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Acid- and Nucleophile-Catalyzed Cleavage of Ethyl Benzenesulfenate in Aqueous Solution. Kinetic Evidence for a Hypervalent Intermediate[1]

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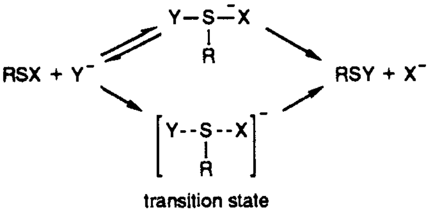
Abstract: Ethyl benzenesulfenate (**1**) undergoes acid-catalyzed hydrolysis to give *S*-phenyl benzenethiosulfinate, which is a condensation product of the initial hydrolysis product, benzenesulfenic acid. The pH-rate profile for the hydrolysis shows a break at pH 2 with limiting catalytic constants 0.13 and 1.3 $M^{-1}\,s^{-1}$ in the low and high pH regions. The break is ascribed to a change in the rate-determining step of the reaction involving a hypervalent sulfuranide intermediate. Nucleophiles including the substrate itself show efficient catalytic effects, though iodide induces the reduction of **1** to afford diphenyl disulfide. The nucleophilic reactivity pattern observed is unusual ($Cl^- < Br^- < I^- < SCN^- < (HOCH_2CH_2)_2S$) but is accommodated by a mechanism involving an incipient hypervalent intermediate, its decay becoming rate determining at least for some of the nucleophiles.

Nucleophilic substitution at a divalent sulfur takes place through a bimolecular mechanism.[2,3] The reaction may proceed in a stepwise manner with a hypervalent sulfur species (sulfuranide) as an intermediate (addition–elimination (A–E) mechanism) or in one step with synchronous bond formation and cleavage (S_N2-type mechanism).



(1)

Various pieces of evidence strongly suggest the possibility of the sulfuranide intermediate. Several stable sulfuranides have been isolated as salts,[4] and an intramolecular hypervalent interaction at divalent sulfur is well established from X-ray crystallography.[5] The recent theoretical calculations also support the formation of a sulfuranide intermediate in the nucleophilic substitution of a sulfenyl derivative.[6] However, the experimental observations reported are only suggestive of the existence of such an intermediate.

Intermediacy of the hypervalent species (sulfurane) for the reaction at trivalent sulfur has been extensively probed by stereochemical studies,[7] but such a study is impossible for the reaction at divalent sulfur. The kinetic method may be the only useful experimental approach to this problem at divalent sulfur. Various structure-reactivity relationships have been discussed in favor of sulfuranide intermediates in the reactions of sulfenyl halides,[8] sulfenate esters,[9,10] thiolsulfinates,[11,12] and thiolsulfonates,[13,14] while similar results on the reactions of disulfides have been taken as evidence for the synchronous S_N2-type mechanism.[15] These results constitute only suggestive but not conclusive evidence for the intermediate.[3] Nonlinear dependence of the rate of aminolysis of sulfenyl chlorides on amine concentrations may be taken as evidence for an intermediate,[16] but this intermediate could be either an ion pair or a hypervalent intermediate.[2,3]

The present paper deals with the kinetics of the acid-catalyzed hydrolysis of a simple sulfenate ester, ethyl benzenesulfenate (**1**), as a typical nucleophilic substitution of this class of compounds, and will present two lines of evidence for a hypervalent intermediate, a change in rate-determining step and an unusual pattern of nucleophilic acceleration. Although the reaction is simple and takes place easily in aqueous acid, it has never been investigated kinetically, probably because of the belief that the instability of the product, sulfenic acid, would complicate the analysis. Only the rates of the alkaline hydrolysis of some sulfenate esters have been measured.[9,17]

Results

On addition of ethyl benzenesulfenate (**1**) to aqueous acid, the UV spectrum of **1** changes to that of *S*-phenyl benzenethiosulfinate (**3**) which has a maximum absorption at 275 nm (ε, 8800) and isosbestic points at 227 and 251 nm as shown in Figure 1. This change is accommodated by the reaction sequence 2, which involves rapid formation of **3** from the primary hydrolysis product, benzenesulfenic acid (**2**). The instability of sulfenic acid is universally recognized, and it is known to undergo facile con-

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Table I. "Initial" Rate Constants (10^3k_i, s^{-1}) in Perchloric Acid at Various Initial Concentrations of the Substrate **1**[a]

	$10^4[\mathbf{1}]_0$, M						
$[HClO_4]$, M	0.678	1.015	1.35	2.02	10^3k_0, s^{-1}	k_{SE}, M^{-1} s^{-1}	k_{SE}^{H},[b] M^{-2} s^{-1}
0.10	24.3	27.3	32.5	38.7	16.8	110	(1100)
0.05	13.2	16.2	20.4	24.9	7.51	88.2	1760
0.020	5.85	7.32	8.35	11.7	2.83	43.2	2160
0.010	3.23	3.86	4.72	5.70	2.02	18.6	1860
0.005	1.98	2.45	2.69	3.24	1.44	9.07	1810
0.0020	1.44	1.54	1.69	1.82	1.26	2.87	(1440)
0.0010		0.842	0.842	0.906	0.76	(0.68)	
0.0005	0.461	0.467	0.469	0.478	0.45	(0.12)	
0.0004[c]		0.397			0.40		
0.0002[c]	0.208	0.204	0.206		0.206		
0.0001[c]	0.102	0.098	0.108		0.103		
0.00005[c]		0.074	0.069		0.072		

[a] Measured at 25 °C and an ionic strength of 0.50 ($NaClO_4$). [b] $k_{SE}^{H} = k_{SE}/[HClO_4]$. The values in parentheses are less reliable (see text). [c] Pseudo-first-order rate constants obtained after an induction period.

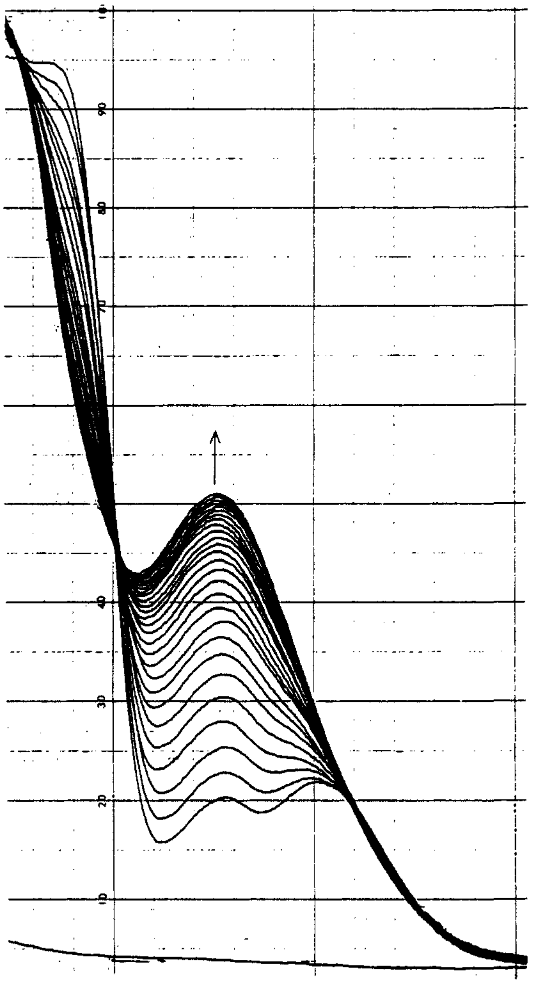

Figure 1. Typical UV spectral changes during the reaction of **1** in aqueous perchloric acid at $[HClO_4] = 5 \times 10^{-3}$ M and $[\mathbf{1}]_0 = 1.2 \times 10^{-4}$ M.

densation to thiosulfinate.[18] Yields of **3** are always >90% as determined by UV and HPLC.

$$\underset{\mathbf{1}}{\text{PhSOEt}} + H_2O \xrightarrow{H^+} \underset{\mathbf{2}}{\text{PhSOH}} + \text{EtOH} \xrightarrow{\text{rapid}} \tfrac{1}{2}\underset{\mathbf{3}}{\text{PhS(O)SPh}} + \tfrac{1}{2}H_2O + \text{EtOH} \quad (2)$$

However, the formation of **3** in aqueous perchloric acid at $[HClO_4] \geq 2 \times 10^{-3}$ M does not follow pseudo-first-order kinetics.

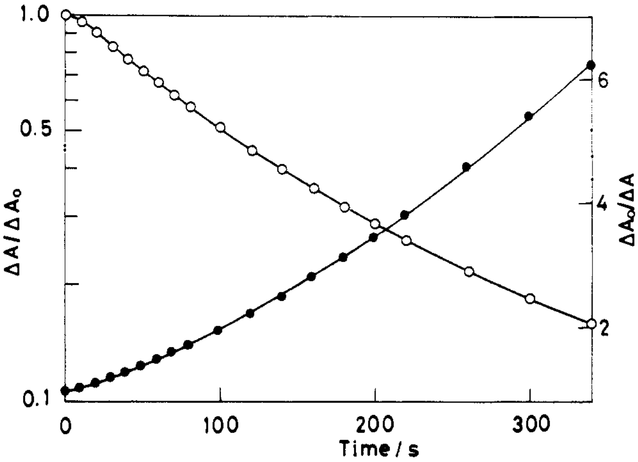

Figure 2. Logarithmic (○) and reciprocal (●) plots of $\Delta A/\Delta A_0$ against reaction time for the increase in absorbance at 275 nm in the reaction of **1** at $[HClO_4] = 0.02$ M and $[\mathbf{1}]_0 = 1.35 \times 10^{-4}$ M.

Neither plots as a first-order reaction (log ΔA vs t) nor as a second-order reaction ($1/\Delta A$ vs t) are linear as shown in Figure 2. There is an induction period followed by decay which gives a curve with decreasing steepness as seen in the log $\Delta A - t$ plot. In these cases, "initial" rate constants k_i were determined from the steepest slope of the log $\Delta A - t$ plots just after the induction period. The value of k_i increases with increasing initial concentration of the substrate $[\mathbf{1}]_0$ (eq 3) as summarized in Table I. The rate constants were measured at 25 °C, and the ionic strength of 0.50 was maintained with $NaClO_4$. The substrate is a catalyst

$$k_i = k_0 + k_{SE}[\mathbf{1}]_0 \quad (3)$$

for the hydrolysis, and the substrate- and water-catalyzed hydrolyses (k_{SE} and k_0) are competing with each other. This is a reason for the deviations from both first-order and second-order kinetics. The induction must be due to the formation of intermediate **2**. However, **2** would always present in a steady-state concentration, and hence the rate constants observed for the formation of **3** (275 nm) should represent those for the hydrolysis of **1**.

With decreasing concentrations of perchloric acid below 5×10^{-3} M, the curvature of the log $\Delta A - t$ plot becomes milder (except for an induction period), and the reaction can practically be analyzed as a first-order reaction after an induction period at $[HClO_4] < 5 \times 10^{-4}$ M to give k_{obsd} which is independent of $[\mathbf{1}]_0$ (Table I).

By contrast, the pseudo-first-order plots are satisfactorily linear after a short induction period in hydrochloric acid. The observed rate constants k_{obsd} are larger in hydrochloric acid than in perchloric acid. It was found that the hydrolysis is accelerated by addition of chloride, bromide, and a neutral dialkyl sulfide. In the presence of these nucleophiles, the UV spectral change closely resembles that observed in perchloric acid, and the reaction follows

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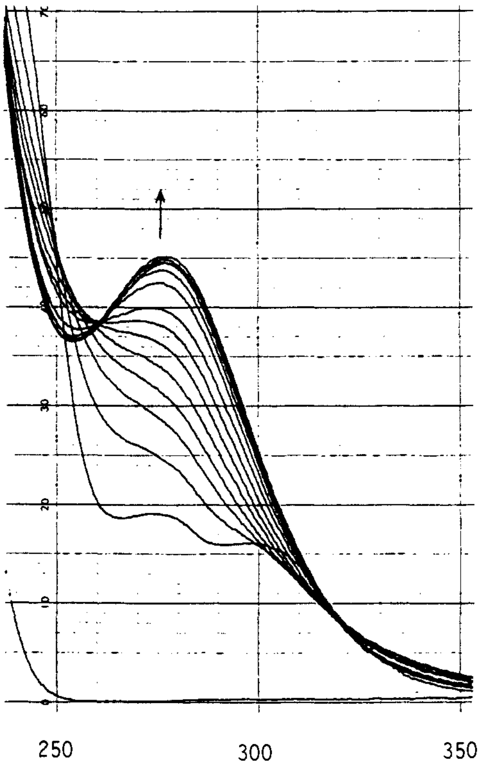


Figure 3. UV spectral changes during the reaction of **1** in the presence of thiocyanate ion, $[SCN^-] = 2 \times 10^{-3}$ M, at $[H^+] = 2 \times 10^{-3}$ M.

Table II. Rate Constants for Nucleophile-Catalyzed Reactions of **1**

$10^3[H^+]$, M	$10^2[Nu]$, M	k_{Nu},[a] $M^{-1}\ s^{-1}$	$k_{Nu}{}^{H}$,[b] $M^{-2}\ s^{-1}$
		Nu = Cl^-	
0.40	10–40	$(7.57 \pm 0.07) \times 10^{-3}$	18.9
0.50	10-40	$(9.86 \pm 0.26) \times 10^{-3}$	19.7
1.0	10-40	$(1.72 \pm 0.12) \times 10^{-2}$	17.2
10	10-40	$(1.64 \pm 0.01) \times 10^{-1}$	16.4
20	10-40	$(3.47 \pm 0.02) \times 10^{-1}$	17.3
		Nu = Br^-	
0.50	0.5-10	$(4.70 \pm 0.06) \times 10^{-2}$	94.0
2.0	1.0–10	$(1.94 \pm 0.02) \times 10^{-1}$	97.0
5.0	1.0–10	$(5.00 \pm 0.05) \times 10^{-1}$	100
10	5.0–20	$(9.26 \pm 0.07) \times 10^{-1}$	92.6
		Nu = $(HOCH_2CH_2)_2S$	
2.0	0.025–0.25	6.90 ± 0.07	3450
10	0.025–0.20	33.6 ± 0.7	3360
1.0–10	0.10	4.03 ± 0.04[c]	4030
		Nu = SCN^-	
2.0	0.05–1.0	5.84 ± 0.03	2940
10	0.05-0.4	28.1 ± 0.2	2810
0.20–50	0.10	3.11 ± 0.02[c]	3110
		Nu = I^-[d]	
2.0	0.50–5.0	2.22 ± 0.03	1110
0.50–5.0	0.50	6.06 ± 0.06[c]	1210

[a] Measured at an ionic strength of 0.50 and 25 °C, and standard deviations are given. [b] $k_{Nu}{}^{H} = k_{Nu}/[H^+]$ or (a slope of the k_{obsd} – $[H^+]$plot)/[Nu]. [c] A slope for acidity dependence at the constant [Nu]. [d] Measured in 10 vol % aqueous acetonitrile.

pseudo-first-order kinetics as monitored by the increase in absorbance at 275 nm. (The k_{obsd} values are summarized in Tables SI–SVI as Supplementary Material.) The k_{obsd} increases linearly with concentration of added nucleophile [Nu], and the slope k_{Nu} is proportional to acid concentration (eq 4). The results are summarized in Table II. The substrate-catalyzed reaction also

$$k_{obsd} = k_0 + k_{Nu}{}^{H}[H^+][Nu] \qquad (4)$$

shows the same trend. The $k_{SE}{}^{H}$ calculated are reasonably constant in the range $[HClO_4] = 0.005–0.05$ M (Table I). The values at lower $[HClO_4]$ are less reliable because of the small dependency on $[\mathbf{1}]_0$. The reason for the much smaller value of $k_{SE}{}^{H}$ obtained at $[HClO_4] = 0.10$ M is not clear, but it may in part be the result from some systematic errors in obtaining k_i.

These hydrolyses catalyzed by added nucleophiles must proceed with intermediate formation of the substitution products (eq 5) which are then easily hydrolyzed and condensed to the final product **3** (eq 6).

$$\mathbf{1} + H^+ \rightleftharpoons PhSO^+(H)Et \xrightarrow{Nu} PhSNu \qquad (5)$$

$$PhSNu + H_2O \rightarrow \mathbf{2} \rightarrow \mathbf{3} \qquad (6)$$

UV spectral changes for the reaction of **1** in the presence of thiocyanate ion are shown in Figure 3. The changes are quite different from those seen in the other hydrolysis reaction (Figure 1). The reaction apparently occurs in a stepwise manner. The latter slow reaction occurs with a good isosbestic point at 261 nm, and the final spectrum is similar to that of **3**. The HPLC analysis also confirms the formation of **3** in this reaction. The log ΔA vs t plots for the increase in absorbance at 275 nm are strongly curved, but the slope for the latter linear part is essentially constant and independent of concentrations of both acid (0.002–0.01 M) and thiocyanate (0.001–0.2 M) to give $k_{obsd} = (2.15 \pm 0.09) \times 10^{-3}\ s^{-1}$. However, the increase in absorbance at 261 nm, the isosbestic point for the latter stage of the reaction, obeys pseudo-first-order kinetics. This pseudo-first-order reaction must reflect the first nucleophilic reaction of **1** with thiocyanate, and hence the reaction should occur in two steps (eq 7). The k_{obsd} determined for both the first reaction (261 nm) and the second reaction are summarized in Table SV (Supplementary Material). The k_{obsd} for the first reaction obeys eq 4 (Table II). The overall reaction must proceed with accumulation of the intermediate PhSSCN. The k_{obsd} for the second reaction is due to the hydrolysis of PhSSCN and is independent of acid catalysis.

$$PhSO^+(H)Et + SCN^- \rightarrow PhSSCN \xrightarrow{H_2O} \mathbf{2} \qquad (7)$$

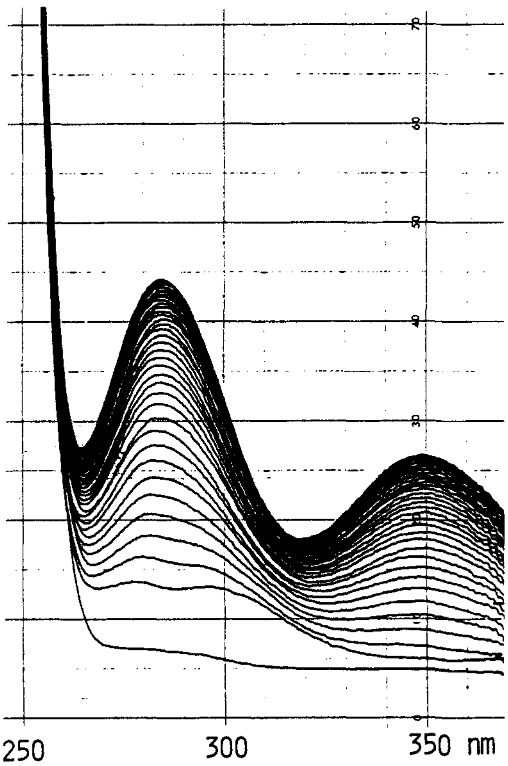


Figure 4. UV spectral changes during the reaction of **1** in the presence of iodide ion, $[I^-] = 0.05$ M, at $[H^+] = 5 \times 10^{-4}$ M.

In the presence of iodide ion, the spectral change is again different from that observed in the simple hydrolysis (Figure 4).

Table III. Nucleophilic Catalytic Constants for the Acid-Catalyzed Reaction of **1**[a] and Relative Nucleophilicities in Some Related Reactions

nucleophile	k_{Nu}^H, M^{-2} s^{-1}	k_{Nu}^H/k_{Cl}^H	rel nucl in reaction 12[b]	13[c]	14[d]
H_2O	0.0024	10^{-4}			
Cl^-	17.9	1.0	1.0	1.0	
Br^-	95.9	5.4	26	35	1.0
I^-	1160[e]	65[e]	1.12 ± 10^3	1.4 ± 10^4	3.0
SCN^-	2950	165	214	5.4×10^3	19
$(HOCH_2CH_2)_2S$	3600	200	9.3[f]	829[g]	
PhSOEt	1900[h]	106			

[a] Measured in aqueous solution at an ionic strength of 0.50 and 25 °C. [b] Relative nucleophilicities for reaction 12 in methanol solution at 25 °C.[20] [c] Relative nucleophilicities for reaction 13 in 60 vol % aqueous dioxane at 39.1 °C.[11] [d] Relative nucleophilicities for reaction 14 in 60 vol % aqueous dioxane at 25 °C.[14] [e] Measured in 10 vol % aqueous acetonitrile. [f] A value for Et_2S. [g] A value for Bu_2S. [h] The average of the values at $[H^+]$ = 0.005–0.05 M (Table I).

The final spectrum showed λ_{max} at 285 and 350 nm and is similar to that of the triiodide ion (eq 8). The reaction was carried out

$$I_2 + I^- \rightleftharpoons I_3^- \qquad (8)$$

in degassed water containing 10 vol % of acetontrile under an argon atmosphere to avoid air oxidation of iodide. Formation of diphenyl disulfide (**4**) was confirmed by HPLC separation and mass spectrometry. Quantitative analysis of the products showed the stoichiometry given in eq 9, reduction, as reported in the previous communication.[19] The wholly aqueous reaction solution became turbid with the progression of the reaction probably because of low solubility of the disulfide formed. Some of the

$$\mathbf{1} + H^+ + I^- \rightarrow \underset{\mathbf{4}}{\tfrac{1}{2}PhSSPh} + \tfrac{1}{2}I_2 + EtOH \qquad (9)$$

hydrolysis product **3** was also found. The increase in absorbance at either 275 or 350 nm followed pseudo-first-order kinetics, and the k_{obsd} obtained from the different wavelengths are essentially identical (data given in Table SVI, Supplementary Material). The k_{obsd} are first order in iodide concentration and follow eq 4 (Table II). This implies that the k_{obsd} reflects the nucleophilic attack of iodide on **1**.

In the pH region 4–5, the hydrolysis of **1** was examined in acetate buffer solution. Positive buffer effects were observed, but details have not been examined in this stage of study. Acetate can also be a nucleophilic catalyst for the hydrolysis.

Nucleophilic catalytic constants for the acid-catalyzed reaction of **1** are summarized in Table III as averages of those given in Table II. These rate constants refer to the acid-catalyzed nucleophilic substitution of **1** (eq 5).

Discussion

pH-Rate Profile. Rate constants k_0 independent of nucleophilic catalysis are logarithmically plotted against pH in Figure 5. The pH-rate profile clearly shows a break at pH ~2 with two different acid-catalyzed processes. The break is accommodated by a change in the rate-determining step with changing pH. The reaction proceeds stepwise with intermediate(s), and the most plausible intermediate for this reaction is a hypervalent sulfuranide. The changeover of the rate-determining step implies a change in the relative magnitude of rate constants for the return (k_{-1}) and the decay (k_2) of the intermediate occurring with changing pH. This must take place because the extent of protonation of the intermediate changes with pH. Such a mechanism for the acid-catalyzed hydrolysis of **1** is given in Scheme I.

At lower pH, the main reaction takes place through the protonated hypervalent intermediate **5a**, and the breakdown of **5a** must be rate determining ($k_{-1} > k_2$). With increasing pH, deprotonation would occur mainly at the more acidic H_2O^+ group of **5a** to give **5b** rather than at the $Et(H)O^+$ group. This would make the decay of the intermediate faster than the return ($k_{-1} < k_2 + K'_ak'_2/[H^+]$), and the formation of the intermediate becomes rate determining at higher pH. According to Scheme I, k_0 is described by eq. 10. The limiting catalytic constants at

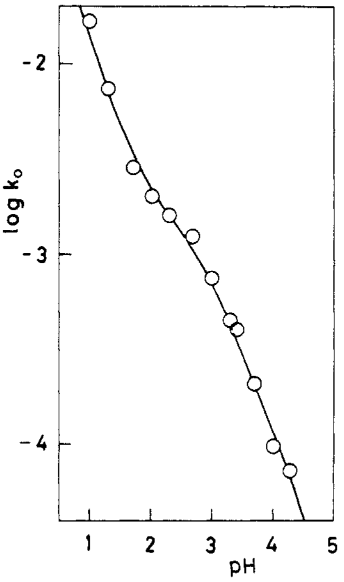
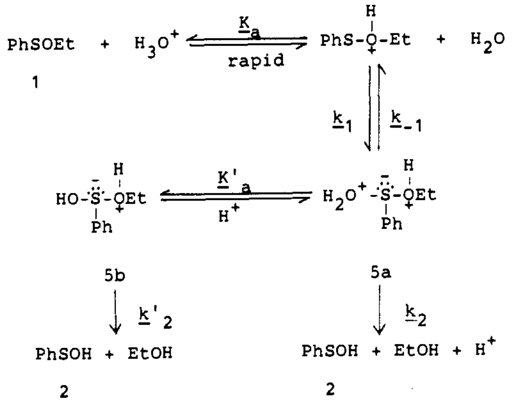


Figure 5. The pH-rate profile for the hydrolysis of **1**. The solid line is a theoretical curve (see text).

Scheme I



$$k_0 = \frac{(k_1/K_a)([H^+] + K'_ak'_2/k_2)[H^+]}{(k_{-1} + k_2)[H^+]/k_2 + K'_ak'_2/k_2} \qquad (10)$$

the lower and higher pH are $k_1k_2/K_a(k_{-1} + k_2)$ = 0.13 and k_1/K_a = 1.3 M^{-1} s^{-1}, respectively. The break occurs at $[H^+] = K'_ak'_2/k_2$ = 0.01 M. The solid curve in Figure 5 is drawn according to eq 10 with these parameters. The break in the pH-rate profile is taken as a new piece of evidence for the hypervalent intermediate that exists on the reaction coordinate for nucleophilic substitution at divalent sulfur.

Nucleophilic Catalysis. Summarized in Table III are the catalytic efficiencies of nucleophiles, which represent nucleo-

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philicities in reaction 11, the rate-determining step of the overall reaction. The unique feature of the reactivity is that thiocyanate

$$PhSO^+(H)Et + Nu^- \rightarrow PhSNu + EtOH \qquad (11)$$

and a neutral sulfide are more reactive than iodide ($R_2S > SCN^- > I^-$). These results are compared with the nucleophilicities observed in a typical S_N2 reaction at carbon (eq 12) in methanol solution[20] and those observed for reaction 13 involved in the nucleophile-catalyzed racemization of the thiolsulfinate.[11] The rate-determining step of the latter reaction is considered to be a nucleophilic attack at the divalent sulfur.[11] In both of the reactions iodide is the strongest nucleophile, $I^- > SCN^- > R_2S$. The unique

$$CH_3I + Nu^- \rightarrow CH_3Nu + I^- \qquad (12)$$

$$PhSS^+(OH)Ph + Nu^- \rightarrow PhSNu + PhSOH \qquad (13)$$

reactivity pattern for the present reaction (11) at the divalent sulfur may imply that the rate-determining step is not a simple nucleophilic reaction. That is, the concerted S_N2-type substitution and the rate-determining formation of a hypervalent addition intermediate can be excluded as a possible mechanism. The reaction must involve a hypervalent intermediate, and the rate-determining step is the decay of the intermediate at least for some of the nucleophiles. A similar reactivity ($SCN^- > I^-$) observed for the nucleophilic reaction of the thiolsulfonate (eq 14) was accommodated by a similar suggestion.[14]

$$PhSS(O)_2Ph + Nu^- \rightarrow PhSNu + PhSO_2^- \qquad (14)$$

This conclusion can be depicted by eq 15. When the leaving ability of Nu^- is greater than that of EtOH ($k_{-1}{}^{Nu} > k_2{}^{Nu}$), the decay of the intermediate is rate determining. This would be the case at least for some of the nucleophiles employed here. The pK_a for the conjugate acids HNu of I^- (−10), Br^- (−9), Cl^- (−7), and Me_2S (−6.99)[21] are much lower than that for EtO^+H_2 (−1.64).[21]

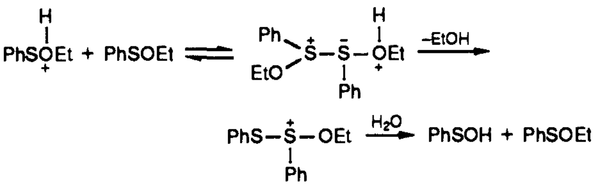
$$PhSO^+(H)Et + Nu^- \underset{k_{-1}{}^{Nu}}{\overset{k_1{}^{Nu}}{\rightleftharpoons}} \underset{\mathbf{6}}{NuS(Ph)O^+(H)Et} \xrightarrow{k_2{}^{Nu}} PhSNu + EtOH \qquad (15)$$

The observed catalytic constant can be described by eq 16 and tends to become smaller as the leaving ability of Nu^- ($k_{-1}{}^{Nu}$) increases. The relatively smaller nucleophilicity observed for iodide may be ascribed to the large value of $k_{-1}{}^{Nu}/k_2{}^{Nu}$.

$$k_{Nu}{}^{H} = k_1{}^{Nu}/K_a(1 + k_{-1}{}^{Nu}/k_2{}^{Nu}) \qquad (16)$$

A pH-dependent change in the rate-determining step did not seem to occur for the nucleophile-catalyzed reaction (eq 15). This is due to the absence of any dissociable proton on the Nu group of the intermediate **6**, which could retard the return ($k_{-1}{}^{Nu}$).

The self-catalysis exerted by the substrate should take place in the same way as that of other nucleophiles, and the reaction may proceed as shown in eq 17. The catalytic efficiency of the sulfenate ester is comparable to that of the sulfide.



(17)

Effects of the self-catalysis on the kinetics and the deviation from the pseudo-first-order kinetics are more clearly seen at higher acidity. This may simply be due to the varying magnitude of the acid-catalytic rate constant in the absence of added nucleophiles. The k_H value is 10 times greater in the high pH region where the formation of the intermediate is rate determining than in the low pH region where the decay of the intermediate is rate determining. The competitive nucleophilic catalysis by the substrate of low concentration can easily be hidden in the unassisted reaction at higher pH.

In conclusion, the break of the pH-rate profile for the acid-catalyzed hydrolysis of a simple sulfenate is taken as a new piece of evidence for the hypervalent sulfuranide intermediate. The unusually low nucleophilic reactivity of iodide toward the sulfenate is also consistent with the formation of the hypervalent intermediate.

Experimental Section

Materials. Ethyl benzenesulfenate (**1**) was prepared according to Armitage[22] and stored under nitrogen. Inorganic salts of the best grade commercially available were dried at about 110 °C when necessary. Bis(2-hydroxyethyl) sulfide was distilled before use.

Product Analysis. Reaction products obtained under kinetic conditions were analyzed on an HPLC analyzer, JASCO BIP-1, equipped with a Finepak SIL $C_{18}S$ column using 1:1 (v/v) CH_3CN-H_2O as an eluent. Retention times and areas of the peaks were compared with those of the authentic samples. Triiodide concentrations were determined from the absorption at 350 nm.

Kinetic Measurements. Acid solutions were prepared from 70% perchloric acid and titrated with a standard NaOH solution. Sodium salts were used for anionic nucleophiles. Solutions of nucleophiles and the substrate **1** were prepared in a volumetric flask by weighing. Ionic strengths were maintained at 0.50 with sodium perchlorate. Iodide solutions were prepared and used under an argon atmosphere.

The UV spectra were recorded on a Shimadzu UV 200 spectrophotometer. Reaction was started by introducing an appropriate amount of a stock solution of **1** in acetonitrile (ca. 2×10^{-2} M) from a microsyringe into 3.0 mL of an acid–nucleophile solution in a quartz cuvette equilibrated at 25.0 + 0.1 °C in a cell compartment of the spectrophotometer. The reaction was usually followed by the absorbance increase at 275 nm. The absorbance data were fed to a personal computer, NEC 9801F, through an A–D converter and were processed with a pseudo-first-order kinetics program. For the well-behaved reactions, the pseudo-first-order rate constants were obtained in the usual way be excluding the initial data during an induction period, typically for about 10% of the total absorbance change.

In perchloric acid at $>5 \times 10^{-4}$ M, the kinetic curves were complicated (Figure 2). The steepest slope, defined as "initial rate constant k_i", was obtained by excluding the data of both the initial and latter parts of the reaction; typically the initial 20 and the final 210 points were excluded out of 250 points of the data fed to the computer. These operations were carried out manually (by trial and error basis) on the computer to get the largest value of k_{obsd} by the pseudo-first-order kinetics program with at least 10 remaining data points.

The thiocyanate reaction was biphasic. The k_{obsd} for the first reaction was obtained from the absorbance increase at 261 nm which is the isosbestic point for the second reaction. The k_{obsd} for the second reaction was obtained from the final slope of the pseudo-first-order plot for the increase in the 275-nm absorption. The iodide reaction was followed both at 275 and 350 nm and gave the same k_{obsd} from the two wavelengths.

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Supplementary Material Available: Tables SI–SVI of k_{obsd} for the nucleophile-catalyzed reactions (6 pages). Ordering information is given on any current masthead page.

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