such as acids and phenols, and dried over $MgSO_4$. Upon evaporation of the ether, 0.0946 g (10–20%) of a light yellow solid was obtained, mp 110–130°. Thin layer chromatography on silica gel using 90:10:1 volume ratio of hexane–ether–acetic acid indicated this product to be mostly one component. The solid was washed with pentane and recrystallized from chloroform–petroleum ether to give a lighter yellow product, mp 135–138°. It had infrared peaks at 2.74, 5.64, 5.84, 6.25, 6.70, 6.91, 7.97, and 9.23 μ. A large nmr peak at 439 cps and very small peaks at 437 and 440 cps were observed in $CDCl_3$ solvent. *Anal.* Found: C, 77.05; H, 5.99; mol wt, 356.

The data are not consistent with *t*-butyl benzyl ether or with 1,2-diphenylethane.

Acknowledgment. We wish to thank the Air Force Office of Scientific Research for financial support, and the Department of Health, Education, and Welfare for a fellowship (G. R. J.).

Mechanisms of Substitution Reactions at Sulfinyl Sulfur. II. Concomitant Electrophilic and Nucleophilic Catalysis of the Solvolysis of Aryl Sulfinyl Sulfones in Acetic Acid–Water[1]

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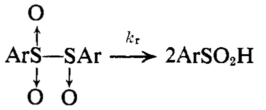
Abstract: In acetic acid–1% water the rate of acid-catalyzed solvolysis (eq 1) of aryl sulfinyl sulfones (II) can be rather dramatically accelerated by the addition of small amounts of various alkyl sulfides. The sulfide-catalyzed solvolysis is first order in both sulfide and sulfinyl sulfone; its rate is proportional to the Hammett acidity function and is strongly dependent on the structure of the sulfide ($\rho^* = -1.6$). Electron-withdrawing substituents in the aromatic ring attached to the sulfonyl sulfur of II enhance the rate of reaction with a given sulfide while the same substituents in the ring attached to the sulfinyl sulfur retard the reaction somewhat. The reaction shows a small solvent isotope effect, $k_H/k_D = 1.15$. Several mechanisms (eq 6 or 8) can be written which are consistent with these data. In each of them one has a nucleophilic attack by the sulfide on the sulfinyl group of II, which displaces the $ArSO_2$ group; this displacement is significantly assisted by the transfer of a proton to the departing $ArSO_2$ group. The mechanisms differ only in the details of how this proton transfer is effected. The sulfide-catalyzed solvolysis of II is thus an example of concomitant nucleophilic and electrophilic catalysis of the scission of a sulfur–sulfur bond involving substitution at sulfinyl sulfur. It is compared with earlier examples[4,5] of such catalysis involving substitution at sulfenyl sulfur.

In moist acetic acid an aryl sulfinyl sulfone (II) hydrolyzes readily to two molecules of the corresponding sulfinic acid (I). In two other papers[2,3] we



$$\underset{\text{II}}{\mathrm{Ar}\overset{\mathrm{O}\atop\uparrow}{\underset{\downarrow\atop\mathrm{O}}{\mathrm{S}}}-\underset{\downarrow\atop\mathrm{O}}{\mathrm{S}}\mathrm{Ar}} \xrightarrow{k_r} \underset{\text{I}}{2\mathrm{ArSO_2H}} \qquad (1)$$

a, Ar = p-$CH_3C_6H_4$
b, Ar = C_6H_5
c, Ar = p-ClC_6H_4
d, Ar = p-$CH_3OC_6H_4$

have shown that one can easily determine the rate of this reaction under a wide variety of reaction conditions. In connection with this work we discovered that the presence of very small amounts of certain alkyl sulfides can profoundly accelerate the rate of acid-catalyzed solvolysis of a sulfinyl sulfone. Investigation of the nature of this catalysis by added sulfides reveals that the phenomenon bears a striking resemblance to several earlier examples of concomitant nucleophilic and electrophilic catalysis of the scission of a sulfur–sulfur bond.[4,5] These other cases, however, involved a substitution at a sulfenyl rather than a sulfinyl sulfur. The similarity in the behavior of the various systems suggests the important conclusion that this type of catalysis is a more general phenomenon in sulfur–sulfur bond scissions that might previously have been suspected.

Study of the mechanism of sulfide catalysis of the solvolysis of II is also of considerable interest in connection with both the mechanism of the normal acid catalyzed solvolysis of sulfinyl sulfones[3] and the general question of mechanisms of substitution at sulfinyl sulfur. The latter area has been the subject of much recent investigation.[6–9]

Results

Kinetic Study of the Solvolysis of II. All the sulfinyl sulfones exhibit a strong absorption maximum near 300 mμ. At the same wavelength, a solution of the corresponding sulfinic acid of comparable concentration is completely transparent. Thus their solvolysis

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(1) (a) This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-106-65. (b) Part of this work appeared in preliminary form: J. L. Kice and G. Guaraldi, *Tetrahedron Letters*, 501 (1966).

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

(3) J. L. Kice and G. Guaraldi, *ibid.*, **31**, 3568 (1966).

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

(5) J. L. Kice and C. G. Venier, *Tetrahedron Letters*, 3629 (1964).

(6) J. Day and D. J. Cram, *J. Am. Chem. Soc.*, **87**, 4398 (1965).

(7) K. Mislow, T. Simons, J. T. Melillo, and A. L. Ternay, *ibid.*, **86**, 1452 (1964).

(8) C. R. Johnson, *ibid.*, **85**, 1020 (1963); C. R. Johnson and D. McCants, Jr., *ibid.*, **87**, 5404 (1965); C. R. Johnson and W. G. Phillips, *Tetrahedron Letters*, 2101 (1965).

(9) D. Landini, F. Montanari, H. Hogeveen, and C. Maccagnani, *ibid.*, 2691 (1964); J. Krueger, *Inorg. Chem.*, **5**, 132 (1966).

Table I. Catalysis of the Solvolysis of Aryl Sulfinyl Sulfones in Acetic Acid–0.56 *M* Water by Benzyl Sulfide[a]

Sulfinyl sulfone[b]	(H_2SO_4), *M*	(R_2S) × 10^3, *M* (R = $PhCH_2$)	$k_r \times 10^3$, sec^{-1}	$k_S = \left[\frac{k_r - k_r^\circ}{(R_2S)}\right]^c$
IIa	0.10	0.69	0.50	0.46
		1.38	0.82	0.46
		2.07	1.07	0.43
	0.20	0.69	1.08	1.1
	0.30	0.69	1.9	1.9
	0.40	0.69	3.2	3.5
b	0.10	0.276	0.29	0.41
		0.69	0.47	0.42
		1.38	0.67	0.36
	0.20	0.69	0.99	1.0
	0.40	0.69	3.1	3.4
c	0.10	0.69	1.16	0.93
		1.38	1.93	1.0
		2.07	2.5	0.97
	0.20	0.69	2.3	2.3
	0.30	0.69	4.2	4.5
	0.40	0.69	6.5	7.2
d	0.10	2.73	2.9	0.26
		4.72	3.3	0.23
III	0.60	0.21	1.72	4.2
		0.62	3.5	4.3
		1.03	5.0	4.1
		2.07	9.2	4.1

[a] All data at 21°. [b] Initial sulfinyl sulfone concentration between 0.5 and 2.8 × 10^{-4} *M* in all runs. [c] k_r° equals the rate of solvolysis in the absence of sulfide. Values used from ref 2 and 3.

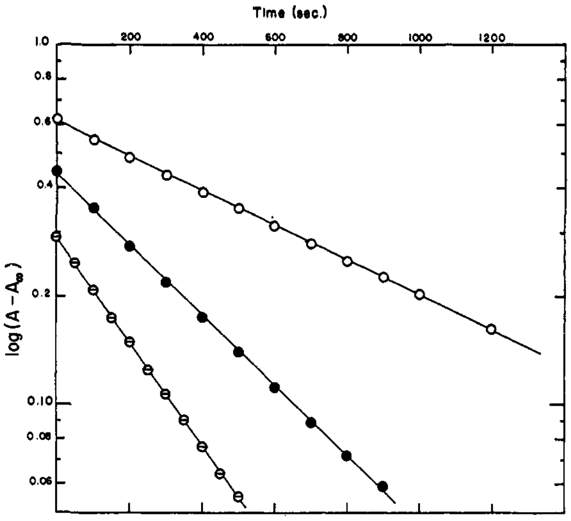


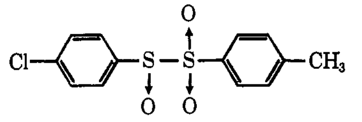
Figure 1. Sulfide-catalyzed solvolysis of sulfinyl sulfones. Representative individual kinetic runs: ○, IIa (benzyl sulfide), 6.9 × 10^{-4} *M*, AcOH–0.56 *M* H_2O–0.20 *M* H_2SO_4; ⊖, IIb (n-Bu_2S), 3.2 × 10^{-4} *M*, AcOH–0.56 *M* H_2O–0.10 *M* H_2SO_4; ●, IIc (benzyl sulfide), 6.9 × 10^{-4} *M*, AcOH–0.56 *M* H_2O–0.20 *M* H_2SO_4.

in acetic acid–water solution can be conveniently followed by observing the decrease in absorbance at this wavelength with time. Since the initial concentration of sulfinyl sulfone is kept low (<2.5 × 10^{-4} *M*) the reverse reaction—formation of II from I—can be neglected, and the final optical density is zero.

All studies of catalyis of the solvolysis by added sulfides were carried out in acetic acid–0.56 *M* water as solvent. Varying amounts (0.10–0.40 *M*) of sulfuric acid were used as acid catalyst. Under these conditions, the disappearance of the sulfinyl sulfone follows good first-order kinetics in all cases. This is evident from Figure 1, which shows plots of log (absorbance) *vs.* time for some representative runs.

The experimental first-order rate constant, k_1, obtained from the slope of such plots is actually the sum of the rate constants for solvolysis, k_r, and thermal decomposition,[10] k_d, of the sulfinyl sulfone. However, for any of the reaction conditions involved in the present studies $k_r \gg k_d$, and k_1 may be taken as equal to k_r.

Our most extensive studies of catalysis by sulfides have involved the use of benzyl and n-butyl sulfides. Data for benzyl sulfide catalyzed solvolysis of the various sulfinyl sulfones, including the unsymmetrical sulfinyl sulfone III, are given in Table I. Data on



III

n-butyl sulfide catalysis are shown in Table II. In addition, four other sulfides have been studied as catalysts for the solvolysis of p-toluenesulfinyl p-tolyl sulfone (IIa) only. These results are summarized in Table III.

Table II. Catalysis of the Solvolysis of Aryl Sulfinyl Sulfones in Acetic Acid–0.56 *M* Water by n-Butyl Sulfide[a]

Sulfinyl sulfone[b]	(H_2SO_4), *M*	(R_2S) × 10^3, *M* (R = n-Bu)	$k_r \times 10^3$, sec^{-1}	$k_S = \left[\frac{k_r - k_r^\circ}{(R_2S)}\right]^c$
IIa	0.10	0.24	1.9	7.2
		0.48	3.9	7.7
		0.69	5.4	7.6
	0.20	0.24	5.5	21
	0.30	0.24	8.3	32
	0.10[d]	0.24	2.8	10.1
	0.10[e]	0.24	4.3	13.8
b	0.10	0.16	1.66	9.2
		0.32	3.4	10
c	0.10	0.16	3.1	16
		0.32	5.8	17

[a] All data at 21° unless otherwise indicated. [b] Initial sulfinyl sulfone concentration between 0.5 and 2.8 × 10^{-4} *M* in all runs. [c] k_r° equals rate of solvolysis under the same conditions in the absence of sulfide. Values used from ref 2 and 3. [d] At 30.0°. [e] At 39.2°.

Table III. Catalysis of the Solvolysis of IIa in Acetic Acid–0.56 *M* Water by Various Alkyl Sulfides[a]

Sulfide	(H_2SO_4), *M*	(R_2S) × 10^3, *M*	k_r × 10^3, sec^{-1}	$k_S = \left[\frac{k_r - k_r^\circ}{(R_2S)}\right]^b$
Tetrahydrothiophene	0.10	0.127	5.0	38
		0.076	3.0	37
Et_2S	0.10	0.334	2.5	6.9
		0.167	1.32	6.8
$(HOOCCH_2CH_2)_2S$	0.10	83	12.2	0.14
		42	5.6	0.13
$(HOOCCH_2)_2S$	0.20	93	0.67	0.0035
		62	0.59	0.0040

[a] All data at 21°. Initial sulfinyl sulfone concentration in thc range 1.0 to 1.5 × 10^{-4} *M*. [b] k_r° equals rate of solvolysis of IIa in the absence of sulfide. Values from ref 2.

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

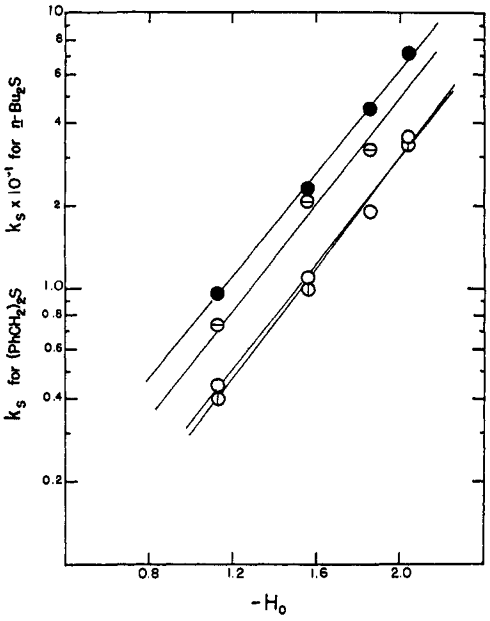

Figure 2. Dependence of sulfide-catalyzed solvolysis rate (k_S) on acidity: O, IIa-benzyl sulfide; ⦶, IIb-benzyl sulfide; ●, IIc-benzyl sulfide; ⊖, IIa-butyl sulfide.

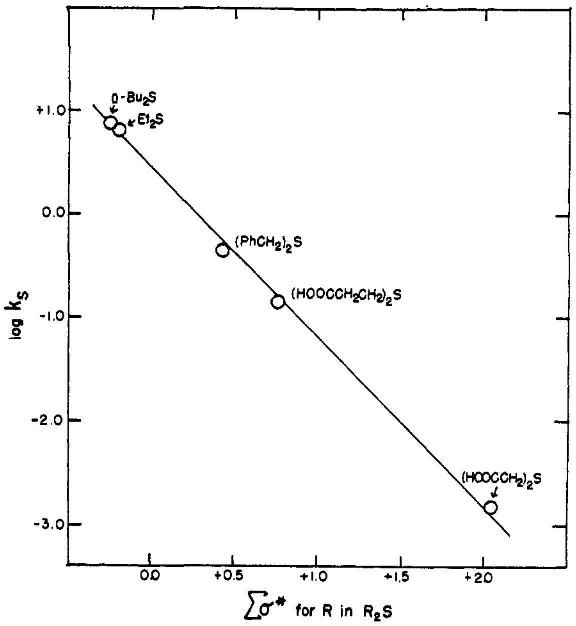

Figure 3. Log k_S for sulfide-catalyzed solvolysis of IIa *vs.* $\Sigma\sigma^*$ for R in R_2S.

Dependence of Rate on Sulfide Concentration. If the sulfide-catalyzed reaction is first order in sulfide, then in the presence of sulfide, k_r will be given by

$$k_r = k_r{}^\circ + k_S(R_2S) \qquad (2)$$

where $k_r{}^\circ$ equals k_r in the absence of sulfide under otherwise identical conditions. Values of $k_r{}^\circ$ are available from our other work.[2,3] Equation 2 may be written in the form

$$k_S = \frac{k_r - k_r{}^\circ}{(R_2S)} \qquad (3)$$

For a given sulfide with a given sulfinyl sulfone at a given sulfuric acid concentration $(k_r - k_r{}^\circ)/(R_2S)$ should be a constant independent of sulfide concentration. The data in Tables I–III show that this is indeed the case for every sulfide-catalyzed solvolysis studied. The sulfide-catalyzed solvolysis is therefore definitely first order in sulfide.

Dependence of k_S on Acidity. The dependence of k_S on the acidity of the medium was investigated for the benzyl sulfide catalyzed solvolyses of three different sulfinyl sulfones. Similar data were obtained for the butyl sulfide catalyzed solvolysis of IIa. In each instance k_S is found to be strongly dependent on the acidity of the medium. Figure 2 shows plots of log k_S for the various sulfide–sulfinyl sulfone combinations studied *vs.* the Hammett acidity function, H_0.[11] All of the plots are satisfactorily linear with slopes of about 0.95. The fact that the slope of a log k_S *vs.* $-H_0$ plot does not depend on the sulfinyl sulfone involved contrasts with the situation observed for the normal acid-catalyzed solvolysis of the same sulfinyl sulfones.[3] There one found a significantly lower slope (0.82) for IIc than for IIa (0.95), with IIb showing intermediate behavior.

Influence of Sulfide Structure. For sulfinyl sulfone IIa we have rate data on the effect of six different sulfides. Comparison of the k_S values for these sulfides at a given sulfuric acid concentration shows one how the rate of the sulfide-catalyzed solvolysis depends on sulfide structure. Table IV summarizes the appropriate data. It is apparent that there is something over a 10,000-fold spread in reactivity between the most reactive sulfide, tetrahydrothiophene, and the least reactive, thiodiacetic acid. Figure 3 shows a plot of the log k_S values for all the sulfides except tetrahydrothiophene *vs.* $\Sigma\sigma^*$ for the R groups in R_2S. The correlation is remarkably good, and the apparent ρ^* value (−1.6) shows that the sulfide sulfur has a significantly lower electron density in the transition state than it has in the original sulfide.

Table IV. Relative Reactivity of Sulfides as Catalysts for the Solvolysis of IIa

Sulfide	k_S, M^{-1} sec^{-1} [a]
Tetrahydrothiophene	38
n-Bu_2S	7.5
Et_2S	6.8
$(PhCH_2)_2S$	0.45
$(HOOCCH_2CH_2)_2S$	0.14
$(HOOCCH_2)_2S$	0.0014[b]

[a] All data are for acetic acid–0.56 M water–0.10 M sulfuric acid at 21°. [b] Extrapolated from 0.2 M sulfuric acid assuming same dependence of k_S on H_0 as for butyl and benzyl sulfides.

Tetrahydrothiophene, in which the alkyl groups are effectively "tied back" by ring formation, is about five times more reactive than ethyl sulfide. This indicates that, despite the excellence of the log k_S *vs.* σ^* correlation for the remaining sulfides, inductive effects are not the only factor influencing k_S; steric effects also play a role.

Effect of Sulfinyl Sulfone Structure on Rate. The data in Table V show the effect of changes in sulfinyl

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[11] The H_0 values used were those of J. Rocek, *Collection Czech. Chem. Commun.*, 22, 1 (1957).

sulfone structure on the rate of a sulfide-catalyzed solvolysis. Comparison of the rates for IIc and III indicates that electron-withdrawing substituents in the aromatic ring attached to the *sulfonyl* sulfur lead to a faster rate of reaction. The same thing was observed in the normal acid-catalyzed solvolysis.[3]

Table V. Effect of Sulfinyl Sulfone Structure on the Rate of the Benzyl Sulfide Catalyzed Solvolysis

Sulfinyl sulfone	$p\text{-X-C}_6\text{H}_4\text{-}\underset{\downarrow}{\text{S}}\text{-}$ X O	$p\text{-Y-C}_6\text{H}_4\text{-}\overset{\text{O}}{\overset{\uparrow}{\underset{\downarrow}{\text{S}}}}\text{-}$ Y O	k_S, M^{-1} sec$^{-1\,a}$
IIb	H	H	0.40
IIc	Cl	Cl	0.97
III	Cl	CH_3	0.26[b]
IIa	CH_3	CH_3	0.45
IId	CH_3O	CH_3O	0.25

[a] All data for acetic acid–0.56 M water–0.10 M sulfuric acid at 21°. [b] Extrapolated from higher acid concentration assuming same dependence on acidity as observed for other sulfinyl sulfones.

The k_S values for IIa and III, on the other hand, suggest that electron-withdrawing substituents in the aromatic ring attached to the *sulfinyl* sulfur result in a somewhat slower rate of solvolysis. The effect, however, is a small one, and, as the k_S values for IIc and IId show, in a symmetrical sulfinyl sulfone it is generally more than counterbalanced by the effect of the same substituent in the $ArSO_2$ group.

The most striking difference between the reactivity pattern in Table V and that for normal acid-catalyzed solvolysis of the same sulfinyl sulfones (Table IV of ref 3) is in the behavior of the p-anisyl compound (IId). The solvolysis rate for IId in the normal acid catalyzed reaction was at least 25 times greater than that of any of the other sulfinyl sulfones. In the sulfide-catalyzed reaction, on the other hand, it is one of the two least reactive compounds.

Solvent Isotope Effect for Benzyl Sulfide Catalyzed Solvolysis of IIa. This was evaluated by determining k_S for this reaction in deuteriated medium (Table VI) and comparing it with the appropriate k_S value in Table I. The solvent isotope effect is small, $(k_S^H/k_S^D) = 1.15$.

Table VI. Catalysis of the Solvolysis of IIa in Acetic Acid-*d* by Benzyl Sulfide

C_{D_2O}, M^a	(D_2SO_4), M	$(R_2S) \times 10^3$, M (R = $PhCH_2$)	$k_r \times 10^3$, sec^{-1}	$k_S = \left[\frac{k_r - k_r^\circ}{(R_2S)}\right]^b$
0.56	0.10	0.00	0.20[c]	
		2.24	1.08[c]	0.39

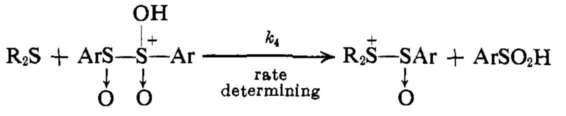
[a] Stoichiometric concentration of water. [b] k_r° equals the rate of solvolysis in the absence of sulfide. [c] Average of two runs.

Activation Energy and Entropy. The rate constant k_S was determined at several temperatures for the butyl sulfide catalyzed solvolysis of IIa in acetic acid–0.56 M H_2O–0.10 M sulfuric acid. From the variation of log k_S with $1/T$ one calculates an activation energy (E_a) for this particular reaction of only 6.5 ± 1.0 kcal. The entropy of activation (ΔS^*) is large and negative, −39 eu.

Discussion

Mechanism of the Sulfide-Catalyzed Solvolysis. The first-order dependence on sulfinyl sulfone and sulfide concentrations indicates that the rate-determining transition state for the sulfide-catalyzed solvolysis involves one molecule each of sulfide and sulfinyl sulfone. The pronounced influence of sulfide structure on rate ($\rho^* = -1.6$) shows that the sulfide sulfur has a significantly lower electron density in the transition state than it had in the original sulfide.

At first glance, given the acid-catalyzed nature of the reaction, as evidenced by the linear relation between log k_S and $-H_0$, a mechanism involving rate-determining nucleophilic attack of the sulfide on the sulfonyl-protonated sulfinyl sulfone (IV) might seem acceptable.

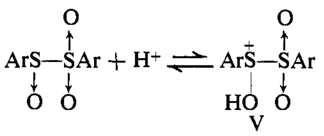


$$R_2S + \underset{\underset{O}{\downarrow}}{ArS}-\overset{OH}{\overset{|+}{\underset{\underset{O}{\downarrow}}{S}}}-Ar \xrightarrow[\text{rate determining}]{k_4} R_2\overset{+}{S}-\underset{\underset{O}{\downarrow}}{S}Ar + ArSO_2H \quad (4)$$

IV

The following arguments, however, demonstrate that this is *not* the case. There is ample evidence[12,13] that sulfonyl groups are extremely weak basic sites. The conjugate acid of dimethyl sulfone, for example, has a pK_a of −12.3.[12] Since the sulfonyl group of a sulfinyl sulfone should be even less basic, the fraction of II present as IV at equilibrium in acetic acid–0.56 M H_2O–0.10 M H_2SO_4 (h_0 = 13) should be *less* than 6 × 10^{-12}. Given the k_S values for the various butyl sulfide catalyzed solvolyses in this medium, this would require that the rate constant (k_4) for reaction 4 be in each case larger than 10^{12} M^{-1} sec^{-1}, a value which is so large as to be patently impossible. For this reason this otherwise plausible mechanism involving IV can be definitely eliminated.

Sulfinyl groups are many orders of magnitude more basic than similarly situated sulfonyl groups; for example, the conjugate acid of dimethyl sulfoxide has a pK_a of around 0.0.[14] Although the sulfinyl group in a sulfinyl sulfone is undoubtedly considerably less basic than this, due to the strong electron-withdrawing inductive effect of the adjacent sulfonyl group, we have no evidence at present which would suggest that it is so weakly basic that mechanisms involving the *sulfinyl*-protonated form (V) as an intermediate can be eliminated *via* arguments of the type just used to exclude IV.[15]



$$\underset{\underset{O}{\downarrow}}{ArS}-\overset{O}{\overset{\uparrow}{\underset{\underset{O}{\downarrow}}{S}}}Ar + H^+ \rightleftharpoons \underset{\underset{HO}{|}}{Ar\overset{+}{S}}-\overset{O}{\overset{\uparrow}{\underset{\underset{O}{\downarrow}}{S}}}Ar \quad (5)$$

V

Mechanisms involving V as an intermediate are not the only possible explanation for the acid-catalyzed nature of the reaction, however. Thus the mechanism shown in eq 6, involving a proton transfer from the catalyzing acid to the departing $ArSO_2$ group which was

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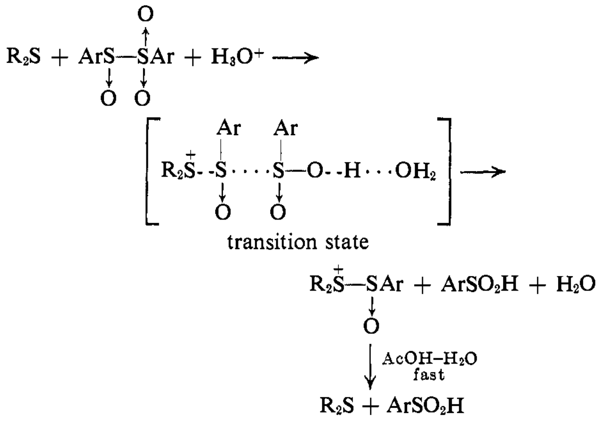
(12) S. K. Hall and E. A. Robinson, *Can. J. Chem.*, **42**, 1113 (1964).

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

(14) P. Nylen, *Z. Anorg. Allgem. Chem.*, **246**, 227 (1941).

(15) One should realize, though, that the pK_a of V is almost certainly such as to require, given k_S for the butyl sulfide catalyzed reactions, that the rate constant for a bimolecular reaction between V and the sulfide have a value of *at least* 10^5 M^{-1} sec^{-1}. In view of the very low (6.5 kcal) over-all activation energy for the butyl sulfide catalyzed reaction this is, however, not an unreasonably large rate constant for such a process.

synchronous with attack of the sulfide, would also exhibit acid catalysis. Such a mechanism can account for the observed dependence of rate on sulfide structure and for the fact that substituents in the Ar group attached to the sulfinyl sulfur have only a modest effect on the rate. It can also account for the fact that electron-withdrawing substituents in the aryl group attached to the sulfonyl sulfur accelerate the rate. Measurements of the equilibrium constant for sulfinyl sulfone formation[3] have shown that electron-withdrawing substituents in the aromatic rings destabilize the sulfinyl sulfone relative to the sulfinic acid. Since the $ArSO_2$ group of II has been in fair measure converted to $ArSO_2H$ in the transition state shown for eq 6, electron-withdrawing substituents in the Ar of $ArSO_2$ would be expected to accelerate the rate.

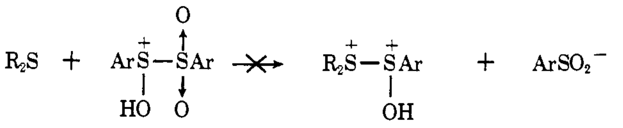


$$R_2S + Ar\underset{O}{\underset{\downarrow}{S}}\!-\!\underset{O}{\underset{\downarrow}{\overset{O}{\overset{\uparrow}{S}}}}Ar + H_3O^+ \longrightarrow \left[R_2\overset{+}{S}\text{- -}\underset{O}{\underset{\downarrow}{\overset{Ar}{S}}}\cdots\underset{O}{\underset{\downarrow}{\overset{Ar}{S}}}\!-\!O\text{- -}H\cdots OH_2\right] \longrightarrow R_2\overset{+}{S}\!-\!\underset{O}{\underset{\downarrow}{S}}Ar + ArSO_2H + H_2O \quad (6) \xrightarrow[\text{fast}]{AcOH-H_2O} R_2S + ArSO_2H$$

There are two arguments that one might advance against eq 6 as the mechanism. These are, first, that eq 6 is a general acid catalyzed reaction and should not therefore show a correlation between rate and H_0, and, second, that this type of general acid catalyzed reaction should have a larger value than 1.15 for the solvent isotope effect (k_H/k_D). In our opinion neither of these arguments can actually be used to exclude eq 6 as the mechanism. In answer to the first criticism one can point out that several cases[16,17] are known in which the rate of a general acid catalyzed reaction is correlated by H_0 in strongly acid solution. In addition, there is considerable question[17] whether a meaningful H_0 function exists in acetic acid, because of the low dielectric constant of the medium. As far as the solvent isotope effect is concerned, Kresge and Preto[18] have recently shown that in general acid catalyzed reactions of this type where hydronium ion is the catalyzing acid,[19] one can in certain circumstances even get a solvent isotope effect where (k_H/k_D) is less than unity. This occurs when the reaction is one in which the proton has been almost completely transferred to the substrate by the time the transition state is reached.[20] Thus, provided the proton is considered to be largely transferred to the $ArSO_2$ group at the transition state for eq 6, the solvent isotope effect of 1.15 is perfectly reasonable for the mechanism.

Although eq 6 represents an acceptable mechanism for the sulfide-catalyzed solvolysis of II, there are also mechanisms involving V as an intermediate which seem in equally good accord with the various experimental data. We shall now outline them briefly.

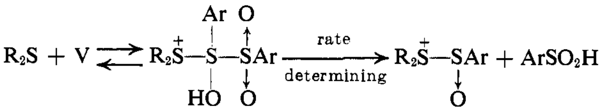
Protonation of the sulfinyl group of II should increase its reactivity toward nucleophilic attack. A direct displacement of $ArSO_2$ by R_2S is unlikely, however, because it would result in the formation of a most unattractive dipositive intermediate VI. This can be avoided if attack of the sulfide on the protonated sulfinyl group is either accompanied, or followed, by transfer of the proton to the departing $ArSO_2$ group. Thus, one could have either actual formation of a valence shell expanded intermediate of sulfur (VII) from V and R_2S, which then underwent rate-determining expulsion of $ArSO_2H$ (eq 7), or, alternatively, the transfer of the proton to the $ArSO_2$ group could be synchronous with the attack of sulfide, as in eq 8. The various experimental results can probably be accommodated about equally well by either mechanism. However, because there is as yet no clear evidence that valence shell expanded species such as VII are generally involved as intermediates in substitutions at sulfinyl sulfur, we have chosen to confine our subsequent discussion to eq 8.



$$R_2S + Ar\underset{HO}{\underset{|}{\overset{+}{S}}}\!-\!\underset{O}{\underset{\downarrow}{\overset{O}{\overset{\uparrow}{S}}}}Ar \not\longrightarrow R_2\overset{+}{S}\!-\!\underset{OH}{\underset{|}{\overset{+}{S}}}Ar + ArSO_2^-$$

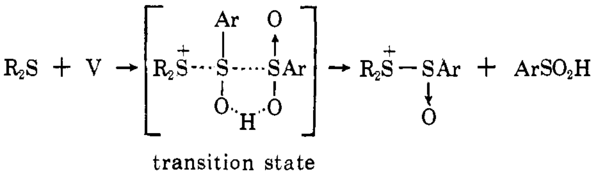
VI

(energetically unfavorable)



$$R_2S + V \rightleftarrows R_2\overset{+}{S}\!-\!\underset{HO}{\underset{|}{\overset{Ar}{\overset{|}{S}}}}\!-\!\underset{O}{\underset{\downarrow}{\overset{O}{\overset{\uparrow}{S}}}}Ar \xrightarrow[\text{determining}]{\text{rate}} R_2\overset{+}{S}\!-\!\underset{O}{\underset{\downarrow}{S}}Ar + ArSO_2H \quad (7)$$

VII



$$R_2S + V \rightarrow \left[R_2\overset{+}{S}\cdots\overset{Ar}{\overset{|}{S}}\cdots\cdots\overset{O}{\overset{\uparrow}{S}}Ar\ \ (O\cdots H\cdots O)\right] \rightarrow R_2\overset{+}{S}\!-\!\underset{O}{\underset{\downarrow}{S}}Ar + ArSO_2H \quad (8)$$

The structures of the transition states for eq 6 and 8 are enough alike that each would lead to essentially the same dependence of rate of sulfide structure and on substituents in the aromatic ring of the $ArSO_2$ group. The modest effect of substituents in the aryl group attached to the sulfinyl sulfur can also be accommodated by eq 8.[21] Since eq 8 involves reaction of the sulfide with the protonated sulfinyl sulfone, a correlation of rate with H_0 would be expected. The solvent isotope

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[16] H. G. Kuivila and K. V. Nahabedian, *J. Am. Chem. Soc.*, **83**, 2159 (1961).

[17] F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957).

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

[19] Hydronium ion would almost certainly be the important acid catalyst for the present reactions in acetic acid–0.56 *M* water solutions of low sulfuric acid content.

[20] Incidentally, Kuivila and Nahabedian[16] have suggested that a process of this type is the kind of general acid catalyzed reaction most likely to show a correlation of rate with H_0.

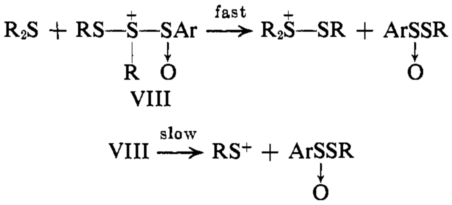
[21] The effect of substituents in the ring attached to the sulfinyl sulfur will depend on the change in the electron density at this sulfur on going from the sulfinyl sulfone to the transition state for eq 8. In particular, if in that transition state bond making between R_2S and this sulfur is slightly ahead of the breaking of the bond to the $ArSO_2$ group, the decrease in electron density at the sulfinyl sulfur on going from II to the transition state may be quite modest.

effect would be the product of that for eq 8 itself times that associated with the II–V equilibrium (eq 5). As indicated in another paper,[3] (K_H/K_D) for eq 5 would probably be something like 0.4 to 0.5. To get the observed over-all isotope effect of 1.15, (k_H/k_D) for eq 8 itself would thus have to have a value of 2.4 to 3.0. Since eq 8 involves a proton transfer, this value seems perfectly reasonable.

It therefore appears that the available experimental data can be adequately reconciled with either eq 6 or 8 being the mechanism for the sulfide-catalyzed solvolysis. However, even though we cannot make a meaningful decision between them at present, they have enough features in common that certain aspects of the mechanism of the sulfide-catalyzed solvolysis seem clearly established. Thus, the reaction obviously involves nucleophilic attack of R_2S on the sulfinyl sulfur. Second, the displacement of the $ArSO_2$ group is assisted by the transfer of a proton to it in the rate-determining step. The principal uncertainty at present is in the specific details of this proton transfer. Hopefully, future study of the reaction in other solvent media may provide information pertinent to this point.

Concomitant Electrophilic and Nucleophilic Catalysis of Sulfur–Sulfur Bond Scission. The sulfide-catalyzed solvolysis of sulfinyl sulfones in acid solution is an example of concomitant electrophilic and nucleophilic catalysis of the scission of an S–S bond. The ability of low concentrations of alkyl sulfides to accelerate the rate of acid-catalyzed solvolysis of II so significantly is undoubtedly due to the following combination of circumstances: (1) except for IId, unimolecular acid-catalyzed heterolysis of the S–S bond in II is relatively slow;[3] (2) in the absence of sulfide there are no species present which are good nucleophiles toward sulfinyl sulfur; (3) polarizable sulfur nucleophiles, like the alkyl sulfides, even though of low proton basicity, can exhibit high nucleophilic reactivity toward sulfinyl sulfur.

We have previously observed concomitant electrophilic and nucleophilic catalysis of sulfur–sulfur bond scission in two cases involving sulfenyl sulfur. In the first of these, the disulfide–sulfinic acid reaction,[4] the bimolecular scission of an S–S bond in **VIII** *via* attack of a sulfur nucleophile on the sulfenyl sulfur is much faster than unimolecular dissociation of the same ion.

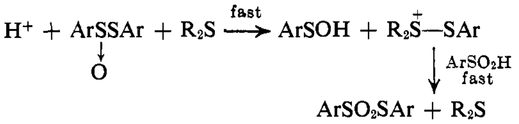


$$\mathrm{R_2S} + \mathrm{RS}-\underset{\underset{\mathrm{R}}{|}}{\overset{+}{\mathrm{S}}}-\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}\mathrm{Ar} \xrightarrow{\text{fast}} \mathrm{R_2\overset{+}{S}-SR} + \mathrm{Ar}\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}\mathrm{SR}$$

VIII

$$\mathrm{VIII} \xrightarrow{\text{slow}} \mathrm{RS^+} + \mathrm{Ar}\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}\mathrm{SR}$$

In the second, the thiolsulfinate–sulfinic acid reaction,[5] the reaction sequence



$$\begin{array}{l} \mathrm{H^+} + \mathrm{Ar}\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}\mathrm{SAr} + \mathrm{R_2S} \xrightarrow{\text{fast}} \mathrm{ArSOH} + \mathrm{R_2\overset{+}{S}-SAr} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \big\downarrow \scriptstyle{\mathrm{ArSO_2H}}\ \text{fast} \\ \qquad\qquad\qquad\qquad\qquad\qquad \mathrm{ArSO_2SAr} + \mathrm{R_2S} \end{array}$$

provides a more rapid route to thiolsulfonate $ArSO_2SAr$ than does the direct reaction of the sulfinic acid with the thiolsulfinate.

The present work shows that similar concomitant catalysis can also be important in a sulfur–sulfur bond scission involving attack at sulfinyl sulfur. It thus suggests that the phenomenon is a more general one than might previously have been suspected and is hardly restricted to reactions involving divalent sulfur.

One of the most striking features of this and the earlier examples[4,5] of this type of catalysis is the extremely small concentrations of weak sulfur nucleophiles which are able to produce quite dramatic catalytic effects. Thus in the present case in acetic acid–0.56 *M* water containing 0.2 *M* sulfuric acid, the rate of solvolysis of IIa is about 15 times faster in the presence of 2×10^{-4} *M* *n*-butyl sulfide than it is in its absence. In the thiolsulfinate–sulfinic acid reaction[5] 10^{-5} *M* butyl sulfide led to a tenfold rate acceleration under the same conditions. Among other things this suggests that in practical work in some cases the success or failure of reactions involving sulfur–sulfur bond scission in acid solution may in actual fact be dependent on the presence of small amounts of nucleophilic impurities in the reagents used. Furthermore, since making and breaking S–S bonds may also be involved in the intermediate stages of reactions in which neither the original reactants nor the final products themselves possess an S–S bond, this may be of wider importance than one might at first think. As a matter of fact, we have seen in another paper[2] that in solutions of low acidity a trace of chloride ion as an impurity can influence significantly the rate of disproportionation of *p*-toluenesulfinic acid, as a result of its catalytic influence on the rates of the forward and reverse reactions of the I–II equilibrium.

Experimental Section

Preparation and Purification of Materials. The various sulfinyl sulfones were synthesized and purified as outlined in another paper.[3] The solvents and solutions used, including deuterated materials, were those described in that same paper.[3]

The purification of all sulfides except tetrahydrothiophene has been described previously.[22] Tetrahydrothiophene (Aldrich Chemical Co.) was purified by fractional distillation.

Procedure for Kinetic Runs. The same apparatus and procedures described in two other papers[2,3] were employed. All runs were made starting with the sulfinyl sulfone and following the disappearance of its absorption maximum. Stock solutions of the sulfides in acetic acid–0.56 *M* water were made up, and an appropriate volume of the stock solution was used in making up the solution used for a particular run.

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