

were dried over magnesium sulfate and the solvent was evaporated. The residue remaining was distilled to yield 8.5 g. (85%) of 1-methylsulfinyl-2-dodecene (I), b.p. 131–137° (0.10–0.14 mm.). It was identical with the I described above as determined by infrared and n.m.r. spectra. On the basis of the relative areas at 3.5–3.9  $\tau$  (due to II) and 3.9–4.8  $\tau$  (due to I) it was determined that the product consisted of 96% I and 4% II.

**Reaction of 1-Methylsulfinyl-2-dodecene with Sodium Deuterioxide in Deuterium Oxide.**—Two-tenths grain (0.009 g.-atom) of sodium was added to 10 ml. of deuterium oxide after which 1.0 g. (0.0043 mole) of 1-methylsulfinyl-2-dodecene was added and the reaction mixture was stirred for 64 hr. at room temperature. The sulfoxide was then extracted with hexane, dried, and the hexane was evaporated to yield 0.85 g. of recovered material. An infrared spectrum was identical with that of starting material except that a new weak band had appeared at 11.6  $\mu$ . The n.m.r. spectrum of this material still had a multiplet at 4.4  $\tau$  (rel. area 1.9) which was only somewhat less complex than that of the starting material. The band at 6.65  $\tau$  in the starting material had disappeared completely. The other bands were the same as in the starting material: 7.6 and 7.9  $\tau$  (combined relative area 4.9), 8.7 and 9.1  $\tau$  (combined rel. area 17.0). The structure 1-methylsulfinyl-1,1-dideuterio-2-dodecene was therefore assigned to the product.

**Reaction of 1-Methylsulfinyl-1-dodecene with Sodium Deuterioxide in Deuterium Oxide.**—One-tenth grain (0.0045 g.-atom) of sodium was added to 5 ml. of deuterium oxide and 0.5 g. (0.0021 mole) of 1-methylsulfinyl-1-dodecene was then added. The

reaction mixture was stirred at room temperature for 66 hr. and was then worked up as described above. An n.m.r. spectrum of the isolated product indicated that 20% of the mixture had been isomerized to  $\beta,\gamma$ -unsaturated isomer (appearance of vinyl proton absorption around 4.4  $\tau$ ), while 80% of the  $\alpha,\beta$ -unsaturated material remained. The relative area of the absorption in the vinyl proton region remained at a value of 2.0, while the peaks at 7.5 and 7.8  $\tau$  still had a combined relative area of 5. The relative areas were based on the area of the terminal methyl group (9.1  $\tau$ , relative area 3.0), since the long-chain methylene protons (8.7  $\tau$ ) would vary depending upon the amount of isomerization that had occurred. Both isomers have allyl protons; hence isomerization does not affect the relative area of the band at 7.8  $\tau$ .

**Reaction of 1-Methylsulfinyl-1-dodecene with Sodium Deuterioxide in Deuterium Oxide.**—Two-tenths gram (0.009 mole) of sodium was added to 10 ml. of deuterium oxide after which 0.5 g. (0.0021 mole) of 1-methylsulfinyl-1-dodecene was added. The reaction mixture was stirred at room temperature for 2 weeks and was then worked up as described above. The recovered material weighed 0.4 g. An n.m.r. spectrum of the recovered material was very similar to the one described above, except that the absorption at 3.5–3.9  $\tau$  was only 35% of the total vinyl proton absorption while the new absorption at 4.0–4.8  $\tau$  accounted for 65%. Again, the allylic proton absorption at 7.8–8.0  $\tau$  was undiminished.

**Acknowledgment.**—We are indebted to Dr. T. J. Flautt for help with the n.m.r. spectra and to Mr. A. L. Voegele for invaluable technical assistance.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE UNIVERSITY, CORVALLIS, OREGON]

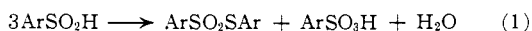
## Mechanisms of Reactions of Sulfinic Acids. VI. The Mechanism of the Disulfide–Sulfinic Acid Reaction<sup>1</sup>

BY JOHN L. KICE AND EVA H. MORKVED

RECEIVED NOVEMBER 20, 1963

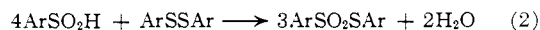
A recent paper<sup>3</sup> described a new reaction between *p*-tolyl disulfide and *p*-toluenesulfinic acid and outlined its probable mechanism. Confirmation of the important details of this mechanism and a significant extension of our understanding of the disulfide–sulfinic acid reaction have now been achieved through study of the reaction of a wide variety of disulfides with *p*-toluenesulfinic acid. For all alkyl disulfides the principal reaction product is the alkyl *p*-toluenethiolsulfonate, accompanied by small amounts of *p*-tolyl *p*-toluenethiolsulfonate and alkyl *p*-tolyl disulfide. Because of the relative availability of the starting materials and the predominant formation of the alkyl *p*-toluenethiolsulfonate, the reaction offers a potentially practical route for the synthesis of unsymmetrical thiolsulfonates. The kinetics of the reaction vary with disulfide structure, being second order in disulfide for nucleophilic primary alkyl disulfides, such as methyl or *n*-butyl, and first plus second order for both less nucleophilic primary ones, such as benzyl, and *sec*-alkyl disulfides, such as isopropyl. This behavior results because the second-order term arises from nucleophilic attack of disulfide on ion II, and such an attack is sterically hindered in the *sec*-alkyl case and inductively disfavored in the case of less nucleophilic disulfides. The disulfide–sulfinic acid reaction can be powerfully catalyzed by suitable alkyl and aryl sulfides. Study of the dependence of such sulfide catalysis on sulfide concentration and sulfide structure shows that it results from the fact that sulfides, being in general more nucleophilic, react more readily with II than the disulfide can. Possible application of such catalysis in other reactions is discussed.

The disproportionation<sup>2</sup> of aromatic sulfinic acids (eq. 1) is a reaction that has seen use<sup>2e</sup> as a preparative



method for the corresponding thiolsulfonates  $\text{ArSO}_2\text{SAr}$ . However, it has one serious shortcoming—as a result of its oxidation to sulfonic acid, one-third of the sulfinic acid is in effect wasted. Recently Kice and Bowers<sup>3</sup> discovered that, under reaction conditions similar to those best employed for its disproportionation, *p*-

toluenesulfinic acid ( $\text{Ar} = p\text{-CH}_3\text{C}_6\text{H}_4$ ) also reacts readily with *p*-tolyl disulfide to give the same thiolsulfonate (eq. 2), but with a reaction stoichiometry that



does not lead to any waste of sulfinic acid. By suitable adjustment of conditions, this latter reaction can be made to predominate over the normal disproportionation.

In moist acetic acid as solvent this disulfide–sulfinic acid reaction was found to be strongly acid catalyzed, strongly retarded by added water, and first order in sulfinic acid. To explain the fact that at the same time it exhibited a first plus second-order dependence on disulfide concentration, the mechanism shown in Chart I was suggested.<sup>3</sup> In it the second-order term in disulfide results from that compound functioning as a

(1) This research supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AFOSR-106-63.

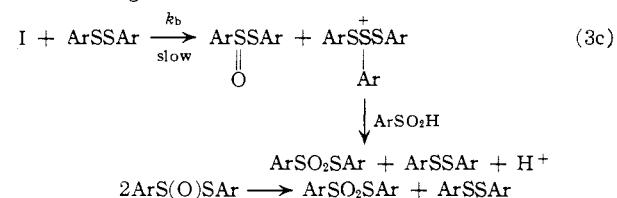
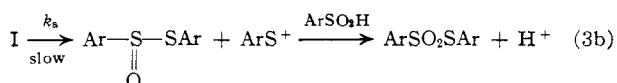
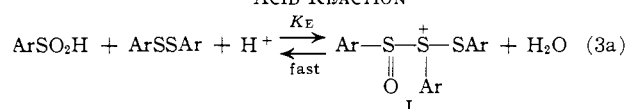
(2) (a) C. Pauly and R. Otto, *Ber.*, **10**, 2182 (1877); (b) J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 605 (1962); (c) H. Bredereck, A. Wagner, E. H. Beck, H. Berlinger, and K. G. Kottenhahn, *Angew. Chem.*, **70**, 268 (1958); (d) P. Allen and L. Reich, *J. Phys. Chem.*, **64**, 1928 (1960); (e) C. M. Bere and S. Smiles, *J. Chem. Soc.*, **125**, 2359 (1924); (f) J. von Braun and K. Weissbach, *Ber.*, **63**, 2837 (1930).

(3) J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 2384 (1962).

nucleophile to promote the breakdown of the intermediate ion I (eq. 3c). Important support for this hypothesis was provided by the observation that the disulfide-sulfinic acid reaction could be catalyzed by phenyl sulfide,<sup>3</sup> a compound which should be a more reactive nucleophile than the disulfide in a reaction such as eq. 3c.

However, although all the experimental evidence obtained in the previous study<sup>3</sup> was in accord with the picture outlined in Chart I, the limited extent of the data hardly constituted a very rigorous test of the correctness of the mechanism. The new results presented here, which consist of an examination of the behavior

CHART I  
MECHANISM OF THE *p*-TOLYL DISULFIDE-*p*-TOLUENESULFINIC ACID REACTION



of a variety of alkyl and aryl disulfides as regards the products and kinetics of their reaction with *p*-toluenesulfinic acid and a systematic study of the phenomenon of sulfide catalysis of the disulfide-sulfinic acid reaction, afford such a test. In addition to establishing the essential correctness of the mechanism outlined in Chart I, these studies have revealed several additional facets of the disulfide-sulfinic acid reaction which are of interest in connection with the general subject of nucleophilic displacements at divalent sulfur. As a bonus, it also appears that in a number of cases the disulfide-sulfinic acid reaction offers a potentially practical synthetic route to unsymmetrical thiolsulfonates.

## Results

**Products of the Reaction of Alkyl Disulfides with *p*-Toluenesulfinic Acid.**—From Chart I one would expect that substitution of an alkyl disulfide (RSSR) for *p*-tolyl disulfide in the reaction with *p*-toluenesulfinic acid should lead to the formation of the alkyl *p*-toluenethiolsulfonate together with some alkyl *p*-tolyl disulfide. A quantitative study of the products formed in such situations was carried out using four different alkyl disulfides—methyl, benzyl, *n*-butyl, and isopropyl. The results are shown in Table I. As expected, the principal product in each case is the alkyl *p*-toluenethiolsulfonate, accompanied by one-third to one-fifth as much alkyl *p*-tolyl disulfide. At first glance, the appearance of some *p*-tolyl *p*-toluenethiolsulfonate may seem surprising. However, when one recalls that unsymmetrical thiolsulfonates have been observed<sup>4</sup> to disproportionate according to both reaction schemes below, the formation of some of the symmetrical thiolsulfonate is understandable. Further consideration of

$$\text{ArSO}_2\text{SAr} + \text{RSSR} \leftarrow 2\text{ArS(O)SR} \rightarrow \text{ArSO}_2\text{SR} + \text{ArSSR}$$

(4) D. Barnard, *J. Chem. Soc.*, 4675 (1957).

the observed stoichiometry, especially in the light of some unpublished observations on the chemistry of thiolsulfonates, will be deferred to the Discussion.

TABLE I

PRODUCTS OF THE REACTION OF ALKYL DISULFIDES WITH *p*-TOLUENESULFINIC ACID

All reactions were carried out at 70° in acetic acid-0.56 *M* water containing the amount of sulfuric acid indicated. The initial sulfinic acid concentration was 0.10 *M* for the experiments with methyl and *n*-butyl disulfides and 0.05 *M* in the other cases

Disulfide, R = <i>M</i>	(H <sub>2</sub> SO <sub>4</sub> ), <i>M</i>	Reacn. time, hr.	Products, mole/mole ArSO <sub>2</sub> H		
			ArSO <sub>2</sub> SR	ArSSR	ArSO <sub>2</sub> SAr
Methyl, 0.15	0.20	0.67	0.56 <sup>a</sup>		0.02
<i>n</i> -Butyl, 0.15	.40	0.75	.58	0.17 <sup>b</sup>	.073
Benzyl, 0.15	.60	2.5	.56	.17 <sup>b</sup>	.086
Isopropyl, 0.15	.60	3.5	.50	.09	.115

<sup>a</sup> Not determined. <sup>b</sup> Moles of alkyl disulfide consumed/mole of sulfinic acid reacting, as estimated from amount of alkyl disulfide recovered unreacted: *n*-butyl, 0.43; benzyl, 0.50.

Under more extreme conditions exchange of the RS group in ArSO<sub>2</sub>SR with the R'S group of the disulfide R'SSR' has been observed.<sup>5</sup> It was therefore important to demonstrate that such an exchange did not occur at an appreciable rate under the reaction conditions used for the experiments in Table I. To this end samples of *p*-tolyl *p*-toluenethiolsulfonate (0.03 *M*) were heated with samples of the three primary alkyl disulfides (0.15 *M*) under the same conditions and for the same length of time as in the reaction of the particular disulfide with *p*-toluenesulfinic acid. The thiolsulfonate was then recovered quantitatively and analyzed. With both methyl and benzyl disulfides less than 5% of the starting thiolsulfonate was found to have been converted to ArSO<sub>2</sub>SR. With *n*-butyl disulfide, there was, for some unknown reason, apparently somewhat more exchange, 20% of the original *p*-tolyl *p*-toluenethiolsulfonate being converted to the butyl ester. However, in all three cases the amount of exchange is low enough that we can say confidently that no significant portion of the alkyl *p*-toluenethiolsulfonate isolated in the disulfide-sulfinic acid reactions of Table I arises from initial formation of *p*-tolyl *p*-toluenethiolsulfonate followed by its subsequent exchange reaction with the alkyl disulfide.

Thiolsulfonates may be separated from disulfides by very rudimentary chromatographic procedures. This, the ready availability of many disulfides, and the high ratio of alkyl to *p*-tolyl thiolsulfonates produced in the reactions in Table I, all suggest that the disulfide-sulfinic acid reaction has considerable potential as a simple synthetic route to unsymmetrical thiolsulfonates.

**Kinetics of the Reaction of Alkyl Disulfides with *p*-Toluenesulfinic Acid.**—The kinetics are most conveniently studied with the disulfide always present in sufficient stoichiometric excess that its concentration remains effectively constant during the course of a run. Under such conditions the disappearance of the sulfinic acid follows good first-order kinetics. From the slope of a plot of log (ArSO<sub>2</sub>H) vs. time one can calculate *k*<sub>1</sub>, the pseudo-first-order rate constant for the disulfide-sulfinic acid reaction.<sup>6</sup> The kinetic dependence on

(5) N. I. Grishko and E. N. Gur'yanova, *J. Gen. Chem. USSR*, **29**, 878 (1959).

(6) To calculate *k*<sub>1</sub> one corrects the experimental first-order rate constant for the small contribution to the over-all rate of disappearance of sulfinic acid due to the normal disproportionation (eq. 1). The procedures for doing this have been outlined in an earlier paper.<sup>3</sup>

TABLE II

DEPENDENCE OF RATE ON DISULFIDE CONCENTRATION FOR THE REACTION OF ALKYL DISULFIDES WITH *p*-TOLUENESULFINIC ACID

All runs at 70° in acetic acid–0.56 *M* water as solvent; initial sulfonic acid concentration, 0.05 *M* unless otherwise noted

Disulfide	(H <sub>2</sub> SO <sub>4</sub> ), <i>M</i>	(RSSR), <i>M</i>	<i>k</i> <sub>1</sub> × 10 <sup>4</sup> , sec. <sup>-1</sup>	$\left[\frac{k_1 \times 10^2}{(\text{RSSR})}\right]$	$\left[\frac{k_1 \times 10^2}{(\text{RSSR})^2}\right]$
MeSSMe	0.20	0.20	20.8	10.4	5.2
		.15	11.7	7.8	5.2
		.10	5.2	5.2	5.2
		.051 <sup>a</sup>	1.46	2.86	5.6
EtSSEt	0.20	.20	5.27	2.64	1.32
		.15	3.15	2.10	1.40
		.10	1.45	1.45	1.45
<i>n</i> -BuS <sub>2</sub>	0.26	.20	9.8	4.9	2.45
		.15	5.60	3.74	2.50
		.10	2.55	2.55	2.55
		.05 <sup>a</sup>	0.75	1.50	3.00
(PhCH <sub>2</sub> S) <sub>2</sub>	0.40	.20	2.20	1.10	0.55
		.15	1.39	0.93	.62
		.10	0.68	.68	.68
<i>i</i> -PrS <sub>2</sub>	0.40	.20	1.15	.58	.29
		.15	0.76	.51	.34
		.10	0.38	.38	.38
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SSBu- <i>n</i>	0.30	.15	5.61	3.74	2.50
		.12	3.60	3.00	2.50
		.10	2.55	2.55	2.55
		.05 <sup>a</sup>	0.79	1.58	3.16

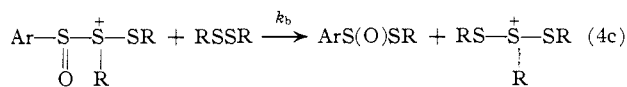
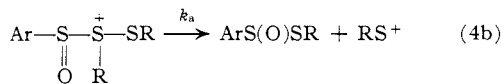
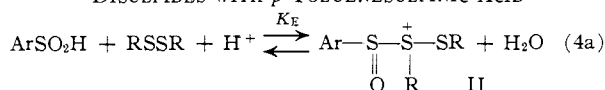
<sup>a</sup> Initial sulfonic acid concentration, 0.03 *M*.

disulfide may then be ascertained from the variation of *k*<sub>1</sub> with disulfide concentration in a series of runs at different initial disulfide concentrations. Table II gives the results of such studies for a variety of alkyl disulfides.

If the basic mechanism of the alkyl disulfide reaction is the same as that for *p*-tolyl disulfide, the kinetically important reactions will be those in Chart II, and the

CHART II

KINETICALLY IMPORTANT STEPS IN THE REACTION OF ALKYL DISULFIDES WITH *p*-TOLUENESULFINIC ACID



dependence of *k*<sub>1</sub> on disulfide concentration will be given by eq. 5. For runs at fixed sulfuric acid and water concentrations a plot of *k*<sub>1</sub>/(RSSR) vs. (RSSR) should be linear with a slope equal to *k*<sub>c</sub>*K*<sub>e</sub> and an intercept equal to *k*<sub>0</sub>*K*<sub>e</sub>. The ratio of intercept to slope, *k*<sub>0</sub>/*k*<sub>c</sub>, gives the relative rate

$$k_1 = K_e(\text{RSSR})[k_0 + k_c(\text{RSSR})] \quad (5)$$

$$K_e = K_E \left[ \frac{a_{\text{H}^+} f_{\text{ArSO}_2\text{H}} f_{\text{RSSR}}}{a_{\text{H}_2\text{O}} f_{\text{II}}} \right]; k_0 = k_a(f_{\text{II}}/f_{*a}) k_c = k_b(f_{\text{II}} f_{\text{RSSR}}/f_{*b})$$

for unimolecular decomposition of intermediate ion II as compared to the rate of nucleophilic attack of disulfide on the same species. For *p*-tolyl disulfide *k*<sub>0</sub>/*k*<sub>c</sub>

was found to be about 0.075 and independent of strong acid concentration.<sup>3</sup>

For three primary alkyl disulfides in Table II—methyl, ethyl, and *n*-butyl—*k*<sub>0</sub>/*k*<sub>c</sub> is about an order of magnitude smaller than for *p*-tolyl disulfide. This is evident both from the appropriate plot of the data for *n*-butyl disulfide in Fig. 1 and from the approximate constancy of *k*<sub>1</sub>/(RSSR)<sup>2</sup> for each set of runs with a given disulfide. In other words, for these disulfides decomposition of II occurs essentially exclusively by nucleophilic attack of RSSR on II. In contrast, with the secondary disulfide isopropyl disulfide, *k*<sub>0</sub>/*k*<sub>c</sub> is 0.11, a value large enough so that at 0.1 *M* disulfide nucleophilic attack by RSSR is responsible for only half of the decomposition of II. Benzyl disulfide, a primary aralkyl disulfide, and the mixed aryl alkyl disulfide, *n*-butyl *p*-tolyl disulfide, show behavior intermediate between these two extremes, *k*<sub>0</sub>/*k*<sub>c</sub> being 0.04 and 0.03, respectively.

**Dependence of Rate on Sulfuric Acid Concentration.**—Although *k*<sub>0</sub>/*k*<sub>c</sub> is independent of sulfuric acid concentration,<sup>3</sup> this is most emphatically not the case for *k*<sub>1</sub>, and therefore for *k*<sub>0</sub>*K*<sub>e</sub> and *k*<sub>c</sub>*K*<sub>e</sub>. Because of the constancy of *k*<sub>0</sub>/*k*<sub>c</sub>, however, the dependence of *k*<sub>1</sub> on sulfuric acid concentration can be completely determined by making a series of runs at a given disulfide concentration but at varying acid concentration. Studies of this sort<sup>3</sup> in acetic acid–0.56 *M* water for the *p*-toluenesulfonic acid–*p*-tolyl disulfide reaction showed that a plot of log *k*<sub>1</sub> vs.  $-H_0$  was linear with a slope of +1.48. A change from 0.3 to 0.4 *M* H<sub>2</sub>SO<sub>4</sub> brought about exactly a twofold increase in *k*<sub>1</sub>.

Similar, although less extensive, experiments have now been carried out for the alkyl disulfide–*p*-toluene-sulfonic acid reaction. The results are shown in Table III. The log *k*<sub>1</sub> values for *n*-butyl disulfide plot linearly

TABLE III

EFFECT OF ACIDITY ON THE RATE OF THE ALKYL DISULFIDE–*p*-TOLUENESULFINIC ACID REACTION

All runs at 70° in acetic acid–0.56 *M* water as solvent; initial sulfonic acid concentration, 0.05 *M*

Disulfide	(RSSR), <i>M</i>	(H <sub>2</sub> SO <sub>4</sub> ), <i>M</i>	<i>k</i> <sub>1</sub> × 10 <sup>4</sup> , sec. <sup>-1</sup>	4 + log <i>k</i> <sub>1</sub>	$-H_0^a$
<i>n</i> -BuS <sub>2</sub>	0.15	0.20	3.07	0.487	1.58
		.26	5.60	.748	1.77
		.30	7.3	.863	1.86
		.40	15.1	1.316	2.07
(PhCH <sub>2</sub> S) <sub>2</sub>	0.15	.30	0.69	–0.162	
		.40	1.39	0.142	

<sup>a</sup> From data of D. S. Noyce and L. R. Snyder, *J. Am. Chem. Soc.*, **80**, 4324 (1958).

against  $-H_0$  with a slope of +1.45. The ratio of rates at 0.4 and 0.3 *M* acid is 2.0 for benzyl disulfide and 2.1 for *n*-butyl disulfide. When taken together with the previous data for *p*-tolyl disulfide,<sup>3</sup> these results strongly suggest that the dependence of rate on sulfuric acid concentration is the same for all the disulfide–toluene-sulfonic acid reactions. That being the case it would seem legitimate to extrapolate the *k*<sub>c</sub>*K*<sub>e</sub> value obtained by a plot such as shown in Fig. 1 for a disulfide at one acid concentration to another sulfuric acid concentration by using the relationship shown in eq. 6b.

$$k_1 = k_c K_e (\text{RSSR}) [(k_0/k_c) + (\text{RSSR})]$$

At constant (RSSR), since  $(k_0/k_c)$  is independent of  $H_0$

$$\left[ \frac{d \log k_1}{dH_0} \right] = \left[ \frac{d \log k_c K_e}{dH_0} \right] \quad (6a)$$

$$\Delta \log k_c K_e = -1.45 \Delta H_0 \quad (6b)$$

**Relative Reactivity of Alkyl Disulfides in the Disulfide-Sulfinic Acid Reaction.**—Using eq. 6b,  $k_c K_e$  values for the various disulfides have all been extrapolated to a common sulfuric acid concentration, 0.3 M. The results, which are shown in Table IV, provide a direct comparison of the reactivity of the various disulfides and illustrate the considerable effect of changes in disulfide structure on the rate of the disulfide-sulfinic acid reaction.

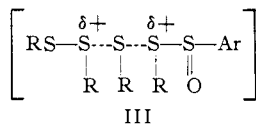
TABLE IV  
RELATIVE REACTIVITY OF DISULFIDES IN THE  
DISULFIDE-SULFINIC ACID REACTION

All data are for reaction with *p*-toluenesulfinic acid at 70° in acetic acid-0.56 M water containing 0.3 M sulfuric acid

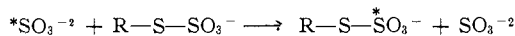
Disulfide	$k_c K_e \times 10^2$	$(k_0/k_c)$
MeSSMe	12.8	0.004
EtSSEt	3.3	.009
( <i>n</i> -BuS) <sub>2</sub>	3.2	.008
(PhCH <sub>2</sub> S) <sub>2</sub>	0.23	.04
( <i>i</i> -PrS) <sub>2</sub>	.094	.11
(HOOCCH <sub>2</sub> CH <sub>2</sub> S) <sub>2</sub> <sup>d</sup>	.02 <sup>b</sup>	..
(HOOCCH <sub>2</sub> S) <sub>2</sub>	<sup>b</sup>	..
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SSBu- <i>n</i>	2.0	0.03
( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> S) <sub>2</sub>	0.29 <sup>c</sup>	.076 <sup>c</sup>
PhSSPh <sup>d</sup>	0.030	.05

<sup>a</sup> Less accurate than other values; based on only two runs at 0.6 M sulfuric acid. <sup>b</sup> Too small to measure at 0.6 M sulfuric acid. <sup>c</sup> Data of ref. 3. <sup>d</sup> See Experimental for runs with this disulfide.

The sizable decrease in  $k_c K_e$  on going from *p*-tolyl to phenyl disulfide and the very low reactivity of dithiodiacetic and dithiodipropionic acids as compared to other alkyl disulfides both show that an increase in the electron-withdrawing character of the alkyl or aryl group attached to sulfur leads to a sharp decrease in  $k_c K_e$ . Such a finding is entirely in accord with the mechanism in Chart II, since in the transition state (III) of reaction 4c there is a full positive charge distributed over several of the disulfide sulfur atoms.



Reaction 4c is a nucleophilic displacement at a divalent sulfur, and such reactions are known to be subject to steric effects of the same sort and magnitude encountered in S<sub>N</sub>2 displacements at tetrahedral carbon. For example, Fava and Iliceto<sup>7</sup> showed that the relative rate of the reaction



varied with the structure of the alkyl group R in the fashion: Me, 100; Et, 50; *i*-Pr, 0.7; *t*-Bu, 0.0006. This is the same reactivity sequence exhibited by the equivalent series of halides, RCH<sub>2</sub>X, in S<sub>N</sub>2 substitution reactions. We believe that a steric effect of this type

(7) A. Fava and A. Iliceto, *J. Am. Chem. Soc.*, **80**, 3478 (1958); A. Fava, A. Iliceto, and F. Camera, *ibid.*, **79**, 833 (1957).

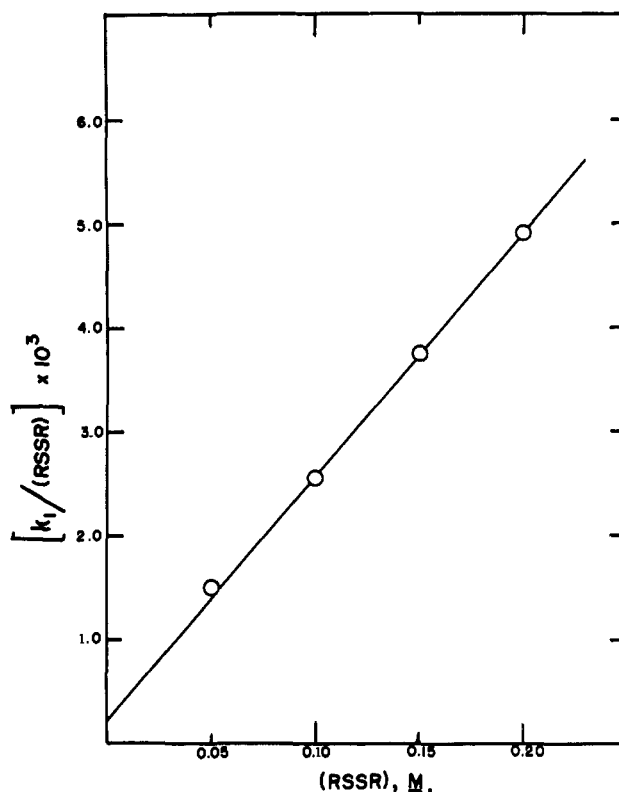


Fig. 1.—Data for *n*-butyl disulfide from Table II plotted according to eq. 5; slope equals  $k_c K_e$ ; intercept,  $k_c K_e$ .

is primarily responsible for the fact that among the series of simple alkyl disulfides—methyl, ethyl, *n*-butyl, and isopropyl—the isopropyl compound shows a value of  $k_c K_e$  one-thirty fifth as large, and the methyl compound a value four times larger, than  $k_c K_e$  for either ethyl or *n*-butyl disulfides. We shall consider additional implications of the data in Table IV in the Discussion.

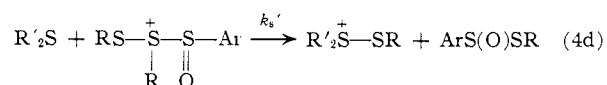
**Sulfide Catalysis of the Disulfide-Sulfinic Acid Reaction.**—In the study of the *p*-tolyl disulfide-*p*-toluenesulfinic acid reaction<sup>8</sup> it was found that the addition of phenyl sulfide led to a pronounced acceleration of the reaction rate, even though in the absence of disulfide this sulfide has no influence on the rate of disappearance of *p*-toluenesulfinic acid. The explanation given for this behavior was that the sulfide, being a better nucleophile than *p*-tolyl disulfide, reacts more rapidly with ion I than does the disulfide and therefore leads to more rapid consumption of this intermediate. In other words, in the presence of added sulfide, reaction 4d ( $R' = \text{Ph}$ ,  $R = \text{Ar}$ ) becomes kinetically important, and  $k_1$  is given by eq. 7, with  $k_s > k_c$ .

$$k_1 = K_e(\text{ArSSAr})[k_0 + k_c(\text{ArSSAr}) + k_s(\text{Ph}_2\text{S})] \quad (7)$$

This hypothesis has several necessary corollaries, none of which were tested in the previous investigation. These are: (1) the phenomenon of sulfide catalysis should be a general one for disulfide-sulfinic acid reactions; (2) for a given disulfide, the efficacy of various sulfides as catalysts should be proportional to their nucleophilicity; (3) the rate of the sulfide-catalyzed reaction should be proportional to the concentration of added sulfide. The experiments to be discussed below have now verified each of these corollaries.

The general reaction for sulfide catalysis of a disulfide-sulfinic acid reaction is shown in eq. 4d. Inclusion

of this additional reaction in the mechanism of Chart II



leads to the following expression for  $k_1$

$$k_1 = k_0K_e(RSSR) + k_cK_e(RSSR)^2 + k_sK_e(RSSR)(R'_2S) \quad (8)$$

with

$$k_s = k_s'(f_{R_2S}/f_{*s})$$

Since the first two terms in eq. 8 are just the rate of the particular disulfide-sulfonic acid reaction in the absence of added sulfide, the contribution of the sulfide-catalyzed reaction to the over-all rate should be given by

$$k_sK_e(RSSR)(R'_2S) = k_1 - K_e(RSSR)[k_0 + k_c(RSSR)] = k_1 - k_1^0 \quad (9a)$$

with  $k_1^0 = k_1$  at  $(R'_2S)$  0.00  $M$ .

**Dependence of Sulfide Catalysis on Sulfide Concentration.**—Equation 9a may also be written in the form

$$k_sK_e = (k_1 - k_1^0)/(RSSR)(R'_2S) \quad (9b)$$

Thus, for a particular disulfide-sulfonic acid reaction a series of runs at a fixed strong acid concentration, but with varying concentrations of a given added sulfide, should all give the same value of  $(k_1 - k_1^0)/(RSSR)(R'_2S)$ . This point was investigated for three widely different systems. The results, which are shown in Table V, demonstrate clearly that the required constancy of  $(k_1 - k_1^0)/(RSSR)(R'_2S)$  with changing sulfide concentration is observed in each case.

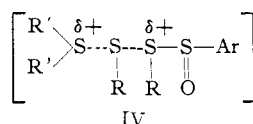
TABLE V

SULFIDE CATALYSIS OF THE DISULFIDE-SULFINIC ACID REACTION. EFFECT OF SULFIDE CONCENTRATION

All runs at 70° in acetic acid-0.56  $M$  water as solvent.  $(ArSO_2H)_0$ , 0.05  $M$

Disulfide	Sulfide	(H <sub>2</sub> SO <sub>4</sub> ), $M$	(RSR), $M$	(R' <sub>2</sub> S), $M$	$k_1 \times 10^4$ , sec. <sup>-1</sup>	$\frac{k_1 - k_1^0}{(RSSR)(R'_2S)} = k_sK_e$
PhSSPh	Ph <sub>2</sub> S	0.60	0.10	0.00	0.22	
				.05	2.24	0.040
				.10	4.21	.040
				.15	6.01	.039
(n-BuS) <sub>2</sub>	n-Bu <sub>2</sub> S	0.20	0.10	.0000	1.24	
				.0025	9.35	3.2
				.0050	17.1	3.2
MeSSMe	Ph <sub>2</sub> S	0.20	0.10	.00	5.2	
				.10	6.6	0.014
				.15	7.3	0.014

**Influence of Sulfide Structure.**—In the rate-determining step of the sulfide-catalyzed reaction (eq. 4d) the structure of the transition state will be as shown in IV. In view of the appreciable positive charge on the



sulfide sulfur in IV, a systematic increase in the electron-releasing character of the group R' in a series of sulfides R'<sub>2</sub>S should lead to an increase in their reactivity as

catalysts for a disulfide-sulfonic acid reaction. This point has been studied with the series phenyl, benzyl, and *n*-butyl sulfides for the phenyl disulfide-*p*-toluenesulfonic acid reaction, and with the first and last named sulfides for four additional disulfide-sulfonic acid reactions. The results are shown in Table VI. In agreement with the picture above, *n*-butyl sulfide is in all five systems markedly more reactive than the phenyl compound, and in the one case where its behavior was investigated, benzyl sulfide shows, as expected, a reactivity intermediate between the other two.

TABLE VI

SULFIDE CATALYSIS OF THE DISULFIDE-SULFINIC ACID REACTION. EFFECT OF SULFIDE STRUCTURE

All runs at 70° in acetic acid-0.56  $M$  water as solvent;  $(ArSO_2H)_0$ , 0.05  $M$

Disulfide	Sulfide	(H <sub>2</sub> SO <sub>4</sub> ), $M$	(RSSR), $M$	(R' <sub>2</sub> S), $M$	$k_1 \times 10^4$ , sec. <sup>-1</sup>	$k_sK_e$					
PhSSPh	Ph <sub>2</sub> S	0.60	a	a	a	0.040					
						(PhCH <sub>2</sub> ) <sub>2</sub> S	.60	0.10	0.005	4.11	0.78
						<i>n</i> -Bu <sub>2</sub> S	.60	0.10	0.005	9.19	1.8
(n-BuS) <sub>2</sub>	<i>n</i> -Bu <sub>2</sub> S	.20	a	a	a	3.2					
						Ph <sub>2</sub> S	.20	0.10	0.10	2.49	0.013
(i-PrS) <sub>2</sub>	None	.40	.10	.10	.00	0.38					
						Ph <sub>2</sub> S	.40	.10	.10	0.8	0.004
						<i>n</i> -Bu <sub>2</sub> S	.40	.10	.005	4.26	0.78
MeSSMe	Ph <sub>2</sub> S	.20	a	a	a	0.014					
						<i>n</i> -Bu <sub>2</sub> S	.20	0.10	0.0025	29.6	9.8
(PhCH <sub>2</sub> S) <sub>2</sub>	None	.40	.10	.00	.00	0.68					
						Ph <sub>2</sub> S	.40	.10	.10	1.60	0.0092
						<i>n</i> -Bu <sub>2</sub> S	.40	.10	.005	13.3	2.5

<sup>a</sup> See Table V for experimental data from which  $k_sK_e$  was calculated.

**Dependence of Sulfide Catalysis on Acid Concentration.**—Previous experiments with phenyl sulfide catalysis of the *p*-tolyl disulfide-*p*-toluenesulfonic acid reaction indicated that  $k_sK_e$  showed almost the same dependence on sulfuric acid concentration as  $k_cK_e$  for the disulfide. Additional experiments with some of the present systems have confirmed this view. Thus, for the system Ph<sub>2</sub>S-(*n*-BuS)<sub>2</sub>-ArSO<sub>2</sub>H the ratio ( $k_s/k_c$ ) has values 1.0 and 0.94 at 0.2 and 0.3  $M$  sulfuric acid, respectively, and for the system *n*-Bu<sub>2</sub>S-(PhCH<sub>2</sub>S)<sub>2</sub>-ArSO<sub>2</sub>H ( $k_s/k_c$ )  $\times 10^2$  is found to be 5.5 at 0.3  $M$  sulfuric acid and 5.4 at 0.4  $M$  acid. This suggests that the various  $k_sK_e$  values in Tables V and VI can all be extrapolated without great error to a common acid concentration using eq. 10. This has been done, and

$$\Delta \log k_sK_e = -1.45 \Delta H_0 \quad (10)$$

the results are shown in Table VII. Also shown is ( $k_s^{Bu}/k_s^{Ph}$ ) for the various disulfides. The accuracy of

TABLE VII

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

All data are for reactions at 70° in acetic acid-0.56  $M$  water containing 0.3  $M$  sulfuric acid

	Disulfide, RSSR, R =				
	Me	<i>n</i> -Bu	<i>i</i> -Pr	PhCH <sub>2</sub>	Ph
$k_sK_e$ for <i>n</i> -Bu <sub>2</sub> S	25	8.2	0.39	1.27	0.33
$k_sK_e \times 10^2$ for Ph <sub>2</sub> S	3.6	3.0	0.2	0.45	.73
( $k_s^{Bu}/k_s^{Ph}$ ) $\times 10^{-2}$	7.0	2.7	2.0	2.8	.45

the values of this ratio, unlike the  $k_sK_e$  values, is in no way dependent on the validity of eq. 10.

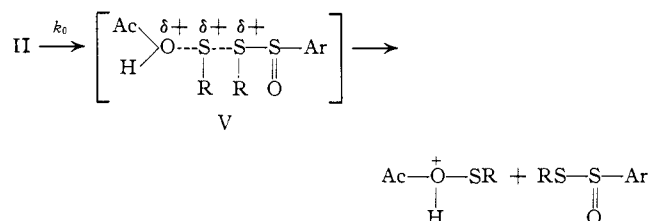
### Discussion

The first point we would emphasize is that the results of the present investigation provide strong support for

the mechanism originally suggested<sup>8</sup> for the tolyl disulfide-toluenesulfonic acid reaction (Chart I) and for its direct counterpart for the alkyl disulfide-sulfonic acid reaction (Chart II). The important central feature of these mechanisms is that they ascribe the one rather unusual aspect of the over-all kinetics—the kinetic term which is second order in disulfide—to a nucleophilic displacement by disulfide on ion II (reaction 4c). Such a hypothesis requires, as observed, that other sulfur nucleophiles be able to catalyze the disulfide-sulfonic acid reaction through related nucleophilic displacements on II (reaction 4d), and that their effectiveness in this role parallel their expected relative nucleophilicities, and be dependent on the first power of their concentration. The experiments in Tables V and VI leave no doubt either as to the generality of this type of catalysis or as to its adherence to the required dependence on structure and concentration. Such a hypothesis also requires, by analogy with other observations on nucleophilic displacements at divalent sulfur,<sup>7</sup> that for the series of alkyl disulfides—methyl, ethyl, *n*-butyl, and isopropyl—the rates of reactions 4c and 4d vary with alkyl group in the fashion: methyl > ethyl  $\cong$  *n*-butyl  $\gg$  isopropyl. Both the  $k_c K_e$  values (Table IV) and the two sets of  $k_s K_e$  values (Table VII) show this type of variation with disulfide structure. While the composite nature of these quantities does not allow us to say unequivocally that the observed effect must be due either entirely, or even principally, to reactions 4c and 4d, nonetheless, it is very reassuring to see that an effect of the expected character and magnitude is uniformly observed. Its failure to appear would have cast considerable doubt on the validity of the mechanisms of Charts I and II.

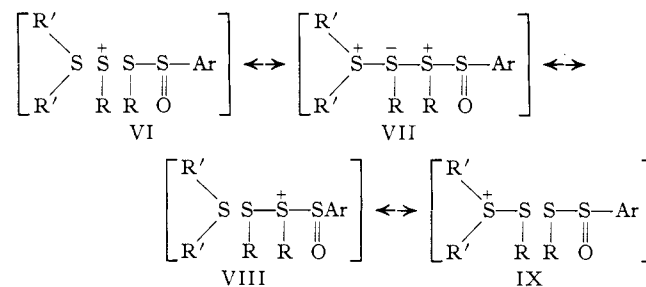
We noted earlier that the decreased reactivity of benzyl disulfide and the very low  $k_c K_e$  for dithiodipropionic acid are consistent with the predicted inductive effect of electron-withdrawing substituents on the stability of III, the transition state for reaction 4c. So too is the increased reactivity of *p*-tolyl disulfide relative to phenyl disulfide, although the magnitude of the difference, a factor of ten, is surprisingly large for a change from *p*-H to *p*-CH<sub>3</sub>. We doubt that it should be considered representative of the average sensitivity of  $k_c K_e$  for *p*-substituted phenyl disulfides to changes in  $\sigma$  for the substituent. Study of the reactivity of other aryl disulfides is planned for the future in an effort to clarify this point.

In Charts I and II the reactions responsible for the kinetic term first order in disulfide (reactions 3b and 4b) have been represented as involving dissociation of ions I and II into a sulfenium ion (RS<sup>+</sup>) and a thiol-sulfinate. However, certain features of the present results suggest that these reactions are probably more accurately pictured as solvolyses of the same ions, involving transition states such as V, and that free sulfenium ions need never be formed.



For example, unless one formulates reaction 4b in this way it is hard to explain why there is not a larger difference in the ( $k_0/k_c$ ) values for *n*-butyl and *n*-butyl *p*-tolyl disulfides, for certainly there should be a large difference in the stability of *n*-BuS<sup>+</sup> and ArS<sup>+</sup>, due to the possibility of resonance stabilization of the latter. Nucleophilic assistance by solvent of the type indicated is a well-established feature of the solvolyses of both primary alkyl and aralkyl tosylates.<sup>8</sup> Since the steric shielding of the reaction site in such compounds is equivalent to that found in the present situation, it is quite reasonable to expect a similar phenomenon to be important in reaction 4b.<sup>9</sup>

From Table VII it is evident that the relative reactivity of *n*-butyl and phenyl sulfides as catalysts varies with the disulfide, ( $k_s^{\text{Bu}}/k_s^{\text{Ph}}$ ) being 700 for methyl disulfide, about 250 for *n*-butyl, benzyl, and isopropyl disulfides, and only 45 for phenyl disulfide. Since the ratio has roughly similar values for isopropyl, *n*-butyl, and benzyl disulfides, the variation in ( $k_s^{\text{Bu}}/k_s^{\text{Ph}}$ ) would not seem to be the result of any steric effect arising from differences in the space requirements of the butyl and phenyl groups; otherwise the isopropyl disulfide results would be abnormal. Tentatively we therefore suggest that the variations in ( $k_s^{\text{Bu}}/k_s^{\text{Ph}}$ ) result mainly from the fact that the amount of positive charge on the sulfide sulfur in the transition state of reaction 4d (IV) varies with the disulfide involved. This could come about if the relative importance of certain resonance contributors to the transition state, VI and VII, were to vary with disulfide structure. In particular, if VI is considerably



more important for the aryl disulfide than for the other disulfides (for the same reasons that an analogous structure is considered to be a more important contributor in the S<sub>N</sub>2 displacement reactions of benzyl halides than it is in the same displacements of *n*-alkyl halides), and if VII plays a somewhat more important role when R equals methyl than in the other cases, one would get a variation of ( $k_s^{\text{Bu}}/k_s^{\text{Ph}}$ ) with disulfide structure of the type observed. Naturally, until much more data are available, this explanation must be considered extremely tentative. One further point is of interest. On the average ( $k_s^{\text{Bu}}/k_s^{\text{Ph}}$ ) has a value of about 250. This is considerably larger than the ratio of 50 observed<sup>11</sup> for the rates of oxidation of the two sulfides by acidic

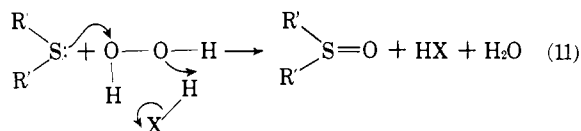
(8) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956).

(9) To those who might argue that the specific involvement of a solvent molecule in the transition state of (4b) should cause  $k_0 K_e$  to exhibit a different dependence on acidity than  $k_c K_e$  and therefore cause ( $k_0/k_c$ ) to be acid dependent (contrary to what is observed), we would note that there are plenty of examples<sup>10</sup> where the involvement of a solvent molecule as a nucleophile in the transition state of the rate-determining step does not lead to a dependence of rate on acidity which is notably different from that which would be expected in its absence.

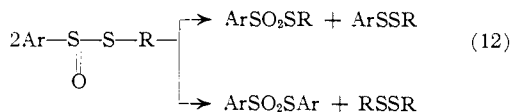
(10) See J. F. Bunnett, *J. Am. Chem. Soc.*, **83**, 4956, 4968, 4978 (1961).

(11) G. Modena and L. Maioli, *Gazz. chim. ital.*, **87**, 1306 (1957).

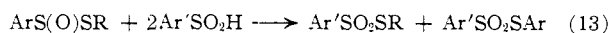
hydrogen peroxide solutions (eq. 11) and illustrates that reaction 4d is indeed markedly sensitive to the nucleophilicity of  $R'S$ .



All three of the kinetically important routes for the disappearance of ion II (reactions 4b,c, and d) produce the thiosulfinate  $\text{ArS(O)SR}$  as one of the products. Since thiosulfinate are known<sup>4</sup> to disproportionate in the manner outlined in eq. 12, and since these reactions are consistent with the final products isolated in the di-



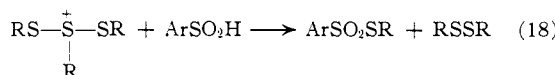
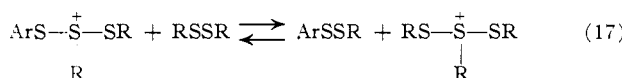
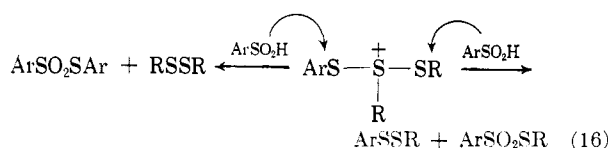
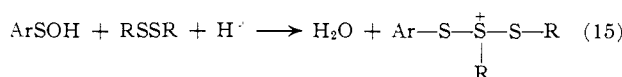
sulfide-sulfenic acid reaction, we have previously assumed that this was the path by which the thiosulfinate produced in the course of the reaction was consumed. However, recent work in this laboratory<sup>12</sup> has shown that in the acetic acid-water-sulfuric acid medium used for the disulfide-sulfenic acid reactions thiosulfinate undergo a direct acid-catalyzed reaction with sulfenic acids which is considerably faster than their disproportionation. The usual stoichiometry of this reaction is shown in eq. 13. At first sight this might seem to make it difficult to account for the formation of unsymmetri-



cal disulfides as one of the products of the alkyl disulfide-sulfenic acid reaction. However, our studies<sup>12</sup> also indicate that the first stage of the thiosulfinate-sulfenic acid reaction involves the formation of a molecule of the sulfenic acid (eq. 14), which under ordinary circumstances then reacts with an additional molecule



of sulfenic acid, giving  $\text{Ar}'\text{SO}_2\text{SAr}$ . We suggest that in the presence of the disulfide the sulfenic acid is intercepted by that reagent (eq. 15), and that this event is then followed by the various reactions shown in eq. 16-18.



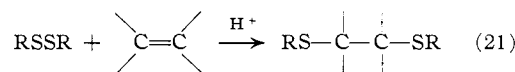
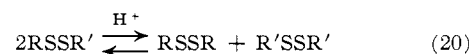
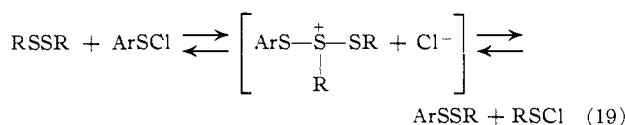
Consideration of the general relationship of the disulfide-sulfenic acid reaction to other reactions of disulfides is very informative and revealing. The two

(12) C. G. Venier, unpublished results.

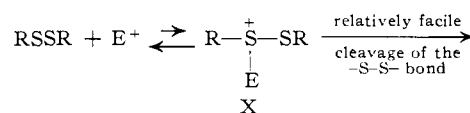
essential features of the disulfide-sulfenic acid reaction are: (1) conversion of a poor leaving group ( $\text{RS}^-$ ) in the normal disulfide to a very good leaving group ( $\text{ArS}^+$ ) through electrophilic addition of  $\text{ArSO}^+$  to one of the sulfur atoms of the disulfide; (2) nucleophilic displacement of  $\text{ArS(O)}^+\text{S}^-$  by either disulfide (reaction

4c) or an added alkyl or aryl sulfide (reaction 4d).

The first of these two features is an example of electrophilic catalysis of the cleavage of an S-S bond. This general phenomenon has been observed before in at least several cases, notably, the exchange of groups between disulfides and sulfonyl chlorides<sup>13</sup> (eq. 19), the disulfide exchange reaction which occurs in concentrated hydrochloric or sulfuric acids<sup>14</sup> (eq. 20) and the acid-catalyzed reaction of olefins with alkyl disulfides<sup>15</sup> (eq. 21). In these three reactions the catalyzing elec-



trophile is thought to be  $\text{ArS}^+$ ,  $\text{H}^+$ , and  $-\text{C}^+$ , respectively. In the disulfide-sulfenic acid reaction it is  $\text{ArSO}^+$ . Since  $\text{ArSO}^+$ ,  $\text{ArS}^+$ , a carbonium ion, and a proton hardly exhaust the list of electrophilic fragments which one can conceive might be able to activate the S-S bond in the general manner shown below, and since, as in the case of  $\text{ArSO}^+$ , such activation can have



as its end result entirely new reactions of disulfides, more extensive future investigation of this type of process seems indicated.

Although electrophilic catalysis of the cleavage of S-S bonds has been recognized in the past, it has usually been thought<sup>14</sup> that the actual decomposition of X was a unimolecular dissociation into  $\text{R}-\text{S}-\text{E}$  and  $\text{RS}^+$ . The present results show most emphatically that this need not be the case, and that, in fact, nucleophilic attack on X by either disulfide or other sulfur nucleophiles can easily be much more important than any unimolecular reaction as the principal path for the disappearance of X. It would be most surprising if such a situation did not generally obtain under suitable conditions for ions of type X.

With this in mind, the phenomenon of sulfide catalysis observed in the disulfide-sulfenic acid reactions takes on considerable potential practical importance. Just

(13) C. G. Moore and M. Porter, *J. Chem. Soc.*, 2890 (1958).

(14) A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 583 (1959).

(15) A. P. Lien, D. A. McCaulay, and W. A. Proell, *General Papers, Division of Petroleum Chemistry, American Chemical Society, No. 28, 1952, p. 159; see p. 590 of ref. 14.*

as we have seen that the rate of a disulfide-sulfenic acid reaction can be dramatically accelerated by the addition of a small amount of a sulfide which is a better nucleophile than the disulfide, and therefore will attack ion II more rapidly, so we might expect that other reactions involving ions of type X could be similarly accelerated. The possible utility of such catalysis is obvious. The use of other nucleophiles besides sulfides as catalysts also is suggested.

### Experimental

**Materials.**—*p*-Toluenesulfenic acid was prepared and purified using previously outlined procedures.<sup>2b</sup> Commercial samples of the following disulfides were purified by careful fractional distillation: methyl disulfide, ethyl disulfide, *n*-butyl disulfide. Isopropyl disulfide was first fractionally distilled, and then was subjected to preparative scale g.l.c. to free it of a small amount of an impurity not removed by fractional distillation. Benzyl and phenyl disulfide were purified by recrystallization as was also true for dithiodiacetic acid and dithiodipropionic acid. *n*-Butyl *p*-tolyl disulfide was prepared and purified by the procedure of Kice and Morkved.<sup>16</sup> The purification of *n*-butyl, benzyl, and phenyl sulfides has been described earlier.<sup>16</sup>

The purification of acetic acid and the preparation of both solutions of acetic acid-0.56 *M* water and stock solutions of sulfuric acid in acetic acid-0.56 *M* water followed previously published procedures.<sup>16</sup>

**Products of the Reaction of *p*-Toluenesulfenic Acid with Alkyl Disulfides.**—A solution of *p*-toluenesulfenic acid and the alkyl disulfide in acetic acid-water-sulfuric acid at the concentrations indicated in Table I was deaerated at room temperature and then heated at 70° for the length of time shown in the table. It was then poured into approximately ten times its volume of water, and the mixture was extracted several times with ether. The combined ether extracts were washed with aqueous 5% sodium bicarbonate until neutral, then with water, and finally were dried over anhydrous sodium sulfate. The ether was removed by careful fractional distillation. The residue was then easily separated by chromatography on acid-washed alumina into two fractions: the first consisting of the excess alkyl disulfide and any alkyl *p*-tolyl disulfide formed in the reaction; the second a mixture of the alkyl and *p*-tolyl *p*-toluenethiolsulfonates.

For all reactions except the one with methyl disulfide the composition of these fractions could be determined by comparing areas of selected n.m.r. peaks. Specifically, for a mixture of benzyl and *p*-tolyl *p*-toluenethiolsulfonates the relative amounts of the two esters may be determined by comparing the area of the CH<sub>2</sub>S singlet at 5.76  $\tau$  with the combined areas of the methyl group absorptions of the *p*-tolyl and *p*-toluenesulfonyl groups. The latter occur as two closely spaced singlets at 7.62 and 7.58  $\tau$ . Similarly, for a mixture of benzyl and benzyl *p*-tolyl disulfides, the relative intensity of the benzyl disulfide CH<sub>2</sub>S singlet at 6.52  $\tau$  and the tolyl methyl at 7.68  $\tau$  provides a satisfactory analytical method. In this connection it is worth pointing out that in benzyl *p*-tolyl disulfide the CH<sub>2</sub>S singlet occurs at slightly lower field (6.17  $\tau$ ) than in benzyl disulfide. For mixtures of isopropyl and *p*-tolyl *p*-toluenethiolsulfonates, the relative areas of the doublet centered at 8.72  $\tau$ , due to the isopropyl methyls, and the previously mentioned peaks due to the *p*-tolyl and *p*-toluenesulfonyl methyls were compared. Mixtures of isopropyl and isopropyl *p*-tolyl disulfide were also analyzed by comparing the areas of the isopropyl methyl doublet and the *p*-tolyl methyl singlet. The procedures for analyzing mixtures of *n*-butyl and *p*-tolyl *p*-toluenethiolsulfonate and mixtures of *n*-butyl *p*-tolyl and *n*-butyl disulfide have been given in an earlier publication.<sup>16</sup>

With the methyl compounds the various CH<sub>2</sub>S singlets all occur at virtually the same  $\tau$ -values as the tolyl methyls, and the n.m.r. method cannot be used. However, by careful chromatography on alumina the thiolsulfonate mixture can be cleanly separated into the two components—methyl *p*-toluenethiolsulfonate,<sup>17</sup> m.p. 58°, and *p*-tolyl *p*-toluenethiolsulfonate,<sup>2b</sup> m.p. 76°. The amount of each ester was determined simply by weighing the appropriate fractions.

For comparison purposes it was necessary to have authentic samples of the various thiolsulfonates and disulfides referred to above. *n*-Butyl,<sup>16</sup> methyl,<sup>17</sup> *p*-tolyl,<sup>2b</sup> and benzyl<sup>18</sup> *p*-toluenethiolsulfonates have already been prepared. So has *n*-butyl *p*-tolyl disulfide.<sup>16</sup> The remaining compounds were synthesized as described below.

**Isopropyl *p*-Tolyl Disulfide.**<sup>19</sup>—Isopropyl mercaptan (6.8 g., 90 mmoles), dissolved in an equal volume of acetic acid, was rapidly added to a well-stirred solution of 4.67 g. (30 mmoles) of *p*-toluenesulfenic acid in 300 ml. of acetic acid-0.56 *M* water-0.6 *M* sulfuric acid at 60°. After 3 min. the solution was poured into water, the water-insoluble products extracted with ether, and the ether solution was washed with aqueous bicarbonate until neutral. After drying over sodium sulfate, the ether was removed, and the residue was fractionally distilled. There were two main fractions. The first, 3.5 g., b.p. 23° (0.6 mm.), was shown to be isopropyl disulfide. The second fraction, 4.1 g., b.p. 93-94° (0.1 mm.), was isopropyl *p*-tolyl disulfide, *n*<sup>25D</sup> 1.5738. Its infrared and n.m.r. spectra were consistent with the assigned structure.

*Anal.* Calcd. for C<sub>10</sub>H<sub>14</sub>S<sub>2</sub>: C, 60.50; H, 7.12; mol. wt., 198. Found: C, 60.60; H, 7.12; mol. wt. (osmometric in CHCl<sub>3</sub>), 195.

**Benzyl *p*-Tolyl Disulfide.**—Benzyl mercaptan was treated with *p*-toluenesulfenic acid using exactly the procedure described above, but at 70°. After a similar work-up, the residue on removal of the ether was separated by fractional crystallization from alcohol into two main fractions. The first of these, m.p. 72°, was benzyl disulfide. The second, obtained in 30% yield, m.p. 34-35°, had infrared and n.m.r. spectra consistent with those expected for benzyl *p*-tolyl disulfide.

*Anal.* Calcd. for C<sub>14</sub>H<sub>14</sub>S<sub>2</sub>: C, 68.24; H, 5.72; mol. wt., 246. Found: C, 68.68; H, 5.77; mol. wt. (osmometric in CHCl<sub>3</sub>), 248.

**Isopropyl *p*-Toluenethiolsulfonate.**—The thiolsulfonate fraction from the isopropyl disulfide-*p*-toluenesulfenic acid reaction in Table I was subjected to molecular distillation in a small Hickman still (bath temp. 90°, pressure 10<sup>-4</sup> mm.). The infrared and n.m.r. spectra of the distillate were in accord with those expected for isopropyl *p*-toluenethiolsulfonate.

*Anal.* Calcd. for C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>S<sub>2</sub>: C, 52.14; H, 6.13. Found: C, 52.10; H, 6.17.

**Procedure for Kinetic Runs.**—Except for the runs using alkyl sulfides as catalysts, the procedure in each case was as follows: samples of disulfide and sulfenic acid were weighed out separately, dissolved in acetic acid-0.56 *M* water, and mixed together in a volumetric flask. The proper amount of a stock solution of sulfuric acid in acetic acid-0.56 *M* water was then added, and the solution was quickly made up to volume with additional acetic acid-0.56 *M* water. The solution was then placed in a reaction vessel of the type previously described,<sup>2b</sup> and from this point on the same procedure<sup>2b</sup> used in earlier kinetic studies of sulfenic acid disproportionation was followed.

For the runs with alkyl sulfides as catalysts the reaction vessel used for the kinetic runs was modified in such a way that a small glass bucket containing a weighed amount of the sulfide could be suspended above the solution in the flask. The solution of the disulfide and the sulfenic acid was made up, placed in the vessel, and deaerated in the usual way. Immediately before placing the reaction flask in the constant temperature bath the bucket containing the sulfide was dropped into the solution, and its contents dissolved. From here on the procedure was the same as before.

For the runs with phenyl sulfide as catalyst the sulfide was weighed out along with the disulfide and the sulfenic acid and dissolved along with them in acetic acid-water in the volumetric flask.

**Kinetic Data for Phenyl Disulfide and Dithiodipropionic Acid.**

—The individual kinetic runs with these two disulfides were not given in Table II. Because of their low reactivity the disulfide-sulfenic acid reaction only competes effectively with the normal disproportionation at high acidity, and even there at the lower disulfide concentrations the disproportionation still contributes sufficiently to the over-all rate of disappearance of sulfenic acid to cause curvature in a plot of log (ArSO<sub>2</sub>H) vs. time. Under such conditions *k*<sub>1</sub> for the disulfide-sulfenic acid reaction must be ob-

(18) J. D. Loudon and A. Livingston, *ibid.*, 896 (1935).

(19) The preparations of this and benzyl *p*-tolyl disulfide were carried out by Mr. G. Bray.

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

(17) D. T. Gibson, *J. Chem. Soc.*, 2637 (1931).



