid reaction does not vary with initial thiolsulfinate concentration.

Dependence on sulfinic acid concentration was investigated with the Ib-p-toluenesulfinic acid system by examining the variation of k_1 for thiolsulfinate disappearance in a series of runs at different initial sulfinic acid concentrations (part B of Table II).

Because of the relatively rapid rate of the thiolsulfinate–sulfinic acid reaction it is inconvenient to operate under conditions where the stoichiometric excess of sulfinic acid is so large that its concentration change during a run is entirely negligible. For this reason the k_1 values for the various runs have been divided, not by $(ArSO_2H)_0$, but by the *average* sulfinic acid concentration during the run, $(ArSO_2H)_{av}$. This

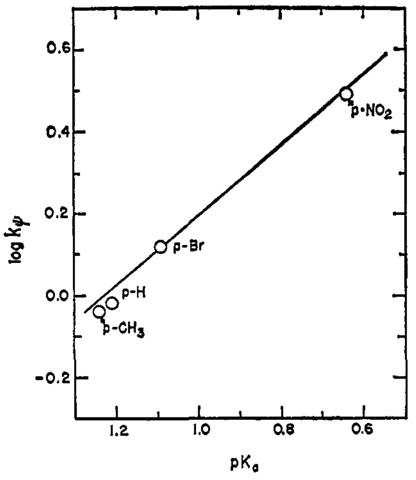

Figure 2. Effect of sulfinic acid structure on the rate of the thiolsulfinate–sulfinic acid reaction. Log k_ψ for reaction of Ib with p-$YC_6H_4SO_2H$ *vs.* pK_a of p-$YC_6H_4SO_2H$.

is equal to

$$(ArSO_2H)_{av} = [(ArSO_2H)_0 + (ArSO_2H)_\infty]/2 \quad (2a)$$

$$(ArSO_2H)_{av} = (ArSO_2H)_0 - (Ib)_0/2a \quad (2b)$$

where a = moles of $ArSO_2H$ consumed per mole of Ib reacting. Because the initial concentration of sulfinic acid in all runs is eight times or more the initial concentration of Ib, the fact that a presumably varies somewhat with exact reaction conditions introduces no significant error in $(ArSO_2H)_{av}$. In the interest of simplicity we have arbitrarily taken a as equal to 1.5 for all the kinetic runs.[6] The constancy of $k_1/(ArSO_2H)_{av}$ with changing sulfinic acid concentration shows that the thiolsulfinate–sulfinic acid reaction is definitely first order in sulfinic acid. In the remainder of the paper the quantity $k_1/(ArSO_2H)_{av}$ will be denoted as k_ψ, the actual second-order rate constant for the thiolsulfinate–sulfinic acid reaction.

Table III. Kinetics of the Reaction between p-Tolyl p-Toluenethiolsulfinate and p-Toluenesulfinic Acid[a]

(Ia) × 10^3, M	$(ArSO_2H)_0$ × 10^2, M	C_{H_2O}, M	$C_{H_2SO_4}$, M	k_1 × 10^4, sec^{-1}	$k_\psi = \left[\frac{k_1}{(ArSO_2H)_{av}}\right]^b$
3.8	12.0	0.56	0.00	3.8	0.0032
	3.0	0.56	0.10	3.9	0.014
			0.20	7.0	0.026
			0.30	9.8	0.036
			0.40	12.4	0.046
		1.13	0.20	7.3	0.027

[a] All runs at 39.4° in acetic acid containing the amounts of water and sulfuric acid indicated. [b] $(ArSO_2H)_{av}$ calculated according to eq 2b using a = 1.5.

Effect of Sulfinic Acid Structure on Rate. The relative reactivity of a series of *para*-substituted benzenesulfinic acids toward Ib was measured under a standard set of conditions (part C of Table II). Figure 2 shows a plot of log k_ψ for the various acids *vs.* their pK_a values as reported by Ritchie, Saltiel, and Lewis.[7] From this plot it is evident that the reactivity of sulfinic acids in the thiolsulfinate–sulfinic acid reaction parallels their acidity, increased acidity being associated with increased reactivity toward the thiolsulfinate. This indicates that electron withdrawal from the sulfinic acid sulfur facilitates the reaction and that the electron density on this sulfur is greater in the transition state than in the sulfinic acid itself.

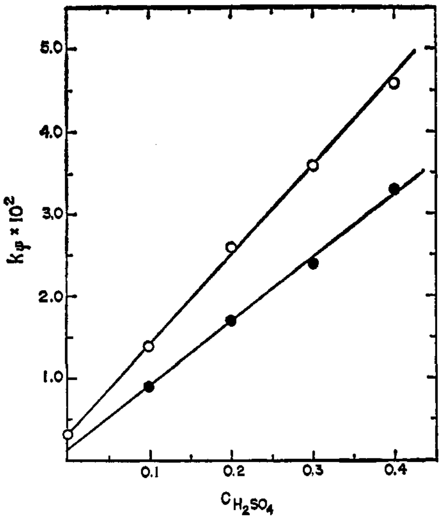

Figure 3. Dependence of k_ψ on (H_2SO_4) in AcOH–0.56 M H_2O medium: ●, Ib-p-$CH_3C_6H_4SO_2H$; ○, Ia-p-$CH_3C_6H_4SO_2H$.

Dependence of Rate on Sulfuric Acid Concentration. The effect on k_ψ of the concentration of sulfuric acid added to the acetic acid–water medium was investigated both for the Ib–p-toluenesulfinic acid reaction (part D of Table II) and the Ia–p-toluenesulfinic acid reaction (Table III). For each set of runs a plot of k_ψ *vs.* (H_2SO_4) is linear with a small intercept (Figure 3). The run with the p-tolyl ester at 0.00 M H_2SO_4 demonstrates that this intercept is real. The dependence of k_ψ on acid concentration in the two cases can be expressed as

$$\text{Ia-}p\text{-}CH_3C_6H_4SO_2H\text{:} \quad k_\psi = 0.0032 + 0.11(H_2SO_4)$$

$$\text{Ib-}p\text{-}CH_3C_6H_4SO_2H\text{:} \quad k_\psi = 0.0015 + 0.077(H_2SO_4)$$

Dependence of Rate on Stoichiometric Concentration of Water. Runs with both Ib–p-toluenesulfinic acid (part E of Table II) and Ia–p-toluenesulfinic acid (Table III) show that k_ψ is practically independent of the stoichiometric concentration of water in the acetic acid–water solvent.

Solvent Isotope Effect. Measurement of the rate of the Ib–p-toluenesulfinic acid reaction in AcOD–0.56 M D_2O–0.10 M H_2SO_4 (part F of Table II) reveals that k_ψ under these conditions is smaller than in the corresponding undeuterated solvent. From the data one calculates a solvent isotope effect of k_H/k_D = 1.27 for the reaction.

The Sulfide-Catalyzed Thiolsulfinate–Sulfinic Acid Reaction. As can be seen from Figure 4, the rate of disappearance of Ib in the presence of p-toluenesulfinic acid is accelerated about sevenfold by the addition of 10^{-5} M n-butyl sulfide to the solution. We have examined the striking catalytic effects of this and other

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[6] This value is undoubtedly quite close to the actual one in most cases. However, even were we to choose values as divergent as 1.3 or 1.7 it would make no difference in the first two significant figures of the $(ArSO_2H)_{av}$ values calculated.

[7] C. D. Ritchie, J. D. Saltiel, and E. S. Lewis, *J. Am. Chem. Soc.*, **83**, 4601 (1961).

Table IV. Stoichiometry of the Sulfide-Catalyzed Reaction of Ib with *p*-Toluenesulfinic Acid[a]

Catalyst, concn, *M*	Initial concn, *M*		Products, mole/mole of thiolsulfinate		$ArSO_2H$ consumed, mole/mole of thiolsulfinate
	PhS(O)SPh	$ArSO_2H$	$ArSO_2SPh$	PhSSPh	
$(PhCH_2)_2S$, 5 × 10^{-4}	0.020	0.100	1.71	0.03	1.97
Ph_2S, 0.051	0.015	0.100	1.7	*b*	1.9

[a] Benzyl sulfide catalyzed data are for acetic acid–0.56 *M* H_2O–0.20 *M* H_2SO_4 solution at 39.4°. Phenyl sulfide same. [b] Not determined.

sulfides in considerable detail, both as regards the kinetics and stoichiometry of the process.

Stoichiometry of the Sulfide-Catalyzed Reaction. Table IV summarizes the stoichiometries observed for the benzyl and phenyl sulfide catalyzed reaction of Ib with *p*-toluenesulfinic acid. Comparison with Table I shows that the stoichiometry of the sulfide-catalyzed reaction is significantly different from that found in the absence of sulfide catalysis. Specifically, in the presence of sulfide there is practically no disulfide formed, and the consumption of sulfinic acid and yield of unsymmetrical thiolsulfonate[8] suggest that the sulfide-catalyzed reaction has the stoichiometry shown in eq 3.

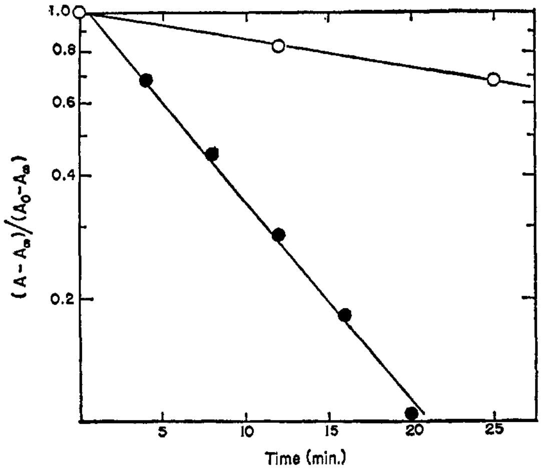
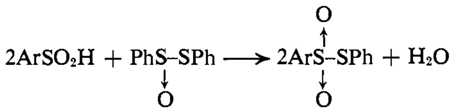


Figure 4. Effect of alkyl sulfides on the rate of the thiolsulfinate–sulfinic acid reaction: ●, (n-Bu_2S), 1 × 10^{-5} *M;* ○, no sulfide added. Both runs with $(Ib)_0$, 0.0038 *M*, and (p-$CH_3C_6H_4SO_2H$), 0.030 *M*, and AcOH–0.56 *M* H_2O–0.10 *M* H_2SO_4 as solvent.



$$2\mathrm{ArSO_2H} + \mathrm{Ph}\underset{\underset{\displaystyle \mathrm{O}}{\downarrow}}{\mathrm{S}}\text{–}\mathrm{SPh} \longrightarrow 2\mathrm{Ar}\overset{\overset{\displaystyle \mathrm{O}}{\uparrow}}{\underset{\underset{\displaystyle \mathrm{O}}{\downarrow}}{\mathrm{S}}}\text{–}\mathrm{SPh} + \mathrm{H_2O} \qquad (3)$$

Kinetics of the Sulfide-Catalyzed Reaction. Runs in the presence of added sulfides give good linear plots of log (thiolsulfinate) *vs.* time (see Figure 4), indicating that the sulfide-catalyzed reaction, like the normal thiolsulfinate–sulfinic acid reaction, is first order in thiolsulfinate. This was further confirmed by the observation that changes in initial thiolsulfinate concentration under otherwise constant reaction conditions lead to no change in the experimental first-order rate constant.

All told we have investigated the catalytic effect of eight different sulfides on the reaction of Ib with several sulfinic acids in acetic acid–0.56 *M* water solvent. Our kinetic results are summarized in Table V. The next to the last column in the table gives the values of k_1, the experimental first-order rate constant for disappearance of the thiolsulfinate, found under the various reaction conditions.

Table V. Kinetics of the Sulfide-Catalyzed Reaction of Phenyl Benzenethiolsulfinate with Sulfinic Acids[a]

$ArSO_2H$, Ar	$(ArSO_2H)_0$ × 10^2, *M*	(R_2S) × 10^4, *M*	$C_{H_2SO_4}$, *M*	k_1 × 10^4, sec^{-1}	$k_s = \left[\frac{k_1 - k_1^{\circ}}{(R_2S)}\right]^b$
		Benzyl Sulfide			
p-$CH_3C_6H_4$	3.0	0.10	0.10	4.5	21
		0.18	0.10	6.1	21
		0.20	0.10	6.4	20
	5.0	0.20	0.10	8.9	23
	6.0	0.20	0.10	9.7	23
	3.0	0.18	0.10	7.0 (DOAc)	28 (DOAc)
C_6H_5	3.1	0.10	0.10	4.6	20
p-$CH_3C_6H_4$	3.0	0.10	0.20	10.4	59
		Benzyl Phenyl Sulfide			
p-$CH_3C_6H_4$	3.0	15	0.10	8.3	0.39
		10	0.10	6.5	0.41
		5.0	0.10	4.5	0.42
	4.5	5.0	0.10	5.9	0.44
	6.0	5.0	0.10	7.1	0.40
	7.5	5.0	0.10	8.8	0.46
	9.0	5.0	0.10	10.0	0.44
p-BrC_6H_4	3.0	10	0.10	7.5	0.39
p-$CH_3C_6H_4$	3.0	5.0	0.20	10.7	1.2
		2.0	0.30	11.6	2.6
		Phenyl Sulfide			
p-$CH_3C_6H_4$	3.0	199	0.10	4.2	0.0090
	5.0	199	0.10	5.9	0.0085
	3.0	99	0.20	6.6	0.021
		71	0.30	10.1	0.053
		195	0.30	16.2	0.051
		97	0.40	15.6	0.072
		n-Butyl Sulfide			
p-$CH_3C_6H_4$	3.0	0.099	0.10	18.2	1.6 × 10^2
		0.020	0.10	5.8	1.7 × 10^2
	6.0	0.020	0.10	8.4	1.7 × 10^2
C_6H_5	3.0	0.024	0.10	6.6	1.7 × 10^2
		Ethyl Sulfide			
C_6H_5	3.0	0.010	0.10	4.5	1.9 × 10^2
		0.021	0.10	6.8	2.1 × 10^2
		Tetrahydrothiophene			
C_6H_5	3.0	0.020	0.10	9.5	3.6 × 10^2
		0.004	0.10	4.0	3.8 × 10^2
		Thiodipropionic Acid			
C_6H_5	3.0	10	0.10	33.4	3.1
		2.0	0.10	8.7	3.1
		Thiodiacetic Acid			
C_6H_5	3.0	600	0.10	5.7	0.0053
		300	0.10	4.2	0.0057

[a] All runs at 39.4° in acetic acid containing 0.56 *M* water and the amount of sulfuric acid indicated. The initial concentration of Ib in all runs with *p*-toluenesulfinic acid was 3.8 × 10^{-3} *M;* in all runs with benzenesulfinic acid it was 4.0 × 10^{-3} *M*. [b] k_1^0 equals $k_\psi \cdot (ArSO_2H)_{av}$ for the particular reaction conditions; k_ψ values taken from Table II; $(ArSO_2H)_{av}$ taken as $(ArSO_2H)_0 - (Ib)_0$.

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(8) The yields of thiolsulfonate in Table IV are probably a few per cent low due to losses during recovery and isolation. The consumption of sulfinic acid, on the other hand, was measured titrametrically.

Dependence of the Rate of the Sulfide-Catalyzed Reaction on Sulfide and Sulfinic Acid Concentration. In the presence of added sulfide the rate of disappearance of the thiolsulfinate will be the sum of the rates of the normal and sulfide-catalyzed reactions. The experimental first-order rate constant, k_1, will thus be given by

$$k_1 = k_\psi(\mathrm{ArSO_2H})_{\mathrm{av}} + k_{\mathrm{cat}} = k_1^0 + k_{\mathrm{cat}}$$

where k_1^0 equals that part of the rate due to the normal thiolsulfinate– sulfinic acid reaction. The experimental first-order rate constant for the sulfide-catalyzed reaction, k_{cat}, can therefore be extracted by the simple expedient of subtracting k_1^0, calculated using the k_ψ values of Table II, from k_1, *i.e.*

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

If for a given sulfide we carry out a series of runs at constant sulfinic acid concentration but at varying sulfide concentrations we can determine the dependence of rate on sulfide concentration. Such data have been obtained for each of the sulfides in Table V, and in every instance one finds that $(k_1 - k_1^0)/(\mathrm{R_2S})$ is independent of sulfide concentration. This shows beyond any doubt that the sulfide-catalyzed reaction is first order in sulfide.

The dependence of the rate on sulfinic acid concentration can be determined by measuring the variation in $(k_1 - k_1^0)/(\mathrm{R_2S})$ with changing sulfinic acid concentration under otherwise constant reaction conditions. The most extensive studies of this type were carried out on the benzyl phenyl sulfide catalyzed reaction (see Table V). These and more limited studies involving the benzyl, *n*-butyl, and phenyl sulfide catalyzed reactions (Table V) all indicate that $(k_1 - k_1^0)/(\mathrm{R_2S})$ for a given sulfide is *effectively independent of sulfinic acid concentration*. One also finds (Table V) that $(k_1 - k_1^0)/(\mathrm{R_2S})$ for a given sulfide is *independent of the structure of the sulfinic acid* reacting with Ib. Thus under a given set of reaction conditions one gets, within the experimental error, the same $(k_1 - k_1^0)/(\mathrm{R_2S})$ for the benzyl phenyl sulfide catalyzed reaction of Ib with *p*-bromobenzenesulfinic acid as with *p*-toluenesulfinic acid, even though these two acids react with Ib at significantly different rates in the normal thiolsulfinate–sulfinic acid reaction (see Table II).

These results demonstrate unequivocally that the rate of the sulfide-catalyzed thiolsulfinate–sulfinic acid reaction is zero order in sulfinic acid concentration and independent of sulfinic acid structure. This means that, despite the fact that the over-all stoichiometry of the sulfide-catalyzed reaction (eq 3) involves the consumption of two molecules of sulfinic acid per molecule of thiolsulfinate, sulfinic acid is *not* a part of the rate-determining transition state. Rather this transition state is derived from a molecule each of the thiolsulfinate and the catalyzing alkyl or aryl sulfide.

Now that we know that the sulfide-catalyzed reaction is first order in both thiolsulfinate and sulfide and zero order in sulfinic acid we can define k_{cat} somewhat more explicitly, *i.e.*

$$k_{\mathrm{cat}} = k_{\mathrm{s}}(\mathrm{R_2S})$$

Here k_{s} is the actual second-order rate constant for the sulfide-catalyzed thiolsulfinate–sulfinic acid reaction.

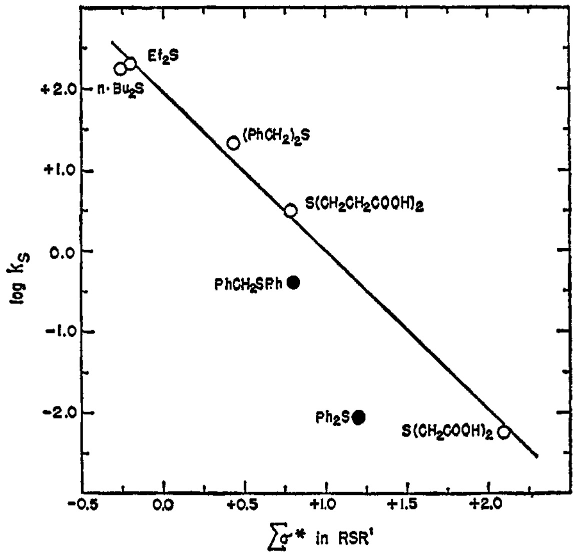

Figure 5. Log k_{s} for the sulfide-catalyzed thiolsulfinate–sulfinic acid reaction *vs.* $\Sigma\sigma^*$ for R and R′ in RSR′.

Variation of k_{s} with Sulfide Structure. Even a cursory inspection of Table V reveals that k_{s} varies tremendously with sulfide structure. In Table VI we have summarized the appropriate data for the various sulfides in a more easily examined form. One sees that there is something like a 60,000-fold spread in reactivity between thiodiacetic acid, the least reactive sulfide, and tetrahydrothiophene, the most reactive. A plot of log k_{s} *vs.* $\Sigma\sigma^*$ for R in $\mathrm{R_2S}$ is shown in Figure 5. The data for all the sulfides except those two having an aryl group attached directly to sulfur fall on a good straight line. Its slope ($\rho^* = -2.0$) indicates that the electron density on the sulfide sulfur is significantly lower in the transition state than it is in the sulfide itself.

Table VI. Relative Reactivity of Various Sulfides as Catalysts for the Thiolsulfinate–Sulfinic Acid Reaction

Sulfide	k_{s}, M^{-1} sec^{-1}[a]
Tetrahydrothiophene	370
Et$_2$S	200
n-Bu$_2$S	170
$(\mathrm{C_6H_5CH_2})_2\mathrm{S}$	21
$(\mathrm{HOOCCH_2CH_2})_2\mathrm{S}$	3.1
$\mathrm{C_6H_5CH_2SC_6H_5}$	0.42
$(\mathrm{C_6H_5})_2\mathrm{S}$	0.0087
$(\mathrm{HOOCCH_2})_2\mathrm{S}$	0.0055

[a] All data are for the sulfide-catalyzed reaction of Ib with sulfinic acids in acetic acid–0.56 M $\mathrm{H_2O}$–0.10 M $\mathrm{H_2SO_4}$ at 39.4°.

The two sulfides with an aryl group attached directly to sulfur, benzyl phenyl and phenyl, are both less reactive than predicted from the log k_{s} *vs.* σ^* correlation line. Similar behavior has been observed[9] in the rates of oxidation of a series of sulfides by hydrogen peroxide in acid solution. Presumably it results from the fact that in reactions where the aryl sulfide functions as a nucleophile there is decreased resonance interaction between the unshared pairs on sulfur and the aromatic ring in the transition state.

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[9] G. Modena and L. Maioli, *Gazz. Chim. Ital.*, **87**, 1306 (1957).

Dependence of k_s on Acidity. The dependence of k_s on the acidity of the medium was investigated both by a series of runs at varying sulfuric acid concentration in acetic acid–0.56 M water solvent (Table V) and also by runs in which the stoichiometric concentration of water in the solvent was varied (see appropriate entries in Table VII). Both the phenyl benzyl and phenyl sulfide catalyzed reactions of Ib with *p*-toluenesulfinic acid were studied. The results are summarized in Table VII; there one sees that for each sulfide log $k_s + H_0$ is effectively constant with both changing sulfuric acid and changing stoichiometric water concentration.

Table VII. Dependence of k_s on Acidity

Sulfide[a]	C_{H_2O}, M	$C_{H_2SO_4}$, M	H_0[b]	k_s, M^{-1} sec^{-1}	Log $k_s + H_0$
$C_6H_5CH_2SC_6H_5$	0.56	0.10	−1.13	0.42	−1.51
		0.20	−1.56	1.2	−1.48
		0.30	−1.86	2.6	−1.45
	1.12	0.10	−0.88	0.28	−1.44
$(C_6H_5)_2S$	0.56	0.10	−1.13	0.0087	−3.19
		0.20	−1.56	0.021	−3.24
		0.30	−1.86	0.052	−3.14
		0.40	−2.08	0.072	−3.22
	1.15	0.20	−1.30	0.013	−3.19

[a] All data are for sulfide-catalyzed reaction of Ib with *p*-toluenesulfinic acid at 39.4°. [b] Values of H_0 for acetic acid–0.56 M H_2O solutions are taken directly from J. Rocek, *Collection Czech. Chem. Commun.*, **22**, 1 (1957); those for acetic acid–1.12 M H_2O and –1.15 M H_2O are interpolated from data in the same reference for acetic acid–0.56 M H_2O, acetic acid–2.80 M H_2O, and acetic acid–5.60 M H_2O.

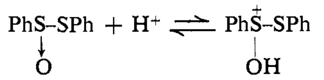
The dependence of k_s on either sulfuric acid or water concentration is strikingly different from the dependence of k_ψ for the normal thiolsulfinate–sulfinic acid reaction on the same variables. In the latter case one found (Table II) essentially no dependence of k_ψ on stoichiometric water concentration and a linear relation between k_ψ and $C_{H_2SO_4}$ in acetic acid–0.56 M H_2O. In the sulfide-catalyzed reactions the increase in k_s with acid concentration is much more marked and is no longer linear with $C_{H_2SO_4}$, and there is a marked decrease in k_s with increasing water content of the medium. Both these changes follow the change in H_0 of the medium.

Solvent Isotope Effect of the Sulfide-Catalyzed Reaction. The rate constant for the benzyl sulfide catalyzed reaction of Ib with *p*-toluenesulfinic acid is found (Table V) to be larger in AcOD–0.56 M D_2O–0.10 M H_2SO_4 than in the corresponding undeuterated medium. The ratio (k_s^{HOAc}/k_s^{DOAc}) is 0.75. The solvent isotope effect for the sulfide-catalyzed reaction is thus in marked contrast to that observed (Table II) for the normal thiolsulfinate–sulfinic acid reaction $(k_\psi^{HOAc}/k_\psi^{DOAc} = 1.3)$.

Discussion

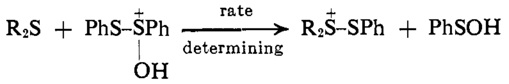
Mechanism of the Sulfide-Catalyzed Thiolsulfinate–Sulfinic Acid Reaction. Although the sulfide-catalyzed reaction has the stoichiometry shown in eq 3 its rate is independent of both sulfinic acid concentration and structure. This means that sulfinic acid does not intervene chemically in the sulfide-catalyzed reaction until *after* the rate-determining step. The nature of that rate-determining step must be such as to be in accord with the following experimental facts: (1) the sulfide-catalyzed reaction is first order in both thiolsulfinate and catalyzing sulfide; (2) its rate is strongly dependent on the structure of the sulfide, electron-releasing groups attached to the sulfur accelerating the rate and electron-withdrawing ones retarding it ($\rho^* = -2.0$); (3) the reaction is strongly acid catalyzed, log k_s responding linearly to changes in the Hammett acidity function, $-H_0$; (4) the solvent isotope effect for the reaction is $(k_{HOAc}/k_{DOAc}) = 0.75$.

The pronounced influence of sulfide structure on rate argues for a mechanism in which the sulfide acts as a nucleophile and is converted in the rate-determining step to a sulfonium species R_2S^+–. The dependence of rate on H_0 and the solvent isotope effect of less than one both suggest that the acid catalysis is of the specific lyonium ion rather than the general acid type. The most straightforward mechanism which one can propose that fits these two criteria is the one shown in eq 4–8. It involves rate-determining nucleophilic attack of the sulfide on the sulfenyl sulfur of the sulfinyl-protonated form (IV) of the thiolsulfinate. The ion R_2S^+–SPh produced in the rate-determining step then reacts rapidly with sulfinic acid in a subsequent fast step (eq 6) to yield the thiolsulfonate. The sulfenic acid (PhSOH) also produced in eq 5 yields the same product, either by being converted first to R_2S^+–SPh (eq 7) and subsequent reaction of the latter species with sulfinic acid, or, alternatively, by direct reaction with sulfinic acid (eq 8).

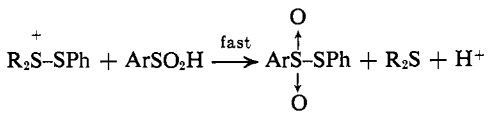


$$\underset{\displaystyle \downarrow \atop \displaystyle O}{PhS}\text{–SPh} + H^+ \rightleftharpoons Ph\underset{\displaystyle | \atop \displaystyle OH}{\overset{+}{S}}\text{–SPh} \qquad (4)$$

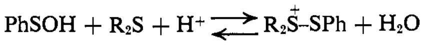
IV



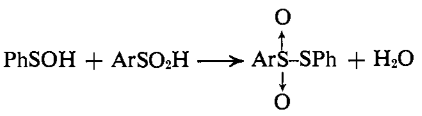
$$R_2S + PhS\text{–}\underset{\displaystyle | \atop \displaystyle OH}{\overset{+}{S}}Ph \xrightarrow[\text{determining}]{\text{rate}} R_2\overset{+}{S}\text{–SPh} + PhSOH \qquad (5)$$



$$\overset{+}{R_2S}\text{–SPh} + ArSO_2H \xrightarrow{\text{fast}} Ar\underset{\displaystyle \downarrow \atop \displaystyle O}{\overset{\displaystyle O \atop \displaystyle \uparrow}{S}}\text{–SPh} + R_2S + H^+ \qquad (6)$$

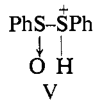


$$PhSOH + R_2S + H^+ \rightleftharpoons R_2\overset{+}{S}\text{–SPh} + H_2O \qquad (7)$$



$$PhSOH + ArSO_2H \longrightarrow Ar\underset{\displaystyle \downarrow \atop \displaystyle O}{\overset{\displaystyle O \atop \displaystyle \uparrow}{S}}\text{–SPh} + H_2O \qquad (8)$$

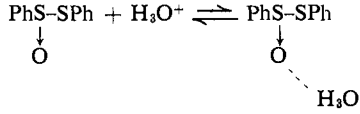
While this mechanism for the sulfide-catalyzed reaction is compatible with all of the known facts regarding the reaction, we must naturally ask if there are any alternative mechanisms which could be in equally good agreement with our experimental observations. One might ask, for example, whether the results actually require that nucleophilic attack by the sulfide occur at sulfenyl sulfur. Could they also be compatible with such attack at the sulfinyl sulfur of either IV or the sulfenyl-protonated thiolsulfinate V? The answer would appear to be that attack on the sulfinyl sulfur



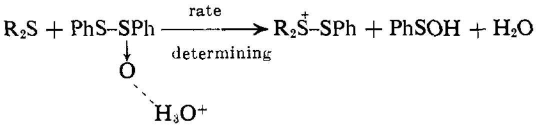
$$\underset{\displaystyle \downarrow \atop \displaystyle O}{PhS}\text{–}\underset{\displaystyle | \atop \displaystyle H}{\overset{+}{S}}Ph$$

V

can in fact be ruled out.[10] Although nucleophilic attack by the sulfide at the sulfenyl sulfur (as in eq 5) thus seems definitely established, the timing of transfer of the proton to the sulfinyl group of Ib is not quite so unequivocally determined. Thus, although the dependence of rate on H_0 and the solvent isotope effect both are those expected for specific lyonium ion catalysis, and, therefore, for IV being a discrete intermediate in the reaction, one must remember that some general acid-catalyzed reactions are now known which exhibit a correlation of rate with H_0[11] and/or a solvent isotope effect of less than one.[12] For this reason, even though we think it unlikely, we cannot completely rule out as an alternative to eq 4 and 5 a general acid catalyzed reaction such as eq 9, in which one has rate-determining



$$\underset{\underset{\displaystyle O}{\downarrow}}{\text{PhS}}\text{-SPh} + H_3O^+ \rightleftharpoons \underset{\underset{\displaystyle O\cdots H_3O^+}{\downarrow}}{\text{PhS}}\text{-SPh} \qquad (9a)$$



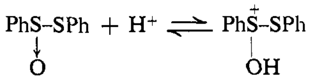
$$R_2S + \underset{\underset{\displaystyle O\cdots H_3O^+}{\downarrow}}{\text{PhS}}\text{-SPh} \xrightarrow[\text{determining}]{\text{rate}} R_2\overset{+}{S}\text{-SPh} + PhSOH + H_2O \qquad (9b)$$

reaction of the sulfide with a hydrogen-bonded complex of the acid and Ib, and in which the proton is assumed to be almost completely transferred from the catalyzing acid to the sulfinyl oxygen by the time the transition state for (9b) is reached. We should stress, however, that for eq 9 to be in accord with the H_0 and solvent isotope effect data, it would be required[12] that the proton be almost completely transferred to the sulfinyl group in the transition state. For this reason the structure of the transition state for eq 9b would be very similar indeed to that for eq 5. Equations 4 and 5 and eq 9 therefore differ in only one rather minor way, namely, the precise details of the timing of the proton transfer to the sulfinyl group.

Concomitant Electrophilic and Nucleophilic Catalysis of Sulfur–Sulfur Bond Scission. We see from examination of its mechanism that the sulfide-catalyzed reaction of Ib with sulfinic acids involves concomitant electrophilic (H^+) and nucleophilic (R_2S) catalysis of the scission of the S–S bond in Ib. We have previously observed this type of catalysis in several other sulfur–sulfur bond scissions[4,5] and have commented[5] upon its possible importance as a rather general phenomenon in reactions involving sulfur–sulfur bond scissions in acid solution. At that time the point was also made that, since the making and breaking of S–S bonds may be involved in the intermediate stages of organosulfur reactions where neither reactants nor final products possess an S–S bond, this type of catalysis may be of wider significance than would first seem apparent.

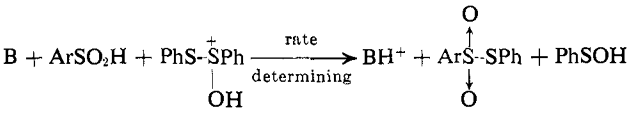
The present results serve to confirm further the frequent occurrence of this type of catalysis in reactions involving S–S bond scission and to underscore its importance in organic sulfur chemistry. A fuller discussion of the entire phenomenon is available in ref 5.

Mechanism of the Normal Thiolsulfinate–Sulfinic Acid Reaction. From the fact that the normal thiolsulfinate–sulfinic acid reaction is first order in both thiolsulfinate and sulfinic acid we know that the transition state of its rate-determining step must be derived from one molecule each of both of these reagents. The normal reaction differs significantly from the sulfide-catalyzed reaction in the response of its rate to changes in the acidity of the medium and in its solvent isotope effect. The observations that k_ψ responds linearly to changes in sulfuric acid concentration, is independent of stoichiometric water concentration, and is larger in HOAc than in DOAc, all suggest that the normal reaction exhibits general acid catalysis, just as the dependence of log k_s on $-H_0$ and $(k_{HOAc}/k_{DOAc}) < 1$ suggested the sulfide-catalyzed reaction was specific lyonium ion catalyzed. Given the evidence from the effect of sulfinic acid structure on rate which shows that the electron density on the sulfinic acid sulfur increases on going from reactant to transition state, and given the likelihood that the mechanisms of the normal and sulfide-catalyzed reactions should have at least a number of features in common, we feel that general acid catalysis of the normal reaction is most satisfactorily explained by a mechanism (eq 10 and 11) involving a



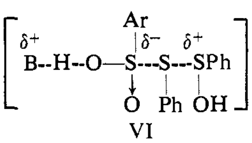
$$\underset{\underset{\displaystyle O}{\downarrow}}{\text{PhS}}\text{-SPh} + H^+ \rightleftharpoons \text{Ph}\underset{\underset{\displaystyle OH}{|}}{\overset{+}{S}}\text{-SPh} \qquad (10)$$

IV



$$B + ArSO_2H + \text{PhS-}\underset{\underset{\displaystyle OH}{|}}{\overset{+}{S}}\text{Ph} \xrightarrow[\text{determining}]{\text{rate}} BH^+ + \text{Ar}\underset{\underset{\displaystyle O}{\downarrow}}{\overset{\overset{\displaystyle O}{\uparrow}}{S}}\text{-SPh} + PhSOH \qquad (11)$$

rate-determining general base catalyzed attack of the sulfinic acid on the sulfinyl-protonated thiolsulfinate. The transition state for eq 11 is envisioned to have structure VI, in which formation of the new S–S bond



$$\left[\overset{\delta+}{B}\text{--H--O—}\underset{\underset{\displaystyle O}{\downarrow}}{\overset{\overset{\displaystyle Ar}{|\,\delta-}}{S}}\text{---}\underset{\underset{\displaystyle Ph}{|}}{\overset{\delta+}{S}}\text{---}\underset{\underset{\displaystyle OH}{|}}{S}\text{Ph}\right]$$

VI

between the sulfinic acid and the sulfenyl sulfur of IV is concerted with base-catalyzed cleavage of the original O–H bond in the sulfinic acid.

That nucleophilic attack of the sulfinic acid on IV should require general base catalysis is easily explained. Sulfone groups have been shown by several groups[13,14] to be extremely weak basic sites (the pK_a of the conjugate acid of dimethyl sulfone, for example, is -12.3).

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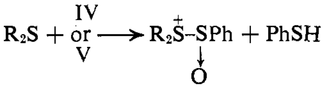
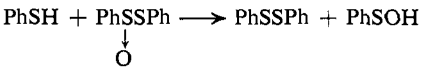
[10] The immediate result of nucleophilic attack by sulfide on the sulfinyl group of either IV or V would presumably be as follows



$$R_2S + \begin{matrix}\text{IV}\\ \text{or}\\ \text{V}\end{matrix} \longrightarrow R_2\underset{\underset{\displaystyle O}{\downarrow}}{\overset{+}{S}}\text{-SPh} + PhSH$$

We know from other experiments that under the present reaction conditions thiophenol not only reacts very rapidly with thiolsulfinates but also that it does so much faster than it reacts with sulfinic acid. One of the products of this reaction is the disulfide



$$PhSH + \underset{\underset{\displaystyle O}{\downarrow}}{\text{PhS}}\text{SPh} \longrightarrow PhSSPh + PhSOH$$

On the other hand, we also know that no disulfide is formed as a product in the sulfide-catalyzed thiosulfinate–sulfinic acid reaction. Thus any mechanism involving attack by the sulfide at the sulfinyl center is incompatible with the observed reaction stoichiometry and can be rejected.

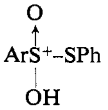
[11] H. G. Kuivila and K. V. Nahabedian, *J. Am. Chem. Soc.*, **83**, 2159 (1961); F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957).

[12] A. J. Kresge and R. J. Preto, *J. Am. Chem.Soc.*, **87**, 4593 (1965).

[13] S. K. Hall and E. A. Robinson, *Can. J. Chem.*, **42**, 1113 (1964).

[14] E. M. Arnett and C. Douty, *J. Am. Chem. Soc.*, **86**, 409 (1964).

This means that the species VII, which would result from a direct displacement by $ArSO_2H$ on IV, would be an extremely unstable intermediate and would presumably therefore be formed only with great difficulty.

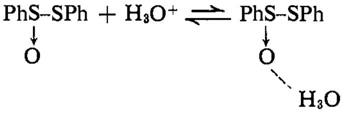


$$\mathrm{Ar}\overset{\substack{\mathrm{O}\\ \uparrow}}{\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{S}}}{}^{+}\mathrm{-SPh}$$

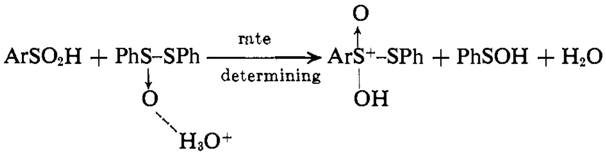
VII

By making transfer of the sulfinic acid proton to a general base concerted with the formation of the new S–S bond the need to go through VII as an intermediate is eliminated, and the reaction can proceed much more readily. Note also that if in the transition state of eq 11 the breaking of the O–H bond is assumed to be slightly ahead of the formation of the SO_2–S bond the observed effect of $ArSO_2H$ structure on rate is also explained.

Although eq 10 and 11 provide an eminently satisfactory explanation of the various kinetic features of the normal thiolsulfinate–sulfinic acid reaction, one must ask, as before, whether there are any alternative mechanisms which are in equally good accord with the data. For example, one might wonder if the general acid catalysis and solvent isotope effect could also be accommodated by a mechanism (eq 12a and b) similar to eq 9, but in which the transfer of the proton to the sulfinyl group has not proceeded as far by the time the transition state is reached as is the case in eq 9b. According to present thinking[11,12] such a difference in the degree of transfer of the proton could lead to k_ψ following $C_{H_2SO_4}$ and having $(k_{HOAc}/k_{DOAc}) > 1$, while k_s is correlated by $-H_0$ and has $(k_{HOAc}/k_{DOAc}) < 1$. However, although the solvent isotope effect and acidity data might be accommodated to this mechanism, eq 12 is not in agreement with the observed effect of sulfinic acid structure on rate, since it predicts that the electron density on the sulfinic acid sulfur should be less in the transition state than in the acid itself, in direct contradiction to the actual result. Equation 12 can therefore be eliminated as a possible mechanism.[15]

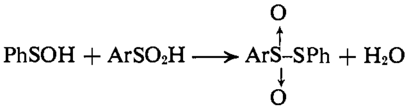


$$\mathrm{Ph}\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{S}}\mathrm{-SPh} + \mathrm{H_3O^+} \rightleftharpoons \mathrm{Ph}\underset{\substack{\downarrow\\ \mathrm{O}\\ \diagdown\\ \mathrm{H_3O^+}}}{\mathrm{S}}\mathrm{-SPh} \tag{12a}$$

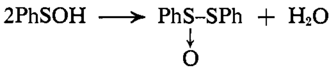


$$\mathrm{ArSO_2H} + \mathrm{Ph}\underset{\substack{\downarrow\\ \mathrm{O}\\ \diagdown\\ \mathrm{H_3O^+}}}{\mathrm{S}}\mathrm{-SPh} \xrightarrow[\text{determining}]{\text{rate}} \mathrm{Ar}\overset{\substack{\mathrm{O}\\ \uparrow}}{\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{S}}}{}^{+}\mathrm{-SPh} + \mathrm{PhSOH} + \mathrm{H_2O} \tag{12b}$$

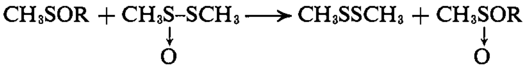
Equations 10 and 11, of course, represent the sequence of events in the normal thiolsulfinate–sulfinic acid reaction only up through the rate-determining step. For a complete description of the mechanism one must indicate the further fate of the sulfenic acid (PhSOH) formed in eq 11. Obviously, reaction with sulfinic acid (eq 13) and formation of Ib (eq 14) cannot be the only routes for disappearance of PhSOH, for, if they were, the over-all stoichiometry of the normal reaction would be the same as that for the sulfide-catalyzed reaction (eq 3), and one also could not account for the small but significant amount of disulfide formed as one of the products of the normal reaction. Clearly, then, there must be some further reaction of PhSOH that leads eventually to disulfide and that occurs in competition with eq 13 and 14. Although we cannot at present specify exactly what this is, we should mention one attractive possibility which is suggested by the work of Moore and O'Connor.[16] They observed the following rapid reaction between a sulfenate ester and a thiolsulfinate.



$$\mathrm{PhSOH} + \mathrm{ArSO_2H} \longrightarrow \mathrm{Ar}\overset{\substack{\mathrm{O}\\ \uparrow}}{\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{S}}}\mathrm{-SPh} + \mathrm{H_2O} \tag{13}$$

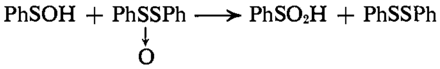


$$\mathrm{2PhSOH} \longrightarrow \mathrm{Ph}\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{S}}\mathrm{-SPh} + \mathrm{H_2O} \tag{14}$$



$$\mathrm{CH_3SOR} + \mathrm{CH_3}\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{S}}\mathrm{-SCH_3} \longrightarrow \mathrm{CH_3SSCH_3} + \mathrm{CH_3}\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{S}}\mathrm{OR}$$

An analogous reaction between the sulfenic acid and Ib would be as shown in eq 15. If eq 15 is in competition with eq 13 and/or 14 the yield of disulfide should increase with an increase in the ratio $(Ib)_0/(ArSO_2H)_0$. Although this is indeed observed (Table I) the actual increase is smaller than would seem to be predicted by the above scheme. For this reason the mechanism of the formation of disulfide in the normal reaction cannot be said to be completely settled at this time.[17]



$$\mathrm{PhSOH} + \mathrm{Ph}\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{S}}\mathrm{SPh} \longrightarrow \mathrm{PhSO_2H} + \mathrm{PhSSPh} \tag{15}$$

Experimental Section

Preparation and Purification of Materials. Thiolsulfinates. *p*-Tolyl *p*-toluenethiolsulfinate (Ia), mp 87.5°, and phenyl benzenethiolsulfinate (Ib), mp 69.5–71°, were both prepared and purified according to the procedures outlined by Backer and Kloosterziel.[18]

Sulfinic Acids. The preparation and purification of the various sulfinic acids have been previously described.[19] In the purification procedures sulfuric acid was used rather than hydrochloric to precipitate the sulfinic acids from aqueous solution.

Sulfides. The alkyl and aryl sulfides were all samples either prepared or obtained from commercial sources in connection with

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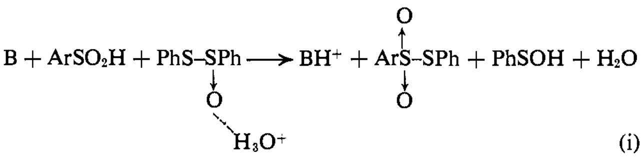
(15) While eq 12b can be definitely ruled out, a general base catalyzed attack of the sulfinic acid on the hydrogen-bonded complex of Ib and H_3O^+ (eq i) is probably tenable as an alternative to eq 11, just as eq 9b represented a possible alternative to eq 5 in the sulfide-catalyzed reaction. However, analogous to our feelings regarding the sulfide-catalyzed reaction, although we cannot completely eliminate eq i as a possibility, we feel eq 11 represents the more straightforward and plausible explanation of the results, and we therefore are strongly inclined to favor it as the mechanism for the rate-determining step.



$$\mathrm{B} + \mathrm{ArSO_2H} + \mathrm{Ph}\underset{\substack{\downarrow\\ \mathrm{O}\\ \diagdown\\ \mathrm{H_3O^+}}}{\mathrm{S}}\mathrm{-SPh} \longrightarrow \mathrm{BH^+} + \mathrm{Ar}\overset{\substack{\mathrm{O}\\ \uparrow}}{\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{S}}}\mathrm{-SPh} + \mathrm{PhSOH} + \mathrm{H_2O} \tag{i}$$

(16) T. L. Moore and D. E. O'Connor, *J. Org. Chem.*, **31**, 3587 (1966).

(17) The difference in the stoichiometry of the sulfide-catalyzed and the normal reaction suggests that whatever the process is by which PhSOH gives disulfide, R_2S^+–SPh does not undergo a comparable reaction, or at least does not undergo it as fast as it reacts with sulfinic acid. Furthermore the difference in stoichiometry also suggests that most of the PhSOH produced in eq 5 in the sulfide-catalyzed mechanism must go on to thiolsulfonate *via* the reaction sequence of eq 7 followed by eq 6, rather than by reacting directly with sulfinic acid as in eq 8.

(18) H. J. Backer and H. Kloosterziel, *Rec. Trav. Chim.*, **73**, 129 (1954).

(19) J. L. Kice, D. C. Hampton, and A. Fitzgerald, *J. Org. Chem.*, **30**, 882 (1965).

earlier work.[5,20] They were purified by previously described procedures.[5,20]

Solvents. Acetic acid was purified as in a previous paper.[21] Acetic acid–0.56 *M* water was made up by weighing out 10.09 g of water and diluting with purified acetic acid to 1-l. total volume. Stock solutions of acetic acid–0.56 *M* water–1.00 *M* H_2SO_4 and acetic acid–0.56 *M* water–2.00 *M* H_2SO_4 were made up as follows. A sample of reagent grade sulfuric acid (Baker and Adamson) was titrated with standard sodium hydroxide and found to be 96.25% sulfuric acid. The remaining 3.75% was assumed to be water. The stock solutions were prepared by weighing out the appropriate amount of sulfuric acid, adding enough water so that the final solution would be 0.56 *M* in water, and then diluting to volume with acetic acid. Acetic acid-*d* was prepared as described in another paper.[22] Stock solutions for the kinetic runs in deuterated solvent were prepared in the same manner as outlined above using acetic acid-*d*, deuterium oxide, and the undeuterated reagent grade sulfuric acid. (Since the final solutions for the runs in acetic acid-*d* were only 0.10 *M* in sulfuric acid, the use of undeuterated sulfuric acid instead of D_2SO_4 leads to no significant isotopic dilution of the solvent medium.)

Procedure for Kinetic Runs. The thiolsulfinate and the sulfinic acid were weighed out directly and dissolved in acetic acid–0.56 *M* water in a volumetric flask. Stock solutions of sulfuric acid and, when appropriate, of the sulfide being used as catalyst were then pipetted into the flask, and the entire solution was made up to volume with acetic acid–0.56 *M* water. (For those few runs with a stoichiometric water concentration other than 0.56 *M*, special stock solutions of acetic acid–water were prepared containing the proper amount of water.)

The final solution was transferred to a reaction vessel of the type previously used[21] to study the kinetics of the disproportionation of sulfinic acids, and the solution was then deaerated by passing prepurified nitrogen through the solution for 5 min. The reaction vessel was then placed in a constant temperature bath, and after allowing 5 min for temperature equilibration a zero-time sample was removed. This sample (1 ml) was immediately pipetted into a volumetric flask containing 95% ethanol and diluted with that solvent to a volume such that the optical density of the solution could be conveniently determined at a wavelength in the 295–310-mμ range. Either a Beckman Model DB or a Cary Model 15 spectrophotometer was used for the determination of the optical density. Other samples were removed from the reaction vessel at appropriate time intervals thereafter, and their absorbance was measured at the same wavelength after dilution with ethanol. After eight to ten half-lives an infinity point was taken in the same manner, and the experimental first-order rate constant for the run was determined from a plot of log $(A_t - A_\infty)$ *vs.* time.

The molar extinction coefficient of Ib in 95% ethanol is 6000 at 295 mμ and 3250 at 310 mμ. In ethanol at these wavelengths the sulfinic acid has no significant absorbance at the concentrations used. The molar extinction coefficient of Ib is from six to ten times larger than the molar extinction coefficient of the thiolsulfonate formed as the major product of the thiolsulfinate–sulfinic acid reaction. It is from three to four times larger than the extinction coefficient of the disulfide formed as a minor product in the nonsulfide-catalyzed reaction. Consequently the occurrence of the thiolsulfinate–sulfinic acid reaction leads to a significant decrease in the optical density of the solution.

Product Studies of the Thiolsulfinate–Sulfinic Acid Reaction. Solutions for the various product studies were prepared in the same manner as for the kinetic studies. The reactions were then allowed to proceed for ten half-lives. At the end of this time an aliquot of the solution was removed and titrated for residual sulfinic acid content with standard sodium nitrite solution.[21] The remainder of the reaction solution was then poured into ten times its volume or water, and the resulting mixture was extracted twice with a total of 400–500 ml of ether. The ether extracts were washed several times with water and then with sodium bicarbonate solution until the washings remained slightly alkaline. After one final washing with water the ether extracts were dried over magnesium sulfate, and the ether was removed under reduced pressure. The residue was then chromatographed on acid-washed alumina to separate the products.

Any disulfide formed was eluted with hexane. Its identity was then determined by infrared and melting point comparisons with known samples of phenyl disulfide and *p*-tolyl disulfide.

The thiolsulfonate formed was eluted with hexane–benzene or benzene. The thiolsulfonate fraction was then recrystallized and the identity of the thiolsulfonate was established by melting point, mixture melting point, and infrared comparisons with samples of either *p*-tolyl *p*-toluenethiolsulfonate[21] or phenyl *p*-toluenethiolsulfonate.[23]

No other reaction products besides disulfide and thiolsulfonate were detected in any of the chromatographic fractions. In the phenyl sulfide catalyzed reaction of Ib with *p*-toluenesulfinic acid the large amount of phenyl sulfide which had to be used as catalyst, and which was recovered in the hexane eluent on chromatography, prevented any determination of the amount of phenyl disulfide formed.

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(20) J. L. Kice and E. H. Morkved, *J. Am. Chem. Soc.*, **85**, 3472 (1963).

(21) J. L. Kice and K. W. Bowers, *ibid.*, **84**, 605 (1962).

(22) J. L. Kice and G. Guaraldi, *J. Org. Chem.*, **31**, 3568 (1966).

(23) F. Klivenyi, *Magy. Kem. Folyoirat*, **64**, 121 (1958); *Chem. Abstr.*, **54**, 16416*f* (1960).

Relative Reactivities of Solid Benzoic Acids[1a]

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Abstract: Reactions of solid *meta-* or *para-*substituted benzoic acids ($RC_6H_4CO_2H$) with solid *meta-* or *para-*substituted potassium benzoates ($R'C_6H_4CO_2K$) have been carried out at 70° in sealed thin-walled glass capillary tubes or in sealed weighing bottles. For all reactions tried: (1) where R and R′ are identical, the product is always the acid salt, $(RC_6H_4CO_2)_2HK$ and (2) where R and R′ are different and Hammett's σ for R is more positive than σ for R′, the reaction, $RC_6H_4CO_2H + R'C_6H_4CO_2K \rightarrow RC_6H_4CO_2K + R'C_6H_4CO_2H$, goes to completion.

Substituent effects on equilibria and rates of reactions in solution involving *meta-* and *para-*substituted benzene derivatives have been extensively investigated and frequently correlated successfully with Hammett[2] substituent constants. The purpose of the present study was to determine if Hammett's σ obtained from studies in solution could be used successfully to predict

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(1) (a) Abstracted in part from the M.S. Thesis of E. J. W., Texas A&M University, Jan 1967. (b) To whom inquiries should be sent.

(2) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).