considered unlikely by other groups of workers[24,29] because it places undue emphasis on the I_π effect. Indeed, Swain and Lupton[24] believe the value should be less than 1, which is certainly true for the correlation of pK_a values[8] and rates of quaternization of substituted pyridines.[30] As already noted, Fischer and Vaughan have shown that electron-withdrawing groups of potential (−I, −M)-type exert only a −I effect in these series, a conclusion amply supported by the work of Schofield,[15] and yet all such groups have a different effect depending on whether they occupy the 3 or 4 position (Table IV).

Table IV

σ_I Values for Substituents in the Pyridine Series

Substituent	(i) σ_I (pK_a values[a]) 3	4	3/4	(ii) σ_I (quaternization[b]) 3	4	3/4
CN	0.64	0.55	1.17	0.62	0.52	1.19
NO_2	0.67	0.63	1.07			
$COOCH_3$	0.35	0.28	1.25			
COC_6H_5	0.33	0.31	1.06	0.30	0.23	1.30

[a] Reference 8. [b] Reference 30.

Another explanation of the increased slope of the σ_p correlation could be a competition between the pyridinium nucleus and the β-vinyl substituent for the π electrons of the double bond, which the former always wins but in varying degrees, so that the assumption of a *constant* negative σ_R(vinyl) value in eq 3 and 4 is incorrect. However, σ_R^0 measurements for the β substituents[31] (NO_2, $\sigma_R^0 = 0.17$; CN, 0.09; COOEt, 0.18; $COCH_3$, 0.22; CHO, 0.24; COC_6H_5, 0.19) show that the −M effect is not proportional to the −I effect for such substituents. Thus to explain the different slope by this phenomena would involve postulation of interaction between the resonance effect of the vinyl group and the inductive effect of the β substituent, a type of interaction previously suggested[31] and also implicitly assumed,[32] but not widely considered, the mutual independence of M and I effects being the general basis for dual substituent parameter correlations.

Stewart and Walker[7] have measured σ_p^- for the β-nitro vinyl group; it is 0.88. Clearly, for this substituent, and presumably for the others studied here, the −M effect of the β substituent fully reasserts itself as expected when conjugation with excess of electronic charge is possible. Thus, these groups fall into the small category of those that have both σ^+ and σ^- values significantly different from σ. The sign of the σ_R^0 values of such groups, measured as 0.13 for $CH{=}CHNO_2$ and 0.10 for $CH{=}CHCOOH$,[31] therefore appears to be in some doubt.

Registry No.—**2b**, 24490-79-7; **2c**, 26505-36-2; **2d**, 10416-53-2; **2e**, 24489-96-1; **2f**, 16208-85-8; **2g**, 28430-32-2; **3a**, 3156-52-3; **3b**, 6443-86-3; **3c**, 28447-15-6; **3d**, 28447-16-7; **3e**, 28447-17-8; **3f**, 4452-13-5; **3g**, 28430-33-3; **5a**, 1075-49-6; **5b**, 28447-20-3; **4** vinylpyridine, 100-43-6.

Acknowledgment.—We thank the directors of Munton and Fison Ltd. for financing this work and granting a leave of absence to G. B. E., and Mr. H. S. Hunt, Head of Science, Ipswich Civic College, for allowing us the use of spectrometers and other facilities.

(29) R. T. C. Brownlee, R. E. J. Hutchinson, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, **90**, 1757 (1968).

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(32) D. W. Farlow and R. B. Moodie, *J. Chem. Soc.*, *B*, 334 (1970).

Mechanisms of Substitution Reactions at Sulfinyl Sulfur. VI. The Kinetics of the Reaction of Mercaptans with Aryl Sulfinyl Sulfones[1]

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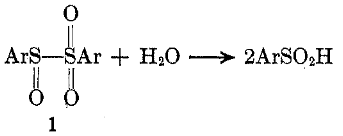
The kinetics of the reaction of *n*-butyl mercaptan with *p*-toluenesulfinyl *p*-tolyl sulfone (**1a**) in 60% dioxane containing 0.001–0.40 *M* perchloric acid have been investigated. In the region 0.001–0.01 *M* $HClO_4$, reaction of $n\text{-BuS}^-$ with **1a** is an important contributor to the rate. At higher acidities the only important contributor to the rate is a reaction between the undissociated mercaptan and **1a**. Reaction of *n*-BuSH with **1a** is not subject to significant acid catalysis, in marked contrast to the butyl sulfide catalyzed hydrolysis of **1a** where nucleophilic attack of $n\text{-Bu}_2S$ on **1a** occurs only if there is accompanying acid catalysis. This difference in the behavior of *n*-BuSH and $n\text{-Bu}_2S$ provides evidence of the probable correctness of the explanation advanced earlier[3] for why acid catalysis is necessary in the sulfide-catalyzed hydrolysis but not in the ordinary hydrolysis of **1a**.

In acidic aqueous dioxane the hydrolysis of aryl sulfinyl sulfones (eq 1) can be markedly catalyzed by the addition of small concentrations of alkyl sulfides such as *n*-butyl sulfide.[3] While the ordinary hydrolysis of **1** under these conditions is *not* subject to acid catalysis, *i.e.*, rate = $k_h(\mathbf{1})$, the sulfide-catalyzed hydrolysis occurs *only* with acid catalysis, *i.e.*, rate = $k_s(H^+)(R_2S)(\mathbf{1})$. To explain this difference in behavior it was suggested[3] that uncharged nucleophiles like H_2O and R_2S are unable to displace sulfinate ion ($ArSO_2^-$) as such from **1**. In the sulfide-catalyzed hydrolysis (eq 2), if R_2S is to effect a substitution on the sulfinyl group of **1**,



$$\mathrm{Ar}\underset{\underset{\textstyle \mathrm{O}}{\|}}{\mathrm{S}}-\overset{\overset{\textstyle \mathrm{O}}{\|}}{\underset{\underset{\textstyle \mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{Ar} + \mathrm{H_2O} \longrightarrow 2\mathrm{ArSO_2H} \qquad (1)$$

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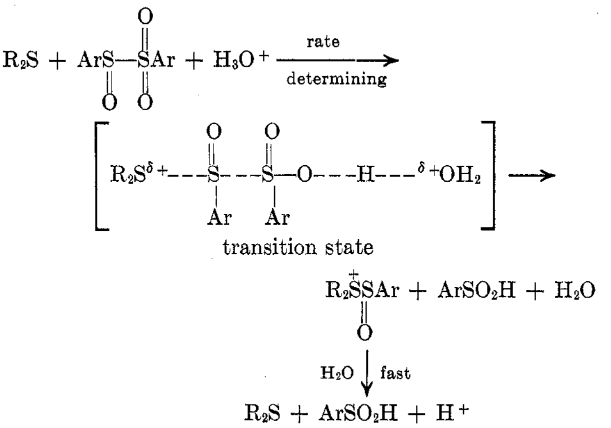
(1) (a) This research was supported by the National Science Foundation, Grant GP-10732X. (b) Preceding paper in this series: J. L. Kice and G. Guaraldi, *J. Org. Chem.*, **33**, 793 (1968).

(2) Department of Chemistry, University of Vermont, Burlington, Vt. 05401.

(3) J. L. Kice and G. Guaraldi, *J. Amer. Chem. Soc.*, **89**, 4113 (1967).



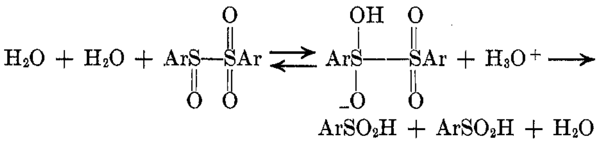
$$R_2S + Ar\underset{O}{S}-\overset{O}{\underset{O}{S}}Ar + H_3O^+ \xrightarrow[\text{determining}]{\text{rate}} \left[R_2S^{\delta+}---\overset{O}{\underset{Ar}{S}}---\overset{O}{\underset{Ar}{S}}-O---H---{}^{\delta+}OH_2\right] \longrightarrow$$

transition state

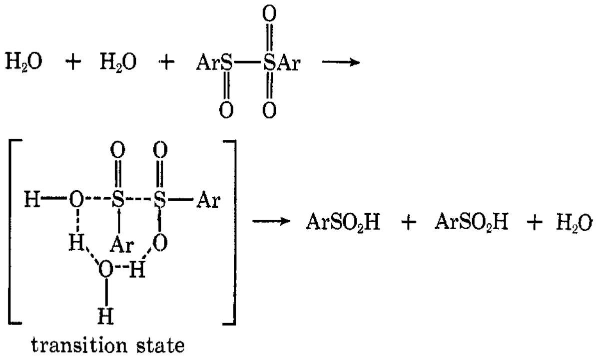
$$R_2\overset{+}{S}\underset{O}{S}Ar + ArSO_2H + H_2O \quad (2)$$

$$\xrightarrow[\text{fast}]{H_2O} R_2S + ArSO_2H + H^+$$

a proton must be transferred to the $ArSO_2$ group coincident with the scission of the $S(O)-SO_2$ bond, so that the $ArSO_2$ group is displaced as $ArSO_2H$.[4] In the ordinary hydrolysis, on the other hand, where water is the attacking nucleophile, the attacking water molecule itself can supply the proton required by the departing $ArSO_2$ group, either *via* a mechanism (eq 3) in which this proton is first transferred to another water molecule and then transferred in a second step from there to the $ArSO_2$ group or *via* a mechanism (eq 4) where this same proton transfer is accomplished in a single encounter. For either eq 3 or eq 4 as the mechanism one will, of course, have no dependence of the hydrolysis rate on (H_3O^+).



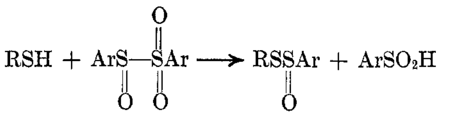
$$H_2O + H_2O + Ar\underset{O}{S}-\overset{O}{\underset{O}{S}}Ar \rightleftarrows Ar\overset{OH}{\underset{^-O}{S}}-\overset{O}{\underset{O}{S}}Ar + H_3O^+ \longrightarrow ArSO_2H + ArSO_2H + H_2O \quad (3)$$



$$H_2O + H_2O + Ar\underset{O}{S}-\overset{O}{\underset{O}{S}}Ar \longrightarrow \left[\begin{array}{c} H-\underset{\vdots}{O}---\overset{O}{\underset{Ar}{S}}---\overset{O}{\underset{O}{S}}-Ar \\ H\cdots O-H \cdots O \\ | \\ H \end{array}\right] \longrightarrow ArSO_2H + ArSO_2H + H_2O \quad (4)$$

transition state

If the above explanation for the difference in the dependence of the rates of the ordinary hydrolysis and the sulfide-catalyzed one on (H_3O^+) is correct, then the reaction of a mercaptan with **1** in acidic aqueous dioxane (eq 5) should, like the ordinary hydrolysis, *not* be significantly acid catalyzed, even though the mercaptan represents a neutral sulfur nucleophile of about the same reactivity as the sulfide, since RSH, like H_2O, and unlike R_2S, has a proton attached to the attacking atom which can be transferred to the departing $ArSO_2$ group in the same manner as shown in eq 3 and 4. For this reason it seemed worthwhile to investigate the kinetics of the reaction of a typical mercaptan with an aryl sulfinyl sulfone in acidic aqueous dioxane. The present paper reports the results of such a study.



$$RSH + Ar\underset{O}{S}-\overset{O}{\underset{O}{S}}Ar \longrightarrow RS\underset{O}{S}Ar + ArSO_2H \quad (5)$$

Results

The particular mercaptan–sulfinyl sulfone combination chosen for study was *n*-butyl mercaptan–*p*-toluenesulfinyl *p*-tolyl sulfone (**1a**, Ar = $p\text{-}CH_3C_6H_4$). The rate of disappearance of **1a** in the presence of added mercaptan could be followed kinetically by the same spectrophotometric procedure used earlier[3] to follow the kinetics of the hydrolysis of **1a**. All runs were carried out with the added mercaptan (0.10–0.15 *M*) present in huge stoichiometric excess over **1a** ($\sim 10^{-4}$ *M*). The disappearance of **1a** followed good first-order kinetics in every case.

The experimental first-order rate constants, k_1, for the disappearance of **1a** under the various reaction conditions investigated are shown in Table I. Each measured rate constant k_1 is the sum of the rate constant for the normal hydrolysis of **1a** (k_h) and the pseudo-first-order rate constant $[k_M(RSH)]$ for the mercaptan–**1a** reaction under that particular set of reaction conditions, *i.e.*

$$k_1 = k_h + k_M(RSH)$$

In a separate set of experiments, values of k_h were determined for **1a** for each set of reaction conditions in Table

TABLE I

KINETICS OF THE DISAPPEARANCE OF *p*-TOLUENESULFINYL *p*-TOLYL SULFONE IN THE PRESENCE OF *n*-BUTYL MERCAPTAN IN 60% DIOXANE AT 21.4°

$(LiClO_4)$, *M*	(*n*-BuSH), *M*	$(HClO_4)$, *M*	$k_1 \times 10^3$, sec^{-1} [a]	$k_M = \left[\frac{k_1 - k_h}{(RSH)}\right]$, $M^{-1}\ sec^{-1}$
0.00	0.150	0.0010	11.5	0.049
		0.0012	10.9	0.045
		0.0015	10.6	0.043
		0.0016	10.5	0.042
		0.0020	9.6	0.037
		0.0025	9.0	0.032
		0.0040	8.3	0.028
		0.0050	7.8	0.025
		0.010	7.3	0.021
		0.050	7.2	0.020
		0.10	7.4	0.022
	0.095	0.10	6.2	0.021
	0.146	0.20	8.4	0.028
		0.40	9.3	0.032
0.30	0.146	0.10	16.7	0.082

[a] All rate constants are the average of several runs. Initial concentration of sulfinyl sulfone, $\sim 1 \times 10^{-4}$ *M* in all runs.

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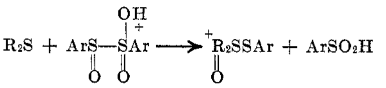
[4] That the proton is transferred in the rate-determining step rather than in an earlier equilibrium is shown by the solvent-isotope effect of $(k_S^{H_2O}/k_S^{D_2O}) = 1.4$. Presumably the reason that the mechanism shown in eq 2 is preferred over one involving attack of R_2S on sulfonyl-protonated **1** formed in a prior equilibrium, *i.e.*, eq i, is simply the fact that, due to the extremely



$$R_2S + Ar\underset{O}{S}-\overset{OH^+}{\underset{O}{S}}Ar \longrightarrow R_2\overset{+}{S}\underset{O}{S}Ar + ArSO_2H \quad \text{(i)}$$

2

low basicity of sulfonyl groups,[5] the equilibrium concentration of **2** is too small for reaction i to be able to compete effectively with eq 2.

[5] S. K. Hall and E. A. Robinson, *Can. J. Chem.*, **42**, 1113 (1964); E. M. Arnett and C. Douty, *J. Amer. Chem. Soc.*, **86**, 409 (1964).

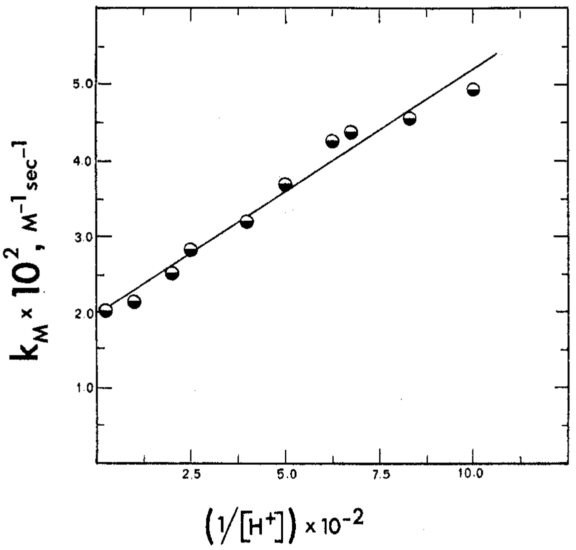


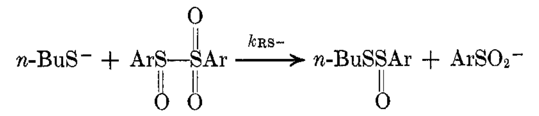
Figure 1.—Plot of k_M, the rate constant for the reaction of **1a** with n-BuSH, *vs.* $1/(H^+)$ for runs in 60% dioxane containing 0.001-0.01 M $HClO_4$.

I, were found to be effectively independent of perchloric acid concentration, and were found to agree within a few per cent with those measured for **1a** earlier[3] under certain of these reaction conditions. Values of k_M calculated from the k_1 values, the k_h values, and the relationship $k_M = [k_1 - k_h/(RSH)]$ are given in the last column of Table I.

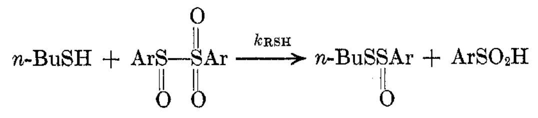
Runs in 0.10 M perchloric acid at two different mercaptan concentrations indicate that k_M is independent of mercaptan concentration, showing that, as expected, the **1a**–mercaptan reaction is first order in mercaptan.

Discussion

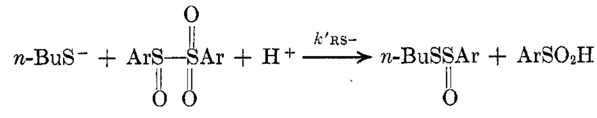
Examination of Table I reveals that in the region 0.001–0.01 M perchloric acid k_M decreases with increasing acid concentration, suggesting that in this region reaction of the mercaptide ion n-BuS$^-$ with **1a** (eq 6) is also contributing significantly to the rate of disappearance of **1a**. In more acid media (0.01–0.10 M $HClO_4$) k_M is independent of acid concentration showing that in this region the only significant contributors to k_M are processes whose rates are independent of (H^+), *i.e.*, either direct reaction of n-BuSH with **1a** (eq 7), or an acid-catalyzed reaction of n-BuS$^-$ with the same substrate (eq 8). If this assessment of the kinetic situation is correct, in the range 0.001–0.10 M $HClO_4$, k_M should be given by



$$n\text{-BuS}^- + \text{Ar}\underset{\text{O}}{\underset{\|}{\text{S}}}\text{—}\overset{\text{O}}{\overset{\|}{\underset{\text{O}}{\underset{\|}{\text{S}}}}}\text{Ar} \xrightarrow{k_{\text{RS}^-}} n\text{-BuS}\underset{\text{O}}{\underset{\|}{\text{S}}}\text{Ar} + \text{ArSO}_2^- \qquad (6)$$



$$n\text{-BuSH} + \text{Ar}\underset{\text{O}}{\underset{\|}{\text{S}}}\text{—}\overset{\text{O}}{\overset{\|}{\underset{\text{O}}{\underset{\|}{\text{S}}}}}\text{Ar} \xrightarrow{k_{\text{RSH}}} n\text{-BuS}\underset{\text{O}}{\underset{\|}{\text{S}}}\text{Ar} + \text{ArSO}_2\text{H} \qquad (7)$$



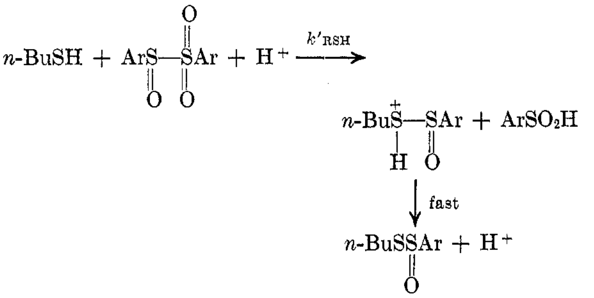
$$n\text{-BuS}^- + \text{Ar}\underset{\text{O}}{\underset{\|}{\text{S}}}\text{—}\overset{\text{O}}{\overset{\|}{\underset{\text{O}}{\underset{\|}{\text{S}}}}}\text{Ar} + \text{H}^+ \xrightarrow{k'_{\text{RS}^-}} n\text{-BuS}\underset{\text{O}}{\underset{\|}{\text{S}}}\text{Ar} + \text{ArSO}_2\text{H} \qquad (8)$$

$$k_M = k_{\text{RS}^-}\left[\frac{K_a^{\text{RSH}}}{(\text{H}^+)}\right] + k'_{\text{RS}^-}K_a^{\text{RSH}} + k_{\text{RSH}} \qquad (9)$$

where K_a^{RSH} is the acid dissociation constant of the mercaptan, and a plot of k_M *vs.* $1/(H^+)$ should be linear. Figure 1 shows that this is indeed the case, thereby demonstrating that the increase in k_M with decreasing (H^+) below 0.01 M $HClO_4$ is indeed due to the fact that reaction of n-BuS$^-$ with **1a** becomes significant at low acidities.

The next question to consider is whether eq 7 or 8 is the major contributor to the acid-independent term in eq 9. For other anionic nucleophiles (Cl^-, Br^-, etc.) reacting with **1a** one has found[3] that the rate constant (k'_{Nu}) for their acid-catalyzed reaction with the sulfinyl sulfone is never larger than five times the rate constant (k_{Nu}) for their uncatalyzed reaction with the same substrate. Assuming the same is true for n-BuS$^-$, this means that $(k'_{RS^-}/k_{RS^-}) \leq 5$. The slope of the plot in Figure 1 is equal to $k_{RS^-}K_a$, the intercept to $k'_{RS^-}K_a + k_{RSH}$. Since the intercept (0.02) is about 700 times greater than the slope (3×10^{-5}), this requires, provided $(k'_{RS^-}/k_{RS^-}) \leq 5$, that essentially all of the acid-independent term be due to eq 7, the reaction of the undissociated mercaptan with **1a**.

Above 0.10 M $HClO_4$ k_M increases slightly with increasing acid concentration (Table I). Does this represent a contribution to the rate from an acid-catalyzed reaction of the undissociated mercaptan with **1a** (eq 10),



$$\begin{gathered} n\text{-BuSH} + \text{Ar}\underset{\text{O}}{\underset{\|}{\text{S}}}\text{—}\overset{\text{O}}{\overset{\|}{\underset{\text{O}}{\underset{\|}{\text{S}}}}}\text{Ar} + \text{H}^+ \xrightarrow{k'_{\text{RSH}}} \\ n\text{-Bu}\underset{\text{H}}{\underset{|}{\overset{+}{\text{S}}}}\text{—}\underset{\text{O}}{\underset{\|}{\text{S}}}\text{Ar} + \text{ArSO}_2\text{H} \qquad (10) \\ \Big\downarrow \text{fast} \\ n\text{-BuS}\underset{\text{O}}{\underset{\|}{\text{S}}}\text{Ar} + \text{H}^+ \end{gathered}$$

analogous to eq 2 for the reaction of n-Bu$_2$S with **1a**? We think not and that the increase in k_M with $(HClO_4)$ in this region is more likely due to a salt effect on k_{RSH}, since the addition of equivalent amounts of $LiClO_4$ in place of $HClO_4$ leads to an even larger increase in k_M (last entry in Table I). However, even if the increase in k_M with $(HClO_4)$ should represent a contribution to the rate from eq 10, such an acid-catalyzed process is *much* less important relative to the rate of the uncatalyzed reaction for the mercaptan reacting with **1a** than for the reaction of the sulfide with **1a**. This can be seen (Table II) by comparing the variation of k_M in the

TABLE II

DEPENDENCE OF RATES OF REACTION OF BUTYL MERCAPTAN AND BUTYL SULFIDE WITH **1a** ON ACID CONCENTRATION[a]

$(HClO_4)$, M	k_M for n-BuSH reaction	k_S for Bu_2S reaction
0.01	0.020	<0.04
0.10	0.021	0.24
0.20	0.028	0.70
0.40	0.032	1.7

[a] All data for 60% dioxane at 21.4°.

region 0.01–0.40 M $HClO_4$ with the variation in k_S for the butyl sulfide catalyzed hydrolysis of **1a** over the same range of acid concentrations.

We conclude from this that the explanation previously offered[3] for why the sulfide-catalyzed hydrolysis of **1a** requires acid catalysis while the ordinary hydrolysis does not is apparently the correct one.

Experimental Section

Preparation and Purification of Materials.—p-Toluenesulfinyl p-tolyl sulfone (**1a**) and dioxane were prepared and/or purified in the manner described in an earlier paper.[3] n-Butyl mercaptan was freshly fractionally distilled under nitrogen, bp 97–98°.

Procedure for Kinetic Runs.—The general procedure for following the kinetics of the disappearance of **1a** was the same as that outlined previously.[3] To initiate a run the proper amount of a stock solution of **1a** in *anhydrous* dioxane was added to an aqueous dioxane solution containing the appropriate amounts of perchloric acid, n-butyl mercaptan, etc., both solutions having been brought to 21.4° before mixing. The disappearance of **1a** was then followed by monitoring the decrease in the optical density, A, of the solution at 300 mμ in the manner described in an earlier paper.[3] Plots of log $(A - A_\infty)$ *vs.* time were nicely linear. One should note that in those runs in which the reaction of mercaptan with **1a** accounts for most of the rate A_∞ is significantly larger than when one is following only the hydrolysis of **1a**, because of the fact that the thiolsulfinate product of the mercaptan–**1a** reaction, n-BuSS(O)Ar, has a significant extinction coefficient at 300 mμ, unlike the sulfinic acid, $ArSO_2H$, which is effectively transparent at this same wavelength. The spectra obtained at the end of the experiments in the presence of mercaptan corresponded to those expected for the formation of a mixture of thiolsulfinate (from the mercaptan–**1a** reaction) and sulfinic acid (from the normal hydrolysis) in the proportions predicted by comparison of k_1 in the presence of mercaptan and in its absence.

Registry No.—**1a**, 788-86-3; n-BuSH, 109-79-5; n-Bu_2S, 544-40-1.

Mechanisms of Substitution Reactions at Sulfinyl Sulfur. VII. General Base Catalysis by a Tertiary Amine of the Hydrolysis of an Aryl Sulfinyl Sulfone[1]

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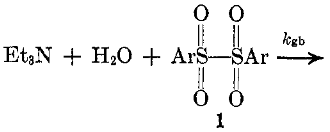
Received January 5, 1971

The hydrolysis of p-anisyl p-methoxybenzenesulfinyl sulfone (**2a**, eq 2) in aqueous dioxane or glyme can be catalyzed by various tertiary amines. The results for N-benzyldiethylamine, $(k^{H_2O}_{R_3N}/k^{D_2O}_{R_3N}) = 2.4$, clearly indicate that the amine is acting in that case as a general base catalyst and represent the first reported example of general base catalysis of a simple substitution at sulfinyl sulfur. On the other hand, the data for catalysis of the hydrolysis by pyridine point toward that amine acting as a nucleophilic rather than a general base catalyst. This, and the behavior of N-benzylpyrrolidine, both suggest that fairly modest changes in amine structure which merely reduce the steric hindrance around nitrogen can be sufficient to switch one from a situation where the tertiary amine acts as a general base catalyst to one where nucleophilic catalysis is observed to predominate instead. This, of course, means that each future example of tertiary amine catalysis of a substitution at sulfinyl sulfur will have to be examined carefully on an individual basis before decision can be reached as to whether nucleophilic or general base catalysis is involved.

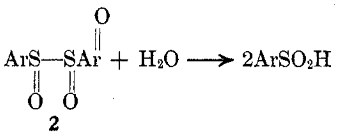
It was shown[3] recently that catalysis of the hydrolysis of aryl α-disulfones (**1**) by triethylamine in aqueous glyme or dioxane involves general base catalysis (eq 1), even though n-alkyl primary and secondary amines react with **1** as nucleophiles. This reaction represented the first reported case of general base catalysis of a substitution at sulfonyl sulfur, although another example has subsequently been reported.[4]



1

$$Et_3N + H_2O + ArS(O_2)\text{—}S(O_2)Ar \xrightarrow{k_{gb}} Et_3NH^+ + ArSO_3H + ArSO_2^- \quad (1)$$

We were interested in determining whether general base catalysis by a tertiary amine could also be observed in an analogous substitution at sulfinyl sulfur. We have accordingly investigated the catalysis of the hydrolysis (eq 2) of an aryl sulfinyl sulfone (**2**) by several tertiary amines under the same conditions. While the rapidity of the catalyzed reaction limited the range of tertiary amines that could be examined, we have still been able to demonstrate that, although certain tertiary amines like pyridine catalyze the hydrolysis by acting as nucleophilic catalysts, the more sterically hindered tertiary alkyl amine, N-benzyldiethylamine, catalyzes the hydrolysis by general base catalysis. To our knowledge this is the first example of general base catalysis of the hydrolysis of a sulfinyl compound, and it shows that this type of catalysis, which has been widely encountered in substitutions of carboxylic acid derivatives[5] and recently observed[3,4] in substitutions at sulfonyl sulfur, can also be important in appropriate substitutions at sulfinyl sulfur.



2

$$ArS(O)\text{—}S(O_2)Ar + H_2O \longrightarrow 2ArSO_2H \quad (2)$$

Results

Catalysis of the hydrolysis of p-anisyl p-methoxybenzenesulfinyl sulfone (**2a**, Ar = p-$CH_3OC_6H_4$) by various tertiary amines was investigated in either 60% glyme–40% water (v/v) or 60% dioxane–40% water (v/v) as

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