teristic of SiOMe and COMe protons, respectively, were assigned to the *trans* isomer. The τ 6.54 (SiOMe) and 6.71 (COMe) bands were assigned to the *cis* isomer. The *trans/cis* ratio based on this tentative assignment was 2.8. Additional bands at τ 6.70 (multiplet overlapping COMe bands), 9.32 (multiplet), and 10.25 (multiplet) were present in the spectrum characteristic of the HCO–, $-CH_2-$, and $SiCH_2-$ protons, respectively, of these isomers.

Reaction of I with Trimethoxysilane. a. In an Ampoule at 125°. A mixture of 8.0 g (0.048 mol) of I and 11.75 g (0.096 mol) of trimethoxysilane was heated in an ampoule at 125° for 16 hr. Glpc analysis (column A) gave an area ratio of $(MeO)_4Si$/(methoxymethyl)trimethoxysilane (IX) of 1.10. Distillation on an 18-in. spinning-band column gave 4.35 g (54.3%) of IX, bp 36–37° (8 mm).

Anal. Calcd for $C_5H_{14}O_4Si$: C, 36.1; H, 8.43; mol wt, 166. Found: C, 36.2, 36.3; H, 8.40, 8.35; mol wt, 166.

The nmr spectrum of IX showed bands at τ 6.48, 6.72, and 6.93 (9:3:2 ratio) due to the –SiOMe, –COMe, and $-CH_2-$ protons, respectively.

b. In the Gas Phase at 250°. A mixture of 16.1 g (0.082 mol) of I and 23.5 g (0.19 mol) of trimethoxysilane was added to the heated quartz tube at a rate of 5.05 ml/hr. Glpc analysis (column A) gave an area ratio of $(MeO)_4Si$/IX of 1.55. Distillation using an 18-in. spinning-band column gave 4.5 g (32%) of IX, bp 36–37° (8 mm).

Acknowledgments. The authors are grateful to Mrs. Barbara Taub for preliminary technical assistance in this study. In addition the assistance and cooperation of our analytical department throughout this work is gratefully acknowledged.

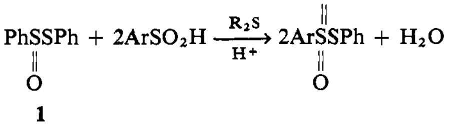
Mechanisms of Reactions of Thiolsulfinates (Sulfenic Anhydrides). III. The Sulfide-Catalyzed Disproportionation of Aryl Thiolsulfinates[1a]

John L. Kice, Clifford G. Venier,[1b] George B. Large, and Leslie Heasley

Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331. *Received September 26, 1968*

Abstract: In acetic acid–1% water containing some sulfuric acid the disproportionation of phenyl benzenethiolsulfinate (**1**) to phenyl disulfide and phenyl benzenethiolsulfonate is markedly catalyzed by added alkyl or aryl sulfides. Although the formal kinetics of this sulfide-catalyzed disproportionation are exactly the same as those of the previously studied sulfide-catalyzed **1**-sulfinic acid[2] and **1**-mercaptan[3] reactions, *i.e.*, the reaction is first-order in both **1** and sulfide and subject to specific-H^+ catalysis, the dependence of its rate on sulfide structure (Table IV) is entirely different from that observed for the other two sulfide-catalyzed reactions. Experiments using esr offer no indication that free radicals are intermediates in the reaction. For this reason the only mechanism for the sulfide-catalyzed disproportionation which appears to be compatible with both the kinetics and the dependence of rate on sulfide structure is the one shown in Chart III. This involves as its key step the sulfenylation of **1** by the ion R_2S^+SPh (**2**); and, while it might seem that this would normally lead to a greater than first power dependence of rate on thiolsulfinate concentration, it is shown that this is not the case, provided the sulfenylation step is faster than the hydrolysis of **2** to PhSOH and sulfide. Since arguments can be given why this should be the case, the mechanism in Chart III appears to be an acceptable one.

In acid solution phenyl benzenethiolsulfinate (**1**) undergoes a rapid sulfide-catalyzed reaction with sulfinic acids which has the stoichiometry shown in eq 1.[2] Kinetic studies[2] have shown that this reaction is first order in both catalyzing sulfide and thiolsulfinate, but that its rate is *independent* of sulfinic acid concentration. The dependence of its rate on the acidity of the medium and the solvent isotope effect both suggest that the acid catalysis of the reaction is of the specific lyonium ion variety. The mechanism shown in Chart I was accordingly suggested.[2] This mechanism, which involves rate-determining nucleophilic attack of the alkyl sulfide on the protonated thiolsulfinate (eq 3), predicts that alkyl sulfides should also catalyze the reaction of other reagents NuH with **1** *via* a mechanism analogous to that shown in Chart I (NuH = $ArSO_2H$). Furthermore, because of the nature of this mechanism, the rate of such a sulfide-catalyzed **1**-NuH reaction should be the same under a given set of conditions as the rate of the sulfide-catalyzed **1**-$ArSO_2H$ reaction. Study[3] of sulfide catalysis of the reaction of **1** with a mercaptan RSH has shown that these predictions are in fact



$$\underset{\underset{O}{\|}}{PhSSPh} + 2ArSO_2H \xrightarrow[H^+]{R_2S} 2Ar\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}SPh + H_2O \qquad (1)$$

1

Chart I. Mechanism of the Sulfide-Catalyzed Thiolsulfinate–Sulfinic Acid Reaction

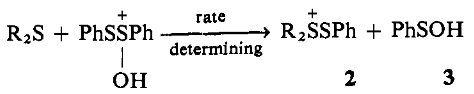
$$\underset{\underset{O}{\|}}{PhSSPh} + H^+ \rightleftharpoons PhS\overset{+}{\underset{\underset{OH}{|}}{S}}Ph \qquad (2)$$

---

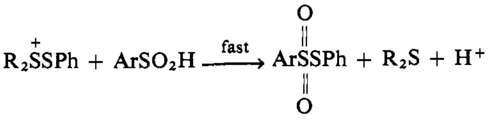
[1] (a) This research supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research under Grants AF-AFOSR-106-63 and 106-65 and by the National Science Foundation under Grant GP-6952. (b) National Science Foundation Cooperative Fellow, 1964–1966.

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

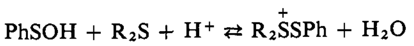
[3] J. L. Kice and G. B. Large, *J. Org. Chem.*, **33**, 1940 (1968).



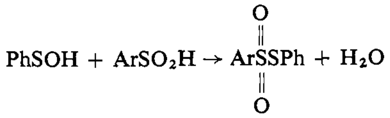
$$R_2S + Ph\underset{\underset{OH}{|}}{\overset{+}{S}}SPh \xrightarrow[\text{determining}]{\text{rate}} \underset{\mathbf{2}}{R_2\overset{+}{S}SPh} + \underset{\mathbf{3}}{PhSOH} \quad (3)$$



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



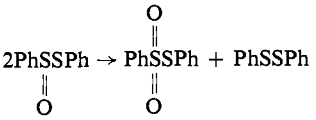
$$PhSOH + R_2S + H^+ \rightleftarrows R_2\overset{+}{S}SPh + H_2O \quad (5)$$



$$PhSOH + ArSO_2H \rightarrow Ar\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}SPh + H_2O \quad (6)$$

borne out by experiment. These sulfide- and acid-catalyzed reactions of **1** with either $ArSO_2H$ or RSH are thus both examples of cooperative nucleophilic and electrophilic catalysis of the scission of an S–S bond, a phenomenon of apparently quite widespread importance in organic sulfur chemistry.[4]

One of the best-known reactions of thiolsulfinates is their disproportionation into thiolsulfonates and disulfides (eq 7).[5] In the study described in this paper we have discovered that in acid solution the disproportionation of



$$2Ph\underset{\underset{O}{\|}}{S}SPh \rightarrow Ph\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}SPh + PhSSPh \quad (7)$$

1 (eq 7) can also be dramatically accelerated by the same sort of concomitant catalysis by acid and alkyl sulfide as the **1**-$ArSO_2H$ and **1**-RSH reactions. However, although the formal kinetics of the catalyzed disproportionation are the same as those of the other two[2,3] sulfide-catalyzed reactions of **1**, *i.e.*, all three reactions show the same dependence on acidity, sulfide concentration, etc., the catalyzed disproportionation shows a considerably different dependence of rate on sulfide structure, particularly for the more reactive sulfides. As we shall see it is no easy matter to find a mechanism for the sulfide-catalyzed disproportionation which is compatible with both these and the additional requirements imposed by certain other experiments which have been carried out on the system. The final picture which emerges is an intricate one which serves to illustrate some of the many complexities that can be encountered in the mechanisms of reactions involving the making and breaking of sulfur–sulfur bonds.

Results

Essentially all of our studies of the sulfide-catalyzed disproportionation of **1** have been carried out at 39.4° in acetic acid–1% water as solvent. Varying amounts (0.10–0.30 *M*) of sulfuric acid were present as an acid catalyst. These are exactly the same reaction conditions used for the previous investigations of the sulfide-catalyzed **1**-$ArSO_2H$[2] and the **1**-RSH[3] reactions, so that the present results can be compared directly to the data for these other systems.

Under such reaction conditions, in the absence of added sulfide, the disproportionation of **1** is quite slow. However, as Figure 1 shows, the addition of as little as 2.5×10^{-4} *M* benzyl sulfide results in a 30-fold acceleration in the rate of disproportionation of **1**. That this rapid, sulfide-catalyzed disappearance of **1** has the usual stoichiometry associated with the disproportionation reaction (eq 7) is evident from Table I.

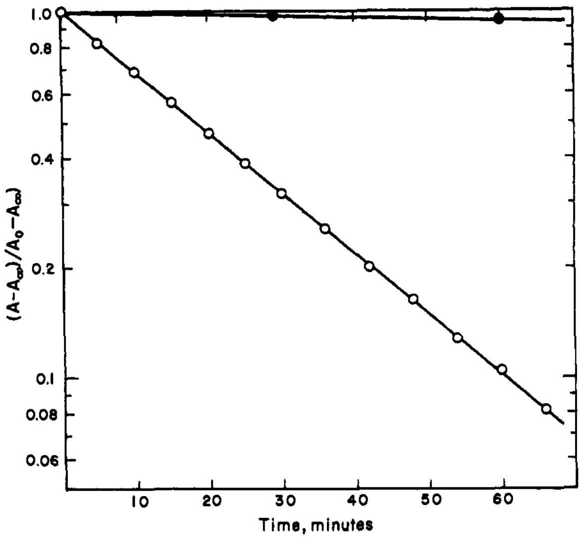


Figure 1. Rate of disproportionation of **1** in the presence and absence of benzyl sulfide: ○, **1**, 8×10^{-3} *M*, $(PhCH_2)_2S$, 2.5×10^{-4} *M*; ●, **1**, 8×10^{-3} *M*, no sulfide. Both runs in AcOH–0.56 *M* H_2O–0.20 *M* H_2SO_4.

Table I. Stoichiometry of the Sulfide-Catalyzed Disproportionation of **1**

Reaction conditions[a]	Products (mole/mole of **1**) $PhSO_2SPh$	PhSSPh
Benzyl sulfide catalyzed[b]	0.50	0.49
Phenyl sulfide catalyzed[c]	0.50	0.50

[a] All runs in acetic acid–0.56 *M* H_2O–0.20 *M* H_2SO_4 at 39.4°. [b] Sulfide concentration, 2.5×10^{-4} *M*. [c] Sulfide concentration, 0.01 *M*.

Kinetics of the Sulfide-Catalyzed Disproportionation. The kinetics of the reaction can be studied conveniently by following the change in absorbance at wavelengths in the range 292–300 mμ. In this region the molar extinction coefficient of **1** is about four times greater than those of the corresponding thiolsulfonate or disulfide.

As Figure 1 shows, a first-order plot of thiolsulfinate disappearance shows excellent linearity over at least four half-lives. Further confirmation of the fact that the reaction is truly first-order in thiolsulfinate is provided by the first two runs with either benzyl sulfide or phenyl sulfide in Table II. These show that doubling the initial thiolsulfinate concentration leads to no change in k_1, the experimental first-order rate constant for the disappearance of **1**. The results of the various kinetic runs with the eight different sulfides studied as catalysts are summarized in Table II.

Dependence of the Rate on Sulfide Concentration. If the sulfide-catalyzed disproportionation is first order in

---

[4] For a review see J. L. Kice, *Accounts Chem. Res.*, **1**, 58 (1968).

[5] (a) H. J. Backer and H. Kloosterziel, *Rec. Trav. Chim.*, **73**, 129 (1954); (b) D. Barnard, *J. Chem. Soc.*, 4675 (1957); (c) D. Barnard and E. J. Percy, *Chem. Ind.* (London), 1332 (1960).

Table II. Kinetics of the Sulfide-Catalyzed Disproportionation of **1**[a]

$[\mathbf{1}]_0 \times 10^3$, M	C_{H_2O}, M	$C_{H_2SO_4}$, M	$[R_2S] \times 10^3$, M	$k_1 \times 10^4$, sec^{-1}	$k_d = \left[\frac{k_1 - k_1^0}{[R_2S]}\right]^b$
			Benzyl Sulfide		
8.0	0.56	0.20	0.25	6.3	2.4
4.0	0.56	0.20	0.25	6.2	2.4
			0.35	8.6	2.4
			0.15	3.8	2.4
		0.10	0.15	1.4	0.89
		0.30	0.15	7.5	4.7
	1.14	0.20	0.40	5.6	1.4
	0.56 (D_2O)	0.10 (D_2SO_4)	0.54	7.0 (DOAc)	1.3
			Tetrahydrothiophene		
4.0	0.56	0.20	0.30	9.5	3.1
			0.15	5.1	3.3
			n-Butyl Sulfide		
4.0	0.56	0.20	0.03	0.85	2.2
			0.24	5.7	2.3
			Ethyl Sulfide		
4.0	0.56	0.20	0.31	5.9	1.8
			0.62	11.1	1.8
			Thiodipropionic Acid		
4.0	0.56	0.20	0.50	6.8	1.3
			0.70	9.3	1.3
			Benzyl Phenyl Sulfide		
4.0	0.56	0.20	0.34	3.3	0.91
			0.67	6.3	0.91
			Phenyl Sulfide		
8.0	0.56	0.20	15.6	6.2	0.038
4.0	0.56	0.20	15.8	6.3	0.039
			31.0	12.1	0.038
		0.10	15.7	2.5	0.0156
		0.30	9.7	7.6	0.074
			Thiodiacetic Acid		
4.0	0.56	0.20	28.6	7.3	0.025
			45.0	11.0	0.024

[a] All runs at 39.4° in acetic acid containing the stoichiometric concentrations of water and sulfuric acid indicated. [b] k_1^0 equals the rate of disproportionation of **1** in the absence of sulfide under otherwise identical conditions. Values used for AcOH–0.56 M H_2O solutions: 0.10 M H_2SO_4, 0.07×10^{-4}; 0.20 M H_2SO_4, 0.20×10^{-4}; 0.30 M H_2SO_4, 0.40×10^{-4}.

sulfide, k_1 should be given by

$$k_1 = k_1^0 + k_d(R_2S)$$

where k_1^0 equals the small rate of disproportionation observed in the absence of the sulfide (see Figure 1), and k_d is the second-order rate constant for the sulfide-catalyzed disproportionation. Accordingly, for a given sulfide under a given set of reaction conditions, the quantity $(k_1 - k_1^0)/(R_2S)$ should be a constant independent of sulfide concentration. The last column of Table II shows that this is true for each of the eight sulfides studied. One can therefore conclude that the sulfide-catalyzed disproportionation is indeed first order in sulfide.

Dependence of k_d on Acidity. The pertinent results with benzyl and phenyl sulfides which indicate the manner in which k_d depends on the acidity of the medium are summarized in Table III. There one sees that whether the Hammett acidity function, H_0, is changed by varying the amount of sulfuric acid or the amount of water in the medium, log $k_d + H_0$ remains effectively constant for a given sulfide. The dependence of k_d on acidity is thus the same as the dependence on this same variable observed[2]. for the rate constant for the sulfide-catalyzed **1**–$ArSO_2H$ reaction, k_s.

Table III. Dependence of k_d on Acidity

Sulfide	C_{H_2O}, M	$C_{H_2SO_4}$, M	H_0[a]	Log $k_d + H_0$
Benzyl	0.56	0.10	−1.13	−1.18
		0.20	−1.56	−1.18
		0.30	−1.86	−1.19
	1.14	0.20	−1.31	−1.16
Phenyl	0.56	0.10	−1.13	−2.94
		0.20	−1.56	−2.98
		0.30	−1.86	−2.99

[a] Values of H_0 for acetic acid–0.56 M water are taken directly from J. Rocek, *Collection Czech. Chem. Commun.*, **22**, 1 (1957); that for acetic acid–1.14 M water is interpolated from data in the same reference.

Solvent Isotope Effect. The rate constant for the benzyl sulfide catalyzed disproportionation of **1** is seen (Table II) to be somewhat larger in AcOD–0.56 M

D_2O–0.10 *M* D_2SO_4 than in the corresponding undeuterated medium, $k_d^{HOAc}/k_d^{DOAc} = 0.68$. Given the experimental uncertainty inherent in our measurements this is not significantly different from the solvent isotope effect, $k_s^{HOAc}/k_s^{DOAc} = 0.75$, observed for the benzyl sulfide catalyzed reaction of **1** with sulfinic acids.[2]

Dependence of k_d on Sulfide Structure. We have seen that the formal kinetics of the sulfide-catalyzed disproportionation are the same as those of the sulfide-catalyzed **1**-$ArSO_2H$ reaction.[2] Thus, both processes are first order in both sulfide and thiolsulfinate, both are acid catalyzed, with log $k + H_0$ essentially a constant, and both show a solvent isotope effect, $k_{HOAc}/k_{DOAc} \cong 0.7$. On this basis one might well expect, *a priori*, that both processes would involve the same rate-determining step and would therefore show the same variation of rate constant with sulfide structure. That this is *most definitely not the case*, however, is evident from Table IV which shows k_d for the sulfide-catalyzed disproportionation and k_s for the sulfide-catalyzed **1**-$ArSO_2H$ reaction[2] for eight different sulfides under the same reaction conditions. One sees that for those sulfides which are most reactive as catalysts for the **1**-$ArSO_2H$ reaction, such a tetrahydrothiophene, benzyl sulfide, etc., k_d is much smaller than k_s. On the other hand for the two least reactive sulfides, phenyl sulfide and thiodiacetic acid, k_d is actually somewhat larger than k_s.

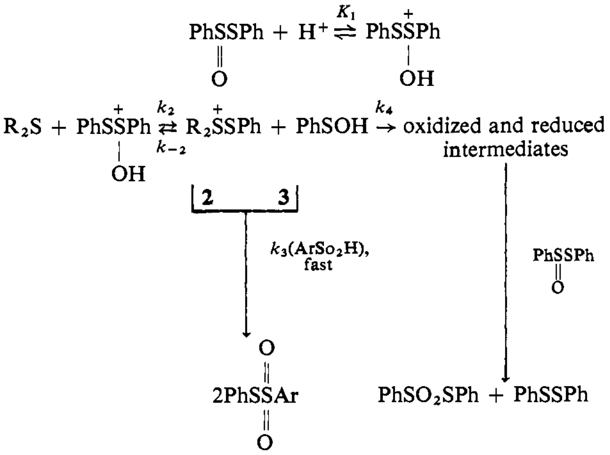
Table IV. Dependence of k_d on Sulfide Structure[a]

Sulfide	k_d, M^{-1} sec^{-1}	k_s, M^{-1} sec^{-1} [b]
Tetrahydrothiophene	3.2	890[c]
$(C_6H_5CH_2)_2S$	2.4	59
n-Bu_2S	2.3	(480)[d]
Et_2S	1.8	620[c]
$(HOOCCH_2CH_2)_2S$	1.3	7.2[c]
$C_6H_5CH_2SC_6H_5$	0.91	1.2
$(C_6H_5)_2S$	0.038	0.021
$(HOOCCH_2)_2S$	0.024	(0.015)[d]

[a] All data are for AcOH–0.56 *M* H_2O–0.20 *M* H_2SO_4 as solvent at 39.4°. [b] k_s is the rate constant for the sulfide-catalyzed reaction of **1** with sulfinic acids in AcOH–0.56 *M* H_2O–0.20 *M* H_2SO_4. Data are from ref 2 except where indicated. [c] Ph.D. Thesis of C. G. Venier, Oregon State University, 1966. [d] Estimated assuming k_s shows same dependence on H_0 as observed for other sulfides.

Thus, a key mechanistic problem is how to explain the very different dependence of k_d and k_s on sulfide structure in the face of the identical formal kinetics exhibited by the two reactions. One way to do this would be *via* a mechanism of the general form shown in Chart II.

Chart II



In the case of the sulfide-catalyzed **1**–$ArSO_2H$ reaction one has a situation where $k_3(ArSO_2H) \gg k_{-2}$ in all cases, and so step k_2 is rate determining for all sulfides and $k_s = k_2K_1h_0$.

In contrast, in the sulfide-catalyzed disproportionation the intermediates **2** and **3** produced in step k_2 must first react further (step k_4) to produce other intermediates before disproportionation can take place. These other intermediates then react with an *additional* molecule of thiolsulfinate to produce the final disproportionation products.

If one assumes for sulfides such as tetrahydrothiophene or benzyl sulfide that $k_4 < k_{-2}$ one can easily see how k_d can be much smaller than k_s for such sulfides. On the other hand, if for sulfides such as phenyl sulfide or thiodiacetic acid one were to have the opposite situation, *i.e.*, $k_4 > k_{-2}$, then, because of the fact that the intermediates formed in the k_4 step consume an additional molecule of **1** in a subsequent reaction (or reactions) one would find $k_d > k_s$ for such sulfides, being in the limit where $k_4 \gg k_{-2}$ equal to $2k_2K_1h_0$, or to $2k_s$. This results because the consumption of the additional molecule of **1** in the disproportionation in the step subsequent to step k_4 means that when k_2 is rate determining one has the overall consumption of twice as much **1** per k_2 reaction in the disproportionation as in the sulfide-catalyzed **1**-$ArSO_2H$ reaction.

Rate of Loss of Optical Activity by (+)-1. The availability of optically active phenyl benzenethiolsul-

Table V. Kinetics of Sulfide-Catalyzed Loss of Optical Activity of Solutions of Optically Active Phenyl Benzenethiolsulfinate[a]

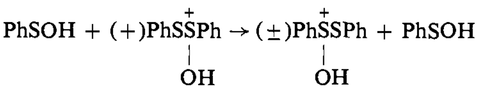
Sulfide	$C_{H_2SO_4}$, *M*	$[R_2S] \times 10^4$, *M*	$k_\alpha \times 10^3$, sec^{-1}	$k_\alpha^s = \left[\frac{k_\alpha - k_\alpha^0}{[R_2S]}\right]^b$	k_d[c]	k_s[d]
$(C_6H_5CH_2)_2S$	0.10	2.0	5.1	25	0.89	21
		4.0	8.6	21		
$(HOOCCH_2CH_2)_2S$	0.10	10	3.5	3.5	0.56[e]	3.1
		20	6.8	3.4		
$C_6H_5CH_2SC_6H_5$	0.20	12.3	2.7	2.1	0.91	1.2
$(C_6H_5)_2S$	0.20	2.2×10^2	1.1	0.044	0.038	0.021

[a] All runs at 39.4° in AcOH–0.56 *M* H_2O containing the amount of sulfuric acid indicated. [b] k_α^0 equals the rate of loss of optical activity in the absence of added sulfide and is equal to 0.07×10^{-3} sec^{-1} for 0.10 *M* H_2SO_4 and to 0.13×10^{-3} sec^{-1} for 0.20 *M* H_2SO_4. [c] Rate of sulfide-catalyzed disproportionation of **1** under same reaction conditions (see Table II). [d] Rate of sulfide-catalyzed **1**-$ArSO_2H$ reaction under same reaction conditions (ref 2). [e] Calculated from data at 0.20 *M* H_2SO_4 assuming k_d shows same dependence on H_0 as k_s.

finate[6] makes it possible for one to test the correctness of certain important aspects of the general scheme which has been suggested in Chart II to account for the very different dependence of k_s and k_d on sulfide structure. Specifically, since intermediates **2** and **3** are incapable of optical activity, the occurrence of the reaction sequence of step k_2 followed by step k_{-2}, even though it leads to no chemical change, will result in the racemization of optically active **1**. Thus the general scheme outlined in Chart II predicts that in the case of sulfides where $k_s \gg k_d$ the rate of sulfide-catalyzed loss of optical activity of optically active **1**, $k_\alpha{}^s$, should be much greater than k_d and, furthermore, that $k_\alpha{}^s$ should be equal, within experimental error, to k_s. On the other hand for those sulfides where $k_4 \geqq k_{-2}$ and $k_d \geqq k_s$ the scheme predicts that $k_\alpha{}^s$ will be equal to $k_s + 0.5k_d$.[7]

The sulfide-catalyzed rate of loss of optical activity of solutions of optically active **1** in acetic acid–0.56 M H_2O was measured for four different sulfides spanning a broad range of k_s and k_d values. The results are summarized in Table V.

One sees that, as required by the scheme in Chart II, for those sulfides like $(C_6H_5CH_2)_2S$ or $(HOOCCH_2CH_2)_2S$ where $k_s \gg k_d$, $k_\alpha{}^s \cong k_s$, while for the two sulfides where $k_s \leqq k_d$, $k_\alpha{}^s$ is significantly larger than k_s and is reasonably close to the predicted value of $k_s + 0.5k_d$. (Actually $k_\alpha{}^s$ seems in each instance to be slightly larger than this, which we attribute to additional racemization as a result of some incursion of reaction 8.)

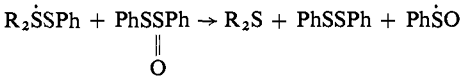


$$\mathrm{PhSOH} + (+)\mathrm{Ph}\underset{\mathrm{OH}}{\overset{+}{\mathrm{S}}}\mathrm{SPh} \rightarrow (\pm)\mathrm{Ph}\underset{\mathrm{OH}}{\overset{+}{\mathrm{S}}}\mathrm{SPh} + \mathrm{PhSOH} \qquad (8)$$

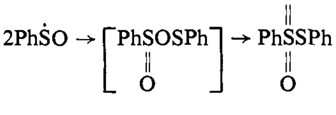
In general the experiments on the behavior of $k_\alpha{}^s$ as a function of sulfide structure seem to provide strong support for the type of mechanistic scheme suggested to account for the different dependence of k_s and k_d on sulfide structure.

Search for Radical Intermediates in the Sulfide-Catalyzed Disproportionation. What sort of process could be involved in step k_4 in the scheme in Chart II? One possibility which seemed attractive initially was the reaction shown in eq 9; this would then be followed by the processes shown as eq 10 and 11. In an effort to obtain evidence for such a mechanism we carried out several experiments that were designed to determine if any radical intermediates were present during the sulfide-catalyzed disproportionation.

$$\mathrm{R_2}\overset{+}{\mathrm{S}}\mathrm{SPh} + \mathrm{PhSOH} \rightarrow \mathrm{R_2}\dot{\mathrm{S}}\mathrm{SPh} + \mathrm{Ph}\dot{\mathrm{S}}\mathrm{O} + \mathrm{H^+} \qquad (9)$$



$$\mathrm{R_2}\dot{\mathrm{S}}\mathrm{SPh} + \mathrm{PhS}\underset{\mathrm{O}}{\underset{\|}{\mathrm{S}}}\mathrm{Ph} \rightarrow \mathrm{R_2S} + \mathrm{PhSSPh} + \mathrm{Ph}\dot{\mathrm{S}}\mathrm{O} \qquad (10)$$



$$2\mathrm{Ph}\dot{\mathrm{S}}\mathrm{O} \rightarrow \left[\mathrm{PhSO}\underset{\mathrm{O}}{\underset{\|}{\mathrm{S}}}\mathrm{Ph}\right] \rightarrow \mathrm{Ph}\underset{\mathrm{O}}{\underset{\|}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}}}\mathrm{SPh} \qquad (11)$$

In the first of these experiments 0.005 M n-butyl sulfide was added to a degassed solution of 0.05 M **1** in AcOH–0.56 M H_2O–0.02 M H_2SO_4 and the solution was examined immediately in a Varian 5400 esr spectrometer. No esr signal could be detected. Since there have been several previous indications[8,9] that Ph$\dot{S}$O radicals are apparently somewhat more stable and chemically less reactive than most other sulfur radicals, one would have expected, if they were involved as intermediates in the sulfide-catalyzed disproportionation, that their steady state concentration would have been high enough to lead to a detectable esr signal.

In a second experiment 0.02 M m-dinitrobenzene was added to a solution containing 4×10^{-3} M **1** and 2.9×10^{-4} M n-butyl sulfide in acetic acid–0.56 M H_2O–0.2 M H_2SO_4, and the rate of disappearance of **1** was monitored in the usual way. The rate constant k_d was the same as in the absence of m-dinitrobenzene. Since m-dinitrobenzene is known[10] to be a good electron transfer agent, and since the k_4 step in Chart II is rate determining with n-butyl sulfide as catalyst, the thought had been that, if the k_4 step actually involved the process shown in eq 9, addition of m-dinitrobenzene might well accelerate the rate by substituting the following hopefully more rapid pair of steps for eq 9.

$$\mathrm{PhSOH} + m\text{-}\mathrm{DNB} \rightarrow \mathrm{Ph}\dot{\mathrm{S}}\mathrm{O} + \mathrm{H^+} + m\text{-}\mathrm{DNB}\cdot^-$$

$$m\text{-}\mathrm{DNB}\cdot^- + \mathrm{R_2}\overset{+}{\mathrm{S}}\mathrm{SPh} \rightarrow m\text{-}\mathrm{DNB} + \mathrm{R_2}\dot{\mathrm{S}}\mathrm{SPh}$$

Since the addition of the dinitrobenzene had no effect, and, more important, since the esr experiment was also negative, one is led to be rather skeptical about the involvement of radical intermediates in the sulfide-catalyzed disproportionation.

Discussion

We have seen that although the sulfide-catalyzed disproportionation exhibits exactly the same formal kinetics as the sulfide-catalyzed **1**–$ArSO_2H$ reaction the two processes show an entirely different dependence of rate on sulfide structure (Table IV). We have also seen that this behavior can be rationalized in terms of the general scheme shown in Chart II, provided one assumes that $k_4 \ll k_{-2}$ for reactive sulfides like tetrahydrothiophene, n-butyl sulfide, benzyl sulfide, etc. and that $k_4 > k_{-2}$ for unreactive sulfides like phenyl sulfide and thiodiacetic acid. This, of course, requires that k_4/k_{-2} be almost as strongly dependent on sulfide structure as k_2, but in an inverse manner. Whereas electron-releasing groups attached to the sulfide sulfur accelerate k_2, the same groups diminish k_4/k_{-2}. Thus any satisfactory mechanism for the sulfide-catalyzed disproportionation must be one that is compatible with this sort of variation of k_4/k_{-2} with sulfide structure. Since the transformation of R_2S^+– to R_2S in step k_{-2} involves an increase in electron density on the sulfide sulfur, k_{-2} will be diminished, at least to some

---

[6] J. L. Kice and G. B. Large, *Tetrahedron Letters*, 3537 (1965); W. E. Savige and A. Fava, *Chem. Commun.*, 417 (1965).

[7] This relationship between k_α^s and k_s and k_d, which is a general one, can be derived as follows. In terms of the scheme in Chart II $k_s = k_2K_1h_0$ and $k_d = 2k_2K_1h_0[k_4/(k_4 + k_{-2})]$. Since $k_\alpha^s = k_2K_1h_0[k_{-2}/(k_4 + k_{-2})] + 2k_2K_1h_0[k_4/(k_4 + k_{-2})]$, it is easily shown that $k_\alpha^s = k_s + 0.5k_d$. (When $k_s \gg k_d$ this, of course, reduces to $k_\alpha^s \cong k_s$.)

[8] J. L. Kice and N. E. Pawlowski, *J. Am. Chem. Soc.*, **86**, 4898 (1964).

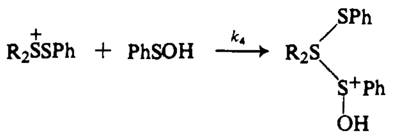
[9] D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *ibid.*, **88**, 3138 (1966); E. G. Miller, D. R. Rayner, and K. Mislow, *ibid.*, **88**, 3139 (1966).

[10] G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, **86**, 1807 (1964).

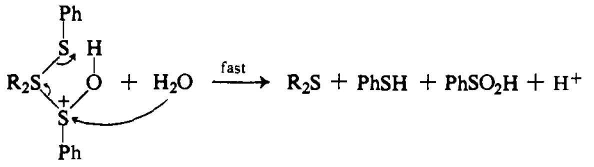
degree, by electron-releasing groups attached to this sulfur, although strong arguments can be made[11] that the effect will be a relatively small one. Nevertheless, this means that in order for k_4/k_{-2} to show the required large decrease with an increase in the electron-releasing character of the R groups, step k_4 must be a reaction in which the electron density on the sulfide sulfur is considerably larger in the transition state than it is in the ion R_2S^+SPh.

A reaction of this type which initially appeared to be an attractive possibility for the k_4 step was eq 9. However, the failure to find any experimental evidence for radical intermediates, while perhaps not conclusively ruling out eq 9, has, nonetheless, made it seem much less probable, and prompted us to search for suitable alternatives.

One alternative which was carefully considered is shown in eq 12 and 13. These two reactions would then be



(12)



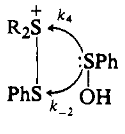
(13)

followed by

$$\mathrm{R_2\overset{+}{S}SPh + PhSH \xrightarrow{fast} PhSSPh + R_2S + H^+}$$

$$\mathrm{R_2\overset{+}{S}SPh + PhSO_2H \xrightarrow{fast} PhSO_2SPh + R_2S + H^+}$$

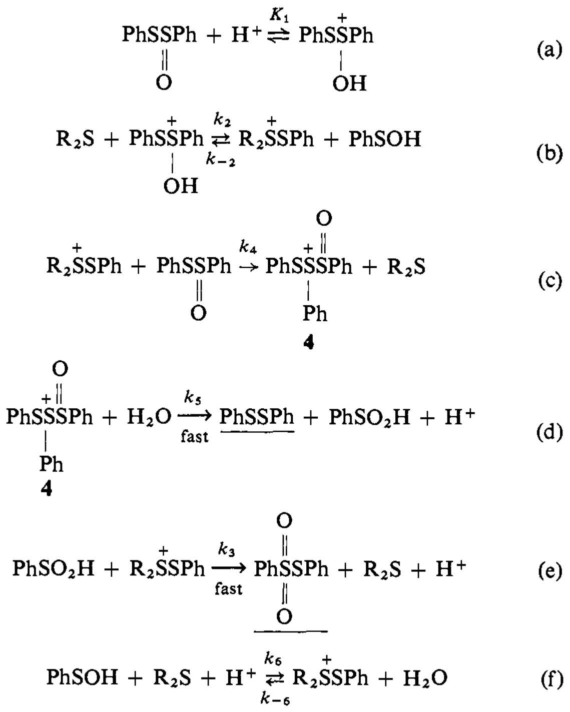
In this mechanism k_4 would involve nucleophilic attack by PhSOH on the trivalent sulfonium sulfur of ion **2**. While it is perfectly reasonable that such a process would be *slower* than nucleophilic attack of the same species on the sulfenyl sulfur of **2** (*i.e.*, $k_4 < k_{-2}$), it does not seem likely, given what is known in general about the relative ease of substitution at sulfenyl and trivalent sulfur, that



2

one would ever have the situation where $k_4 > k_{-2}$; and yet this is what is required by our data for both phenyl sulfide and thiodiacetic acid as catalysts. For this reason this mechanism is regarded as even less probable than eq 9.

Chart III. Proposed Mechanism for the Sulfide-Catalyzed Disproportionation of **1**



$$\mathrm{Ph\underset{\underset{O}{\|}}{S}SPh + H^+ \overset{K_1}{\rightleftharpoons} Ph\underset{\underset{OH}{|}}{\overset{+}{S}}SPh} \qquad \text{(a)}$$

$$\mathrm{R_2S + Ph\underset{\underset{OH}{|}}{\overset{+}{S}}SPh \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R_2\overset{+}{S}SPh + PhSOH} \qquad \text{(b)}$$

$$\mathrm{R_2\overset{+}{S}SPh + Ph\underset{\underset{O}{\|}}{S}SPh \xrightarrow{k_4} PhS\underset{\underset{Ph}{|}}{\overset{+}{S}}\overset{\overset{O}{\|}}{S}Ph + R_2S} \qquad \text{(c)}$$

4

$$\mathrm{PhS\underset{\underset{Ph}{|}}{\overset{+}{S}}\overset{\overset{O}{\|}}{S}Ph + H_2O \xrightarrow[fast]{k_5} \underline{PhSSPh} + PhSO_2H + H^+} \qquad \text{(d)}$$

4

$$\mathrm{PhSO_2H + R_2\overset{+}{S}SPh \xrightarrow[fast]{k_3} Ph\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}SPh + R_2S + H^+} \qquad \text{(e)}$$

$$\mathrm{PhSOH + R_2S + H^+ \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} R_2\overset{+}{S}SPh + H_2O} \qquad \text{(f)}$$

Since there are no other reasonable interactions of PhSOH and R_2S^+SPh which would have the required dependence of k_4 on R and also yield intermediates that would give the correct stoichiometry and products, one appears at first glance to have reached an impasse and to be forced to accept eq 9, despite the lack of positive evidence for radical intermediates, as the least unsatisfactory alternative.

However, although it may not appear so initially, it turns out that, given certain, in our view, reasonable assumptions, the mechanism in Chart III can also lead to the proper formal kinetics and can account satisfactorily for the peculiar dependence of k_d on sulfide structure. In this mechanism the k_4 step becomes the sulfenylation of **1** by R_2S^+SPh. The intermediate which results, **4**, then breaks up in the manner indicated in Chart III to give the disulfide and benzenesulfinic acid.[15] The latter then

---

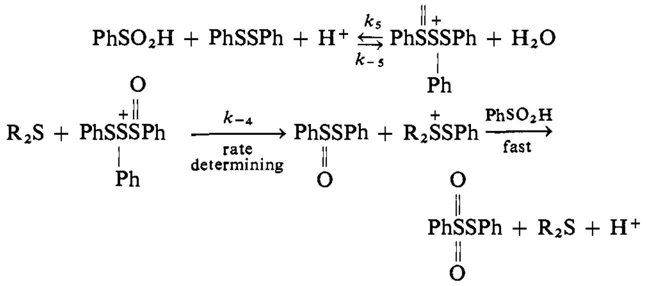
[11] The transition state for step k_{-2} is almost certainly much closer to the reactants (R_2S^+SPh + PhSOH) in structure than it is to the products (R_2S + $PhSS^+(OH)Ph$).[12] For this reason, k_{-2} will be considerably less sensitive than k_2 to changes in the electronic character of R.

[12] Several considerations suggest this: (a) the equilibrium constant for the equilibrium represented by steps k_2 and k_{-2} strongly favors R_2S + protonated **1**;[13] (b) the incredible rapidity of certain nucleophilic substitutions involving ions R_2S^+SR'[4] suggests that many such reactions are exothermic processes with little E_a. According to Hammond's principle[14] their transition states should therefore resemble the reactants much more closely than the products.

[13] C. G. Venier, Ph.D. Thesis, Oregon State University, 1966.

[14] G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

[15] Reactions c and d in Chart III and/or their reverse steps are involved as key steps in the mechanism of the sulfide-catalyzed disulfide–sulfinic acid reaction,[16] *i.e.*



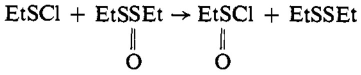
$$\mathrm{PhSO_2H + PhSSPh + H^+ \underset{k_{-5}}{\overset{k_5}{\leftrightarrows}} PhS\underset{\underset{Ph}{|}}{\overset{+}{S}}\overset{\overset{O}{\|}}{S}Ph + H_2O}$$

$$\mathrm{R_2S + PhS\underset{\underset{Ph}{|}}{\overset{+}{S}}\overset{\overset{O}{\|}}{S}Ph \xrightarrow[\text{rate determining}]{k_{-4}} Ph\underset{\underset{O}{\|}}{S}SPh + R_2\overset{+}{S}SPh \xrightarrow[fast]{PhSO_2H} Ph\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}SPh + R_2S + H^+}$$

Kinetic studies[16] of this reaction in AcOH–0.56 *M* H_2O containing added sulfuric acid show that even at higher sulfide concentrations than those used in the present work $k_{-4}(R_2S) \ll k_5(H_2O)$. Thus we can rest assured that under the present reaction conditions step k_5 will be considerably faster than the reverse of reaction c. Because of this step k_{-4} will not be kinetically important under our conditions and need not be included in any kinetic analysis.

reacts rapidly with another R_2S^+SPh ion (reaction e) to yield the other disproportionation product, the thiolsulfonate. That this latter reaction occurs very readily has already been shown by studies[2] of the **1**-$ArSO_2H$ reaction.

Since Douglass and Koop[17] have shown that EtSCl, almost certainly a poorer sulfenylating agent than R_2S^+SPh, reacts readily with ethyl ethanethiolsulfinate



$$\mathrm{EtSCl} + \mathrm{Et}\underset{\underset{\displaystyle O}{\|}}{\mathrm{S}}\mathrm{SEt} \rightarrow \mathrm{Et}\underset{\underset{\displaystyle O}{\|}}{\mathrm{S}}\mathrm{Cl} + \mathrm{EtSSEt}$$

the postulated reaction sequence involving R_2S^+SPh and **1** and the subsequent break-up of ion **4** appears a most reasonable one indeed. However, one's first reaction is that, despite this fact, it cannot be acceptable, because in those cases where k_4 is rate determining it would lead to a higher than first-order dependence of rate on thiolsulfinate concentration. Surprisingly, though, under the right circumstances this turns out not to be the case, as the following kinetic analysis will show.

Application of the steady-state hypothesis to the concentrations of **2**, **3**, **4**, and sulfinic acid gives the steady-state concentrations of these intermediates as

$$[4] = \frac{k_4[R_2S^+SPh][PhS(O)SPh]}{k_5[H_2O]}$$

$$[PhSO_2H] = \frac{k_4}{k_3}[PhS(O)SPh]$$

$$[R_2S^+SPh] = \frac{K_1k_2[R_2S][PhS(O)SPh]h_0 + k_6[R_2S][PhSOH]h_0}{k_{-2}[PhSOH] + 2k_4[PhS(O)SPh] + k_{-6}[H_2O]}$$

$$[PhSOH] = \frac{K_1k_2[R_2S][PhS(O)SPh]h_0 + k_{-6}[R_2S^+SPh][H_2O]}{k_{-2}[R_2S^+SPh] + k_6[R_2S]h_0}$$

where $H_0 = -\log h_0$. Substituting the expression for $[R_2S^+SPh]$ into that for $[PhSOH]$ and solving for the latter one obtains

$$[PhSOH] = \frac{k_4[PhS(O)SPh]}{2k_{-2}} \times \left[\left[1 + \frac{4k_{-2}k_2K_1}{k_6k_4}\left(1 + \frac{k_{-6}[H_2O]}{k_4[PhS(O)SPh]}\right)\right]^{\frac{1}{2}} - 1\right]$$

Now, if it should be the case that $k_4[PhS(O)SPh] \gg k_{-6}[H_2O]$, *i.e.*, that ion **2** reacts more readily with **1** than it hydrolyzes to PhSOH, then

$$[PhSOH] = \frac{k_4[PhS(O)SPh]}{2k_{-2}}\left[\left(1 + \frac{4k_{-2}k_2K_1}{k_6k_4}\right)^{\frac{1}{2}} - 1\right]$$

and

$$[R_2S^+SPh] = \frac{[R_2S]h_0}{k_4} \times \left\{\frac{2K_1k_2 + \dfrac{k_6k_4}{k_{-2}}\left(\left[1 + \dfrac{4k_{-2}k_2K_1}{k_6k_4}\right]^{\frac{1}{2}} - 1\right)}{3 + \left[1 + \dfrac{4k_{-2}k_2K_1}{k_6k_4}\right]^{\frac{1}{2}}}\right\}$$

For the mechanism in Chart III the rate of the sulfide-catalyzed disproportionation will be given by eq 14 which

$$-\frac{d[PhS(O)SPh]}{dt} = K_1k_2[R_2S][PhS(O)SPh]h_0 + k_4[R_2S^+SPh][PhS(O)SPh] - k_{-2}[R_2S^+SPh][PhSOH] \quad (14)$$

upon substituting in the expressions for [PhSOH] and $[R_2S^+SPh]$ given above becomes

$$-\frac{d[PhS(O)Ph]}{dt} = K_1k_2[R_2S][PhS(O)SPh]h_0 \times \left\{\frac{4 + \dfrac{2k_6k_4}{K_1k_2k_{-2}}\left(\left[1 + \dfrac{4K_1k_2k_{-2}}{k_6k_4}\right]^{\frac{1}{2}} - 1\right)}{3 + \left[1 + \dfrac{4K_1k_2k_{-2}}{k_6k_4}\right]^{\frac{1}{2}}}\right\} \quad (15)$$

Thus one sees that provided the situation is such that $k_{-6}[H_2O] < k_4[PhS(O)SPh]$, the mechanism in Chart III does lead to the proper formal kinetics, *i.e.*, a first-order dependence on both sulfide and thiolsulfinate and a proportionality between rate and h_0.

Rate constant k_s for the sulfide-catalyzed **1**-$ArSO_2H$ reaction[2] is, of course, equal to $K_1k_2h_0$, so that according to eq 15 the relationship between k_s and k_d should be

$$\frac{k_d}{k_s} = \frac{4 + \dfrac{2k_6k_4}{K_1k_2k_{-2}}\left(\left[1 + \dfrac{4K_1k_2k_{-2}}{k_6k_4}\right]^{\frac{1}{2}} - 1\right)}{3 + \left[1 + \dfrac{4K_1k_2k_{-2}}{k_6k_4}\right]^{\frac{1}{2}}} \quad (16)$$

(One should note too that the mechanism in Chart III, like that of Chart II, also yields the observed relation $k_{\text{a}}^{\text{s}} = k_s + 0.5k_d$.) Equation 16 indicates that k_d/k_s will vary with the magnitude of the rate constant ratio $(k_6k_4/K_1k_2k_{-2})$. Calculated values of k_d/k_s for a range of values of this ratio are shown below.

$(k_6k_4/K_1k_2k_{-2})$	4	0.4	0.04	0.004	4×10^{-4}	4×10^{-6}
Calcd (k_d/k_s)	1.7	0.93	0.36	0.12	0.04	0.004

Since the smallest value of k_d/k_s in Table IV is about 0.004 and the largest about 1.7 this requires that $k_6k_4/K_1k_2k_{-2}$ must decrease by about 10^6 on going from unreactive sulfides like thiodiacetic acid and phenyl sulfide to those most reactive in the **1**-$ArSO_2H$ reaction like tetrahydrothiophene and *n*-butyl sulfide. One can ask whether it is reasonable to expect such a large variation in this ratio. The answer would appear to be in the affirmative, provided one can assume that the rate of step k_6 is somewhat less dependent on sulfide structure than is

---

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

(17) I. B. Douglass and D. A. Koop, *J. Org. Chem.*, **27**, 1398 (1962).

k_2. The detailed arguments are given in a footnote.[18] In our opinion, then, the mechanism in Chart III would appear to be fully capable of explaining all the known facts regarding the sulfide-catalyzed disproportionation, to have analogy[17] and precedent[16] for its key step, the reaction of R_2S^+SPh with **1**, and to be able to do all this without the need of invoking intermediates for which there is no experimental evidence in the present system, which is, of course, the shortcoming of the mechanism in eq 9–11.

We would stress, however, that the mechanism in Chart III fits the experimental facts only if one assumes that $k_4[PhS(O)SPh] > k_{-6}[H_2O]$, and some may feel that this is unrealistic. We do not think it so for the following reasons. Recent studies[19] have shown that in the terminology of the Theory of Hard and Soft Acids and Bases[20] sulfenyl sulfur is a very soft electrophilic center; and, accordingly, it undergoes nucleophilic substitution by soft nucleophiles much more readily than by hard ones. This would indicate that the divalent sulfur of **1** (a soft nucleophile) should enjoy a considerable advantage over water (a hard nucleophile) in ease of nucleophilic attack on the sulfenyl sulfur of R_2S^+SPh. Thus we feel it not unreasonable that $k_4 \gg k_{-6}$.

In any event, the mechanism in Chart III and the one in eq 9–11 appear to represent the only tenable possibilities for the mechanism of the sulfide-catalyzed disproportionation of **1**. For the reasons outlined, we currently favor the one shown in Chart III. However, no matter which is correct, one fact emerges clearly from the present study, and that is that, perhaps as befits an element generally considered to have strong nether world and Mephistophelian connections, the mechanisms of reactions involving the making and breaking of sulfur–sulfur bonds can be simply devilish in their intricacy and complexity.

Experimental Section

Preparation and Purification of Materials. The preparation and purification of **1**, and the purification of the various sulfides used as catalysts have already been described.[2]

Solvents. Acetic acid was purified as outlined in a previous paper.[21] The preparation of the various solutions of acetic acid–water and acetic acid–water–sulfuric acid has already been outlined.[2] The same is true of the details of the preparation of solutions of acetic acid-*d*.

Procedure for Kinetic Runs. The thiolsulfinate was weighed out directly and dissolved in acetic acid–0.56 *M* water in a volumetric flask. Stock solutions of sulfuric acid and 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 runs with a stoichiometric water concentration other than 0.56 *M*, special stock solutions of acetic acid–water were prepared.) The final solution was transferred to a reaction vessel of the type previously used[2] to study the kinetics of the **1**-$ArSO_2H$ reaction, the solution carefully deaerated, and the course of the reaction followed by the same procedure[2] used to monitor the disappearance of **1** in the **1**-$ArSO_2H$ reaction.

Product Studies of the Disproportionation. Solutions for product studies were prepared in the same manner as for the kinetic runs. The solutions used were initially 0.03 *M* in **1**. The reactions were run for eight to ten half-lives. The final solution was poured into ten times its volume of 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 separated into its various components by chromatography on acid-washed alumina in the manner described in an earlier paper.[2] Phenyl benzenethiolsulfonate was identified by comparison with a known sample,[5a] mp 45–46°.

Rate of Loss of Optical Activity of Optically Active 1. The desired amount of optically active[6] **1** was weighed into a 10-ml volumetric flask and some acetic acid–0.56 *M* water was added. Aliquots of stock solutions of catalyzing sulfide and sulfuric acid were pipetted into the flask, and the solution was made up to volume with acetic acid–0.56 *M* water. The solution was poured into a jacketed, 1-dm polarimeter tube kept at 39.4°. The rate of loss of optical activity was then followed by measuring the decrease in optical rotation of the solution *vs.* time at 436 mμ with a Perkin-Elmer Model 141 polarimeter.

---

(18) Let us consider the effect of changing the structure of the sulfide from thiodiacetic acid to *n*-butyl sulfide on each of the rate constants in the ratio in turn. Since K_1 does not involve the sulfide it is unaffected. The behavior of k_s indicates that k_2 will increase by about 4×10^4 on going from $(HOOCCH_2)_2S$ to $n\text{-}Bu_2S$ ($\rho^* = -2.0$). The nature of the k_4 step is such as to suggest that k_4 will probably have a larger positive ρ^* than k_2 has a negative one. Taking ρ^* for k_4 equal to $+2.5$ as a reasonable value, k_4 would decrease by something like a factor of 6×10^5 on going from thiodiacetic acid to *n*-butyl sulfide. We have already noted[11] that while k_{-2} should also decrease on going from $(HOOCCH_2)_2S$ to $n\text{-}Bu_2S$ the change should be a relatively small one. We suggest a decrease of a factor of 50 ($\rho^*_{k_{-2}} \cong 0.75$) as a not unreasonable estimate. This leaves only k_6 to be considered. Clearly it will increase on going from thiodiacetic acid to *n*-butyl sulfide, but if the increase is less pronounced than for k_2, *i.e.*, a factor of 7.5×10^2 (corresponding to a ρ^* for k_6 of -1.25) then the expected value of

$$\left(\frac{k_4k_6}{K_1k_2k_{-2}}\right)_{n\text{-}Bu_2S} = \frac{(6 \times 10^5)^{-1}(7.5 \times 10^2)}{1 \times (4 \times 10^4)(1/50)}\left(\frac{k_4k_6}{K_1k_2k_{-2}}\right)_{(HOOCCH_2)_2S}$$

$$\left(\frac{k_4k_6}{K_1k_2k_{-2}}\right)_{n\text{-}Bu_2S} = 1.6 \times 10^{-6}\left(\frac{k_4k_6}{K_1k_2k_{-2}}\right)_{(HOOCCH_2)_2S}$$

which is essentially what is required by the difference in (k_d/k_s) observed for the two sulfides.

(19) J. L. Kice and G. B. Large, *J. Am. Chem. Soc.*, **90**, 4069 (1968).

(20) R. G. Pearson, *ibid.*, **85**, 3533 (1963); R. G. Pearson and J. Songstad, *ibid.*, **89**, 1827 (1967).

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