# The Mechanism of the Disproportionation of Sulfinic Acids[1]

BY JOHN L. KICE[2] AND KERRY W. BOWERS

The disproportionation of p-toluenesulfinic acid has been studied in acetic acid containing 0.5–5.0% water and 0.0–1.3 M sulfuric acid. The reaction is second order in sulfinic acid. At constant stoichiometric water concentration, the rate is only moderately accelerated by increasing sulfuric acid concentration, the magnitude of the change being considerably smaller than the change in H_0. At constant strong acid concentration, the rate is strongly retarded by increasing water concentration. The reaction shows a small negative salt effect. The rate of hydrolysis of p-toluenesulfinyl p-tolyl sulfone (I) is much faster than any reaction of I with p-toluenesulfinic acid. With the observed second-order kinetics, this rules out a previously suggested[6] mechanism for the reaction. A mechanism is proposed involving a rapid reversible equilibrium between the sulfinic acid and I, followed by rate-determining rearrangement of I to a sulfonic-sulfenic anhydride II, which can then yield the observed products by a variety of routes.

The disproportionation of aromatic sulfinic acids (eq. 1) has long been known[3] and has proved

$$3ArSO_2H \longrightarrow ArSO_2SAr + ArSO_3H + H_2O \quad (1)$$
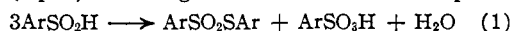
useful[4] for the preparation of certain aryl arenethiolsulfonates. Mechanistically, it is interesting in that (1) there are a number of plausible mechanisms for the reaction and (2) it represents a conveniently studied example of mutual oxidation-reduction reactions involving organic sulfur compounds—reactions frequently postulated as key steps in the transformations of organic sulfur chemistry.[5] Since the inception of our work, two papers[6,7] have reported studies of this particular reaction, albeit under rather different reaction conditions from those employed here. The mechanisms suggested by these other workers[6,7] cannot, however, be reconciled with the behavior of the reaction under the present conditions.

We have studied the disproportionation of p-toluenesulfinic acid in acetic acid containing 0.5–5.0% water. The reaction proceeds much more rapidly under these conditions than in aqueous solution; furthermore, the thiolsulfonate product remains in solution, in contrast to its separation as a second phase when only water is used as a solvent. Since most previous investigators[6–8] have felt the reaction was subject to acid catalysis, known amounts of sulfuric acid have normally been added to our acetic acid–water mixtures, and we have carefully determined the dependence of rate on acid concentration.

Results

In moist acetic acid, p-toluenesulfinic acid rapidly undergoes disproportionation at 70° according to eq. 1, both in the presence and absence of sulfuric acid. The initial yield of p-tolyl p-toluenethiolsulfonate is that expected from the stoichiometry of eq. 1 and the amount of sulfinic acid reacted.

However, on prolonged heating of the solutions, the yield of thiolsulfonate slowly decreases, due to its hydrolysis. Thus solutions of sulfinic acid (0.1–0.2 M) in acetic acid containing water (0.22–0.55 M) and sulfuric acid (0.0–1.0 M) at 70° for 2–6 hr. gave the thiolsulfonate in 98–99% yield; but in acetic acid–1.10 M H_2O after 48 hr. the yield was only 87%. These facts suggested that the thiolsulfonate could best be prepared, when this is desired, in dry acetic acid, and indeed conversion proved to be complete after only 15 min. at 70°. In view of the marked retarding effect of water on the rate of reaction 1 (*vide infra*) and the decreased yield of thiolsulfonate on prolonged heating, the usual procedure of carrying out the reaction in aqueous solution seems hardly defensible.

Kinetics of the Reaction.—Reaction 1 could be followed by measuring the disappearance of sulfinic acid. The sulfinic acid concentration was determined by removing aliquots and, after dilution with water, titrating the unreacted sulfinic acid with standard sodium nitrite solution.[9] Although not of the highest precision, this method seemed preferable to others investigated in that there were no interferences by the other compounds present. As a precautionary measure all kinetic runs were carried out on deaerated solutions under nitrogen.

Kinetic Order with Respect to Sulfinic Acid.—A series of runs was made in which the initial concentration of sulfinic acid was varied. These runs (Part A of Table I) are shown in Fig. 1, plotted as reactions second order in sulfinic acid. The reaction is clearly second order in sulfinic acid. An equally good fit to second-order kinetics was exhibited by all the runs shown in Table I.[10]

(1) Presented at the 140th Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

(2) To whom inquiries should be sent: Department of Chemistry, Oregon State University, Corvallis, Ore.

(3) R. Otto, *Ann.*, **145**, 13, 317 (1868); *Ber.*, **9**, 1640 (1876); C. Pauly and R. Otto, *ibid.*, **10**, 2182 (1877).

(4) C. M. Bere and S. Smiles, *J. Chem. Soc.*, **125**, 2359 (1924).

(5) See generally such works as Houben-Weyl, "Methoden der Organischen Chemie," v. 9, 4th edition, Georg Thieme Verlag, Stuttgart, 1955.

(6) H. Bredereck, A. Wagner, E. H. Beck, H. Berlinger and K. G. Kottenhahn, *Angew. Chem.*, **70**, 268 (1958).

(7) P. Allen and L. Reich, *J. Phys. Chem.*, **64**, 1928 (1960).

(8) J. v. Braun and K. Weissbach, *Ber.*, **63**, 2837 (1930).

(9) C. S. Marvel and R. S. Johnson, *J. Org. Chem.*, **13**, 822 (1948).

(10) One complicating factor which influences slightly the accuracy of some of the rate constants in Table I is the fact that reaction 1 produces, along with thiolsulfonate, a molecule each of water and strong acid ($ArSO_3H$), both of which affect, albeit in opposite ways, the rate of the reaction. Fortunately the effect of added strong acid is small, and one can calculate from eq. 2 that even in the worst case, *i.e.*, when no H_2SO_4 is added initially, a change in strong acid concentration of 0.033 M (the total amount from decomposition of a 0.10 M sulfinic acid solution) would increase the second-order rate constant by only 10%. The measured experimental rate constant would naturally be changed somewhat less. By carrying out all but a few runs at initial water concentrations of at least 0.56 M, we have kept any decrease in k_2 due to increasing water concentration to less than 8%. Even in the few runs at lower initial water concentrations the maximum decrease should be no more than 12%.

In many cases the accelerating effect of increasing acid and the decelerating effect of increasing water effectively cancel. In others,
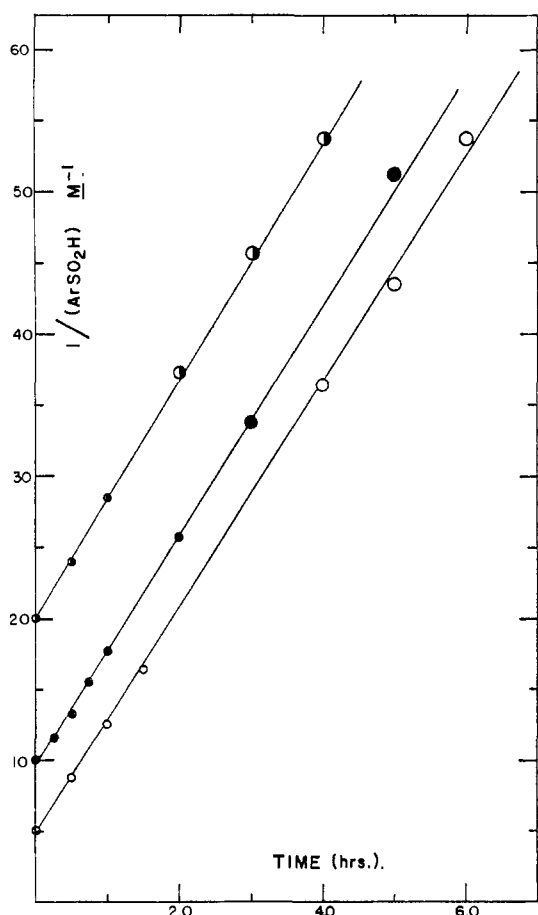
Fig. 1.—Plot of $1/(\text{ArSO}_2\text{H})$ vs. time for disproportionation of p-toluenesulfinic acid in acetic acid-0.56 M H_2O, 1 M H_2SO_4, at 70°. O, initial sulfinic acid conc., 0.2 M; ●- 0.1 M; ◑- 0.05 M.

Dependence of Rate on Sulfuric Acid Concentration.—In the runs in Part B of Table I the sulfuric acid concentration was varied between 0.0 and 1.3 M. Surprisingly, the rate constant varies relatively little with acid concentration, the rate in 1.3 M H_2SO_4 being only about five times greater than the rate in the absence of H_2SO_4. To a good approximation the rate constant k_2 is given by

$$k_2 = 0.61 \times 10^{-3} + 1.66 \times 10^{-3} (\text{H}_2\text{SO}_4) \, M^{-1}\text{sec.}^{-1} \quad (2)$$

On the other hand, a plot of log k_2 vs. H_0[11] is not linear. Moreover, even if one assumes that only the second term on the right should depend on H_0 and plots log k_2' vs. H_0, where $k_2' = k_2 - k_{2\text{st}}$ $(\text{H}_2\text{SO}_4) = 0.0 \, M$, the plot although approximately linear has a slope of slightly less than 0.5.

Dependence of Rate on Water Concentration.—Although relatively insensitive to changing acid concentration, the rate was markedly dependent on

one or the other predominates, but in no case should the measured rate constant differ by more than 6–7% from the true rate constant for the initial experimental conditions.

The slight decrease in k_2 in Part A of Table I with increasing initial sulfinic acid concentration is probably due to such an effect, the larger initial ArSO_2H concentrations leading to slightly larger average water concentrations during a run, and the retarding effect of increasing water predominating due to the high initial strong acid concentration.

(11) (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).

TABLE I

KINETICS OF THE DISPROPORTIONATION OF p-TOLUENE-SULFINIC ACID

In all runs the solvent is acetic acid containing the amount of water indicated, and the temperature is 70°.

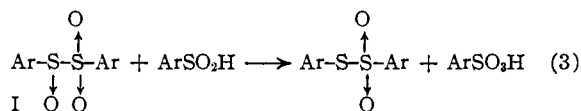| (H_2O), M	(H_2SO_4), M	$(\text{ArSO}_2\text{H})_i$ M	$k_2 \times 10^3$, M^{-1} sec.$^{-1}$	$-H_0{}^a$
A, Effect of initial sulfinic acid concentration			
0.56	1.00	0.200	2.21	
		.100	2.24	
		.050	2.30	
B, Effect of sulfuric acid concentration			
0.56	1.30	0.100	2.84	
	1.00		2.24	
	0.80		1.93	
	.50		1.47	
	.30		1.19	
	.10		0.82	
	.00		0.60	
0.53	1.00	0.100	2.33	2.79
	0.80		2.06	2.61
	.60		1.62	2.38
	.40		1.32	2.07
	.20		1.03	1.58
C, Effect of water concentration			
0.22	1.00	0.100	6.95	
0.56			2.24	
1.10			0.87	
1.67			.50	
2.28			.31	
2.78			.24	
0.28	0.00	0.100	1.26	
.56			0.60	
.83			.36	
.97			.31	
1.10			.25	
D, Effect of added inert salt				(NaOTs), M
0.56	0.00	0.100	0.60	0.00
			.58	.10
			.52	.20
			.54	.30

From data of ref. 8.

water concentration. This was true both in the presence of sulfuric acid (top half, Part C of Table I) and in its absence (lower half, Part C of Table I). With 1 M H_2SO_4 in acetic acid, the rate is about nine times faster in a solution 0.56 M in water than in one 2.8 M in water. Similarly, in the absence of sulfuric acid k_2 is five times larger in 0.28 M H_2O than in 1.10 M H_2O. Although there is no simple exact relationship between k_2 and water content, roughly the rate constant is inversely proportional to somewhat greater than the first power of the stoichiometric concentration of water.

Effect of Added Inert Salt (Sodium p-Toluene-sulfonate).—The effect of an added inert salt on reaction rate in the absence of sulfuric acid was briefly investigated. Regrettably lithium bisulfate, whose salt effect would probably be most closely comparable to that of sulfuric acid, proved too insoluble in acetic acid. Perchlorates oxidized the sulfinic acid. For this reason measurements

were made with sodium p-toluenesulfonate. Part D of Table I shows this salt produces a slight negative salt effect.

Evidence that Reaction of p-Toluenesulfinyl p-Tolyl Sulfone (I) and p-Toluenesulfinic Acid is not Involved in Reaction 1.—Bredereck[6] has postulated p-toluenesulfinyl p-tolyl sulfone (I) as a key intermediate in the mechanism of the disproportionation. He has suggested reaction 3 as the final step of reaction 1, and he has shown that in *anhydrous* dioxane, at least, a reaction having

$$\underset{\underset{O}{\overset{\uparrow}{\underset{\downarrow\downarrow}{\text{Ar-S-S-Ar}}}}}{\text{I}} + \text{ArSO}_2\text{H} \longrightarrow \underset{\underset{O}{\overset{\uparrow}{\underset{\downarrow}{\text{Ar-S-S-Ar}}}}}{} + \text{ArSO}_3\text{H} \quad (3)$$

the stoichiometry of eq. 3 will take place quite readily.[12] Although reaction 3 may be involved in the disproportionation under certain conditions, there is compelling evidence that it cannot be involved in the disproportionation of p-toluenesulfinic acid under our reaction conditions. The experiments leading to this conclusion are summarized below.

First, hydrolysis of I to two molecules of sulfinic acid is extremely rapid in the acetic acid–water mixtures used. Thus 0.28 mmole of I was dissolved in acetic acid containing 2.8 M water, and the solution was heated at 70° for five minutes. At the end of this time an iodometric test[6,12] showed that no I remained, while nitrite titration[9] showed 0.55 mmole (98%) of p-toluenesulfinic acid had been formed.

Second, one can show that any reaction of sulfinic acid with I (eq. 3) is not rapid enough to compete with this hydrolysis. Thus p-toluenesulfinic acid (0.41 mmole) was dissolved in 5 ml. of acetic acid–2.8 M H$_2$O. To this solution was then added 0.26 mmole of *solid* I, solution of I effected, and the final solution heated at 70° for five minutes. After this time iodometric analysis for I was again negative. Nitrite titration[9] gave 0.86 mmole of sulfinic acid, or 93% of the amount expected from combination of that originally present (0.41 mmole) with that which should be formed by hydrolysis of I (0.52 mmole). Similarly, in acetic acid containing only 0.56 M water, adding 0.045 mmole of I to a solution containing 0.122 mmole of sulfinic acid gave after five minutes at 70° 0.202 mmole of sulfinic acid (95%).

These experiments show that if the mechanism were to include reaction 3, it would have to be the rate-determining step, because it is clearly much slower than the hydrolysis of I (reverse step of equilibrium shown in eq. 4). *In such a situation the over-all kinetics of reaction 1 would have to be third rather than second order in sulfinic acid.* For these reasons reaction 3 cannot be part of the mechanism of the disproportionation under the present conditions.
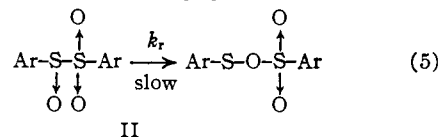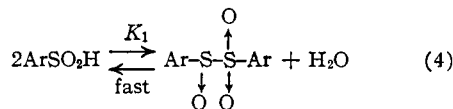
Discussion

Any acceptable mechanism for the disproportionation must be compatible with the principal kinetic features of the reaction: (1) The pro-
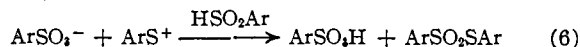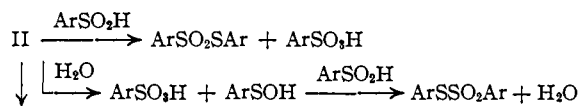
(12) H. Bredereck, A. Wagner, H. Beck and R. J. Klein, *Ber.*, **93**, 2736 (1960).

nounced retardation by water, (2) the rather small effect of added strong acid, and (3) the fact the reaction is second-order in sulfinic acid. Although these restrictions rule out many mechanisms, there are still a number which with varying degrees of credibility can be accommodated to the experimental results. The mechanism outlined in the succeeding paragraphs is, then, not the only one consistent with the data. It is, however, the one which at the present state of our knowledge seems the most plausible, and it has in addition the virtue of simplicity.

Although in a previous section we ruled out the intervention of reaction 3, we have not ruled out the possibility that Compound I may be a key intermediate in the mechanism of reaction 1. On the contrary, on several counts such a hypothesis seems an attractive one. First, despite the ready hydrolysis of the sulfinyl sulfone to sulfinic acid, it is known[18] that under certain conditions in the absence of water p-toluenesulfinic acid can be converted to I. Second, the observation[12,13] that I decomposes on all attempts at recrystallization suggests the sulfinyl sulfone is thermally unstable. For these reasons we favor a mechanism involving a highly unfavorable initial equilibrium between the sulfinic acid and I (eq. 4) followed by rate-determining decomposition of I. For the rate-determining step we suggest the rearrangement of I to a mixed sulfonic-sulfenic anhydride (II), as in eq. 5; II could then decompose by a variety of

$$2\text{ArSO}_2\text{H} \underset{\text{fast}}{\overset{K_1}{\rightleftarrows}} \underset{\underset{O\ O}{\overset{\uparrow}{\underset{\downarrow\downarrow}{\text{Ar-S-S-Ar}}}}}{} + \text{H}_2\text{O} \quad (4)$$

$$\underset{\underset{O\ O}{\overset{O}{\underset{\downarrow\downarrow}{\overset{\uparrow}{\text{Ar-S-S-Ar}}}}}}{} \overset{k_r}{\underset{\text{slow}}{\longrightarrow}} \underset{\underset{O}{\overset{O}{\underset{\downarrow}{\overset{\uparrow}{\text{Ar-S-O-S-Ar}}}}}}{\text{II}} \quad (5)$$

$$\text{II} \xrightarrow{\text{ArSO}_2\text{H}} \text{ArSO}_2\text{SAr} + \text{ArSO}_3\text{H}$$

$$\left\downarrow\right. \underset{}{\overset{\text{H}_2\text{O}}{\longrightarrow}} \text{ArSO}_3\text{H} + \text{ArSOH} \xrightarrow{\text{ArSO}_2\text{H}} \text{ArSSO}_2\text{Ar} + \text{H}_2\text{O}$$

$$\text{ArSO}_2{}^- + \text{ArS}^+ \xrightarrow{\text{HSO}_2\text{Ar}} \text{ArSO}_3\text{H} + \text{ArSO}_2\text{SAr} \quad (6)$$

routes, such as those in eq. 6, but all would lead to thiolsulfonate and sulfonic acid as final products.[14]

For the proposed mechanism the rate would be given by eq. 7 where f_{*r} is the activity coefficient of the transition state for reaction 5, and the other quantities are self-explanatory. The experimental second-order rate

$$-\text{d}(\text{ArSO}_2\text{H})/\text{d}t = k_r K_1 \frac{(\text{ArSO}_2\text{H})^2 f^2{}_{\text{ArSO}_2\text{H}}}{a_{\text{H}_2\text{O}} f_{\pm r}} \quad (7)$$

constant, k_2, would therefore be

$$k_2 = \text{const.} \times \frac{(f^2{}_{\text{ArSO}_2\text{H}}/f_{\pm r})}{a_{\text{H}_2\text{O}}} \quad (8)$$

Qualitatively this mechanism clearly accounts for the second-order kinetics, the pronounced

(13) E. Knoevenagel and L. Pollack, *ibid.*, **41**, 3323 (1908).

(14) There is no reason why Bredereck's[12] observed reaction between I and ArSO$_3$H in *anhydrous* dioxane may not take this course rather than one involving direct reaction of I and sulfinic acid. We hope to conduct experiments designed to test this point in the future.
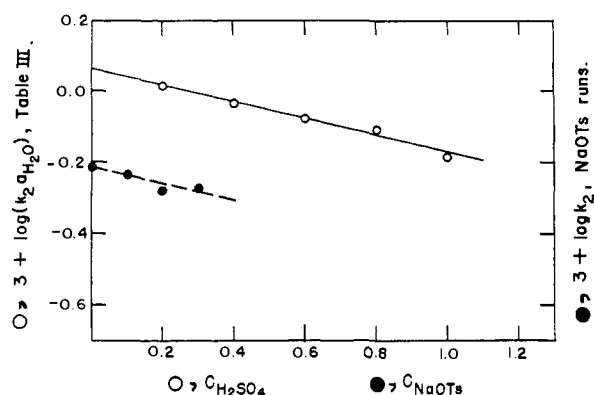
Fig. 2.—Correlation of rate with acid concentration: O, plot of log $(k_2 a_{H_2O})$ values from Table II for runs with 0.53 M H_2O $vs.$ (H_2SO_4); ●, plot of log k_2 $vs.$ $(NaOTs)$ for runs at 0.56 M H_2O with added sodium p-toluenesulfonate.

retardation by added water, and as the following arguments indicate, for the rather limited effect of strong acid, which should influence the rate only insofar as it affects the activity of water.

Some results by Noyce and Snyder[11b] on the reaction sequence shown in eq. 9 seem to provide the best currently available estimate of the relative activity of water in acetic acid solutions 0.53 M in water and 0.2–1.0 M in sulfuric acid.[15]

$$CH_3CH = CCH_3 \qquad (9)$$
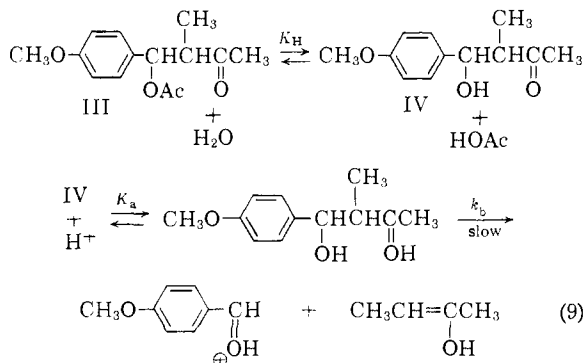
Their calculated values for the relative activity of water in these solutions are shown in the second column of Table II. The activity of water decreases by only a factor of 3.5 on going from 0.2 to

(15) Noyce and Snyder[11b] showed that the rates of esterification and hydrolysis of the β-hydroxyketone IV and its ester III were rapid compared to the cleavage of IV to aldehyde and ketone. As a result the experimental rate constant for cleavage, k_{20}, is given by

$$k_{20} = k_b K_a K_H \frac{a_{H^+} a_{H_2O} f_{III}}{a_{HOAc} f_{*b}} = k^0{}_{20} (a_{H^+} f_{IV}/f_{*b}) \frac{a_{H_2O} f_{III}}{a_{HOAc} f_{IV}}$$

The quantity in parentheses should equal h_0; the ratio of the activity coefficients of the neutral species III and IV should presumably vary little with changing acid concentration; and the activity of acetic acid, the solvent, is naturally nearly constant. Hence to a good approximation

$$\log k_{20} + H_0 = \text{constant} + \log a_{H_2O}$$

From measured k_{20} and H_0 values Noyce and Snyder[11b] calculated relative water activities for solutions 0.53 M in water and 0.2–1.0 M in sulfuric acid.

The possible alternate suggestion that one can take log $a_{H_2O} = H_R - H_0$ seems unworthy of serious consideration; for although H_R differs from H_0 by log a_{H_2O} under certain conditions, as in 85–100% H_2SO_4, this is not generally true,[16] and certainly it has not been demonstrated for the present system.

(16) R. W. Taft, Jr., $J.$ $Am.$ $Chem.$ $Soc.$, 82, 2965 (1960); R. Stewart and T. Mathews, $Can.$ $J.$ $Chem.$, 38, 602 (1960).

1.0 M H_2SO_4, although h_0 changes by a factor of almost 16. Since k_2 increases by a factor of 2.3 over the same range, the change in k_2 is certainly qualitatively comparable to that expected from the change in a_{H_2O} with changing acid concentration.

Whether the results are in good quantitative agreement with the requirements of the mechanism is more difficult to determine with certainty. Equation 8 may be rewritten as

$$\log(k_2 \times a_{H_2O}) = \text{constant} + \log(f^2{}_{ArSO_2H}/f_{\pm r}) \quad (10)$$

Accordingly the mechanism requires that log-$(k_2 a_{H_2O})$ change with changing reaction conditions only insofar as these affect the ratio of activity coefficients in the second term on the right.

Values for a_{H_2O} are available for the 0.53 M H_2O solutions containing 0.2–1.0 M H_2SO_4[11b] and for the solutions of varying water content containing no sulfuric acid.[17] The pertinent data for these two systems are shown in Tables II and III. Unfortunately no measurements of a_{H_2O} are, to our knowledge, available for the solutions of varying water content containing 1 M H_2SO_4.

TABLE II

CORRELATION OF k_2 WITH ESTIMATED a_{H_2O} FOR RUNS AT 0.53 M WATER

(H_2SO_4), M	$a'_{H_2O}{}^a$	$3 + \log (k_2 a'_{H_2O})$
0.20	(1.00)	+0.012
.40	0.70	− .037
.60	.51	− .082
.80	.38	− .109
1.00	.28	− .188

a Activity shown is $a_{H_2O}/a_{H_2O(0.2 M H_2SO_4)}$ as taken from data of ref. 11b.

TABLE III

CORRELATION OF k_2 WITH a_{H_2O} FOR RUNS IN ABSENCE OF SULFURIC ACID

(H_2O), M	$a_{H_2O}{}^a$	$5 + \log (k_2 a_{H_2O})$
0.28	0.040	0.70
.56	.076	.66
.83	.108	.59
.97	.123	.58
1.10	.137	.54

a Based on $a_{H_2O} = 1.00$ for pure water; data of ref. 17.

Table III and Fig. 3 show that $\log(k_2 a_{H_2O})$ decreases slowly with increasing water concentration in a regular manner. To be consistent with the mechanism this requires that $(f^2{}_{ArSO_2H}/f_{*r})$ decrease with increasing water content of the medium. In deciding whether this is reasonable to expect one should note evidence suggesting I must be extremely insoluble in water.[18] Provided then that the transition state for reaction 5 is similar to I in its solubility behavior, a decrease in $(f^2{}_{ArSO_2H}/f_{*r})$ seems reasonable, for certainly the solubility of the sulfinic acid should be decreased much less than that of I by addition of water.

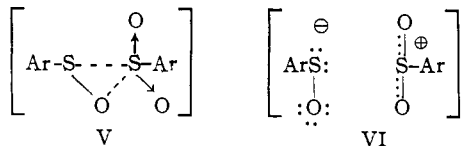(17) R. S. Hansen, F. A. Miller and S. D. Christian, $J.$ $Phys.$ $Chem.$, 59, 391 (1955).

(18) In preparing I both Bredereck[12] and Knoevenagel[13] poured the reaction mixture into water, filtered off the I which precipitated, and then washed it in each case with more water. In view of the very ready hydrolysis of I, it seems unlikely this workup procedure would have succeeded were it not that the sulfinyl sulfone is almost totally insoluble in water.

Furthermore, the magnitude of the change in $(f^2_{ArSO_2H}/f_{*r})$ required is not too large.

Table II and Fig. 2 show that $\log(k_2 a_{H_2O})$ also decreases slowly in a linear manner with increasing sulfuric acid concentration. We have already seen that addition of an inert salt (sodium p-toluenesulfonate) decreases k_2, and to the extent that sulfuric acid is converted in 0.53 M H_2O–acetic acid to the ion pairs ($H_3O^+HSO_4^-$) and ($AcOH_2^+HSO_4^-$) it should influence k_2 similarly. Addition of water to acetic acid apparently decreases log $(f^2_{ArSO_2H}/f_{*r})$, and it seems reasonable that molecular sulfuric acid, also a highly polar, high dielectric solute, might also decrease this activity coefficient ratio. For both these reasons an increase in sulfuric acid concentration should lead to a slow decrease in log $(k_2 a_{H_2O})$ of the sort observed.
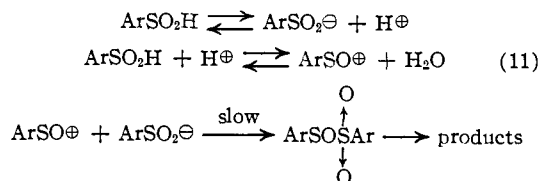
Thus insofar as they can be tested quantitatively the experimental results do not seem inconsistent with the proposed mechanism.

At present we can only speculate about the detailed mechanism of the proposed rearrangement of I to II (eq. 5). However, the apparent behavior of the activity coefficient ratio $(f^2_{ArSO_2H}/f_{*r})$ suggests the transition state does not have any considerable degree of ion pair character, and for this reason a process involving concomitant formation of the new S–O bond and cleavage of the S–S bond, as in V, seems preferable to an ionization–recombination mechanism involving intermediates such as VI. An intermediate such as V is perhaps rendered more plausible by the known ability of sulfur to expand its valence shell.

$$\left[\begin{array}{c} O \\ \uparrow \\ Ar-S- - - S-Ar \\ \diagdown O \diagup \diagdown O \end{array} \right] \quad \left[\begin{array}{cc} \ominus & O \\ \ddot{Ar}\ddot{S}: & \overset{\ddot{..}}{\overset{\oplus}{S}}-Ar \\ :\ddot{O}: & O \end{array} \right]$$

$$V \qquad\qquad VI$$

The individual steps in the initial equilibrium between $ArSO_2H$ and I (eq. 4) can be formulated as originally suggested by Bredereck, et al.[6]; or other alternative sequences can be proposed. However, as long as the hydrolysis of I is much faster than its rearrangement to II only the over-all equilibrium represented by eq. 4 will be of kinetic consequence.

Although we prefer the mechanism represented by eq. 4 and 5, we should re-emphasize that alternatives such as eq. 11 could perhaps lead to a similar dependence on the various reaction variables.

$$ArSO_2H \rightleftarrows ArSO_2^\ominus + H^\oplus$$

$$ArSO_2H + H^\oplus \rightleftarrows ArSO^\oplus + H_2O \qquad (11)$$

$$ArSO^\oplus + ArSO_2^\ominus \xrightarrow{\text{slow}} Ar\overset{O}{\overset{\uparrow}{S}}OSAr \xrightarrow{} \text{products}$$

Our reasons for preferring 4 and 5 to 11 are outlined in a footnote below.[19]

(19) First, one would expect the concentration of $ArSO_2^-$ to be very small in these rather acid solutions, so that a reaction of this type with $ArSO^+$ would be much more likely to involve $ArSO_2H$; yet, any rate-determining reaction between $ArSO^+$ and $ArSO_2H$ is ruled out by the absence of any pronounced effect of strong acid on the rate. Second, even if $ArSO_2^-$ were sufficiently more reactive toward $ArSO^+$ to
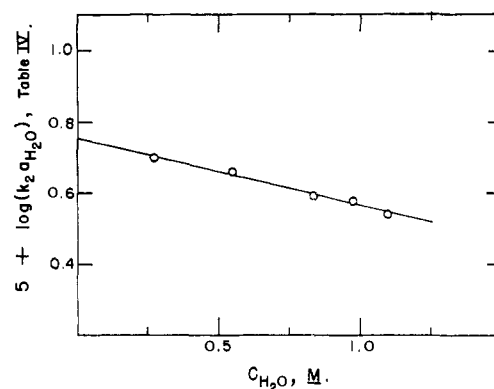

Fig. 3.—Correlation of rate with water concentration. Plot of log $(k_2 a_{H_2O})$ values from Table III for runs at 0.0 M H_2SO_4 vs. stoichiometric concentration of water.

Finally we would point out that an entirely different mechanism may be operative in aqueous solution where the rate of the present mechanism would be very slow due to the high concentration of water. For this reason, and also because Allen and Reich[7] actually studied the much more rapid iodide-ion catalyzed conversion of sulfinic acid to thiolsulfonate, we shall not attempt to compare critically our results with theirs. However, we would note that their contention that the sole function of iodide ion is to catalyze attainment of

the equilibrium $Ar\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}OH \rightleftarrows Ar\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}H$ seems rather

unlikely, and their postulate of two different sulfinate anions, $Ar\overset{O}{\overset{\|}{S}}O^-$ and $Ar\overset{O}{\overset{\|}{\underset{\|}{S}}}:^-$, one in equilibrium

only with $Ar\overset{..}{\underset{O}{\overset{}{\underset{\|}{S}}}OH$, the other only with $Ar\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}H$, is

clearly in error.

Experimental

p-Toluenesulfinic Acid.—Sodium p-toluenesulfinate was prepared by the usual method,[20] recrystallized from water twice, and stored in this form. The free acid was prepared from the salt as follows: The sodium salt was dissolved in water, the solution filtered and then acidified with 6 N hydrochloric acid. The precipitated sulfinic acid was dried under vaccum. It was then twice recrystallized by dissolving it in the minimum amount of ether and then adding an equal volume of hexane, the acid crystallizing out in long needles. After vacuum drying the pure sulfinic acid, m.p. 85°, was stored in a desiccator at −20° in the dark until used, but never was any sample kept longer than one week.

monopolize capture of this intermediate, it seems far more probable that the product of this reaction would be I rather than II. Third, it seems unlikely the transition state for the $ArSO^+$–$ArSO_2^-$ reaction would show a variation of activity coefficient with reaction conditions consistent with that required by the experimental data.

(20) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941; p. 492.

Gravimetric analysis as its ferric salt[21] showed it to be of at least 99.9% purity.

p-Toluenesulfinyl p-Tolyl Sulfone (I).—The procedure was a modification of that of Bredereck, et al.[12] The entire preparation and purification of the sulfinyl sulfone was carried out in a glove-box in an anhydrous nitrogen atmosphere. Anhydrous sodium p-toluenesulfinate (1.0 g.), prepared by heating the dihydrate at 185° and 0.1 mm. for 5 hr., was dispersed in 20 ml. of anhydrous ether. To this suspension p-toluenesulfinyl chloride[22] was added dropwise with vigorous shaking until the yellow color of the sulfinyl chloride persisted. After a short time the ether was decanted, and the residual solid was washed several times with anhydrous ether. The solid was then treated with dry benzene to dissolve the sulfinyl sulfone. The benzene solution was filtered, and the solvent was removed under reduced pressure at room temperature. The crystalline product was washed several times with ether, and dried under vacuum at room temperature; m.p. 76° (lit.[13] 75°; Bredereck,[12] on the other hand, reports a m.p. of 87° but says his product is identical by infrared with the compound of m.p. 75° prepared by Knoevenagel and Pollack.[13]

The sulfinyl sulfone reacted quantitatively in acetone or acetic acid with two equivalents of iodide. For determination of its purity, compound I ($\sim$ 0.1 g.) was treated with a solution of excess sodium iodide in reagent grade acetone. The flask was warmed gently until all the sulfinyl sulfone dissolved. The liberated iodine was then determined by diluting the solution with an equal volume of water and titrating with 0.1 N thiosulfate. The reaction of iodide with I is apparently faster than the hydrolysis of I to sulfinic acid, since when the above procedure was applied using acetic acid–0.56 M H$_2$O as the solvent rather than acetone, 92% of the expected amount of iodine was liberated. Control experiments showed that under these conditions none of the other substances involved in the disproportionation—thiolsulfonate, sulfinic and sulfonic acids—liberate iodine from sodium iodide.

Solvents and Standard Solutions.—Reagent grade acetic acid was refluxed with acetic anhydride for 24 hr. followed by distillation through a 4-ft. glass helices-packed column using a reflux ratio of 100:1. A large middle fraction was collected and redistilled under the same conditions; freezing point of the purified acid was 16.67°. Water content, as determined by titration with Karl Fischer reagent,[23] was less than 0.01%. Reagent grade concentrated sulfuric acid was dissolved in the purified acetic acid, sufficient acetic anhydride added to take up most of the water, and the solution made up to a volume such that the final sulfuric acid concentration was 5 M. This stock solution was used as the source of sulfuric acid for the kinetic runs. Its residual

water content, determined by titration with Karl Fischer reagent,[23] was taken into account in the preparation of solutions for kinetic runs.

Stoichiometry of the Disproportionation Reaction.—The yield of thiolsulfonate was compared with that expected from the stoichiometry of reaction 1 as follows: An aliquot was removed from the solution and titrated for remaining sulfinic acid by the nitrite titration described in Procedure for Kinetic Runs. Another aliquot was then removed, thrown into ten times its volume of water, and the resulting mixture extracted several times with ether. The combined ether extracts were washed with aqueous bicarbonate until neutral, dried, and the ether removed under reduced pressure. The last traces of solvent and any tolyl disulfide (from hydrolysis of the thiolsulfonate) were removed by prolonged high vacuum drying at room temperature. The residue was quite pure p-tolyl p-toluenethiolsulfonate, m.p. 76° (lit.[24] 76°) and infrared spectrum identical with a known sample. The yield of thiolsulfonate was determined simply by weighing this residue.

Procedure for Kinetic Runs.—Solutions for kinetic runs were prepared as follows. An exact amount of p-toluenesulfinic acid was weighed into a 100-ml. volumetric flask, the required amount of water was added from a microburet, and about 30 ml. of acetic acid was added. The required amount of sulfuric acid (as a 5 M solution in acetic acid) was then added, and the solution was made up to volume with acetic acid. The solution was then placed in the reaction vessel—a 125-ml. flask equipped with a nitrogen inlet, a spiral condenser connected by capillary tubing to a mineral oil trap which prevented back diffusion of air into the system, and a series of tubes and stopcocks which made it possible to use nitrogen pressure to remove a sample from the flask without opening it to the atmosphere. Before starting a run air was removed from the system by slowly bubbling prepurified nitrogen through the solution. Once the solution was deaerated, the nitrogen flow was stopped, except when removing samples from the reaction vessel, and the flask was immersed in a constant temperature bath kept at 70 ± 0.02°. Samples (5 ml.) were withdrawn from time to time, and the reaction was quenched by the addition of an equal volume of cold water. The solution was then titrated with 0.2 N sodium nitrite solution using a 5-ml. microburet with the tip held below the surface of the liquid. The solution was stirred throughout with a Teflon-covered magnetic stirring bar. After each addition of nitrite solution (0.01 to 0.05 ml.) a small drop of the solution was touched to a strip of potassium iodide–starch paper. The end-point is reached when a faint pink color is developed. The indicator blank using this procedure was less than 0.01 ml. Trials with known samples of sulfinic acid showed the method gave accurate results and that the other substances present did not interfere. The method is adapted from that mentioned by Marvel and Johnson.[9] The reaction of nitrite with sulfinic acids in acid solution leads to the formation of the insoluble hydroxylamine, $(ArSO_2)_2NOH$.

(21) J. Mitchell, I. M. Kolthoff, E. S. Proskauer and A. Weissberger, "Organic Analysis," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1953, p. 378.

(22) Org. Syntheses, 34, 93 (1954).

(23) J. Mitchell and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948, pp. 105 ff.

(24) R. Otto, J. Lowenthal and A. v. Gruber, Ann., 149, 101 (1869).

Bicyclic Phosphites[1]

BY WILLIAM S. WADSWORTH, JR., AND WILLIAM D. EMMONS

The bicyclic phosphites 1-alkyl-4-phospha-3,5,8-trioxabicyclo[2.2.2]octanes (I) represent a new class of organophosphorus compounds. They may be prepared easily in high yields and have a number of unique properties as a result of their bridged structure. Notable in this respect is the fact that they undergo a stereospecific Arbuzov reaction.

No thorough study of the preparation of phosphites containing a bridged structure, I, has been reported. Recently Verkade and Reynolds[2] prepared a bicyclic phosphite (I, R = CH₃) in 40%

yield by treating trimethylolethane with phosphorus trichloride under conditions of high dilution and by using pyridine as an acid-binding agent. Barnes and Hoffman[3] have prepared the same phosphite in 50–55% yield by heating the triol and phosphorus trichloride in the absence of a sol-

(1) Presented at the 137th Meeting of A.C.S., New York, N. Y., September, 1960.

(2) J. G. Verkade and L. T. Reynolds, J. Org. Chem., 25, 663 (1960).

(3) R. A. Barnes, private communication.