Analogous reduction of lithium aluminum hydride gave a product identical in infrared spectrum to that cited in Table IV, footnote *j*. The n.m.r. spectrum of this sample showed all the expected signals; phenyl, methine (quartet), methyl (doublet), SCH_2 (triplet), OCH_2 (triplet) and OH. The peak assigned to OCH_2 was missing in the n.m.r. spectrum of the deuterated material.

Reduction of 4-Phenyl-3-thia-1,1-dideuteriopentanol. (a) **With Lithium Aluminum Hydride-Aluminum Chloride.**—The hydride solution was prepared from 13.34 g. (0.1 mole) of aluminum chloride in ether and 20 ml. (0.025 mole) of 1.26 *M* ethereal lithium aluminum hydride. The alcohol (5.5 g., 0.03 mole) was added in ether solution and the reaction allowed to proceed for 19 hours at reflux with stirring. The usual work-up procedure yielded an oil which was purified by chromatography in hexane solution on basic alumina and then distilled; yield 2.35 g. (74% taking into account 2.0 g. of starting material recovered by ether elution of the chromatogram), b.p. 114–116° (20 mm.), n^{20}_D 1.5370 (*cf.* Table IV for the corresponding unlabeled material).

The infrared spectrum and n.m.r. spectrum of the recovered starting material were identical with the spectra of the material put into the reaction. The n.m.r. spectrum of the product was compared with that of unlabeled α-phenethyl ethyl thioether (Table IV, footnote *s;* the same material was obtained by treating α-phenethyl β-hydroxyethyl thioether with mixed hydride in the way described above for the deuterated compound). The unlabeled material showed signals for C_6H_5, CH_3-CH (doublet), C*H* (quartet) CH_2S (quartet) and CH_2CH_3 (triplet). In the spectrum of the deuterated product, the CH_2S peak was a doublet instead of a quartet and was also diminished in intensity relative to the other peaks. The CH_3 peak of the ethyl group was nearly a singlet (with perhaps small satellites on either side) and was also diminished in intensity. This is what one would predict for a mixture of $C_6H_5CH(CH_3)SCH_2CHD_2$ (A) and $C_6H_5CH(CH_3)SCD_2CH_3$ (B); the observations are incompatible with a product which is all A. Thus rearrangement of the ethyl group has taken place during reduction. From the relative areas of the methyl (0.32) and methylene signals (0.18) of the ethyl group, the ratio of A to B was 1:1 within the limit of experimental error.

(b) **With Lithium Aluminum Deuteride-Aluminum Chloride.**—This reduction was carried out in similar fashion, except that solid $LiAlD_4$ (1.05 g.) was used instead of hydride solution. The product boiled at 106–110° (12 mm.), n^{20}_D 1.5380. The n.m.r. spectrum in this case showed only singlets for both the methylene and the methyl groups of the ethyl thioether function and the ratio of the two signal areas ($CH_3:CH_2$ = 9.00:8.75) was within limits of experimental error of that expected for a 1:1 mixture of $C_6H_5CH(CH_3)SCD_2CH_2D$ and $C_6H_5CH(CH_3)SCH_2CD_3$.

Other Hydrogenolyses. (a) ***trans*-4-*t*-Butylcyclohexyl β-hydroxyethyl sulfide** (5.6 g., 0.026 mole) was treated with mixed hydride from 6.9 g. (0.052 mole) of aluminum chloride and 15.5 ml. (0.013 mole) of 0.83 *M* lithium aluminum hydride at reflux for 6 hours. There was obtained 1.4 g. (60.5% considering 2.5 g. of starting material recovered) of *trans*-4-*t*-butylcyclohexyl ethyl sulfide, b.p. 82° (0.25 mm.), n^{20}_D 1.4893 (*cf.* Table IV).

(b) **β-Hydroxyethyl Benzyl Sulfide.**—Using 20.5 g. (0.154 mole) of aluminum chloride and 28 ml. (0.0384 mole) of 1.4 *M* lithium aluminum hydride for 6.0 g. (0.0357 mole) of benzyl β-hydroxyethyl sulfide, very little reduction occurred even after 48 hours at reflux and 24 hours at room temperature. Only 0.7 g. of benzyl ethyl sulfide, b.p. 100° (10 mm.), n^{20}_D 1.5355 (lit.[27] b.p. 98–99° (13 mm.)) was isolated by chromatography on alumina, in addition to 4.7 g. of starting material.

Acknowledgment.—Our work in the area of hydride chemistry has been aided by a grant from Merck and Co., Inc. We are indebted to J. Wilson and W. Breivogel for the preparation of 3-thio-1-propanol.

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[27] J. Büchi, M. Prost, H. Eichenberger and R. Lieberherr, *Helv. Chim. Acta*, **35**, 1527 (1952).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF OREGON STATE UNIVERSITY, CORVALLIS, ORE., AND THE UNIVERSITY OF SOUTH CAROLINA, COLUMBIA, S. C.]

Mechanisms of Reactions of Sulfinic Acids. II. The Reaction of *p*-Tolyl Disulfide with *p*-Toluenesulfinic Acid

BY JOHN L. KICE[1] AND KERRY W. BOWERS

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A new oxidation–reduction reaction involving a sulfinic acid and a disulfide is described. The reaction, studied with *p*-toluenesulfinic acid and *p*-tolyl disulfide, has the stoichiometry shown in eq. 2. In acetic acid–1% H_2O containing reasonable amounts of sulfuric acid this reaction can be made to predominate over the normal disproportionation of sulfinic acids. Kinetic study of the reaction shows it to be first-order in sulfinic acid, with the rate strongly accelerated by increasing concentration of added strong acid and strongly retarded by increasing concentration of water. These facts, the somewhat unexpected dependence of the rate on disulfide concentration (eq. 4) and the catalysis of the reaction by added diphenyl sulfide, all seem most consistent with a mechanism involving equilibrium formation of the intermediate ion (I) (eq. 8 and 9) and its rate-determining decomposition, either by eq. 10, or by nucleophilic attack of disulfide (or sulfide) on this same ion, eq. 11. The thiolsulfonate is then presumably formed by the reactions 12, 13 and 15.

In the first paper of this series[2] the disproportionation of *p*-toluenesulfinic acid (eq. 1) was studied in acetic acid containing 0.5–5.0% water and 0.0–1.3 *M* sulfuric acid. The reaction was found to be second order in sulfinic acid, markedly

$$3ArSO_2H \longrightarrow ArSO_2SAr + ArSO_3H + H_2O \quad (1)$$

$$Ar = p\text{-}CH_3C_6H_4\text{–}$$

retarded by added water, and only slightly accelerated by added strong acid. In the slower runs at 1 *M* H_2SO_4 we noticed the experimental second-order rate constant increased slightly toward the end of the run. Because of the large initial concentration of sulfuric acid and the relative insensitivity of the rate to strong acid, this was clearly not due to the small amount of sulfonic acid produced in the decomposition. Nor was it due to the thiolsulfonate produced, since a run with 0.03 *M* added thiolsulfonate showed no change in the initial second-order rate constant. However, it did show a more pronounced acceleration toward the end of the run. This led us to suspect that perhaps *p*-tolyl disulfide, a known hydrolysis product of *p*-tolyl *p*-toluenethiolsulfonate, accelerated the rate of disappearance of sulfinic acid. Since the extent of hydrolysis of the thiolsulfonate

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[1] To whom inquiries should be sent: Department of Chemistry, Oregon State University.

[2] J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 605 (1962).

under these reaction conditions is no more than a few per cent. it was evident, if this picture were correct, that at reasonable concentrations of disulfide a disulfide–sulfinic acid reaction might well predominate over eq. 1. This has indeed proved true, and the present paper is devoted to the course and mechanism of this, to our knowledge, previously unreported reaction between a disulfide and a sulfinic acid (eq. 2).

Results

Figure 1A, which shows runs with and without disulfide, demonstrates that the presence of *p*-tolyl disulfide can greatly accelerate the rate of disappearance of sulfinic acid. The progress of the reaction was followed by the method described previously.[2]

Kinetic Order with Respect to Sulfinic Acid.—Not only is the rate of disappearance of sulfinic acid much faster in the presence of disulfide, but also the kinetics are no longer second order in sulfinic acid. That the kinetics are in fact first order in sulfinic acid can be seen from Fig. 1B.

Products of the Disulfide-Sulfinic Acid Reaction.—The run shown in Fig. 1B was stopped after one hour (90.3% reaction) and the unreacted sulfinic acid was separated from the water-insoluble compounds present. The latter were then separated by chromatography. From a volume of solution containing initially 10 mmoles of *p*-toluenesulfinic acid and 20 mmoles of *p*-tolyl disulfide there was obtained 6.5 mmoles of *p*-tolyl *p*-toluenethiolsulfonate. This is 216% of the theoretical yield according to eq. 1, showing that the disulfide alters not only the kinetics but also the stoichiometry of the disappearance of sulfinic acid. On the other hand, the observed yield is 96% of theoretical for reaction according to eq. 2. The only other substance isolated from

$$4ArSO_2H + ArSSAr \longrightarrow 3ArSO_2SAr + 2H_2O \quad (2)$$

the chromatography was a large amount of unreacted tolyl disulfide.

The dependence of rate on disulfide concentration was investigated in a series of runs (Part A of Table I). In these runs, for the reasons outlined in footnote 3, the change in disulfide concentration during the course of any run is small enough (<10%) that within the accuracy of the kinetic measurements the disulfide concentration may be considered effectively constant during the run.

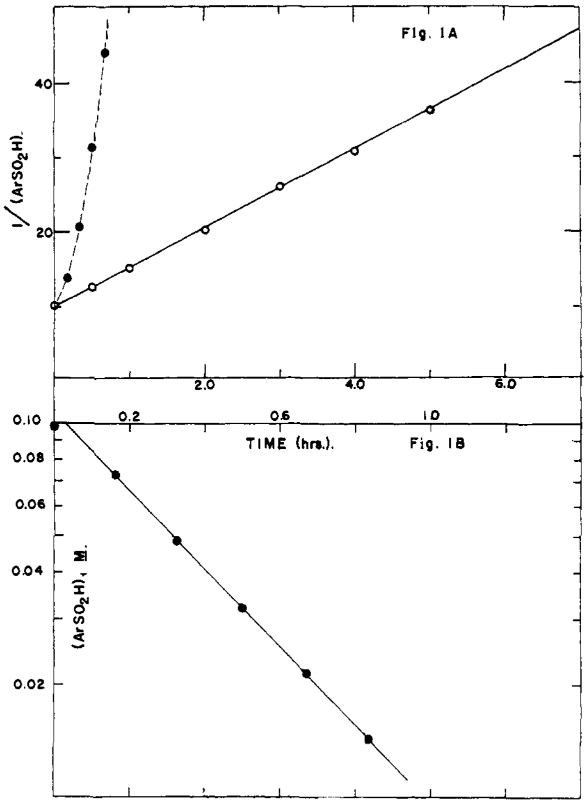

Fig. 1.—Rate of disappearance of $ArSO_2H$ in presence and absence of *p*-tolyl disulfide. All runs with 0.5 *M* H_2SO_4, 0.56 *M* H_2O and initial $ArSO_2H$ concn. of 0.1 *M*; ●, disulfide, 0.20 *M*; ○, disulfide, 0.00 *M*.

To the extent there is any contribution from the normal disproportionation (eq. 1) the runs will display the kinetic behavior (eq. 3) expected for disappearance of $ArSO_2H$ by both a first- and second-order process.

$$-\,d(ArSO_2H)/dt = k_1(ArSO_2H) + k_2(ArSO_2H)^2 \quad (3)$$

In all runs at 0.5 *M* H_2SO_4 and in the 0.3 *M* disulfide run at 0.3 *M* H_2SO_4 the k_2 term in eq. 3 is sufficiently small that the decomposition behaves for all practical purposes as one first-order in sulfinic acid (Fig. 1B). However, consideration of the magnitude of the previously determined[2] k_2 values and the size of the observed experimental first-order rate constants shows that, even though the kinetics appear clearly first order, there is a small but not always negligible contribution to $-d(ArSO_2H)/dt$ from the $k_2(ArSO_2H)^2$ term. In determining k_1 we have therefore proceeded as follows: The average value of $k_2(ArSO_2H)$ during a given run was determined from the k_2 values of ref. 2 and sulfinic acid concentration range over which the run was followed. This quantity, $k_2(ArSO_2H)_{av}$, was then subtracted from the experimental first-order constant, *i.e.*, the slope of the log $(ArSO_2H)$ *vs.* time plot. The result, $k_{exp} - k_2(ArSO_2H)_{av}$, was taken as k_1.

In the other runs at 0.3 *M* sulfuric acid the disulfide–sulfinic acid reaction occurs at a rate comparable to eq. 1, and a plot of log $(ArSO_2H)$ *vs.* time shows upward curvature. To evaluate k_1 in these cases we used the procedure[4] of plotting $(ArSO_2H)$

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[3] From the stoichiometry of eq. 2 the amount of disulfide consumed should equal only one-fourth the amount of sulfinic acid reacting. For the runs at 0.5 *M* H_2SO_4, even for the worst case, *i.e.*, 0.1 *M* disulfide, this would mean at most a 12% change in disulfide concentration during the run. However, since under these conditions, on the average, about 15% of the sulfinic acid decomposes by eq. 1, and since the reaction is not followed to completion, the actual change in the disulfide concentration is less than this, probably about 8–9%.

For the same reasons in the 0.3 *M* H_2SO_4 runs containing 0.1 and 0.2 *M* disulfide the actual change in disulfide concentration during a run should be much less than would be obtained if all the sulfinic acid reacted according to eq. 2. In fact from the rate constants for reactions 1 and 2 and the concentration range, 0.1–0.2 *M* $ArSO_2H$, over which the reaction was followed, one can estimate that the actual change in disulfide concentration during the 0.1 *M* disulfide run was only about 0.008 *M*, rather than the 0.025 *M* calculated for complete reaction by eq. 2.

[4] A. Frost and R. Pearson, "Kinetics and Mechanism," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 165.

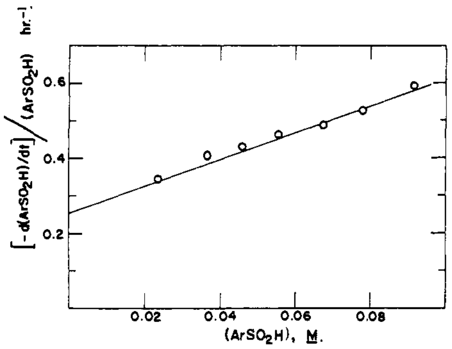


Fig. 2.—Plot of data according to procedure of ref. 4 for run with 0.20 M H_2SO_4, 0.56 M H_2O, 0.20 M disulfide and 0.10 M $(ArSO_2H)_0$. Slope (3.41 M^{-1} hr.$^{-1}$) equals k_2 (compare 3.5 M^{-1} hr.$^{-1}$ estimated from data of ref. 2). Intercept is k_1 (see Table I).

vs. time and determining $-d(ArSO_2H)/dt$ at various points along a smooth curve through the experimental data. We then plotted $[-d(ArSO_2H)/dt/(ArSO_2H)]$ vs. $(ArSO_2H)$, as in Fig. 2. The slope of such a plot should equal k_2, a quantity already known from rate studies in the absence of disulfide.[2] The intercept is k_1. The footnotes to Table I indicate which method was used in a given case to determine k_1.

From the stoichiometry of eq. 2 one would probably expect the disulfide–sulfinic acid reaction to be first order in disulfide. Surprisingly, this is not so, the $k_1/(ArSSAr)$ values in Table I increasing markedly with increasing disulfide concentration. Figure 3 shows, however, that the data are well accommodated by the following expression for k_1

$$k_1 = K_e[k_0 + k_c(ArSSAr)](ArSSAr) \qquad (4)$$

Such an expression would result if the reaction of disulfide and sulfinic acid had the kinetic form outlined in eq. 5. One way in which the disulfide might promote decomposition of the intermediate (eq. 5c) is through nucleophilic attack by one of the unshared pairs on sulfur. If so, then other sulfur nucleophiles might also promote decomposition of the intermediate. Demonstration of this sort of catalysis of reaction 2 would constitute powerful evidence in favor of the above picture. The succeeding paragraphs describe just such a demonstration.

$$ArSO_2H + ArSSAr \underset{\text{fast}}{\overset{K_e}{\rightleftarrows}} \text{intermediate} \qquad (5a)$$

$$\text{intermediate} \underset{\text{slow}}{\xrightarrow{k_0}} \text{products} \qquad (5b)$$

$$\text{intermediate} + ArSSAr \underset{\text{slow}}{\xrightarrow{k_0}} \text{products} + (ArSSAr) \qquad (5c)$$

Catalysis by Diphenyl Sulfide.—Diphenyl sulfide, which should be a better nucleophile than tolyl disulfide in a reaction such as 5c, is by itself completely without effect on the disproportionation. On the other hand, when it is added at 0.1 M to a solution 0.2 M in disulfide and 0.05 M in sulfinic acid the rate of reaction 2 is increased by a factor of four. The details of these experiments are shown in Table II.

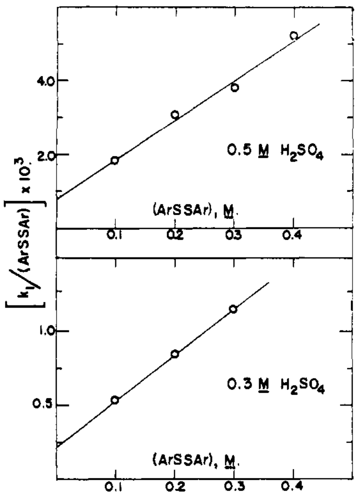


Fig. 3.—Dependence of rate on disulfide concentration. Data of Part A of Table I plotted according to eq. 4. Slope equals K_ek_c; intercept, K_ek_0.

This powerful catalysis of the disulfide–sulfinic acid reaction by a sulfur nucleophile which is by itself without effect on the rate of disappearance of sulfinic acid seems readily compatible only with intervention of reaction 5d.

Table I

Kinetics of the Decomposition of *p*-Toluenesulfinic Acid in the Presence of *p*-Tolyl Disulfide

Solvent acetic acid with water as indicated at 70°

(H_2O), M	(H_2SO_4), M	$(ArSO_2H)_0$, M	$(ArSSAr)$, M	$k_1 \times 10^3$,[a] sec.$^{-1}$	$\frac{k_1 \times 10^3}{(ArSSAr)}$
A: Effect of *p*-tolyl disulfide concentration					
0.56	0.50	0.050	0.40	2.1	5.2
			.30	1.14	3.8
			.20	0.63	3.1
			.10	.186	1.86
0.56	0.30	0.100	.30	.34	1.15
			.20	.17[b]	0.85
			.10	.053[b]	0.53
B: Effect of sulfuric acid concentration					
0.56	0.70	0.100	0.20	1.5	7.5
	.60			1.0	5.0
	.50			0.61	3.1
	.40			.34	1.70
	.30			.17[b]	0.85
	.20			.070[b]	0.35
C: Effect of water concentration					
0.34	0.50	0.100	0.20	1.1	5.5
.56				0.61	3.1
.78				.33	1.65
1.10				.211	1.05
1.67				.083	0.42
2.22				.038	0.19

[a] Unless otherwise noted k_1 is determined from the experimental first-order rate constant and $k_2(ArSO_2H)_{av.}$; see text. [b] k_1's determined by method of ref. 4 (see text).

$$(C_6H_5)_2S + \text{intermediate} \xrightarrow{k_s} \text{products} + [(C_6H_5)_2S] \qquad (5d)$$

Assuming k_1 is given in the presence of diphenyl sulfide by eq. 6 and in its absence by eq. 4 one can

TABLE II

EFFECT OF DIPHENYL SULFIDE ON THE RATE OF THE *p*-TOLUENESULFINIC ACID–*p*-TOLYL DISULFIDE REACTION

All runs solvent acetic acid, 0.56 *M* water, at 70°

(H_2SO_4), *M*	$(ArSO_2H)_0$, *M*	(ArSSAr), *M*	(Ph_2S), *M*	$k_1 \times 10^3$, sec.$^{-1}$	$k_2 \times 10^3$, M^{-1} sec.$^{-1}$
1.00	0.100	0.00	0.00	..	2.24[a]
			.10	..	2.2[b]
0.30	.050	.20	.00	0.17	..
			.10	.69	..
0.50	.050	.20	.00	.63	..
			.10	~2.6	..

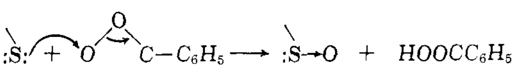
[a] Data of ref. 2. [b] Run follows second-order kinetics in sulfinic acid.

calculate values for the ratios (k_0/k_c) and (k_s/k_c).

$$k_1 = K_e[k_0 + k_c(\text{ArSSAr}) + k_s(\text{Ph}_2\text{S})](\text{ArSSAr}) \quad (6)$$

The value of (k_s/k_c) calculated from the 0.3 *M* H_2SO_4 data is 8.4.

The initial step in the perbenzoic acid oxidation of sulfides and disulfides is believed to involve nucleophilic attack by sulfur on the –O–O– bond (eq. 7). In this reaction Marangelli, Modena and Todesco[5] found that the initial rate of oxidation of diphenyl sulfide was 30 times greater than that of diphenyl disulfide. From data on the ease of


(7)

oxidation of other disulfides,[5] *p*-tolyl disulfide should be about 1.5 times more reactive than diphenyl disulfide, or about one-twentieth as reactive as the diphenyl sulfide. This is close enough to the ninefold difference between k_s and k_c to demonstrate that the relative effectiveness of tolyl disulfide and diphenyl sulfide in promoting the decomposition of the intermediate in eq. 5 parallels their relative nucleophilicities in another reaction.

The mechanism in eq. 5 suggests that, although the over-all rate of reaction 2 could be markedly sensitive to sulfuric acid concentration, the ratio (k_0/k_c) should not be, since the acidity of the medium should have little influence on this ratio of rate constants. The k_0/k_c values calculated from the data at 0.5 and 0.3 *M* sulfuric acid are 0.076 and 0.072, respectively, in gratifying accord with these expectations, especially when one remembers that the over-all rates differ by a factor of 3.6 in the two media.

In the Discussion we will see that the structure for the "intermediate" in eq. 5 which is suggested by the dependence of the over-all rate on water and strong acid concentration is also one which should be readily subject to decomposition through nucleophilic attack.

Dependence of Rate on Sulfuric Acid Concentration.—A series of runs at 0.2 *M* disulfide was made in which the sulfuric acid concentration was varied between 0.2 and 0.7 *M* (Part B of Table I). Since k_0/k_c is independent of sulfuric acid concentration the variation of log k_1 with (H_2SO_4) at a given disulfide concentration should be independent of disulfide concentration. As a result the measurements in Part B suffice to delineate fully the variation of over-all rate with acid concentration.

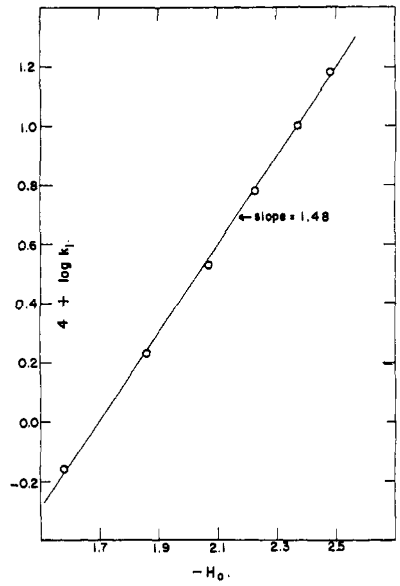


Fig. 4.—Dependence of rate on strong acid concentration. Data of Part B of Table I plotted *vs.* $-H_0$.

The effect of acid concentration on the rate of reaction 2 is in dramatic contrast to its effect on the normal disproportionation. Thus changing the sulfuric acid concentration from 0.2 to 0.6 *M* produces about a 15-fold increase in k_1. A similar change in acid concentration produced only a 1.6-fold increase in the rate of eq. 1.[2] A plot of log k_1 *vs.* H_0[6] is linear but with a slope of 1.48 (Fig. 4). The significance of this finding will be considered more fully in the Discussion, but clearly the rate of the disulfide–sulfinic acid reaction is strongly dependent on the acidity of the medium.

Dependence of Rate on Water Concentration.—The effect of the stoichiometric concentration of water on the rate was also studied (Part C of Table I). Although the response of the rate to changing water concentration is greater than that of the normal disproportionation, the difference in behavior is not as great as the difference in the response of the two reactions to changes in strong acid concentration. Thus going from 0.56 to 2.22 *M* water decreases the rate of reaction 2 by a factor of 16, while a similar change in water content changed the rate of eq. 1 by a factor of about seven.[2] In view of the pronounced dependence of the rate on H_0 (see above) and the fact that an increase in water content at fixed sulfuric acid concentration decreases the acidity of the medium, the greater sensitivity of eq. 2 to changes in water content seems readily understandable.

Discussion

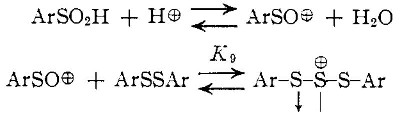
The mechanism shown in eqs. 8–15, involving the positive ion I as the "intermediate" of eq. 5, seems the one the most consistent with the experimental results. The succeeding paragraphs

(5) U. Marangelli, G. Modena and P. E. Todesco, *Gazz. chim. ital.*, **90**, 681 (1960).

(6) (a) V. Gold and B. W. V. Hawes, *J. Chem. Soc.*, 2102 (1951); (b) D. S. Noyce and L. R. Snyder, *J. Am. Chem. Soc.*, **80**, 4324 (1958).

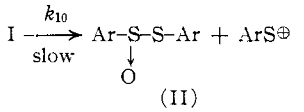
will be devoted to discussion of this mechanism and demonstration of its experimental justification.

$$ArSO_2H + H^{\oplus} \underset{}{\overset{K_8}{\rightleftarrows}} ArSO^{\oplus} + H_2O \qquad (8)$$



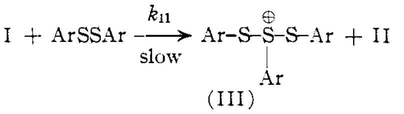
$$ArSO^{\oplus} + ArSSAr \overset{K_9}{\rightleftarrows} Ar{-}\underset{\downarrow \atop O}{S}{-}\overset{\oplus}{\underset{| \atop Ar}{S}}{-}S{-}Ar \qquad (9)$$

(I)



$$I \xrightarrow[\text{slow}]{k_{10}} Ar{-}\underset{\downarrow \atop O}{S}{-}S{-}Ar + ArS^{\oplus} \qquad (10)$$

(II)



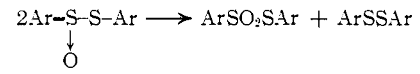
$$I + ArSSAr \xrightarrow[\text{slow}]{k_{11}} Ar{-}S{-}\overset{\oplus}{\underset{| \atop Ar}{S}}{-}S{-}Ar + II \qquad (11)$$

(III)

$$ArS^{\oplus} + ArSO_2H \longrightarrow ArSO_2SAr + H^{\oplus} \qquad (12)$$

$$III + ArSO_2H \longrightarrow ArSSAr + ArSO_2SAr + H^{\oplus} \qquad (13)$$

$$III \longrightarrow ArSSAr + ArS^{\oplus} \qquad (14)$$



$$2Ar{-}\underset{\downarrow \atop O}{S}{-}S{-}Ar \longrightarrow ArSO_2SAr + ArSSAr \qquad (15)$$

With reactions 10 and 11 the slow steps the rate expression for the mechanism is given by eq. 16, and k_1 by eq. 17. We have already seen that

$$\left[\frac{-d(ArSO_2H)/dt}{(ArSO_2H)}\right] = K_8K_9k_{10}\left[\frac{a_{H^+}f_{ArSO_2H}f_{ArSSAr}}{a_{H_2O}\,f_{*10}}\right]\left\{1 + \frac{k_{11}f_{ArSSAr}f_{*10}}{k_{10}f_{*11}}(ArSSAr)\right\}(ArSSAr) \qquad (16)$$

$$k_1 = K_8K_9k_{10}(ArSSAr)\left[\frac{a_{H^+}f_{ArSO_2H}f_{ArSSAr}}{a_{H_2O}\,f_{*10}}\right]\left\{1 + \frac{k_{11}f_{ArSSAr}f_{*10}}{k_{10}f_{*11}}(ArSSAr)\right\} \qquad (17)$$

an expression of the form of eq. 17 will adequately represent the variation in k_1 with variation in disulfide concentration (see Fig. 3).

Consider now the variation in k_1 with sulfuric acid concentration. The earlier demonstration that k_0/k_c is independent of sulfuric acid concentration requires $(k_{11}f_{ArSSAr}f_{*10}/k_{10}f_{*11})$ be independent of (H_2SO_4). This is quite reasonable considering the nature of the activity coefficient ratio involved. Then, since all runs at varying acid were at the same disulfide concentration, for these runs we should have

(for runs in Part B, Table I)

$$k_1 = \text{const.} \times \left[\frac{a_{H^+}f_{ArSO_2H}f_{ArSSAr}}{a_{H_2O}\,f_{*10}}\right] \qquad (18)$$

From eq. 18, k_1 should clearly increase rapidly with increasing acidity of the medium, as it indeed does; but its exact behavior is somewhat uncertain due to uncertainty about the effect of changing acid concentration on the activity coefficient ratio in eq. 18. However, the change in k_1 would probably lie somewhere within the limits outlined below.

At one extreme, if the behavior of the ratio $(f_{ArSO_2H}f_{ArSSAr}/f_{*10})$ were to approximate that of (f_{ArSO_2H}/f_{ArSO^+}) or (f_{ROH}/f_{R^+}), $-\log k_1$ should approximately follow the acidity function H_R. For the present solutions Gold[6a] reports $H_R = 2H_0 +$ constant, although an actual plot of his data, which show some scatter, suggests a better estimate is $H_R = 1.8H_0 +$ constant. At the other extreme, if the ratio varied in the same way with acid concentration as (f_B/f_{BH^+}) for a typical Hammett base, $-\log(k_1a_{H_2O})$ would follow the Hammett acidity function, H_0.

The actual experimental results do in fact lie between these two extremes, being somewhat closer to the second alternative than the first. Values for the relative activity of water in the solutions in question are given by Noyce and Snyder[6b] and are shown in Table III.[7] Table III shows that $\log(k_1a_{H_2O}) + H_0$, while not constant, increases only slightly with acid concentration—the slope of a plot of $-\log(k_1a_{H_2O})$ *vs.* H_0 being 1.10. A plot of $\log k_1$ *vs.* $-H_R$ is naturally also linear (see above and Fig. 4) and has a slope of 0.80. The variation of k_1 with acidity therefore seems consistent with the requirements of the mechanism.

TABLE III

CORRELATION OF RATE WITH ACIDITY AT 0.56 M H_2O

(H_2SO_4), M	a_{H_2O}[a]	$\log (k_1a_{H_2O})$	H_0	$\log (k_1a_{H_2O}) + H_0$
0.20	(1.00)	−4.16	−1.58	−5.74
.30	0.83	−3.85	−1.86	−5.71
.40	.70	−3.62	−2.07	−5.69
.50	.60	−3.44	−2.23	−5.67
.60	.51	−3.29	−2.37	−5.66
.70	.44	−3.18	−2.48	−5.66

[a] Activity shown is $a_{H_2O}/a_{H_2O(0.2\ M\ H_2SO_4)}$ as taken from data of ref. 6b.

At present lack of data on a_{H_2O}, H_0 and H_R for most of the solutions involved precludes any meaningful correlation of the variation of k_1 with water concentration. This much, however, can be said. Since k_1 is proportional to a_{H^+}/a_{H_2O} it should certainly decrease markedly with increasing water concentration and furthermore should do so more rapidly than the rate constant for the normal disproportionation (k_2) which is,[2] to a first approximation, equal to $1/a_{H_2O}$. This is what is observed, and to this extent the dependence of rate on water concentration is, at the least, not inconsistent with the mechanism.

There is good reason to believe that the intermediate I should be readily subject to nucleophilic attack by disulfide (eq. 11) or sulfide (eq. 5d). The excellent review of Kharasch and Parker[8] provides ample evidence from the work of Fava[9] and others that nucleophilic displacements at divalent sulfur occur with unusual ease, especially relative to the rates of the same displacements at tetrahedral carbon. Moreover, intermediate I has $ArS(O)\overset{+}{\underset{|}{S}}Ar$ as the leaving group. This should be a very good leaving group, particularly in comparison to such as RS– in a disulfide, RSO_2– in a thiolsulfonate, and perhaps even to Cl– in a sulfenyl chloride. In the case of sulfenyl

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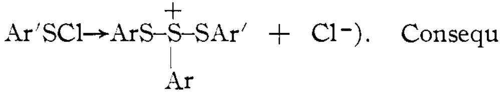
[7] Reasons have been given in ref. 2 indicating why these data seem the best presently available estimates of a_{H_2O} for these solutions.

[8] A. J. Parker and N. Kharasch, *Chem. Revs.*, **59**, 583 (1959).

[9] A. Fava, A. Iliceto and E. Camera, *J. Am. Chem. Soc.*, **79**, 833 (1957); A. Fava and A. Iliceto, *ibid.*, **80**, 3478 (1958).

chlorides the recent studies of Moore and Porter[10] suggest clearly that disulfides are strong enough nucleophiles to attack the S–Cl group (ArSSAr +  $Ar'SCl \rightarrow ArS\text{–}\overset{+}{\underset{\underset{Ar}{|}}{S}}\text{–}SAr' + Cl^-$). Consequently it seems probable the disulfide should react with I at a quite rapid rate.

The conversion of thiolsulfinate II to thiolsulfonate is postulated to occur by reaction 15. This is a well-known reaction of thiolsulfinates.[11] Furthermore, Vinkler and Klivényi have shown[12] that this reaction occurs most readily in the presence of acid. This suggests it should occur very rapidly under the present reaction conditions.

Examination of the mechanism shows that substitution of an aliphatic disulfide (RSSR) for tolyl disulfide should lead to the production of the unsymmetrical thiolsulfonate $ArSO_2SR$. This has indeed been found to be the case. Dimethyl disulfide (0.2 *M*) was found to react very rapidly with *p*-toluenesulfinic acid (0.1 *M*) in acetic acid–0.56 *M* H_2O containing 0.3 *M* sulfuric acid, the sulfinic acid being completely consumed in 10 minutes at 70°. Examination of the products showed that a large amount of methyl *p*-toluenethiolsulfonate had been formed. Some *p*-tolyl *p*-toluenethiolsulfonate was also formed, but this would be expected from Barnard's[11b] observation that the disproportionation of thiolsulfinates (eq. 15) is not just a simple transfer of an oxygen atom between the two ArS(O)SAr molecules. The extension of this reaction to other aliphatic disulfides and a more quantitative study of its course are currently under study.

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Experimental

***p*-Toluenesulfinic** acid was prepared as previously described.[2] ***p*-Tolyl disulfide** (Columbia Organic Chemicals) was purified by chromatography on alumina using hexane as eluents followed by one recrystallization from methanol; m.p. 45–46°. **Diphenyl sulfide** (Eastman Kodak Co. white label) was distilled before use; b.p. 152–153° (15 mm.). **Dimethyl disulfide** (Eastman Kodak Co.) was fractionally distilled before use; b.p. 110–111°.

Procedure for Kinetic Runs.—The preparation of the solvents and standard solutions has been described.[2] The procedure was basically that previously used for the normal disproportionation.[2] The disulfide was weighed out and added to the solution before the sulfuric acid was added. Diphenyl sulfide, when used, was added as a 2.0 *M* stock solution in acetic acid. Test experiments showed the presence of sulfide or disulfide did not affect the determination of sulfinic acid by the nitrite method.

Stoichiometry of the Tolyl Disulfide–Sulfinic Acid Reaction.—*p*-Toluenesulfinic acid (10.0 mmoles) and *p*-tolyl disulfide (20.0 mmoles) were dissolved in 100 ml. of a solution of acetic acid–0.56 *M* water containing 0.5 *M* sulfuric acid. The solution was heated for 1 hour at 70° using the procedure of the kinetic runs. At the end of this time titration of a 5-ml. aliquot showed 90.3% of the sulfinic acid had reacted. The reaction was stopped at this point, and the reaction mixture poured into 1 liter of distilled water. The resulting mixture was extracted several times with ether. The combined ether extracts were washed with aqueous bicarbonate until neutral. After drying, the ether was removed by distillation and the residue chromatographed on a 2 × 40 cm. column of acid-washed alumina. Elution with 400 ml. of pentane gave 3.4 g. (14 mmoles) of recovered disulfide in a state of high purity. Subsequent elution with 400 ml. of ether gave 1.81 g. (6.5 mmoles) of *p*-tolyl *p*-toluenethiolsulfonate, m.p. 76°. No other products were found. No attempt was made to determine whether the workup method leads to a quantitative recovery of unreacted disulfide. Trial experiments did show that it was quantitative for the thiosulfonate.

Reaction of Dimethyl Disulfide and Sulfinic Acid.—Dimethyl disulfide (20 mmoles) and *p*-toluenesulfinic acid (10 mmoles) were dissolved in 100 ml. of a solution of acetic acid–0.56 *M* H_2O containing 0.3 *M* sulfuric acid. The solution was heated at 70° using the usual procedure. After 10 min., titration of an aliquot with standard nitrite solution showed all the sulfinic acid was gone. The reaction mixture was then poured into water, extracted with ether, etc., in the manner described above. The residue after removal of the ether was chromatographed on a 2 × 80 cm. acid-washed alumina column, eluting with the following solvent mixtures: pentane, 800 ml.; pentane–ether 19:1, 200 ml.; 9:1, 200 ml.; 7.1, 200 ml.; 4:1, 100 ml.; 3:1, 100 ml.; ether, 700 ml. Fractions of 20 ml. were collected, and the solvents were removed by fractional distillation through a micro-Widmer column to minimize product loss. The following products were obtained: Methyl *p*-toluenethiolsulfonate (0.61 g., 3.0 mmoles) was identified by infrared and mixed m.p. comparison with a known sample, m.p. 58°, prepared by the method of Gibson.[13] Only 0.43 g. (1.5 mmoles) of *p*-tolyl *p*-toluenethiolsulfonate was isolated. A large amount of dimethyl disulfide was recovered unreacted. No methyl methanethiolsulfonate could be found. A significant amount of a compound believed from its infrared spectrum and point of elution from the chromatographic column to be methyl *p*-tolyl disulfide was isolated. Definitive identification is planned for the future, but such a disulfide would be one of the products expected to the extent that disproportionation of methyl *p*-toluenethiolsulfinate occurs according to the equation

$$2ArS(O)SMe \longrightarrow ArSO_2SMe + ArSSMe$$

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

(11) (a) H. J. Backer and H. Kloosterziel, *Rec. trav. chim.*, **73**, 129 (1954); (b) D. Barnard, *J. Chem. Soc.*, 4675 (1957).

(12) E. Vinkler and F. Klivényi. *Acta Chim. Acad. Hung.*, **22**, 345 (1960); *Magyar Kémiai Folyóirat*, **62**, 48 (1956).

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