used without further purification. The n-butyl sulfide was fractionally distilled before use.

Procedure for Measurement of Exchange Rates. Standard solutions of perchloric acid, the catalyzing nucleophile, and lithium perchlorate in 60% dioxane (v/v) were prepared as described in the accompanying paper.[15] To initiate a run a weighed amount of **1**-^{18}O was dissolved in 60% dioxane, the proper amounts of the various stock solutions were added, and the solution was made up to volume with additional 60% dioxane. The final solution was then transferred to a reaction vessel of a type described previously[23] and the solution was deaerated by passing prepurified nitrogen through it for 5 min. Solutions were kept under nitrogen during the course of the exchange.

At appropriate times aliquots of the reaction solution were removed and the aliquot was added to a large volume of water. The resulting mixture was extracted several times with portions of chloroform. The combined chloroform extracts were washed with water and dried over magnesium sulfate, and the solvent was removed under reduced pressure.

The thiolsulfinate was then separated in a pure state from the residue by means of preparative thin-layer chromatography on silica gel (1 mm thickness, 1% acetic acid in benzene as solvent). Clean separations were achieved in all cases with the disulfide showing the largest and the thiolsulfinate the smallest R_f value. After development of the tlc plate was complete and the developing solvent had been allowed to evaporate, the thiolsulfinate was removed from the plate using dry ether. The ether was removed under reduced pressure and the thiolsulfinate residue was recrystallized from warm hexane to which just enough chloroform had been added to effect solution of the thiolsulfinate. The use of this isolation and work-up procedure on a sample of ^{18}O-labeled **1**, which had not been subjected to exchange, led to no detectable loss of ^{18}O label, provided that care was taken to use scrupulously dry ether for the removal of the chromatographed thiolsulfinate from the tlc plate.

The oxygen-18 content of the thiolsulfinate samples was determined by using the Doering and Dorfman[24] procedure. The ratio of mass 46:44 in the samples of CO_2 resulting from the pyrolyses was measured using an Atlas CH-7 mass spectrometer. The atom percentage of oxygen-18 in the thiolsulfinate, P, was then calculated using the equation given by Doering and Dorfman[24]

$$P = \frac{0.00408R - 0.00204}{0.9959 + 0.00408R} \times 10^2$$

where

$$R = (I_{46}/I_{44})/(I^0{}_{46}/I^0{}_{44})$$

and I^0 represents the intensity of a particular mass peak in a sample of standard (or tank) carbon dioxide and I represents the intensity of the same mass peak in the sample of carbon dioxide from the pyrolysis of the thiolsulfinate.

The rate of the exchange reaction (eq 5) was then determined by plotting log $(P - P_\infty)/(P_0 - P_\infty)$ *vs.* time, where P_0 = atom % oxygen-18 in the starting thiolsulfinate and P_∞ that which would be present after exchange was complete. Since there is from 400 to 1600 times more water than **1**-^{18}O present, depending on the initial thiolsulfinate concentration, P_∞ was taken in all runs as being equal to 0.204, the natural abundance of oxygen-18.

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

[24] W. von E. Doering and E. Dorfman, *ibid.*, **75**, 5595 (1953).

The Nucleophile- and Acid-Catalyzed Disproportionation of Phenyl Benzenethiolsulfinate in Aqueous Dioxane. Confirmation of a Previously Suggested Mechanism for the Disproportionation[1a]

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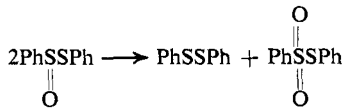
Received June 23, 1972

Abstract: In 60% dioxane the acid- and nucleophile-catalyzed disproportionation of phenyl benzenethiolsulfinate exhibits a three-halves-order dependence on thiolsulfinate concentration, in contrast to the first-order dependence on thiolsulfinate observed in acetic acid–1% water. In both media the reaction is first order in both acid and catalyzing nucleophile. It is shown that this is exactly the change in kinetics that would be expected for the mechanism shown in Chart I upon transfer of the reaction from a medium of very low water content to one of much higher water content. The results therefore constitute important evidence for the probable correctness of this mechanism.

One of the important reactions of thiolsulfinates (sulfenic anhydrides) is their disproportionation into thiolsulfonates and disulfides (eq 1).[2] It has been found[3] that in acetic acid–1% water as solvent the disproportionation can be dramatically accelerated *via*



$$2\mathrm{Ph}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{SPh} \longrightarrow \mathrm{PhSSPh} + \mathrm{Ph}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{SPh} \qquad (1)$$

catalysis by added strong acid and nucleophiles. Kinetic study of this acid- and nucleophile-catalyzed disproportionation showed that in AcOH–1% H_2O the reaction was first order in both thiolsulfinate and nucleophile and had the same dependence of rate on acidity as other[4] acid- and nucleophile-catalyzed reactions of thiolsulfinates, but exhibited a significantly

[1] (a) This research was supported by the National Science Foundation, Grant GP-10732X; (b) to whom correspondence should be addressed: Department of Chemistry, University of Vermont, Burlington, Vt. 05401; (c) National Institutes of Health Postdoctoral Fellow, 1969–1970.

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

[3] J. L. Kice, C. G. Venier, G. B. Large, and L. Heasley, *J. Amer. Chem. Soc.*, **91**, 2028 (1969).

[4] (a) J. L. Kice, C. G. Venier, and L. Heasley, *ibid.*, **89**, 3557 (1967); (b) J. L. Kice and G. B. Large, *J. Org. Chem.*, **33**, 1940 (1968).

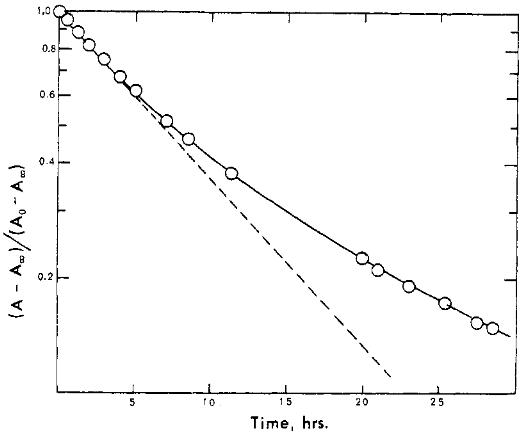
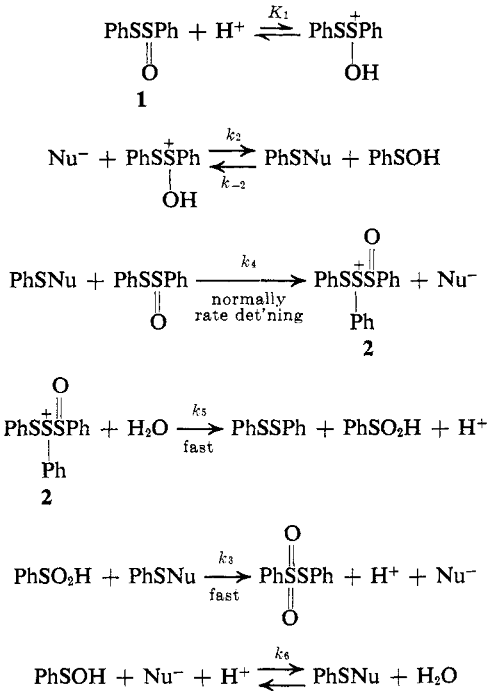


Figure 1. Plot of log $(A - A_\infty)/(A_0 - A_\infty)$ *vs.* time for an acid- and nucleophile-catalyzed disproportionation of **1** in 60% dioxane: **1**, 0.0147 *M*; *n*-Bu_2S, 0.02 *M*; $HClO_4$, 0.10 *M*; $LiClO_4$, 0.40 *M*; temperature, 39.6°.

different dependence of rate on nucleophile structure than did these other reactions. After consideration of all the evidence the final conclusion was that the most probable mechanism for the acid- and nucleophile-catalyzed disproportionation was the one shown in Chart I, despite the fact that at first sight it would appear that with k_4 rate determining one would get a higher than first-order dependence of rate on thiolsulfinate concentration. However, a detailed kinetic analysis of the scheme in Chart I showed[3] that provided $k_{-6}[H_2O] \ll k_4[PhSOSPh]$ the kinetics of the reaction will, surprisingly, be first order in thiolsulfinate, and a number of arguments were advanced[3]—very low concentration of water in AcOH–1% H_2O, preference of PhSNu for reaction with "soft" rather than "hard" nucleophiles[5]—to support the idea that it was not unreasonable to expect $k_{-6}[H_2O] \ll k_4[PhSOSPh]$ under these particular reaction conditions.

Chart I. Proposed Mechanism for the Acid- and Nucleophile-Catalyzed Disproportionation of Phenyl Benzenethiolsulfinate



$$\underset{\mathbf{1}}{\mathrm{PhS(O)SPh}} + \mathrm{H^+} \overset{K_1}{\rightleftharpoons} \mathrm{Ph}\overset{+}{\mathrm{S}}\mathrm{(OH)SPh}$$

$$\mathrm{Nu^-} + \mathrm{Ph}\overset{+}{\mathrm{S}}\mathrm{(OH)SPh} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{PhSNu + PhSOH}$$

$$\mathrm{PhSNu + PhS(O)SPh} \xrightarrow[\text{normally rate det'ning}]{k_4} \underset{\mathbf{2}}{\mathrm{PhS}\overset{+}{\mathrm{S}}\mathrm{(Ph)S(O)Ph}} + \mathrm{Nu^-}$$

$$\underset{\mathbf{2}}{\mathrm{PhS}\overset{+}{\mathrm{S}}\mathrm{(Ph)S(O)Ph}} + \mathrm{H_2O} \xrightarrow[\text{fast}]{k_5} \mathrm{PhSSPh + PhSO_2H + H^+}$$

$$\mathrm{PhSO_2H + PhSNu} \xrightarrow[\text{fast}]{k_3} \mathrm{PhS(O_2)SPh + H^+ + Nu^-}$$

$$\mathrm{PhSOH + Nu^- + H^+} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} \mathrm{PhSNu + H_2O}$$

In the event that $k_{-6}[H_2O] > k_4[PhSOSPh]$ the mechanism in Chart I leads (see Discussion for derivation) to the kinetics for the disproportionation being greater than first order in thiolsulfinate. If the mechanism in Chart I is in fact correct, one would therefore expect that going from acetic acid–1% water to a highly aqueous medium where the concentration of water is much greater might lead to a significant change in the kinetics observed for the acid- and nucleophile-catalyzed disproportionation. Should such a change be observed and should it be in accord with the kinetics predicted for the situation where $k_{-6}[H_2O] > k_4[PhSOSPh]$, this would constitute strong additional evidence that the mechanism in Chart I is the correct one.

In connection with a study of the acid- and nucleophile-catalyzed exchange of the oxygen-18 of PhS(^{18}O)SPh described in an accompanying paper it was necessary to determine the rate of acid- and nucleophile-catalyzed disproportionation of phenyl benzenethiolsulfinate in 60% aqueous dioxane. These kinetic studies, which form the subject of this paper, show that the kinetics of the disproportionation are indeed different in aqueous dioxane than they are in acetic acid–1% water, and since the change in the kinetics is the one expected for a change from a situation where $k_{-6}[H_2O] \ll k_4[PhSOSPh]$ to one where $k_{-6}[H_2O] > k_4[PhSOSPh]$, they provide confirmation for the validity of the mechanism shown in Chart I.

Results

In 60% dioxane (v/v) the course of the disproportionation (eq 1) can be followed kinetically by monitoring the change in absorbance at 296 nm in the same general manner as for runs in acetic acid.[3]

All of the runs in the present study were carried out at 39.6°. In the absence of added acid and nucleophile the rate of disappearance of the thiolsulfinate under these conditions is so slow that it can be neglected. The runs were carried out using perchloric acid (0.10–0.50 *M*) as the acid catalyst and with either chloride ion, bromide ion, or *n*-butyl sulfide as the nucleophilic catalyst.

Figure 1 shows the data for a typical *n*-butyl sulfide catalyzed run plotted assuming that the disappearance of the thiolsulfinate follows first-order kinetics. Such a plot is clearly not linear, and the curvature is in such a direction as to indicate that the dependence of rate on thiolsulfinate concentration is higher than first order. Figure 2 shows a plot of the data for the same run assuming that the disappearance of the thiolsulfinate depends on the three-halves-power of thiolsulfinate concentration. This plot is nicely linear, and since the data points extend to almost 90% reaction, it definitely appears that under these conditions the rate of the disproportionation is proportional to $[PhSOSPh]^{3/2}$. All of the other runs with *n*-butyl sulfide, as well as the runs with chloride or bromide ions as nucleophilic catalyst, also gave linear plots of $(A - A_\infty)^{-1/2}$, so that the three-halves-order dependence on thiolsulfinate concentration appears to be quite general for the acid- and nucleophile-catalyzed disproportionation in aqueous dioxane.

Table I summarizes the kinetic data obtained for the

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[5] J. L. Kice and G. B. Large, *J. Amer. Chem. Soc.*, **90**, 4069 (1968).

Table I. Kinetics of the Acid- and Nucleophile-Catalyzed Disproportionation of Phenyl Benzenethiolsulfinate in 60% Dioxane[a]

Nucleophilic catalyst	$[HClO_4]$, M	$[Nu^-]$, M	$10^3[\mathbf{1}]_0$, M	$10^3k_{3/2}$, $M^{-1/2}$ sec^{-1}	$k_d = [k_{3/2}/([H^+][Nu^-])] \times 10^2$
n-Bu_2S	0.50	0.02	8.2	1.35	13.5
		0.01	8.2	0.65	13.0
	0.10	0.02	14.7	0.26	13.0
Br^-	0.20	0.30	3.9	1.48	2.5
			8.0	1.50	2.5
	0.10	0.30	3.8	0.75	2.5
			8.4	0.69	2.3
Cl^-	0.40	0.10	8.4	0.25	0.63
			14.6	0.25	0.63

[a] All runs at 39.6° with the ionic strength held constant at 0.50 by addition of lithium perchlorate as needed.

various catalysts and reaction conditions investigated; the values of $k_{3/2}$ in each case are the experimental rate constants as measured from the slope of a plot of $(A - A_\infty)^{-1/2}$ *vs.* time of the type shown in Figure 2. One notes that for given concentrations of nucleophile and perchloric acid there is no variation in $k_{3/2}$ with variation in initial thiolsulfinate concentration. This fact also demonstrates that in 60% dioxane the acid- and nucleophile-catalyzed disproportionation shows a three-halves-order dependence on thiolsulfinate concentration.

The last column in Table I lists values of k_d; these are equal in each case to $k_{3/2}/[H^+][Nu^-]$ for that run. For each particular nucleophile the value of k_d appears not to be influenced by changes in $[H^+]$ or $[Nu^-]$. This indicates that the acid- and nucleophile-catalyzed disproportionation is first order in both acid and nucleophile in aqueous dioxane. This is the same dependence on acidity and nucleophile concentration observed for the acid- and nucleophile-catalyzed racemization of (+)-PhS(O)SPh in this same medium.[5]

Discussion

We have just seen that in aqueous dioxane the acid- and nucleophile-catalyzed disproportionation of phenyl benzenethiolsulfinate shows a three-halves-order dependence of rate on thiolsulfinate concentration and a first-order dependence on both acid and nucleophile concentration. The key question now is whether these are the kinetics that would be expected for the mechanism shown in Chart I in a situation where $k_{-6}[H_2O] > k_4[PhSOSPh]$.

Using the mechanism in Chart I and assuming that under our reaction conditions the steady-state hypothesis is applicable to the concentrations of **2**, PhSNu, PhSOH, and $PhSO_2H$, one gets

$$[\mathbf{2}] = k_4[PhSNu][\mathbf{1}]/k_5[H_2O]$$

$$[PhSO_2H] = (k_4/k_3)[\mathbf{1}]$$

$$[PhSNu] = \frac{K_1k_2a_{H^+}[Nu^-][\mathbf{1}] + k_6a_{H^+}[Nu^-][PhSOH]}{k_{-2}[PhSOH] + 2k_4[\mathbf{1}] + k_{-6}[H_2O]}$$

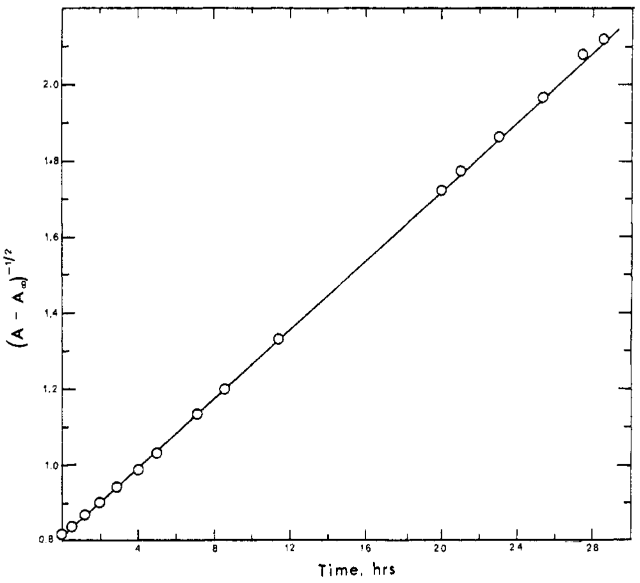

Figure 2. Plot of $1/(A - A_\infty)^{1/2}$ *vs.* time for the same acid- and nucleophile-catalyzed disproportionation of **1** as in Figure 1.

$$[PhSOH] = \frac{K_1k_2a_{H^+}[Nu^-][\mathbf{1}] + k_{-6}[PhSNu][H_2O]}{k_{-2}[PhSNu] + k_6a_{H^+}[Nu^-]}$$

If one substitutes the expression for [PhSNu] into the one for [PhSOH], one obtains

$$[PhSOH] = \frac{k_4[\mathbf{1}]}{2k_{-2}}\left\{\left[1 + \frac{4K_1k_2k_{-2}}{k_6k_4}\left(1 + \frac{k_{-6}[H_2O]}{k_4[\mathbf{1}]}\right)\right]^{1/2} - 1\right\} \quad (2)$$

The rate of disproportionation is given by

$$-d[\mathbf{1}]/dt = K_1k_2a_{H^+}[Nu^-][\mathbf{1}] + k_4[\mathbf{1}][PhSNu] - k_{-2}[PhSNu][PhSOH]$$

On substituting into this the expression for [PhSNu] given above, this becomes

$$-d[\mathbf{1}]/dt = a_{H^+}[Nu^-]\left\{\frac{3K_1k_2k_4[\mathbf{1}]^2 + K_1k_2k_6[\mathbf{1}][H_2O] + k_4k_6[\mathbf{1}][PhSOH] - k_{-2}k_6[PhSOH]^2}{k_{-2}[PhSOH] + 2k_4[\mathbf{1}] + k_{-6}[H_2O]}\right\}$$

Upon substitution into this of the expression for [PhSOH] given in eq 2 and collection of like terms, this can be expressed as shown in eq 3.

The previous study[3] of the acid- and sulfide-catalyzed disproportionation of **1** in acetic acid–1% water strongly indicated that for n-Bu_2S as the nucleophilic catalyst $k_{-2}k_2K_1/k_6k_4$ was very large. For situations involving this catalyst where $k_{-6}[H_2O]$ becomes significantly larger than $k_4[\mathbf{1}]$ this means that

$$\left[1 + \frac{4K_1k_2k_{-2}}{k_6k_4}\left(1 + \frac{k_{-6}[H_2O]}{k_4[\mathbf{1}]}\right)\right]^{1/2} \cong \left(\frac{4K_1k_2k_{-2}k_{-6}[H_2O]}{k_6k_4^2[\mathbf{1}]}\right)^{1/2}$$

$$-d[\mathbf{1}]/dt = 2k_4a_{H^+}[Nu^-][\mathbf{1}]^{3/2}\left[\frac{2K_1k_2[\mathbf{1}]^{1/2} + \left(\frac{k_4k_6}{k_{-2}}\right)[\mathbf{1}]^{1/2}\left\{\left[1 + \frac{4K_1k_2k_{-2}}{k_6k_4}\left(1 + \frac{k_{-6}[H_2O]}{k_4[\mathbf{1}]}\right)\right]^{1/2} - 1\right\}}{k_4[\mathbf{1}]\left\{\left[1 + \frac{4K_1k_2k_{-2}}{k_6k_4}\left(1 + \frac{k_{-6}[H_2O]}{k_4[\mathbf{1}]}\right)\right]^{1/2} + 3\right\} + 2k_{-6}[H_2O]}\right] \quad (3)$$

and it also suggests that $(4K_1k_2k_{-2}k_{-6}[\mathrm{H_2O}]/k_6k_4{}^2[\mathbf{1}])^{1/2}$ itself is almost certainly considerably larger than one so that to a good approximation under such conditions

$$-\mathrm{d}[\mathbf{1}]/\mathrm{d}t = 2k_4a_{\mathrm{H^+}}[\mathrm{Nu^-}][\mathbf{1}]^{3/2} \times \left[\frac{K_1k_2[\mathbf{1}]^{1/2} + \left(\dfrac{K_1k_2k_6k_{-6}[\mathrm{H_2O}]}{k_{-2}}\right)^{1/2}}{\left(\dfrac{K_1k_2k_{-2}k_{-6}[\mathrm{H_2O}]}{k_6}\right)^{1/2}(\mathbf{1})^{1/2} + k_{-6}[\mathrm{H_2O}]}\right]$$

Suitable factoring operations reduce this expression to eq 4. Equation 4 has exactly the kinetic form that we

$$-\mathrm{d}[\mathbf{1}]/\mathrm{d}t = 2k_4\left(\frac{K_1k_2k_6}{k_{-2}k_{-6}[\mathrm{H_2O}]}\right)^{1/2} a_{\mathrm{H^+}}[\mathrm{Nu^-}][\mathbf{1}]^{3/2} \quad (4)$$

have observed for the *n*-Bu_2S catalyzed disproportionation in 60% dioxane, namely, a first-order dependence on both acid and catalyzing nucleophile and a three-halves-order dependence on thiolsulfinate concentration. Thus the kinetics found for the *n*-Bu_2S catalyzed disproportionation in 60% dioxane are those that would be expected for the mechanism in Chart I in the situation where $k_{-6}[\mathrm{H_2O}] > k_4[\mathrm{PhSOSPh}]$ just as the different kinetics previously observed[3] for this reaction in acetic acid–1% water were those expected for Chart I in the alternate situation where $k_{-6}[\mathrm{H_2O}] \ll k_4[\mathrm{PhSOSPh}]$. The change in the kinetic dependence on thiolsulfinate with increasing water content of the medium for the *n*-Bu_2S catalyzed disproportionation therefore provides a significant further indication that the mechanism for this reaction is indeed the one shown in Chart I ($\mathrm{Nu^-}$ = *n*-Bu_2S).

Because, unlike the situation for *n*-Bu_2S, we have no independent measurement for either $\mathrm{Cl^-}$ or $\mathrm{Br^-}$ as catalysts of $k_{-2}k_2K_1/k_6k_4$ for these systems, we cannot really say that the fact that the kinetics of both the chloride and bromide catalyzed disproportionations also follow eq 4 in 60% dioxane constitutes proof that these reactions also follow the mechanism in Chart I with $k_{-6}[\mathrm{H_2O}] > k_4[\mathrm{PhSOSPh}]$. However, since it seems rather unlikely that eq 3 would reduce to a clean three-halves-order dependence on [**1**] except when $(K_1k_2k_{-2}/k_4k_6) \gg 1$ and $k_{-6}[\mathrm{H_2O}] > k_4[\mathbf{1}]$, we think it likely that $K_1k_2k_{-2}/k_4k_6$ for these systems is also large and that the mechanism involved is that in Chart I with $\mathrm{Nu^-}$ equal to either $\mathrm{Cl^-}$ or $\mathrm{Br^-}$, as appropriate.

One can obtain independent evidence that $k_6[\mathrm{H_2O}] > k_4[\mathbf{1}]$ under our conditions in the following way. In an accompanying paper[6] we show that k_{exch}, the rate constant for the acid- and nucleophile-catalyzed exchange of oxygen-18 in $\mathrm{PhS(O^{18})SPh}$ under the same conditions, is given by

$$k_{\mathrm{exch}} = \frac{k_2K_1a_{\mathrm{H^+}}[\mathrm{Nu^-}]}{1 + (k_2K_1k_{-2}[\mathbf{1}]/k_6k_{-6}[\mathrm{H_2O}])^{1/2}}$$

From eq 4 $k_{3/2}$ in Table I is seen to be

$$k_{3/2} = 2k_4(K_1k_2k_6/k_{-2}k_{-6}[\mathrm{H_2O}])^{1/2}a_{\mathrm{H^+}}[\mathrm{Nu^-}]$$

Suitable manipulation of these two expressions yields

$$\frac{k_{-6}[\mathrm{H_2O}]}{k_4[\mathbf{1}]} = \frac{2k_{\mathrm{exch}}}{k_{3/2}[\mathbf{1}]^{1/2}}\left\{\frac{1}{1 - (k_{\mathrm{exch}}/k_\alpha)}\right\} \quad (5)$$

where k_α is the rate of acid- and nucleophile-catalyzed racemization[5] of (+)-PhS(O)SPh under the conditions. Substitution of values of k_{exch}, $k_{3/2}$, and k_α into eq 5 reveals that for the *n*-Bu_2S catalyzed reaction even at the highest thiolsulfinate concentration used in Table I $k_{-6}[\mathrm{H_2O}]/k_4[\mathbf{1}]$ is 20, while for the analogous situation for the $\mathrm{Cl^-}$ or $\mathrm{Br^-}$ catalyzed runs it is in each case at least 10, so that clearly for all the runs in Table I it is reasonable to assume that $k_{-6}[\mathrm{H_2O}] > k_4[\mathbf{1}]$.

Experimental Section

Preparation and Purification of Materials. Phenyl benzenethiolsulfinate (**1**) was prepared and purified as previously described.[4a] Dioxane was purified by the method described by Wiberg[7] and was freshly distilled from the sodium ketyl of benzophenone[7] as needed. *n*-Butyl sulfide was purified by fractional distillation before use.[4a] Anhydrous reagent grade lithium perchlorate, sodium bromide, and sodium chloride were used without further purification.

Procedure for Kinetic Runs. Standard solutions of perchloric acid, the catalyzing nucleophile, and lithium perchlorate in 60% dioxane (v/v)[8] were prepared. To initiate a run a weighed quantity of **1** was dissolved in 60% dioxane, the proper amounts of the various stock solutions were added, and the solution was made up to volume with additional 60% dioxane. The final solution was then transferred to a reaction vessel of a type described previously[9] and the solution was deaerated by passing prepurified nitrogen through the solution for 5 min. Solutions were normally kept under nitrogen throughout the reaction although independent experiments indicated that air apparently had no effect upon the rate of disproportionation. The rate was then followed at 39.6° by removing 1-ml aliquots of the reaction solution, diluting these to either 25 or 50 ml with 95% ethanol and immediately determining the absorbance of the solution at 296 nm. Measured A_∞ values in every case corresponded well with those expected for the stoichiometry shown in eq 1, *i.e.*, 2 mol of **1** yield 1 mol of PhSSPh and 1 mol of $\mathrm{PhSO_2SPh}$.

Plots of $1/(A - A_\infty)^{1/2}$ *vs.* time were always linear while those of log $(A - A_\infty)$ were always noticeably curved. The value of $k_{3/2}$, the experimental three-halves-order rate constant for a run, was obtained from the slope of the plot of $1/(A - A_\infty)^{1/2}$ *vs.* time using the following relationship

$$k_{3/2} = \frac{2 \times \mathrm{slope}(\epsilon_1 - \epsilon_{\mathrm{products}})^{1/2}}{F^{1/2}}$$

where $\epsilon_{\mathrm{products}} = {}^1/_2(\epsilon_{\mathrm{PhSSPh}} + \epsilon_{\mathrm{PhSO_2SPh}})$ at 296 nm and F was the dilution factor (either 1:25 or 1:50) used in diluting the aliquots in that particular run with 95% ethanol prior to determining the absorbance.

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(6) J. L. Kice and J. P. Cleveland, *J. Amer. Chem. Soc.* **95**, 104 (1973).

(7) K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill, New York, N. Y., 1960, p 245.

(8) The per cent dioxane was calculated after the fashion of Bunton, *et al.*, *J. Chem. Soc.*, 2327 (1957).

(9) J. L. Kice and K. W. Bowers, *J. Amer. Chem. Soc.*, **84**, 605 (1962).