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Acid-Catalyzed Hydrolysis of Methoxymethyl Phenyl Sulfoxide without Concomitant Racemization

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Methoxymethyl phenyl sulfoxide **1** undergoes acid-catalyzed hydrolysis to give *S*-phenyl benzenethiosulfinate **5**, which is formed rapidly from a primary product, benzenesulfenic acid **3**. Formation of **5** follows pseudo-first-order kinetics. Rate constants obtained spectrophotometrically in perchloric acid show that the reaction is dependent on the protonated substrate with the Bunnett–Olsen ϕ=−0.15. Rate constants for the loss of optical activity of the enantiomeric **1** measured in 80 vol% aqueous dioxane are identical with those obtained spectrophotometrically for the formation of **5**. Racemization of the substrate does not take place more rapidly than the fragmentation. The reaction is accelerated by chloride and bromide ions. The halide reaction is first order in acid concentration.

Dithioacetal monooxides are hydrolyzed to the aldehydes in acid solution more easily than the dithioacetals, and this conversion is widely used in organic syntheses as deprotection of the carbonyl group[1] and as a dethiolation step after alkylation of the carbanions derived from sulfoxides.[1b,2] Details of the mechanism of this transformation remain to be solved probably because the reaction is too slow under mild conditions appropriate for mechanistic investigations.[3] A more reactive sulfoxide, methoxymethyl phenyl sulfoxide **1**, is chosen here as a substrate for mechanistic studies, and acid-catalyzed hydrolysis of **1** has been kinetically investigated. The hydrolysis was found to be accelerated by added chloride and bromide ions. Racemization of the substrate was not observed during the reaction.

Closely related acid-catalyzed reactions of sulfoxides are racemization[4–9] and oxygen exchange.[9,10] These reactions are also catalyzed by halide ions. *t*-Butyl and phenethyl sulfoxides were found to undergo fragmentation leading to hydrolysis in aqueous solution.[6] This fragmentation was, however, not influenced by halide ions. Similarities and differences between these reactions and the present reaction will be discussed in terms of reaction mechanisms.

Results

When the sulfoxide **1** was added to aqueous acid, the UV absorption spectrum changed smoothly to develop a new spectrum with isosbestic points at about 238 and 247 nm. The product spectrum closely resembles that of *S*-phenyl benzenethiosulfinate **5**: Absorbances at wavelengths of maximum (275 nm), minimum (253 nm), and shoulder (220 nm) absorptions were about 90—95% of those calculated from the extinction coefficients determined with the authentic sample of **5** prepared independently. Formation of **5** was also confirmed by HPLC. In prolonged reactions, diphenyl disulfide and *S*-phenyl benzenethiosulfonate, disproportionation products from **5**, were also formed (HPLC). The dimeric product **5** is reported to be formed very rapidly from benzenesulfenic acid **3**,[11] a primary hydrolysis product. A possible reaction sequence is thus described by Eqs. 1—3.

$$\underset{\mathbf{1}}{PhS(O)CH_2OMe} + H_3O^+ \rightleftharpoons \underset{\mathbf{2}}{PhS^+(OH)CH_2OMe} + H_2O$$

$$\underset{\mathbf{2}}{PhS^+(OH)CH_2OMe} \longrightarrow \underset{\mathbf{3}}{PhSOH} + \underset{\mathbf{4}}{MeOCH_2OH} \quad (1)$$

$$\mathbf{2}\ \mathbf{3} \xrightarrow{\text{rapid}} \underset{\mathbf{5}}{PhS(O)SPh} + H_2O \quad (2)$$

$$\mathbf{4} + H_2O \xrightarrow{\text{rapid}} CH_2(OH)_2 + MeOH \quad (3)$$

Time-dependent absorbance changes at 275 nm were recorded on a conventional spectrophotometer, and the changes were found usually to follow pseudo-first-order kinetics. In some slow runs, induction periods were observed. Pseudo-first-order rate constants k_{obsd} were calculated from the later part of reaction and are considered to reflect rates of hydrolysis of **1**. This is confirmed by the observation that the k_{obsd} obtained spectrophotometrically agrees well with that for the loss of optical activity of the enantiomeric substrate (see below).

Observed rate constants k_{obsd} obtained under various reaction conditions are summarized in Tables 1—4. Table 1 shows acidity dependence, and the k_{obsd} measured in HCl are greater than those in $HClO_4$. The rate constant obtained in deuterium media was 2.77 times greater than that in H_2O as measured at [H(D)Cl]=0.20 M (1 M=1 mol dm^{-3}). Effects of chloride and bromide ions were examined in 10 vol% aqueous acetonitrile solution while the ionic strength was maintained at 0.45 with $NaClO_4$ (Tables 2 and 3). The rates increase linearly with halide concentrations as seen in Fig. 1. Second-order rate constants for the halide reactions are proportional to acid concentration (Fig. 2). The catalytic constants at 25 °C are:

Table 1. Rate Constants for the Hydrolysis of **1** in Aqueous Perchloric and Hydrochloric Acids at 25 °C[a]

$[HClO_4]$/M	$10^4 k_{obsd}/s^{-1}$	[HCl]/M	$10^4 k_{obsd}/s^{-1}$
0.200	0.498	0.20	(0.687)[b]
0.295	0.743	0.40	(1.84)
0.400	0.999 (1.20)	0.50	(2.61)
0.590	1.60	0.75	(4.78)
1.00	3.15	1.00	(8.23)
1.18	3.96 (4.30)		
2.36	13.1		
2.95	19.5 (22.1)		
3.54	32.9		
4.72	83.1		
5.90	216		
7.08	595		
8.26	1402		

a) The ionic strength was not adjusted. Values in parentheses were obtained in aqueous solution containing 10 vol% of acetonitrile. b) k_{obsd} was 1.90×10^{-4} s^{-1} in D_2O at 0.20 M of DCl.

Table 2. Effects of Chloride Ion Concentrations on the Hydrolysis Rate of **1** in 10 vol% Aqueous Acetonitrile Solution at 25 °C[a]

$[Cl^-]$/M	$[H^+]$/M			
	0.10	0.20	0.30	0.40
0	0.325	0.602	0.911	1.18
0.10			1.04	1.36
0.20	0.408	0.771	1.16	1.54
0.30	0.450	0.840	1.28	1.67
0.40	0.473	0.906	1.39	1.85
$10^4 k_{Cl}/M^{-1} s^{-1}$	0.379	0.764	1.20	1.65

a) $10^4 k_{obsd}$ are given in s^{-1}. The ionic strength was maintained at 0.45 with $NaClO_4$.

Table 3. Effects of Bromide Ion Concentrations on the Hydrolysis Rate of **1** in 10 vol% Aqueous Acetonitrile Solution[a]

$[Br^-]$/M	$[H^+]$/M				
	0.20			0.10	0.40
	25 °C	30 °C	35 °C	25 °C	25 °C
0	0.602	1.22	2.36	0.325	1.18
0.05	0.808	1.56	2.95		
0.10	0.981	1.89	3.48		1.86
0.15	1.125	2.10	4.05		
0.20	1.28	2.41	4.50	0.639	2.50
$10^4 k_{Br}/M^{-1} s^{-1}$	3.35	5.84	10.76	1.67	6.60

a) $10^4 k_{obsd}$ are given in s^{-1}. The ionic strength was maintained at 0.45 with $NaClO_4$.

$k_H=2.95\times10^{-4}M^{-1} s^{-1}$; $k_{Cl}^H=4.12\times10^{-4}M^{-2} s^{-1}$; $k_{Br}^H=1.66\times10^{-3}M^{-2} s^{-1}$.

$$k_{obsd} = k_H[H^+] + k_X^H[H^+][X^-] \quad (4)$$

Table 4. Rate Constants for the Hydrolysis and the Optical Activity Loss of Active **1** in Aqueous Dioxane Solution at 25 °C

Dioxane vol%	$[H^+]$ M	$[Cl^-]$ M	$[Br^-]$ M	$10^3 k_h$ s^{-1}	$10^3 k_\alpha$ s^{-1}
20	0.40	0	0	0.118	
50	0.40	0	0	0.158	
80	0.40	0	0	0.521	0.518
80	0.40	0.10	0	1.22	1.22
80	0.40	0.20	0	1.81	1.89
80	0.40	0.30	0	2.38	2.42
80	0.40	0.40	0	2.89	2.83
80	0.40	0	0.20	5.95	5.82
80	0.40	0	0.40	11.1	10.8

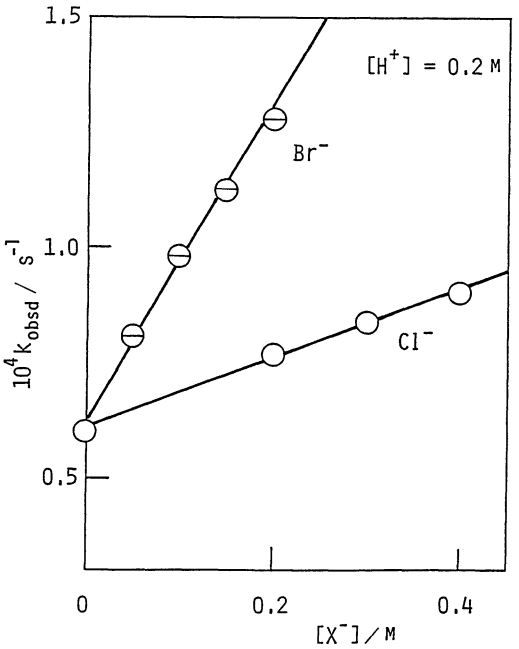


Fig. 1. Dependence of the hydrolysis rate of **1** on halide ion concentrations at 25 °C and $[HClO_4]$= 0.20 M in 10 vol% aqueous acetonitrile.

Table 3 also gives rate constants at varying temperatures: activation enthalpies $\Delta H^{\neq}$ for the acid-catalyzed and bromide ion-catalyzed reactions are calculated to be 24.3 and 20.7 kcal mol^{-1} (1 cal=4.184 J), while the activation entropies $\Delta S^{\neq}$ for k_H and k_{Br}^H are 0.5 and −8.3 cal K^{-1} mol^{-1}, respectively.

In Table 4, hydrolysis rate constants k_h obtained spectrophotometrically in aqueous dioxane are compared with rate constants k_α for the loss of optical activity of the enantiomeric substrate. Both rate constants are identical within experimental errors. The optically active substrate of **1** was prepared by the Sharpless oxidation of methoxymethyl phenyl sulfide in the presence of diethyl tartrate.[12] Data in Table 4 also show that hydrolysis rates increase with increasing content of dioxane in the reaction media.

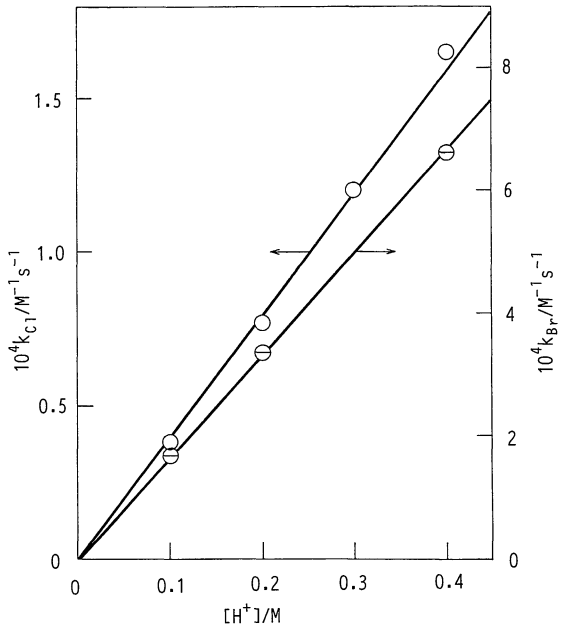


Fig. 2. Acidity dependence of the halide ion-catalyzed hydrolysis of **1**.

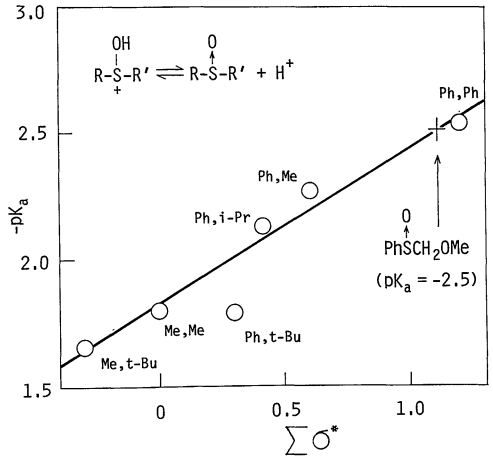


Fig. 3. Correlation of pK_a of protonated sulfoxides RS(O)R′ with the σ^* constants. Data are taken from Ref. 13 and R, R′ are given.

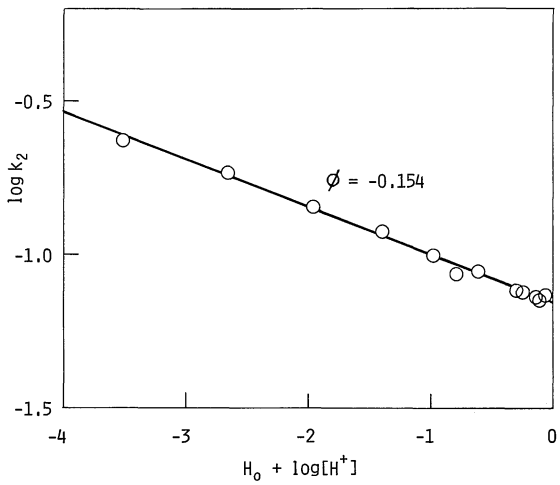


Fig. 4. The Bunnett–Olsen correlation for the acid-catalyzed hydrolysis of **1** in aqueous perchloric acid.

Discussion

Rates of formation of *S*-phenyl benzenethiosulfinate **5** were measured spectrophotometrically. Formation of this dimeric product was found to be in the first order with respect to concentration of the substrate **1** except for the very early stage of the reaction where the induction was observed. The observed first-order rate constants k_{obsd} must reflect the formation of benzenesulfenic acid **3**, which is a primary hydrolysis product and undergoes very rapidly condensation to **5**.[11] The spectrophotometric rate constants agree very well with the rate constants for loss of optical activity of the substrate **1**. These observations strongly support that the rate-determining step of the reactions responsible for the two rate constants is identical and should be the cleavage of the S–C bond. The loss of optical activity must be due to the fragmentation of **1**, and the racemization of the optically active **1** does not occur more rapidly than the fragmentation.

The observed rate constants increase with increasing acidity of perchloric acid as given in Table 1. Deuterium solvent isotope effects are inverse and the reaction is likely to involve a pre-equilibrium protonation followed by the rate-determining breakdown of the protonated intermediate. The pK_a value for **1** may be evaluated from the linear free energy correlation in the following way. Values of pK_a of protonated sulfoxides measured and compiled by Scorrano[13] are correlated with sums of the Taft σ^* constants[14] of substituents as shown in Fig. 3 to give pK_a for **1** being −2.5. On the other hand, the ratio of the conjugate acid to the substrate were found to follow the Bunnett and Olsen equation (Eq. 5)[15] with ϕ=0.50±0.05. The fraction of the ptotonated substrate **2** (SH^+) can be calculated by Eq. 5 and the rate constant k_2 for the breakdown of **2** is given by Eq. 6.

$$\log([SH^+]/[S]) + H_0 = \phi(H_0 + \log[H^+]) + pK_a \quad (5)$$

$$k_2 = k_{obsd}(h_{SO} + K_a)/h_{SO} \quad (6)$$

where $h_{SO}=10^{-H_{SO}}$ and $H_{SO}=H_0-0.50\ (H_0+\log[H^+])$. The rate constants k_2 are then analyzed according to the Bunnett and Olsen linear free energy approach[15] and values of $\log(k_2)$ are plotted against $H_0+\log[H^+]$ in Fig. 4 to give a slope $\phi=-0.154\pm0.003$. The negative value of ϕ suggests according to the Bunnett-Olsen criterion[15] that any water molecule is not involved in the rate-determining step. That is, the rate-determining process is uni-molecular in accord with the

A-1 mechanism. This conclusion suggesting rate-determining formation of methoxymethyl cation intermediate is, however, incompatible with the recently accepted belief that methoxymethyl cation has too short a lifetime (10^{-13} — 10^{-15} s) to be a discrete intermediate.[16-19]

A similar fragmentation reaction of *t*-butyl phenyl sulfoxide **6** observed previously had the value of ϕ of -0.25.[6] The reaction of **6** was found to undergo a concomitant racemization (i.e., the racemization is faster than the fragmentation)[6] while the present reaction of **1** is not accompanied by a possible racemization at the sulfinyl sulfur. The reactions of **6** were rationalized by the occurrence of return to the sulfoxide from the ion-sulfenic acid pair (Eq. 7).[6]

$$\underset{\mathbf{6}}{PhS(O)Bu^t} + H^+ \rightleftharpoons PhS^+(OH)Bu^t \overset{\text{racemization}}{\rightleftharpoons} [PhSOH\ {}^+Bu^t] \longrightarrow PhSOH + {}^+Bu^t \longrightarrow PhSOH + {}^tBuOH \quad (7)$$

By contrast, the present reaction does not involve such a return to the sulfoxide. It is not reasonable that the return from the intermediate ion pair cannot occur with the methoxymethyl derivative **1** while it does occur with the *t*-butyl derivative **6**. The return with the former derivative may be occurring in a different way, the carbocation recombining with the sulfenic acid at the oxygen but not at the sulfur atom. That is, the return may give rise to the sulfenate ester **7** but not to the sulfoxide **1** (Eq. 8). Methoxymethyl benzenesulfenate **7** is hydrolyzed much more rapidly than the sulfoxide **1**,[20] and the return (racemization) could not be observed. The mechanism involving rate-determining formation of **7** is in accord with the Bunnett-Olsen analysis suggesting that the rate-determining step does not involve any water molecule. The observed value of $\Delta S^{\neq}$ close to zero also conforms to this mechanism. Furthermore, free methoxymethyl cation, an impossible intermediate, is avoided.

$$2 \xrightarrow{\text{r.d.s.}} [PhSOH\ {}^+CH_2OMe] \xrightarrow{\text{return}} \underset{\mathbf{7}H^+}{PhS\overset{H}{\overset{|}{\overset{+}{O}}}CH_2OMe} \xrightarrow[\text{rapid}]{H_2O} PhSOH + HOCH_2OMe \quad (8)$$

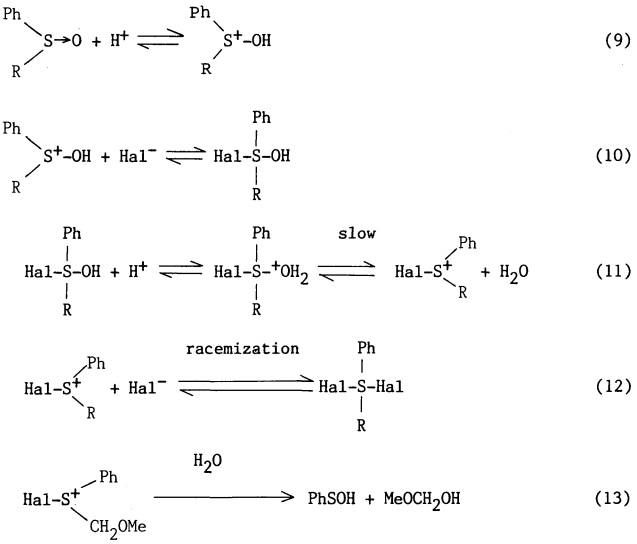
The return to form the sulfenate may take place because **7** is more stable than the sulfoxide **1**. The stability of **7** was previously observed when the sulfoxide **1** was found to rearrange thermally to **7**.[21] The stability of this sulfenate is not unexpected and may be attributed to the anomeric type interaction (or negative hyperconjugation) of geminal oxygen atoms which is widely recognized for acetal and orthoester derivatives.[22,23]

$$PhSO\text{-}CH_2\text{-}OMe \longleftrightarrow PhSO^-\ CH_2{=}\overset{+}{O}Me \longleftrightarrow PhS\overset{+}{O}{=}CH_2\ {}^-OMe$$

7

The observed solvent effects on the hydrolysis rate are unusual, the rate increasing with increasing content of the organic component of aqueous solution (Table 4) contrary to the expectation for an ionic reaction. Rates of the A-1 hydrolysis of acetals were actually found to decrease with increasing content of dioxane.[24] This anomaly may have arisen from an intramolecular nature of the rate-determining step (rearrangement) and/or from differential solvation requirements between sulfur and oxygen compounds.[13,25]

The hydrolysis is faster in HCl than in $HClO_4$ at the same acidity, and was found to be accelerated by added halide ions. The reaction is third order, first order in each of the substrate, acid, and halide ion concentration. Halide ion catalysis has also been observed for the acid-catalyzed racemization of primary alkyl phenyl sulfoxides (but not for tertiary alkyl sulfoxides).[5] The halide-catalyzed racemization was found to be of the *second order in acid concentration*.[5] The second-order dependence was accommodated by a reaction sequence of Eqs. 9—12 where the rate-determining step is the formation of the halosulfonium ion from the protonated sulfurane intermediate.



(9)

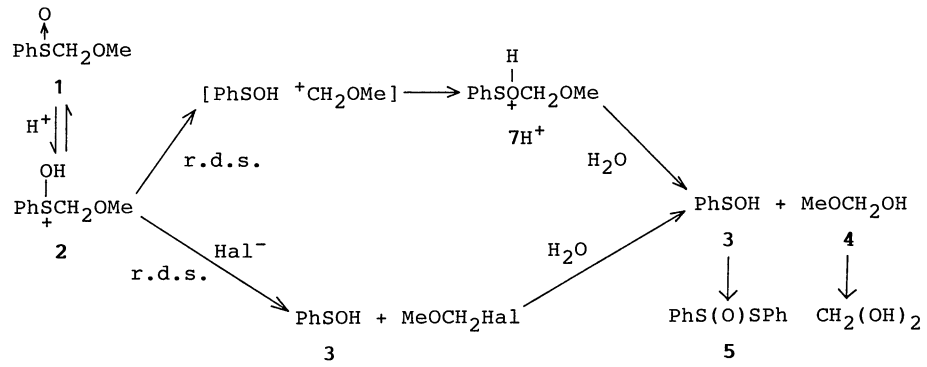
(10)

(11)

(12)

(13)

The halosulfonium ion may readily lead to hydrolysis products (Eq. 13), if formed. However, the rate of the present reaction depends on the *first power of acid concentration* and the rate-determining step must be initial attack of halide ion on the protonated sulfoxide **2** or the ensuing step which does not involve a second proton. It is hard to consider that the reaction of **1** follows the same mechanism as described in Eqs. 9—13 but only the rate-determining step is changed by the



Scheme 1.

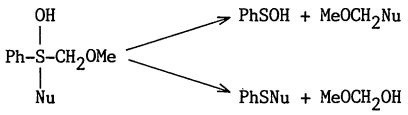
methoxy substitution.

The initial halide attack could be at the carbon atom of the protonated sulfoxide **2** (Eq. 14). The sulfenic acid-ion pair may be trapped by halide ion in the rate-determining step before it rearranges to the sulfenate **7**. However, this is imcompatible with the suggestion that formation of the ion pair is rate determining in the water reaction. The S_N2-type reaction (Eq. 14) is preferred because of high nucleophilicity of halide ion.

$$PhS^+(OH)CH_2OMe + Hal^- \longrightarrow PhSOH + HalCH_2OMe \quad (14)$$

The most plausible mechanism of the overall reaction is summarized in Scheme 1 as a conclusion.

Another possibility that a sulfurane intermediate formed by the initial nucleophilic attack at the sulfur atom of **2** undergoes fragmentation in a way different from simple alkyl sulfoxides cannot completely be excluded. A heteroatom ligand (OH or Nu) may couple with the methoxymethyl residue within the sulfurane intermediate (Eq. 15). This type of intramolecular reaction, ligand coupling, has recently been observed for some sulfurane intermediates.[26] The only weak evidence against this mechanism is the observed negative ϕ value suggesting that the water molecule is not involved in the rate-determining step of the water reaction.



(15)

Experimental

Materials. Acetonitrile and dioxane were distilled from calcium hydride and sodium, respectively. Inorganic salts were of the best grade commercially available.

Methoxymethyl phenyl sulfoxide (**1**). Four mmol of methoxymethyl phenyl sulfide, which was prepared from chloromethyl methyl ether and benzenethiol, was dissolved in 15 cm³ of chloroform and 20 cm³ of chloroform solution of *m*-chloroperbenzoic acid (4 mmol) was added from a dropping funnel and stirred for 1 h under cooling with an ice bath. The mixture was washed with 5% NaOH and water and dried over $MgSO_4$. Evaporation of the solvent gave a practically pure sample of **1**. Kinetic and analytical samples were purified just before use by chromatography (silica gel, hexane–ethyl acetate). IR (film) 1047 cm^{-1} (S=O). ^1H NMR (CCl_4) δ=3.68 (s, 3H), 4.34 (s, 2H), 7.4—7.7 (m, 5H). Distillation at >0.5 mmHg (1 mmHg=133.322 Pa) and ca. 100 °C resulted in rearrangement to methoxymethyl benzenesulfenate.

Optically active **1** was prepared according to the literature.[12] Reaction was carried out at 0 °C for 20 h. Chromatographic separation gave a chemically pure sample in about 60% yield. $[\alpha]_D$, +76° (*c* 1.23, CH_3CN).

Kinetic Measurements. Acid solutions were prepared from 70% perchloric acid and concentrated hydrochloric and hydrobromic acids and titrated with a standard NaOH solution. Sodium chloride and sodium bromide were also used for halide solutions. Ionic strengths were maintained with sodium perchlorate when necessary.

The UV spectra were recorded on a Shimadzu UV 200 spectrophotometer. Reaction was started by introducing 0.03 cm³ of a stock solution of **1** in acetonitrile (ca. 10^{-2} mol dm^{-3}) from a microsyringe into 3 cm³ of acid solution in a quartz cuvette equilibrated at the constant temperature in the cell compartment of the spectrophotometer. The absorbance increase at 275 nm was followed usually for about 6 halflives and pseudo-first-order rate constants were calculated by a modified Guggenheim method.

Rates of the loss of optical activity were measured in the same way on a Union PM 101 polarimeter. About 0.01 cm³ of the substrate was directly introduced to 3 cm³ of aqueous dioxane solution.

Product Analysis. Hydrolysis product obtained under kinetic conditions were analyzed on an HPLC analyzer, JASCO BIP-1, equipped with a Finepak SIL $C_{18}S$ column (eluent, 1:1 (v/v) CH_3CN–H_2O) after neutralization with NaOH. Retention times were compared with those of the authentic samples.

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