References and Notes

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Catalysis of the Reaction of Morpholine with Phenyl Benzenethiolsulfonate by Halide Ions and Thiocyanate. Possible Evidence for an Intermediate on the Reaction Coordinate in a Substitution at Sulfenyl Sulfur[1a]

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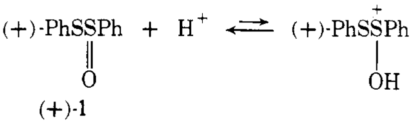
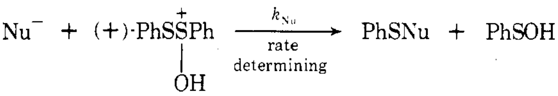
The reaction of morpholine with phenyl benzenethiolsulfonate (2) in aqueous dioxane to form the sulfenamide can be catalyzed by the addition of bromide, iodide, or thiocyanate ions. Data on their catalytic effectiveness can be used to measure the rates of attack of each of these three nucleophiles on the sulfenyl sulfur of 2. One finds that SCN^- is 6.3 times more reactive than I^- and 19 times more reactive than Br^-. This reactivity pattern is markedly different than the one previously observed for attack of the same nuclophiles on the sulfenyl sulfur of $PhSS^+(OH)Ph$; there (k_{Nu}/k_{Br}) is SCN^-, 150; I^-, 400; Br^-, (1.0). It is shown that this marked change in reactivity pattern can be easily explained if nucleophilic attack on the sulfenyl sulfur of 2 by these nucleophiles involves an addition–elimination mechanism with an intermediate (4) on the reaction coordinate, and with loss of $PhSO_2^-$ from 4 being rate determining, while in the case of $PhSS^+(OH)Ph$ attack of the nucleophile is instead rate determining.

In aqueous dioxane optically active phenyl benzenethiolsulfinate, (+)-1, undergoes an acid- and nucleophile-catalyzed racemization via the mechanism shown in eq 1.[2] Both iodide and thiocyanate ion are much more reactive than bromide ion as catalysts for this reaction, k_{Nu}/k_{Br} being 400 for I^- and 150 for SCN^-.

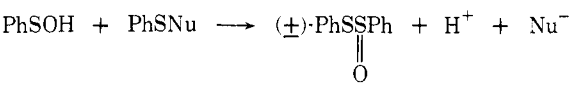


$$(+)\text{-PhS}\underset{\substack{\|\\ \text{O}}}{\text{S}}\text{Ph} + \text{H}^+ \rightleftharpoons (+)\text{-PhS}\overset{+}{\underset{\substack{|\\ \text{OH}}}{\text{S}}}\text{Ph} \qquad (1a)$$

(+)-1

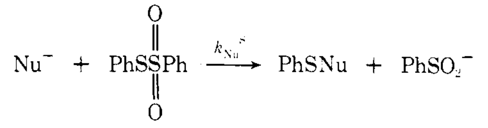


$$\text{Nu}^- + (+)\text{-PhS}\overset{+}{\underset{\substack{|\\ \text{OH}}}{\text{S}}}\text{Ph} \xrightarrow[\text{rate determining}]{k_{\text{Nu}}} \text{PhSNu} + \text{PhSOH} \qquad (1b)$$



$$\text{PhSOH} + \text{PhSNu} \longrightarrow (\pm)\text{-PhS}\underset{\substack{\|\\ \text{O}}}{\text{S}}\text{Ph} + \text{H}^+ + \text{Nu}^- \qquad (1c)$$

Phenyl benzenethiolsulfonate (2) undergoes nucleophilic substitution reactions (eq 2) easily with many nucleophiles, and we have recently reported[3] kinetic data on the reactivity of 15 common nucleophiles toward 2 in aqueous dioxane.



$$\text{Nu}^- + \text{PhS}\overset{\substack{\text{O}\\ \|}}{\underset{\substack{\|\\ \text{O}}}{\text{S}}}\text{Ph} \xrightarrow{k_{\text{Nu}}^{\text{S}}} \text{PhSNu} + \text{PhSO}_2^- \qquad (2)$$

2

Thiocyanate ion and the halide ions were not among the nucleophiles studied, however, because of several complications. First, benzenesulfenyl halides undergo hydrolysis easily in aqueous dioxane, and under some conditions[4] the hydrolysis product, the sulfenic acid PhSOH, can react readily with 2 to produce 1; this has the potential for greatly complicating the kinetics. Second, the reaction of $PhSO_2^-$ with PhSX (reverse of eq 2 for Nu = X) can be fast enough compared to hydrolysis of PhSX so that, even if subsequent reactions of PhSOH produce no kinetic complications, reversal of attack of X^- on 2 can be kinetically significant, and one cannot equate k_X^S with the rate of disappearance of 2, since attack of X^- on 2 will not be rate determining.

These several complications to determining the reactivity of halides and thiocyanate toward 2 can be circumvented if one can find some other nucleophile to add to the reaction medium which, at the concentration employed, is reactive enough toward PhSX compared to water or $PhSO_2^-$ so that it will capture essentially every PhSX produced by eq 2 before they can react with either water or $PhSO_2^-$. This added nucleophile should also react with PhSX to give a product which will be stable under the reaction conditions. The only other requirement is that the nucleophile added to trap PhSX must not itself react directly with 2 at too rapid a rate. If it does, the contribution of the X^--induced disappearance of 2 to the overall rate will be too small to be detected.

It appeared to us that morpholine might meet all the re-

Table I
Kinetics of the Nucleophile-Catalyzed Reaction of Morpholine with Phenyl Benzenethiolsulfonate (2) in 60% Dioxane at 25°[a]

Nucleophile	[Morpholine] = [morpholine H$^+$], M	[Nu$^-$], M	$10^3 k_{\mathrm{exp}}$, sec^{-1}	$k_X{}^S = (k_{\mathrm{exp}} - k_M[\mathrm{morph}])/[\mathrm{Nu}^-]$, M^{-1} sec^{-1}
None	0.01	0.00	3.3	
SCN$^-$	0.01	0.01	6.8	0.25
		0.03	10.9	0.25
I$^-$	0.01	0.03	4.5 ± 0.1	0.039
		0.05	5.3 ± 0.1	0.038
Br$^-$	0.01	0.03	3.7 ± 0.1	0.013
		0.05	4.0 ± 0.1	0.013

[a] All runs at a constant ionic strength of 0.04 except those containing 0.05 M Br$^-$ or I$^-$. In these runs the ionic strength is 0.06. Data for each set of conditions for iodide and bromide are average of several runs.

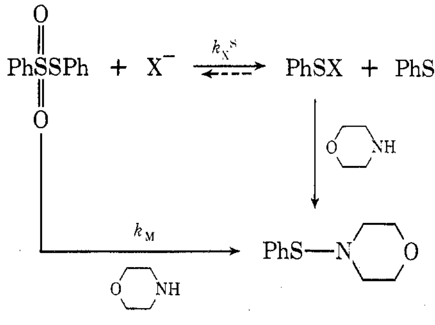
quirements just set forth. Thus, it would react readily with PhSX or PhSSCN to give a sulfenamide, and these are stable under the reaction conditions.[3] On the other hand, it is not too reactive toward 2.[3]

Indeed, we have found that it is possible to measure the reactivity of Br$^-$, I$^-$, and SCN$^-$ toward 2 using morpholine to trap the reactive sulfenyl derivative formed in eq 2. The results are reported in this paper and are especially interesting because they indicate a quite different reactivity pattern for these three nucleophiles toward 2 than the one observed earlier[2] toward protonated 1. A possible explanation for this is presented.

Results

The kinetics of the disappearance of 2 (2×10^{-4} M) in 1:1 morpholine–morpholine H$^+$ buffers containing 0.01–0.04 M morpholine in 60% dioxane at 25° at a constant ionic strength of 0.04 have been previously measured.[3] In the present work the addition of 0.01–0.05 M bromide, iodide, or thiocyanate ion to such solutions was found to result in a definite increase in the rate of disappearance of 2. This was more marked with thiocyanate than with the two halide ions. Even though the concentration of PhSO$_2^-$ in these runs increases from zero at the start to a final value equal to $[2]_0$, there is no decrease during the course of a run in the experimental first-order rate constant for the disappearance of 2, showing that morpholine is trapping the reactive sulfenyl derivatives formed in eq 2 and preventing their return to 2 via reaction with the PhSO$_2^-$ produced. The experimental first-order rate constants for the disappearance of 2 under the various reaction conditions are summarized in Table I.

Chart I
Mechanism of Catalysis of the Disappearance of 2 by Halide Ions and Thiocyanate in the Presence of Morpholine



(X = Br$^-$, I$^-$, or SCN$^-$)

If the reaction scheme shown in Chart I applies under our reaction conditions, the experimental first-order rate constant for the disappearance of 2 in any given run will be given by

$$k_{\mathrm{exp}} = k_M[\mathrm{morph}] + k_X{}^S[X^-]$$

and for a given X$^-$

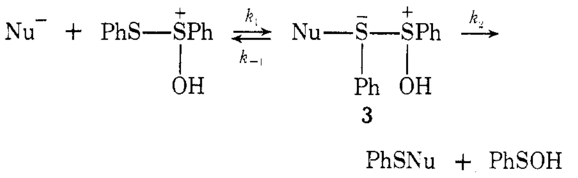
$$k_X{}^S = \frac{k_{\mathrm{exp}} - k_M[\mathrm{morph}]}{[X^-]}$$

should be a constant independent of the concentration of X$^-$. The last column of Table I shows that this is indeed the case. We therefore believe that the values of $k_X{}^S$ shown in that column are accurate measures of the reactivity of Br$^-$, I$^-$, and SCN$^-$ toward 2.

Discussion

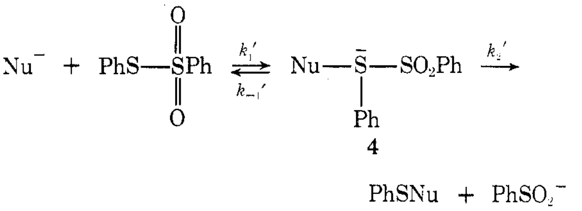
From the last column in Table I one sees that for eq 2 the reactivity toward 2 of I$^-$ or SCN$^-$, as compared with Br$^-$, i.e., $(k_{\mathrm{Nu}}{}^S/k_{\mathrm{Br}}{}^S)$, is SCN$^-$, 19; I$^-$, 3.0; Br$^-$, (1.0). This contrasts markedly with the reactivity pattern observed for these same three nucleophiles toward protonated 1, where $(k_{\mathrm{Nu}}/k_{\mathrm{Br}})$ for eq 1b is SCN$^-$, 150; I$^-$, 400; Br$^-$, (1.0). Particularly striking is the fact that SCN$^-$ is more reactive than I$^-$ toward 2 in the substitution at the sulfenyl sulfur in eq 2 while I$^-$ is more reactive than SCN$^-$ in the substitution at a sulfur of similar oxidation state in eq 1b. The only difference in the two substitutions is that in one the leaving group is PhSO$_2^-$ while in the other it is PhSOH.

Can this peculiar change in the rate pattern be simply explained? We think that it can provided one assumes that the substitutions depicted in eq 1b and 2 do not actually involve synchronous bond making and bond breaking but instead occur in each case with the formation of an intermediate (3 or 4) as shown in eq 3a and 3b.



$$\mathrm{Nu^- + PhS{-}\overset{+}{S}Ph(OH)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{Nu{-}\overset{-}{S}(Ph){-}\overset{+}{S}Ph(OH)} \xrightarrow{k_2} \mathrm{PhSNu + PhSOH} \tag{3a}$$

3



$$\mathrm{Nu^- + PhS{-}S(=O)_2Ph} \underset{k_{-1}'}{\overset{k_1'}{\rightleftarrows}} \mathrm{Nu{-}\overset{-}{S}(Ph){-}SO_2Ph} \xrightarrow{k_2'} \mathrm{PhSNu + PhSO_2^-} \tag{3b}$$

4

In eq 3a we feel that PhSOH will be a better leaving group than I$^-$, SCN$^-$, or Br$^-$, so that $k_2 > k_{-1}$ in all cases, with the result that attack of the nucleophile on protonated 1 (step k_1) will be rate determining, and the experimentally measured rate constants for the three nucleophiles will be directly proportional in each case to k_1.

On the other hand, in the reaction of Br^-, I^-, and SCN^- with **2** we think that each of these anions should be a better leaving group than $PhSO_2^-$, so that k_2'/k_{-1}' will be less than unity in all cases. In this situation step k_2', rather than attack of Nu^- on **2** (step k_1'), will be rate determining and $k_{Nu}{}^S$ will be given by $k_1'k_2'/(k_{-1}' + k_2')$.

Furthermore, it would be reasonable to expect $k_2'/(k_{-1}' + k_2')$ to be considerably smaller for I^- than for the other two nucleophiles, because k_2' should be effectively independent of Nu^-, while k_{-1}' would probably be much larger for I^- than for either Br^- or SCN^-, since I^- is in all probability a considerably better leaving group than the other two anions. Thus, even though k_1' for I^- attacking **2** was larger than k_1' for SCN^- by about the same amount as in the attack of these two nucleophiles on protonated **1**, it would be easy for $k_I{}^S$ to be significantly less than $k_{SCN}{}^S$, simply because $k_2'/(k_{-1}' + k_2')$ for I^- was so much smaller than $k_2'/(k_{-1}' + k_2')$ for SCN^-.

The presence of intermediates on the reaction coordinate in eq 3a and 3b and a change of rate-determining step from attack of Nu^- on protonated **1** to departure of $PhSO_2^-$ from **4** with a change in the leaving group ability of the group to be displaced in the substitution can thus provide a simple and straightforward rationalization for the marked difference in the reactivity pattern for Br^-, I^-, and SCN^- in eq 1b vs. eq 2. We recognize that other more complex explanations are doubtless conceivable. For this reason the difference in the reactivity pattern for the three nucleophiles toward the two substrates can be considered only as suggestive, rather than compelling, evidence for the presence of an intermediate on the reaction coordinate in the substitutions in question.

This is not the first occasion in which kinetic evidence of one type or another has been obtained suggestive of an intermediate being on the reaction coordinate in a simple nucleophilic substitution at sulfenyl sulfur. The work of Ciuffarin provides several additional examples.[5,6] While these, like the present example, are suggestive rather than compelling, and while there have been other cases[7,8] where the evidence seemed to point to synchronous bond making and bond breaking, rather than to an addition–elimination mechanism involving an intermediate, we feel that the present results and those of Ciuffarin,[5,6] together with the known ability of sulfur to expand its valence shell, make it generally desirable to picture nucleophilic substitutions at sulfenyl sulfur as proceeding through an intermediate, except in those specific cases where there is definite experimental evidence that bond making and bond breaking are synchronous.

Experimental Section

Preparation and Purification of Materials. The preparation and purification of phenyl benzenethiolsulfonate (**2**) and the purification of dioxane and morpholine followed previously described procedures.[3] Sodium thiocyanate, potassium iodide, potassium bromide, lithium perchlorate, and perchloric acid were all reagent grade and were used without further purification.

Procedure for Kinetic Runs. A 1:1 morpholine–morpholine H^+ buffer in 60% dioxane was prepared by adding a known amount of standard perchloric acid to a known amount of morpholine in 60% dioxane. To this was then added the appropriate amount of the catalyzing nucleophile (bromide, iodide, or thiocyanate) along with the amount of lithium perchlorate needed to bring the ionic strength up to the desired value. Four milliliters of this solution was thermostatted in a quartz uv cell in the cell compartment of a Perkin-Elmer Model 402 spectrophotometer. The reaction was then initiated by adding to this solution with efficient mixing 40 μl of a relatively concentrated stock solution of **2** in dioxane. The disappearance of **2** was then followed by monitoring the change in optical density at 272 nm. Plots of log $(A - A_\infty)$ vs. time showed excellent linearity in every case and rate constants were reproducible to within ±3%. A run without added catalyzing nucleophile gave the same rate as previously observed by Kice, Rogers, and Warheit.[3]

Registry No.—**2**, 1212-08-4; morpholine, 110-91-8; thiocyanate, 302-04-5; iodide, 20461-54-5; bromide, 24959-67-9.

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New Synthesis of *S*(*Se*)-Alkylphosphorothio(seleno)lates from the Corresponding Phosphoroanilidates. Stereospecific Cleavage of the Phosphorus–Nitrogen Bond in Chiral Phosphoroanilidates

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Reaction of sodio derivatives of phosphoroanilidates and their thio and seleno analogues with carbon disulfide or carbon dioxide, followed by treatment of the resulting phosphorothioate or phosphoroselenoate sodium salt with methyl iodide, gave the corresponding S or Se methyl esters. The stereochemistry of P–N bond cleavage was studied using optically active *O*-ethyl ethylphosphonoanilidate and *O*-ethyl ethylphosphonoanilidothioate and diastereoisomeric 2-*N*-phenylamino-2-oxo(-seleno, -thio)-4-methyl-1,3,2-dioxaphosphorinanes. In all cases P–N cleavage proceeds with high stereospecificity and retained configuration around the phosphorus atom. Chemical correlation of absolute configuration at phosphorus in a family of chiral ethylphosphonic acid derivatives is also described.

Although the reaction of anions derived from dialkyl phosphoroanilidates with carbonyl and thiocarbonyl compounds, leading to isocyanates, isothiocyanates, and carbodiimides, was described in the early sixties,[1] the fate of the