program, the amount of **2a** remaining as a function of time. The results indicated that there is enough **2a** left when the maximum in the $A - A_0$ plot is reached for the steady state assumption regarding the concentrations of $PhSO^-$ and PhS^- to still be valid at that point.

To determine the expected behavior of the concentration of **1a** with time during the initial stage of its alkaline hydrolysis a Runge-Kutta program[12] was constructed for a Xerox Sigma 6 computer which would provide a simultaneous solution of the kinetic differential equations corresponding to the reaction scheme represented by eq 7-9. The computer output was displayed graphically on a Tektonix 4013 terminal and directly compared to experimental data which had been plotted on a transparent plastic sheet. Particular attention was focused on the change in the shape of the curves representing $[\mathbf{1a}]/[\mathbf{1a}]_0$ for different reaction conditions with fairly marked changes in k_7 and k_8. Fortunately, as one can see from Figure 6, the same values of k_7 and k_8 which can provide the excellent fit for the initial stage of the hydrolysis of **2a** shown in Figure 5 also appear to be consistent with the experimentally observed data for the hydrolysis of **1a.**

Detection of 1b as an Intermediate in the Hydrolysis of 2b *via* a Product Study. To 2.01 g (7.2 mmol) of *p*-tolyl *p*-toluenethiolsulfonate (**2b**) in 200 ml of 60% dioxane was rapidly added with stirring an equimolar amount (7.2 mmol) of sodium hydroxide, also dissolved in 60% dioxane. The solution, which immediately turned from colorless to pale yellow, was allowed to stand at room temperature for 10 min and then extracted with two 100-ml portions of ether. The ether extracts were dried over anhydrous magnesium sulfate, and the solvent was then removed under reduced pressure. The residue was chromatographed on a 2 × 29-cm column of silica gel (40-140 mesh) according to a procedure described by Koch, Ciuffarin, and Fava.[13] The fractions eluted early contained 0.34 g (1.4 mmol) of *p*-tolyl disulfide, then came fractions containing 0.31 g (1.1 mmol) of unreacted **2b,** and finally fractions containing 0.32 g (1.2 mmol) of *p*-tolyl *p*-toluenethiolsulfinate (**1b**). The identity of all of these compounds was proven by spectral and melting point comparisons with known samples.

The aqueous layer from the ether extraction was also evaporated under reduced pressure. The amount of sodium *p*-toluenesulfinate present was estimated by titration with sodium nitrite, using the procedure described by Kice and Bowers.[10] The amount found, 6.5 mmol, was in reasonable agreement with that expected (after correcting for the amount of **2b** unreacted) from the presumed stoichiometry of the reactions involved, 7.2 mmol.

References and Notes

(1) This research supported by the National Science Foundation, Grants GP-25799 and GP-35927X.
(2) (a) W. E. Savige and J. A. Maclaren in "The Chemistry of Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. Y. Meyers, Ed., Pergammon Press, Oxford, 1966, p 374, Chapter 15, (b) W. E. Savige, J. Eager, J. Maclaren, and C. M. Roxburgh, *Tetrahedron Lett.*, 3289 (1964).
(3) R. Otto and A. Rossing, *Ber.*, **20,** 2079 (1887); R. Otto, A. Rossing, and J. Troger, *J. Prakt. Chem.*, **47** (2), 94 (1893); H. Limpricht, *Justus Liebigs Ann. Chem.*, **278,** 239 (1894).
(4) (a) S. Oae, Y. Yoshikawa, and W. Tagaki, *Bull. Chem. Soc. Jap.*, **42,** 2899 (1969); (b) S. Oae, R. Nomura, Y. Yoshikawa and W. Tagaki, *ibid.*, **42,** 2903 (1969).
(5) J. L. Kice and T. E. Rogers, *J. Amer. Chem. Soc.*, **96,** 8015 (1974).
(6) W. H. Stanley, M.S. Thesis, Oregon State University, 1966.
(7) J. L. Kice and J. P. Cleveland, *J. Amer. Chem. Soc.*, **95,** 104 (1973).
(8) The scheme of eq 3-5 plus eq 7 predicts that there should be much less decrease in the slope of the plot of $A - A_0$ *vs.* time during the first stage of the hydrolysis than is actually observed.
(9) J. L. Kice, C. G. Venier, and L. Heasley, *J. Amer. Chem. Soc.*, **89,** 3557 (1967).
(10) J. L. Kice and K. W. Bowers, *J. Amer. Chem. Soc.*, **84,** 605 (1962).
(11) We are grateful to Professor George Kasperek of Connecticut College for his assistance with the analog computer programming.
(12) This program was written by Mr. William Crow, Academic Computing Center, University of Vermont.
(13) P. Koch, E. Ciuffarin, and A. Fava, *J. Amer. Chem. Soc.*, **92,** 5971 (1970).

A Kinetic Study of the Reaction of Mercaptans with Phenyl Benzenethiolsulfinate and Benzenethiolsulfonate in Aqueous Dioxane[1]

John L. Kice* and Thomas E. Rogers

Contribution from the Department of Chemistry, University of Vermont, Burlington, Vermont 05401. *Received May 30, 1974*

Abstract: The kinetics of the reaction of mercaptans with both phenyl benzenethiolsulfinate (**1**) and phenyl benzenethiolsulfonate (**2**) have been studied in a series of carboxylate buffers in 60% aqueous dioxane as solvent. The dependence of reaction rate on pH shows that in each instance the mercaptide ion RS^- is at least 10^7 more reactive toward **1** or **2** than is the corresponding RSH, a much larger difference in reactivity than might have been expected based on their relative reactivity in other substitutions. The thiolsulfonate **2** reacts considerably faster with mercaptide ion than does the thiolsulfinate **1**, in marked contrast to the thermal stability of the two compounds, where **1** undergoes homolytic dissociation of the S-S bond much more readily than **2.** As might be expected from the fact that attack of $-S^-$ anions on dicoordinate sulfur is generally very facile, the rate constants for reaction of mercaptide ions with **1** or **2** are all very large (10^5 to 2×10^7 M^{-1} sec^{-1}).

Thiolsulfinates, RS(O)SR, sometimes also referred to as "sulfenic anhydrides," are generally many orders of magnitude more reactive than the corresponding disulfide RSSR in reactions leading to both homolytic and heterolytic cleavage of the sulfur-sulfur bond.[2] This, combined with the fact that they can be formed by oxidation of disulfides with a variety of oxidizing agents, including singlet oxygen sources,[3] suggests they should be considered as potentially important reactive intermediates in disulfide chemistry and argues for the desirability of more extensive study of their chemical behavior.

If thiolsulfinates are ever produced from disulfides in living systems, it seems likely that their subsequent reaction with some of the free sulfhydryl groups present in such systems will be important. That thiolsulfinates react readily with thiols is known.[4] The stoichiometry of the reaction is shown in eq 1. The antimicrobial and antibiotic activity of alkyl thiolsulfinates has been attributed to the ability of

$$2R'SH + RS(O)SR \longrightarrow 2RSSR' + H_2O \qquad (1)$$

Table I. Kinetics of the Reaction of Phenyl Benzenethiolsulfinate with Thiophenol in 60% Dioxane at 25°[a]

10^5[1]$_0$, M	Buffer	Buffer ratio [RCOO$^-$]:[RCOOH][b]	10^3[PhSH]$_0$, M	k_1,[c] sec^{-1}	k_1/[PhSH]$_{av}$[d]
7.2	Acetate	10:1	0.92	6.7	7.9×10^3
			1.44	10.2	7.5×10^3
		5:1	0.92	3.3	3.9×10^3
			1.44	5.6	4.1×10^3
		1:1	0.92	0.68	0.80×10^3
			1.44	1.14	0.83×10^3
		1:2	1.47	0.50	0.36×10^3
7.2	Formate	2:1	1.47	0.130	93
		1:1	1.47	0.067	48
		1:2	1.47	0.036	26
16	Trifluoroacetate	10:1	2.98	0.00062	0.22
		5:1	2.98	0.00028	0.10
		1:1	2.98	0.000092	0.033

[a] All runs at an ionic strength of 0.05. [b] Concentration of carboxylate ion, 0.05 M in all runs. [c] k_1 is experimental first-order rate constant. [d] [PhSH]$_{av}$ is the average concentration of thiophenol during the run and is equal to [PhSH]$_0$ − [1]$_0$.

Table II. Kinetics of the Reaction of Phenyl Benzenethiolsulfonate with Thiophenol in 60% Dioxane at 25°[a]

10^4[2]$_0$, M	Buffer	Buffer ratio [RCOO$^-$]:[RCOOH][b]	10^3[PhSH]$_0$, M	k_1,[c] sec^{-1}	k_1/[PhSH]$_{av}$[d]
2.3	Acetate	10:1	1.44	3.8×10^2	2.9×10^5
		5:1	1.44	1.8×10^2	1.37×10^5
		1:1	1.44	38.9	0.30×10^5
		1:2	1.44	16.9	0.13×10^5
2.3	Formate	5:1	1.47	10.0	7.56×10^3
		2:1	1.47	4.11	3.04×10^3
		1:1	1.47	2.01	1.49×10^3
		1:2	1.47	1.15	0.85×10^3
2.3	Chloracetate	2:1	1.47	0.88	0.66×10^3
		1:1	1.47	0.44	0.33×10^3
		1:2	1.47	0.23	0.175×10^3
4.4	Trifluoroacetate	10:1	1.51	0.0064	4.6
		5:1	1.51	0.0032	2.3
		1:1	1.51	0.00062	0.45

[a] All runs at an ionic strength of 0.05. [b] Concentration of carboxylate ion, 0.05 M in all runs. [c] k_1 is experimental first-order rate constant. [d] [PhSH]$_{av}$ is the average concentration of thiophenol during run and is equal to [PhSH] − $\frac{1}{2}$[2]$_0$.

these compounds to react readily with biologically essential sulfhydryl groups.[4c]

In earlier work Kice and Large[4b] investigated the mechanism of this reaction in rather strongly acid media. Much more germane to the question of reaction of thiolsulfinates with sulfhydryl groups under physiological conditions would be a study of the kinetic behavior of the reaction in roughly neutral media. This was the major objective of the present work. In it we have investigated the kinetics of the reaction of phenyl benzenethiolsulfinate (**1**, R = Ph in eq 1) with both thiophenol (R′ = Ph) and 1-butanethiol (R′ = *n*-Bu) in a series of carboxylate buffers in 60% aqueous dioxane as solvent.

In conjunction with a study of the alkaline hydrolysis of both PhS(O)SPh, **1**, and phenyl benzenethiolsulfonate (**2**), $PhSO_2SPh$, described in an accompanying paper,[5] it was important also to investigate the kinetics of the reaction of the thiolsulfonate with these thiols[4c] (eq 2) in the same

$$R'SH + PhS(=O)_2SPh \longrightarrow R'SSPh + PhSO_2H \qquad (2)$$

buffers. The results of this study of the kinetics of reaction 2 form the other principal part of this paper.

Results

Kinetics of the Reaction of Phenyl Benzenethiolsulfinate (1) and Phenyl Benzenethiolsulfonate (2) with Thiophenol. The kinetics of the reaction of PhSH with either **1** or **2** were studied at 25° in 60% dioxane in RCOOH–RCOO$^-$ buffers under conditions where the thiol was present in sufficient stoichiometric excess over **1** or **2** so that the concentration of the thiol remained effectively constant over the course of the reaction. The buffers used were all ones in which only a small fraction of the total thiol was present as the anion PhS$^-$. (For exact determination of the fraction of thiol present as the anion *vide infra.*) The ionic strength was kept constant at 0.05 in all runs.

The course of the reactions was followed by monitoring the change in the optical density of the solution at 295 nm. In the case of thiolsulfinate **1**, reaction with thiophenol leads to a decrease in the optical density of the solution at this wavelength; in the case of thiolsulfonate **2** it leads to an increase. In each instance, however, good first-order kinetics were observed for the disappearance of **1** or **2**. For all of the runs except those in CF_3COOH–CF_3COO^- buffers, the rates were so rapid that they were followed by stopped-flow spectrophotometry.

The experimental first-order rate constants, k_1, for the reaction of **1** with PhSH in the various buffers are collected in Table I. In the 10:1, 5:1, and 1:1 acetate buffers, runs were made at two different mercaptan concentrations. As indicated by the constancy of k_1/[PhSH] with variation in [PhSH], k_1 varies, as expected, linearly with thiophenol concentration.

Table II presents the data on experimental first-order rate constants for the reaction of **2** with thiophenol. By

comparison with Table I one can see at once that for any particular set of reaction conditions the thiolsulfonate reacts about 30 times faster than does the thiolsulfinate.

The data in the two tables also show that the rate of both reactions is strongly dependent on pH in all buffers used, including the rather acidic trifluoroacetate buffers, and that the rate increases as the pH increases. A quantitative examination of the pH–rate profiles of the two reactions will be given in a subsequent section.

Determination of Degree of Dissociation of Thiophenol in Different Buffers. One can take advantage of the marked difference in the molar extinction coefficients of PhSH and PhS^- in the 285–300-nm region to determine spectrophotometrically the actual degree of dissociation of PhSH in 10:1 and 20:1 AcO^-:AcOH buffers. The molar extinction coefficient of PhS^- in 60% dioxane in the 285–310-nm region was determined by measurements of the optical density of solutions prepared by mixing known amounts of thiophenol with sufficient excess standard sodium hydroxide to convert the thiol completely to its anion. The molar extinction coefficient of undissociated PhSH in the same solvent was determined by standard procedures. Throughout the region in question ϵ for PhS^- is much larger than ϵ for PhSH. For example, at 295 nm $\epsilon_{PhS^-}/\epsilon_{PhSH} = 26$. The optical densities of solutions of thiophenol in 20:1 and 10:1 AcO^-:AcOH buffers were then measured. From the measured optical densities at 295 and 300 nm and the known values of the ϵ's for PhS^- and PhSH at these wavelengths, one could estimate the fraction of the thiol present as the anion. The results in the two buffers were internally consistent. They indicated that in the most basic buffer used for the kinetic studies, the 10:1 AcO^-:AcOH buffer, the thiol was 9% ionized to PhS^-. The extent of dissociation of PhSH in the other buffers can then be calculated from this and a knowledge of the difference between the pH of the 10:1 acetate buffer and the solutions in question.

Estimated pK_a's of Buffer Carboxylic Acids in 60% Dioxane. Precise measurements of the pK_a's of acetic (7.44) and formic (6.10) acids in 60% dioxane are available in the literature.[6] No such data are available for chloroacetic and trifluoroacetic acids, however. To get a reasonably accurate value of the pK_a of chloroacetic and trifluoroacetic acids, we obtained titration curves for these acids and formic acid in 60% dioxane and then used these to estimate the pK_a difference between the two acids and formic acid in this solvent.

From this the pK_a for chloroacetic acid was estimated to be 5.48, and that of trifluoroacetic acid to be 2.81.

pH–Rate Profiles for Reactions of 1 and 2 with Thiophenol. From the estimated pK_a's for the various carboxylic acids and the buffer ratios, we calculated the pH of the various buffer solutions. The circles in Figure 1 represent a plot of log $k_1/[PhSH]_{total}$ *vs.* pH for the kinetic data of Tables I and II. The two lines of unit slope drawn on the figure fit almost all the data for the two reactions in the various buffers very well. Even in the relatively acidic trifluoroacetate buffers, where no more than one part in 10^6 of the thiol is present as PhS^-, the kinetically important reaction for both **1** and **2** is still that with the thiolate anion and not reaction with the undissociated mercaptan.

Kinetics of the Reaction of 1 and 2 with 1-Butanethiol. The kinetics of the reaction of 1-butanethiol with either **1** or **2** can also be followed in $RCOO^-$–RCOOH buffers in 60% dioxane using the same general procedures employed to study the reaction of thiophenol with these substrates. The results of an investigation of the kinetic behavior of these two reactions in acetate and formate buffers are shown in Table III. Comparison with Tables I and II shows that in a given buffer the rate of reaction of *n*-BuSH with either **1** or **2** is roughly 10^3 slower than the rate of reaction of PhSH with the corresponding compound.

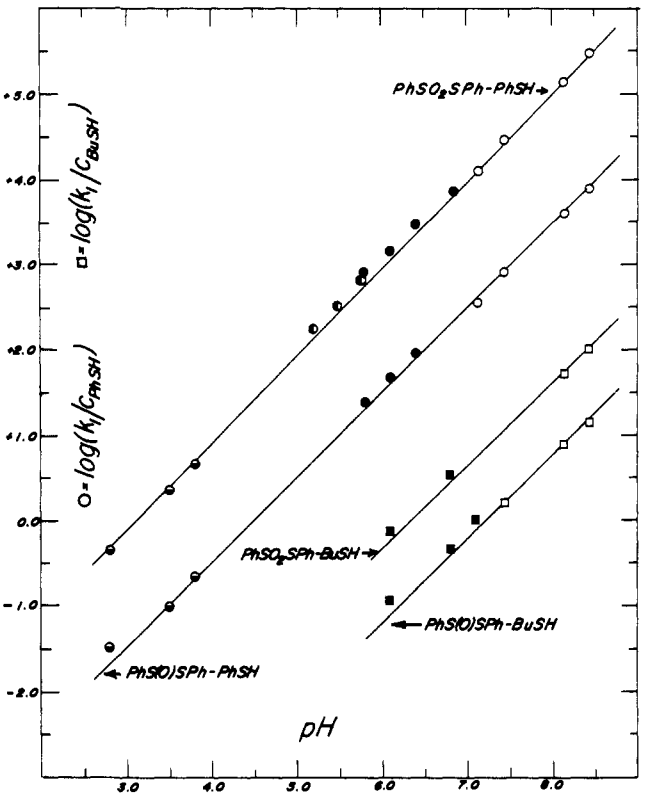


Figure 1. pH–rate profiles for reactions of thiophenol (circles) and *n*-butyl mercaptan (squares) with phenyl benzenethiolsulfonate and benzenethiolsulfinate in carboxylate buffers in 60% dioxane at 25°. Ordinate equals logarithm of experimental first-order rate constant, k_1, divided by stoichiometric mercaptan concentration. Runs are in: acetate buffers, ○ and □; formate buffers, ● and ■; chloroacetate buffers, ◐; trifluoroacetate buffers, ⊖. Ionic strength = 0.05 in all runs.

The squares in Figure 1 represent a plot of log $k_1/[BuSH]_{total}$ *vs.* pH for the runs in Table III. The lines on the plot are drawn with unit slope. It is evident that the dependence of rate on pH is similar to that observed with thiophenol, and that reaction with *n*-BuS^- rather than *n*-BuSH is the kinetically dominant term for either substrate in this pH region.

Discussion

The pH–rate profiles in Figure 1 demonstrate that under all the reaction conditions used in the present work attack of the thiolate anion on either **1** or **2** is much more important kinetically than attack of the undissociated thiol. This is true even in buffer solutions in which less than one part in a million of the total thiol is present as the anion. For example, from spectrophotometric measurements thiophenol is 9% dissociated into PhS^- in 60% dioxane in a 10:1 CH_3COO^-:CH_3COOH buffer. Given the pK_a difference between acetic acid and trifluoroacetic acid, it should therefore be only about 10^{-4}% dissociated in a 5:1 CF_3COO^-:CF_3COOH buffer, and yet in this solution where only 1 part in 10^6 of the thiol is present as PhS^-, one can see from Figure 1 that over 90% of the measured reaction rate is still due to nucleophilic attack of PhS^-, rather than PhSH, on **1** or **2**. Therefore PhS^- must be at least 10^7 more reactive as a nucleophile toward either of these substrates than is PhSH.

Although, lacking a measured pK_a for 1-butanethiol in 60% dioxane, we cannot say exactly what fraction of this thiol is dissociated in the acetate and formate buffers used

Table III. Kinetics of the Reaction of Phenyl Benzenethiolsulfinate (1) and Benzenethiolsulfonate (2) with 1-Butanethiol in 60% Dioxane at 25°[a]

Substrate, concn (M)	10^3[BuSH]$_0$, M	Buffer	Buffer ratio RCOO$^-$:RCOOH[b]	10^2k_1[c], sec^{-1}	k_1/[BuSH]$_{av}$[d]
1, 7.6×10^{-5}	1.43	Acetate	10:1	1.91	14.2
			5:1	1.07	7.9
			1:1	0.22	1.63
		Formate	10:1	0.14	1.04
			5:1	0.065	0.48
			1:1	0.0158	0.117
2, 2.3×10^{-4}	1.43	Acetate	10:1	13.4	101
			5:1	6.8	52
	1.33	Formate	5:1	0.43	3.5
			1:1	0.089	0.74

[a] All runs at an ionic strength of 0.05. [b] Concentration of carboxylate ion, 0.05 M in all runs. [c] k_1 is the experimental first-order rate constant. [d] [BuSH]$_{av}$ is the average concentration of 1-butanethiol during the run.

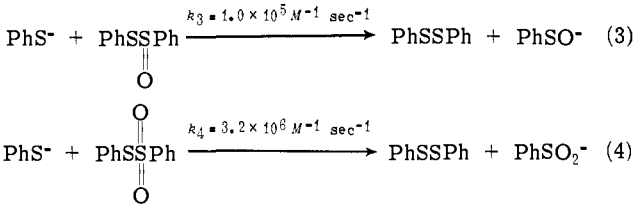
for the kinetic runs, we can probably make a reasonably good estimate by assuming that the pK_a *difference* between PhSH and *n*-BuSH will be approximately the same as what it is in water,[7] which is 4.1 pK units. If that is so then 1-butanethiol should be dissociated into *n*-BuS$^-$ to the extent of only about 1 part in 10^5 in the 10:1 CH_3COO^-:CH_3COOH buffer. Since Figure 1 shows that a strict proportionality between rate constant and pH is maintained at least down to formate buffers having a pH 1.5 units lower than the 10:1 acetate buffer, it is clear that *n*-BuS$^-$ must also be at least 10^7 more reactive toward **1** or **2** than is *n*-BuSH.

Although from previous work[8,9] a thiolate ion would be expected to be a much more reactive nucleophile than the corresponding thiol, what is surprising about the present results is that the magnitude of the difference in reactivity is much larger than those reported earlier. Thus, Pearson, Sobel, and Songstad[8] state that in methanol PhS$^-$ is 2×10^4 more reactive than PhSH toward CH_3I and 10^3 more reactive toward $Pt(py)_2Cl_2$, while Davis, *et al.*,[9] report that in water $H_3N^+CH_2CH_2S^-$ is about 500 times more reactive than $H_3N^+CH_2CH_2SH$ toward β-propiolactone. All of these are *much* smaller than the ratio of $k_{RS^-}/k_{RSH} \geq 10^7$ for nucleophilic attack on **1** and **2** in 60% dioxane. One should note, however, that both the reaction of 1-butanethiol with *p*-toluenesulfinyl *p*-tolyl sulfone[10a] and also the addition of $HOCH_2CH_2SH$ to quinazoline[10b] exhibit very large k_{RS^-}/k_{RSH} ratios, comparable to or greater than that found for the reaction of **1** or **2** with mercaptans.

Quite frankly, at present we have no satisfying explanation of why k_{RS^-}/k_{RSH} for the reaction of mercaptans with **1, 2,** or the sulfinyl sulfone[10a] in 60% dioxane, or for the reaction of $HOCH_2CH_2SH$ with the quinazoline,[10b] is so much larger than for the other substitutions[8,9] mentioned. Certainly, however, given the results discussed in another accompanying paper,[11] it *cannot* be attributed for **1** and **2** to substitutions at sulfenyl sulfur being markedly more sensitive to nucleophile basicity than those at the sp^3 carbon.

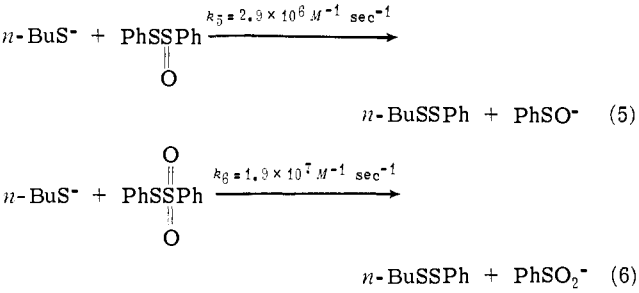
In initiating kinetic studies of the reaction of mercaptans with **1** and **2** in carboxylic acid buffers, we had hoped that it would be possible to find conditions where general base catalysis of the reaction of RSH with these substrates could be observed and studied. The very large value of k_{RS^-}/k_{RSH}, however, now indicates that such a search is almost certain to be fruitless, because in any solution where one has a significant concentration of any reasonably effective general base one will also probably have enough RS$^-$ ion for its reaction with **1** or **2** to be the kinetically dominant process.

Since we know the extent of dissociation of PhSH in the various buffers, we can calculate from the rate data in Figure 1 the actual second-order rate constants for the reaction of PhS$^-$ with both **1** and **2.** The values so obtained are shown over the arrows in eq 3 and 4. One sees that the thiolsulfonate (eq 4) is approximately 30 times more reactive than the thiolsulfinate (eq 3). We are inclined to attribute the greater reactivity of the thiolsulfonate to the fact that $PhSO_2^-$, being almost certainly less basic than PhSO$^-$, is probably a better leaving group. The greater reactivity of the thiolsulfonate in such a nucleophilic substitution stands in marked distinction to the thermal stability[12] of the two compounds. There homolytic dissociation of the S-S bond in the thiolsulfinate occurs much more readily than for the thiolsulfonate.



Reviews discussing nucleophilic substitution in organic sulfur chemistry[13] usually suggest that substitutions involving attack of -S$^-$ anions on dicoordinate, or sulfenyl, sulfur are normally very rapid. The size of the rate constants for eq 3 and 4 is entirely consistent with this picture.

As pointed out earlier, although we do not know the exact pK_a of *n*-BuSH in 60% dioxane, a good approximation to the correct value is to assume that its pK_a differs from that of PhSH by the same number of pK_a units as in water. Using that assumption in conjunction with the rate data in Figure 1, one can arrive at the estimated values for the rate constants for reaction of *n*-BuS$^-$ with **1** and **2** shown in eq 5 and 6.



On comparing these rate constants with k_3 and k_4 one sees that the increase in reactivity on going from PhS$^-$ to *n*-BuS$^-$ is somewhat larger for **1** ($k_5/k_3 = 29$) than for **2** ($k_6/k_4 = 6$). A possible explanation for this could be that in the case of **2** the rate constant for reaction of *n*-BuS$^-$ has

become so large ($>10^7\ M^{-1}\ sec^{-1}$) that one is entering the region where the rate constant is close enough to the diffusion-controlled limit that changes in inherent nucleophile reactivity now cause much less change in rate than would normally be the case.[14]

It is interesting to note that (k_{BuS^-}/k_{PhS^-}) for **1** is very similar to the relative reactivity of EtS^- and PhS^- in another substitution involving nucleophilic attack on dicoordinate sulfur. Ritter and Krueger[15] measured the rates of reaction of EtS^- and PhS^- with trithionate ion (eq 7) and found

$$RS^- + {}^-O_3S-S-SO_3^- \xrightarrow{k_{RS^-}} RS-S-SO_3^- + SO_3^{2-} \quad (7)$$

(k_{EtS^-}/k_{PhS^-}) = 26, which is, of course, very similar to the value of 29 observed for reaction of **1** with BuS^- and PhS^- in the present work.

Experimental Section

Preparation and Purification of Reagents. Phenyl benzenethiolsulfinate (**1**) was prepared as described previously.[2c] Phenyl benzenethiolsulfonate (**2**), mp 43–44.5° after recrystallization from absolute ethanol, was prepared by oxidation of phenyl disulfide with 2 mol of *m*-chloroperbenzoic acid in chloroform in a procedure patterned after that of Marangelli, Modena, and Todesco.[16] Dioxane was purified by the procedure described by Wiberg.[17] The freshly distilled material was then frozen and stored in the freezer to prevent formation of peroxides prior to use. Acetic acid was also purified by a procedure described by Wiberg.[18] Sodium acetate, sodium formate, lithium trifluoroacetate, formic acid, trifluoroacetic acid, and monochloroacetic acid were all analytical reagent grade and were used without further purification. *n*-Butyl mercaptan and thiophenol were purified by fractional distillation under reduced pressure and were redistilled frequently.

pK_a Determinations in 60% Dioxane. The pK_a's of chloroacetic and trifluoroacetic acids in 60% dioxane were estimated in the following way. A 0.10 *N* solution of formic acid in 60% dioxane (using CO_2-free distilled water) was titrated with standard 0.10 *N* sodium hydroxide solution, also in 60% dioxane. The titration was followed using a pH meter and the *apparent* pK_a determined from the titration curves of duplicate runs. The same titration procedure was then applied to 0.10 *N* solutions of chloroacetic and trifluoroacetic acids in 60% dioxane. The measured differences between the *apparent* pK_a's of these acids and formic acid were 0.62 pK units for chloroacetic and 3.29 pK units for trifluoroacetic. Using the known pK_a of formic acid in 60% dioxane[6] (6.10) as the standard, the pK_a's of $ClCH_2COOH$ and CF_3COOH are calculated to be 5.48 and 2.81, respectively.

The pK_a of thiophenol in 60% dioxane was determined as follows. First, the ultraviolet spectrum of a solution of freshly distilled thiophenol in 60% dioxane was determined. Then, the ultraviolet spectrum of PhS^- was determined over the same wavelength range by adding excess sodium hydroxide to a solution of PhSH in 60% dioxane and measuring the absorbance of the resulting solution. The ultraviolet spectra of solutions of a known amount of PhSH in 10:1 and 20:1 acetic acid:acetate buffers in 60% dioxane were then determined. At any given wavelength the concentration of PhS^- can be calculated from the relationship

$$[PhS^-] = \frac{A - \epsilon_{PhSH} C_{PhSH}}{\epsilon_{PhS^-} - \epsilon_{PhSH}}$$

where A is the measured absorbance of the buffer solution, C_{PhSH} is the stoichiometric concentration of thiophenol, and the ϵ's are the extinction coefficients for the various species involved. The ratio of $[PhS^-]/[PhSH]$ in each buffer was then calculated from these data. The results for the two buffers were internally consistent. Since the pK_a of acetic acid in 60% dioxane is known,[6] one can also calculate the pK_a for thiophenol in this same solvent. This was estimated to be 9.48.

Procedure for Kinetic Runs. All solutions were prepared fresh immediately prior to use. The procedure for the stopped-flow runs was as follows. A stock solution of the proper concentration of either **1** or **2** was prepared and placed in one of the reservoir syringes of a Durrum-Gibson Model D-110 stopped-flow spectrophotometer. A stock stolution of either *n*-BuSH or PhSH in the desired buffer in 60% dioxane was prepared and placed in the other reservoir syringe. The course of the reactions was then monitored at 295 nm on the storage oscilloscope. In all cases duplicate runs showed excellent reproducibility.

For the runs that were followed by conventional spectrophotometry 4 ml of a solution of the mercaptan in the appropriate buffer was placed in a 1-cm spectrophotometer cell and thermostated at 25° in the cell compartment of a Perkin-Elmer Model 402 spectrophotometer. Once the solution had reached thermal equilibrium, the reaction was initiated by the rapid mixing of 50 μl of a relatively concentrated solution of either **1** or **2** with the solution in the cell, and the change in absorbance was followed at 295 nm.

Pseudo-first-order rate constants for each run were determined from the slope of plots of log ($A - A_\infty$) or log ($A_\infty - A$) *vs.* time. Excellent linearity was observed in all the plots.

References and Notes

(1) This research supported by the National Science Foundation, Grants GP-25799 and GP-35927X.
(2) (a) E. Block, *J. Amer. Chem. Soc.*, **94**, 642 (1972); E. Block and S. W. Weidman, *ibid.*, **95**, 5046 (1973); (b) P. Koch, E. Cuiffarin, and A. Fava, *ibid.*, **92**, 5971 (1970); (c) J. L. Kice and J. P. Cleveland, *ibid.*, **95**, 104, 109 (1973); J. L. Kice, C. G. Venier, and L. Heasley, *ibid.*, **89**, 3557 (1967).
(3) R. W. Murray, R. D. Smetana, and E. Block, *Tetrahedron Lett.*, 299 (1971).
(4) (a) A. Schoberl and H. Grafje, *Justus Liebigs Ann. Chem.*, **617**, 71 (1958); (b) J. L. Kice and G. B. Large, *J. Org. Chem.*, **33**, 1940 (1968); (c) L. D. Small, J. H. Bailey, and C. J. Cavallito, *J. Amer. Chem. Soc.*, **69**, 1710 (1947); **71**, 3565 (1949).
(5) J. L. Kice and T. E. Rogers, *J. Amer. Chem. Soc.*, **96**, 8009 (1974).
(6) (a) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, N.Y., 1950, p 581; (b) S. S. Danyluk, H. Taniguchi, and G. J. Janz, *J. Phys. Chem.*, **61**, 1679 (1957).
(7) M. M. Kreevoy, E. T. Harper, R. E. Duvall, H. S. Wilgus, III, and L. R. Ditsch, *J. Amer. Chem. Soc.*, **82**, 4899 (1960).
(8) R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, **90**, 319 (1968).
(9) R. E. Davis, L. Suba, P. Klimishin, and J. Carter, *J. Amer. Chem. Soc.*, **91**, 104 (1969).
(10) (a) J. L. Kice and J. D. Campbell, *J. Org. Chem.*, **36**, 2288 (1971); (b) M. J. Cho and I. H. Pitman, *J. Amer. Chem. Soc.*, **96**, 1843 (1974).
(11) J. L. Kice, T. E. Rogers, and A. Warheit, *J. Amer. Chem. Soc.*, **96**, 8020 (1974).
(12) J. L. Kice, "Sulfur in Organic and Inorganic Chemistry," Vol. 1, A. Senning, Ed., Marcel Dekker, New York, N.Y., 1971, pp 158–163.
(13) (a) E. Ciuffarin and A. Fava, *Progr. Phys. Org. Chem.*, **6**, 81 (1968); (b) R. E. Davis, *Surv. Progr. Chem.*, **2**, 189 (1964); (c) A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 583 (1959); (d) O. Foss, *Kgl. Nor. Vidensk. SelsK. Skr.*, **No. 2** (1945).
(14) D. S. Kemp and M. L. Casey, *J. Amer. Chem. Soc.*, **95**, 6670 (1973).
(15) R. D. Ritter and J. H. Krueger, *J. Amer. Chem. Soc.*, **92**, 2316 (1970).
(16) U. Marangelli, G. Modena, and P. E. Todesco, *Gazz. Chim. Ital.*, **90**, 681 (1960).
(17) K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill, New York, N.Y., 1960, p 245.
(18) Reference 17, p 249.