Buffer Catalysis of the Hydrolysis of Phenyl and Methyl Benzenesulfinates. Contrasting Behavior between Acyclic and Cyclic Analogs

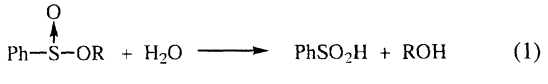
Tadashi Okuyama

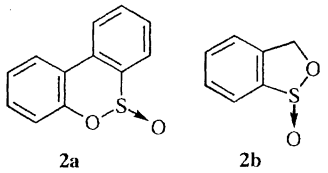
Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

(Received May 29, 1996)

The hydrolysis of phenyl benzenesulfinate is catalyzed by both acid and base, and is strongly accelerated by the carboxylate and amine base components of the buffer. Carboxylates and amines constitute different groups in the Brønsted plots, falling nearly on two separate lines of $\beta = 1$. The carboxylates are about 400-times more effective catalysts than the amines of similar basicity. Solvent deuterium isotope effects on the catalytic constants are small, and the buffer catalysis is considered to be nucleophilic. By contrast, the hydrolysis of the methyl ester was only weakly affected by the buffer, if at all. High efficiencies of oxygen nucleophiles in the catalysis of the hydrolysis of acyclic sulfinates are distinctive compared with the cyclic analogs, and are rationalized by a concerted S_N2-like mechanism of the nucleophilic reaction at sulfur.

The hydrolysis of sulfinate esters is a typical nucleophilic reaction of sulfinyl compounds. The modes of the nucleophilic reaction at the sulfinyl sulfur are one of the central problems in the organic reactions of sulfur compounds,[1] and the mechanistic aspects of the hydrolysis of sulfinates have attracted the interest of organic chemists.[1—10] Although the *alkaline* hydrolysis of sulfinate esters has generally been considered to take place through a hypervalent addition intermediate, a concerted S_N2-like mechanism cannot be excluded.[8,11] We have recently presented some evidence for a single-step S_N2-like mechanism for the *acid* hydrolysis of alkyl sulfinate esters[9] as well as cyclic sulfinates.[10] However, the base-catalyzed hydrolysis (ring opening) of cyclic sulfinates showed interesting buffer catalysis behavior, suggesting the formation of a hypervalent intermediate during the course of this reaction.[12] The ring opening of cyclic sulfinates with a phenolic leaving group nudergoes strong buffer catalysis, while that with an pliphatic leaving group does little buffer catalysis. We now examine in detail the buffer effects on the hydrolysis of acyclic esters, phenyl and methyl benzenesulfinates (**1a** and **1b**, Eq. 1); the results are compared with those obtained for the cyclic analogs, **2a** and **2b** (Scheme 1).[12] Distinctive differences in buffer catalysis were observed between the acyclic and cyclic sulfinates, and a concerted S_N2-like mechanism is proposed for the former, while a stepwise mechanism involving a hypervalent intermediate is suggested for the latter.





Scheme 1.

Results and Discussion

The hydrolysis of the sulfinate esters **1** was carried out in aqueous solution at 25 °C, and was monitored spectrophotometrically. The ionic strength was usually maintained at 0.10 with $NaClO_4$.

Hydrolysis of the Phenyl Ester. The hydrolysis of the phenyl ester **1a** proceeded smoothly with an isosbestic point at 267 nm at pH > 4, where one of the products is benzenesulfinate ion ($pK_a = 1.45$),[13] or with an essentially isosbestic region of 270—280 nm in a strong acid. The absorbance at 245 nm decreased with time, nicely following pseudo-first-order kinetics in all of the runs examined. The observed pseudo-first-order rate constants (k_{obsd}) increased linearly with the concentration of perchloric acid, while they showed an upward curvature against [HCl], following $k_{obsd} = k_1[HCl] + k_2[HCl]^2$, as shown in Fig. 1. Acid-catalyzed reaction must be accelerated by chloride ion, as was observed for the alkyl sulfinates.[8]

The hydrolysis of **1a** was strongly buffer dependent in all the buffers examined. The spectral changes were smooth with a sharp isosbestic point, and identical for teriary, secondary, and primary amines as well as carboxylates and dimethylarsinate (cacodylate) or phosphate. That is, no symp-

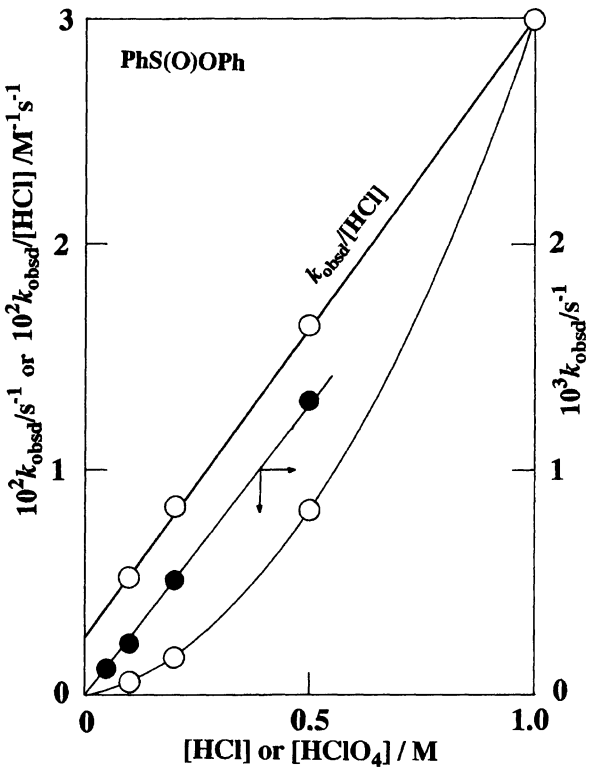


Fig. 1. Rates for the hydrolysis of **1a** in perchloric (●, right ordinate) and hydrochloric acids (○, left ordinate) at 25 °C.

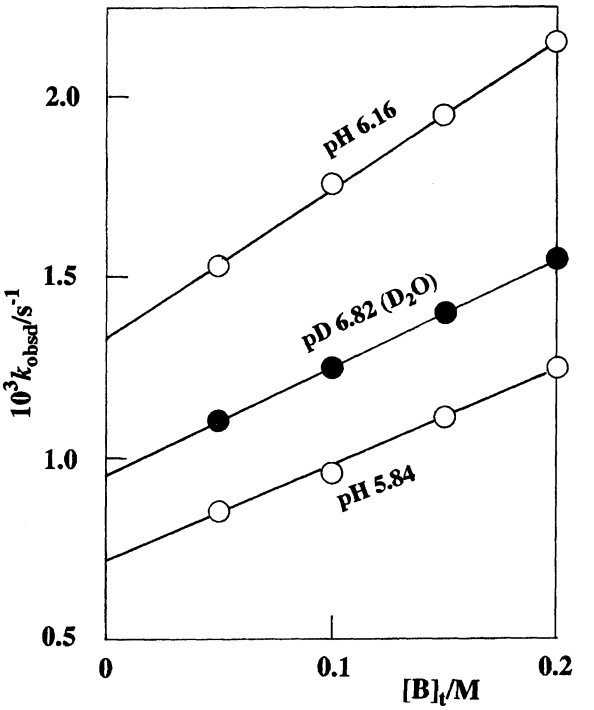


Fig. 2. Buffer effects on the hydrolysis rate of **1a** in MES buffer solutions at 25 °C and the ionic strength of 0.10.

tom of the accumulation of an intermediate or the formation of any other nucleophilic products was found. These observations indicate that the buffer is operating as a catalyst. Typical buffer dependences are shown in Figs. 2, 3, and 4. The observed pseudo-first-order rate constants (k_{obsd}) are linearly dependent on the total buffer concentration, $[B]_t$ ($k_{obsd}=k_0+k_B[B]_t$). The obtained rate constants are summarized in Table 1.

The rate constants (k_0) extrapolated to a zero buffer concentration are logarithmically plotted against the pH together

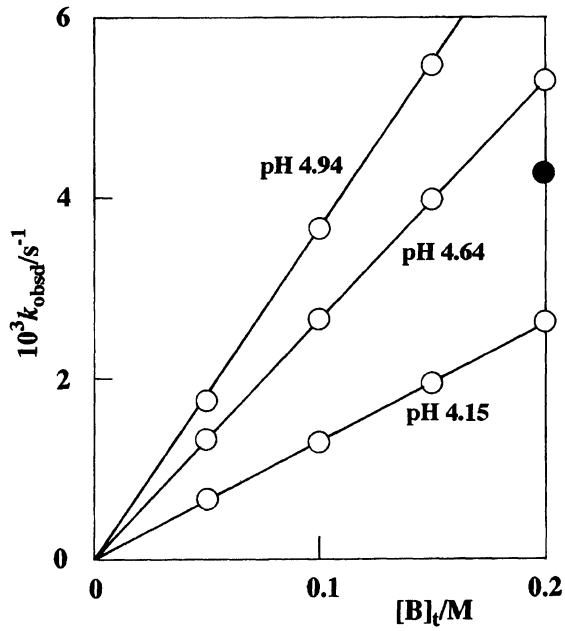


Fig. 3. Buffer effects on the hydrolysis rate of **1a** in acetate buffer solutions at 25 °C and the ionic strength of 0.10. The rate constant obtained in D_2O at the buffer ratio of 1 (pD=5.22) is shown with a closed circle.

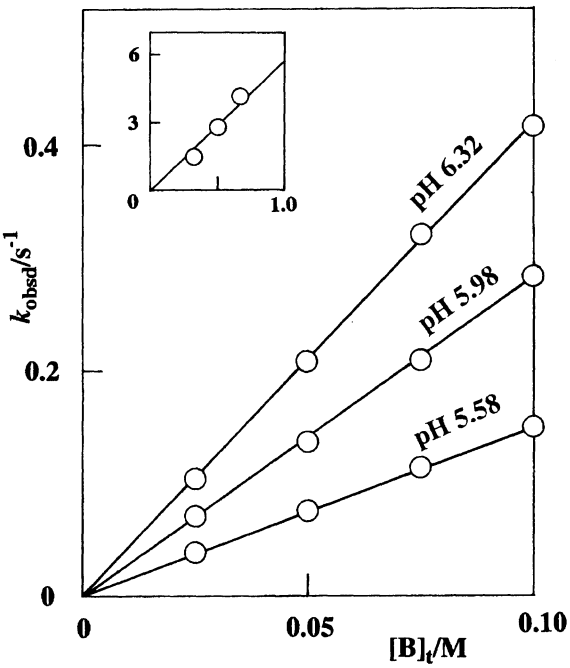


Fig. 4. Buffer effects on the hydrolysis rate of **1a** in cacodylate buffer solutions at 25 °C and the ionic strength of 0.10. The inset shows a plot of $k_B/M^{-1}\ s^{-1}$ against base fraction.

Table 1. Rate Constants for the Hydrolysis of **1a** in Buffer Solutions[a)]

Buffer base[b)]	Buffer ratio[c)]	pH	$10^3 k_0/s^{-1}$	$10^2 k_B/M^{-1} s^{-1}$
N-Ethylmorpholine	1	7.85	51	5.0
N-Methylmorpholine	1	7.51	24.8	12.5
MOPS	1	7.15	10	31
MOPSO	1	6.84	7.8	1.44
MES	1/2	6.53	2.98	0.47
MES	1	6.16	1.35	0.40
MES(D_2O)[d)]	1	(6.82)	0.93	0.31
MES	2	5.84	0.65	0.30
$NCCH_2CH_2NMe_2$	1	5.38	0.19	2.65
$Me_2N^+HCH_2CH_2NMe_2$	1	5.62	0.44	1.96
Imidazole	1	7.00	6.2	15
$MeN^+H_2CH_2CH_2NHMe$	1[e)]	5.74	0.55	1.82
$(NCCH_2CH_2)_2NH$	1	5.30	0.215	0.155
$EtOOCCH_2NH_2$	1[e,f)]	6.98	8.5	4.4
$H_3N^+CH_2CH_2NH_2$	1[e)]	6.85	6.2	10
$CF_3CH_2NH_2$	1[f)]	5.65	0.43	2.3
$NCCH_2NH_2$	1[f)]	5.38	0.19	0.265
Phosphate	1	6.80	13	112
Cacodylate	1/2	6.32		418
Cacodylate	1	5.98		280
Cacodylate	2	5.58		146
Pivalate	1	4.95		8.9
Acetate	1/2	4.94		3.6
Acetate	1	4.64		2.65
Acetate	3	4.15		1.31
3-Chloropropanoate	1	3.98		0.75
Glycolate	1	3.71		0.31
Formate	1	3.58		0.176
Chloroacetate	1	2.5		0.045

a) Determined at 25 °C and the ionic strength of 0.10 ($NaClO_4$) unless noted otherwise. Values are estimated to be accurate to within ±10%. b) MOPS=3-morpholinopropanesulfonate, MOPSO=3-morpholino-2-hydroxypropanesulfonate, MES=2-morpholinoethanesulfonate. c) [conjugate acid]/[base]. d) The ionic strength was maintained with $LiClO_4$ in D_2O. The pD value is given. e) Measured at the ionic strength of 0.20. f) Hydrochloride salts were used.

with the k_{obsd} obtained in perchloric acid (Fig. 5). The reaction is catalyzed by both the acid and base ($k_{H^+}=2.4\times10^{-3}$ $M^{-1} s^{-1}$ and $k_{OH}=1.0\times10^5$ $M^{-1} s^{-1}$).[14)] The phenyl ester **1a** is about 60 (H^+) and 10^4 (OH^-) times more reactive than the methyl ester **1b** in acid and base hydrolysis, respectively, reflecting the higher nucleofugality of phenol than methanol. The phenyl ester **1a** is about 14-times as reactive as the cyclic analog **2a** toward hydroxide. However, the methyl ester **1b** is somewhat less reactive than the five-membered ring analog **2b**, but 25-times more reactive than the six-membered cyclic analog.[10)] The five-membered cyclic analog is highly activated by the ring strain.[10)]

The buffer-dependent second-order rate constants (k_B) are plotted against the base fraction in Fig. 6 for acetate and MES (2-morpholinoethanesulfonate) buffers and the inset of Fig. 4 for cacodylate buffers. These plots indicate that only the conjugate base of the buffer acts as a catalyst but the acid component has essentially no effect at least in the pH region studied. The catalytic constants (k_{N_u}) dependent on the base component were usually evaluated from the k_B obtained at a buffer ratio of unity ($k_{N_u}=2k_B$ at $[B]=[BH^+]$); k_{N_u} are plotted against pK_a of the conjugate acid of the catalyst in Fig. 7. Statistical corrections were made in these plots for the number of ionizable protons of the acid (p) and that of the protonation sites in the conjugate base (q). Plots for the carboxylates and amines constitute different lines of slope β close to unity, though the points for the amines are greatly scattered, the carboxylates being about 400-times more effective catalysts than the amines of the corresponding basicity. Although cacodylate is also a very effective catalyst, phosphate is in between the carboxylates and amines.

The rates were also determined in deuterium buffer solutions of MES and acetate at a buffer ratio of unity, as indicated by the closed circles in Figs. 2 and 3. Solvent deuterium isotope effects on the buffer-dependent rate constants k_B (that for acetate was evaluated from k_{obsd} at $[B]_t=0.2$ M since $k_0\approx0$) are $k_B^H/k_B^D=1.28$ and 1.24 for MES and acetate, respectively. The deuterium oxide-dependent rate constant can be evaluated from the k_0 obtained in the MES buffer solution and $pk_w(D_2O)=14.869$;[15)] $k_{OH}/k_{OD}=0.96$. Although all of those isotope effects data are rather crude, the base-dependent rate constants are considered not to be greatly affected by the solvent isotopes. These results are consistent with a mechanism involving the nucleophilic catalysis of the hydrolysis of **1a**, rather than that involving a general base catalysis.

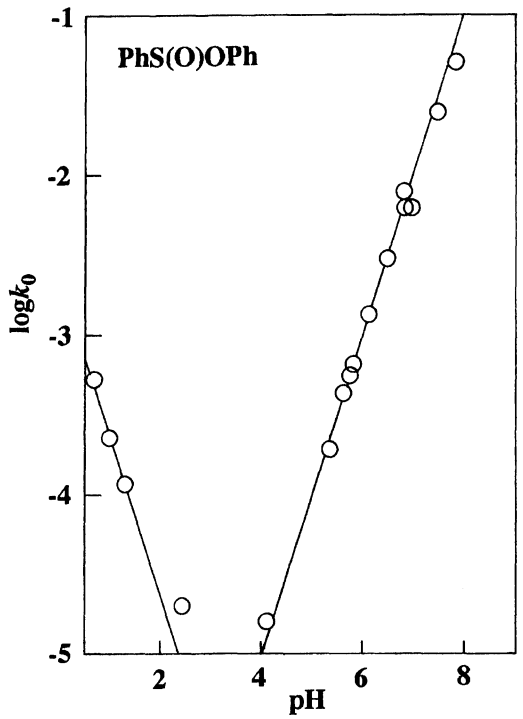


Fig. 5. pH-rate profile for the hydrolysis of **1a** at 25 °C.

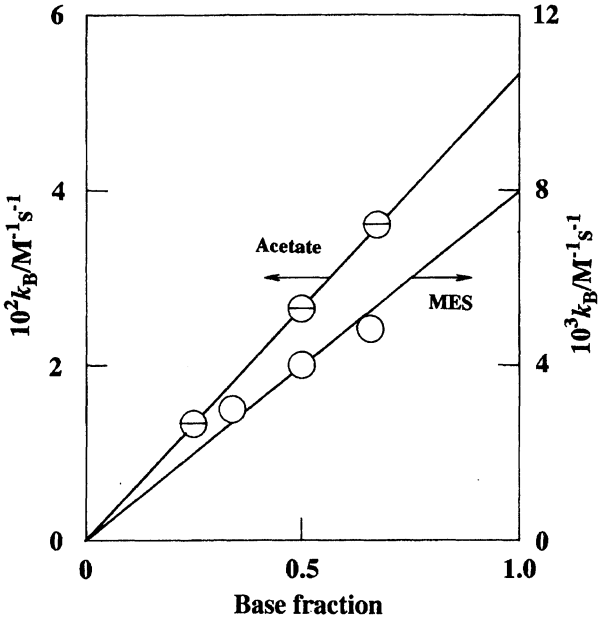


Fig. 6. Plots of buffer-dependent rate constants against base fraction of the buffer, MES (○) and acetate (⊖).

Nucleophilic catalysis by carboxylates and amines was also observed for the hydrolysis (ring opening) of the cyclic analog **2a**. However, a distinctive difference in the buffer catalysis of the hydrolysis of **1a** and **2a** is apparent in that the carboxylate ions are highly efficient nucleophilic catalysts for the former, while they are normal in the catalysis of the hydrolysis of the cyclic analog. The acetate point falls on the line of amine catalysis in the Brønsted plot for the latter.[12]

Hydrolysis of the Methyl Ester. The hydrolysis of

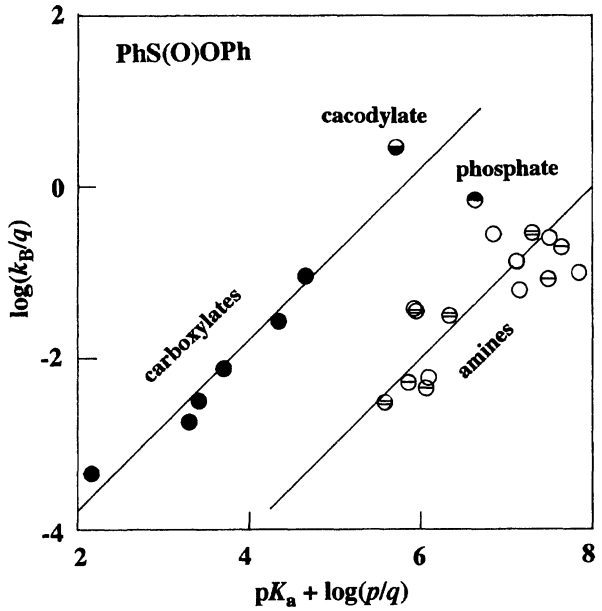


Fig. 7. The Brønsted plots for the catalytic constants for the hydrolysis of **1a**. Numbers, p and q, are that of ionizable protons in the acid and that of protonation sites in the conjugate base, respectively. ●, carboxylates; ○, tertiary amines; ⊖, secondary amines; ⊖, primary amines.

Table 2. Observed Rate Constants ($10^4k_{obsd}/s^{-1}$) for the Hydrolysis of **1b** in Buffer Solutions[a]

Buffer	pH	$[B]_t$/M			
		0.05	0.10	0.15	0.20
DABCO[b]	8.85	0.732	0.730	0.745	0.754
$HOCH_2CH_2NMe_2$[c]	9.40	2.3	2.7	3.1	3.4
$Me_2NCH_2CH_2Me_2$	9.52	2.60	2.60	2.54	2.46
$MeOCH_2CH_2NH_2$	9.78	5.04	5.13	5.01	4.95
$HOCH_2CH_2NH_2$[c]	9.90	7.3	7.8	8.3	8.9
$^-OOCCH_2NH_2$	10.05	7.57	7.81	8.10	8.34
Carbonate[d]	10.30	14.3	14.9		
N-Methylpiperidine	10.47	19.8	19.4	18.5	17.2
N-Ethylpiperidine	10.83	43.8	42.2	39.8	37.2
Triethylamine[e]	11.35	131	131	122	121

a) Determined at 25 °C and the ionic strength of 0.10 ($NaClO_4$) unless otherwise noted. b) 1,4-Diazabicyclo[2.2.2]octane. c) A short induction period was observed. d) Measured at the ionic strength of 0.20 and 10^4k_{obsd} at $[B]_t$=0.025 and 0.075 M are 14.4 and 14.9 s^{-1}, respectively. e) Measured at the ionic strength of 0.20 maintained with NaCl.

the methyl ester **1b** in alkaline solutions proceeds with an isosbestic point at 259 nm, and the absorbance decrease at 240 nm usually follows first-order kinetics for at least 4 half-lives.[8] In buffer solutions, the dependences of the rates on the buffer concentrations are rather small in contrast to the results for **1a**, as summarized in Table 2 and illustrated in Figs. 8 and 9. The buffer effects observed for **1b** are divided into three categories: (1) Negligible effects of the buffer concentration were observed for 1,4-diazabicyclo[2.2.2]octane (DABCO), 2-methoxyethylamine, and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, which are amines of lower basicity.

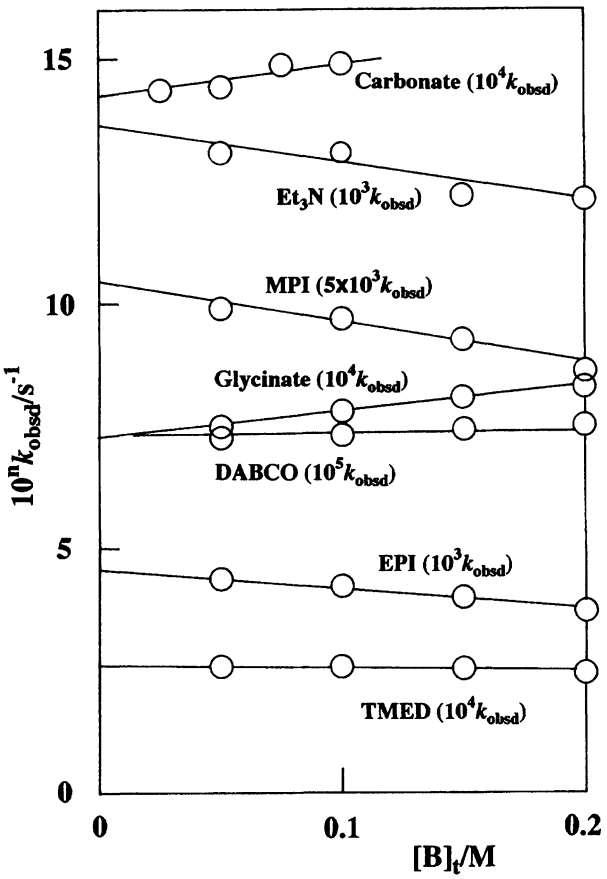


Fig. 8. Buffer effects on the hydrolysis rate of **1b** in various buffer solutions at 25 °C and the ionic strength of 0.10. Carbonate, pH=10.30; triethylamine, pH=11.35; MPI, pH=10.47; glycinate, pH=10.05; DABCO, pH=8.85; EPI, pH=10.83; TMED, pH=9.52.

(2) Small positive effects were found with *N*,*N*-dimethyl-2-hydroxyethylamine, 2-hydroxyethylamine, glycinate, and carbonate, which are hydroxy amines or bases bearing a basic oxygen center. Furthermore, some induction was observed in these reactions. (3) Small negative effects are apparent with *N*-methylpiperidine, *N*-ethylpiperidine, and triethylamine, tertiary amines of higher basicity. Although these results are similar to those observed for the cyclic analog **2b**, positive effects of hydroxy amines have never been found for **2b**.[12]

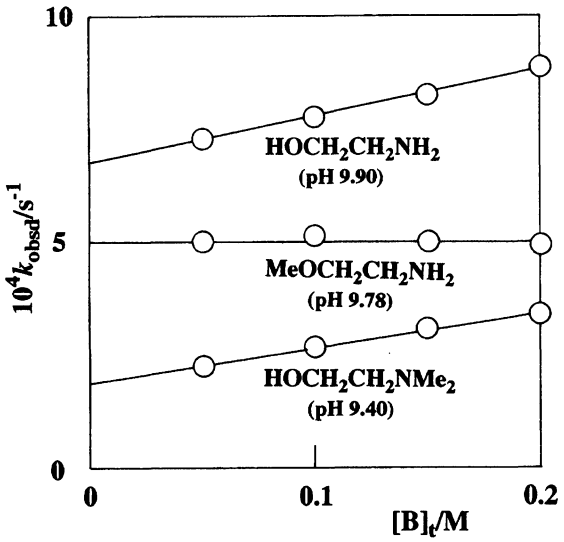


Fig. 9. Buffer effects on the hydrolysis rate of **1b** in 2-hydroxyethylamine and related buffer solutions at 25 °C and the ionic strength of 0.10.

This noticeable feature, that only the hydroxy amines show positive buffer effects on the hydrolysis of **1b**, was further examined as to whether these effects arise from the hydroxy function. Thus, the effects of some alcohols and related organic additives were examined for the hydrolysis of **1b** at pH 9.8 maintained by a 2-methoxyethylamine buffer. The results are given in Table 3, and illustrated in Fig. 10. Alcohols of lower pK_a, such as 2,2,2-trifluoroethanol, choline, and 2-chloroethanol, accelerate the hydrolysis, while 2-methoxyethanol and ethanol as well as acetonitrile decelerate the hydrolysis of **1b**. Some induction was also found when the alcoholic acceleration was apparent.

From all of these results, it may be concluded that the amine base group has no detectable catalytic effects on the hydrolysis of the methyl ester **1b**, while some oxygen bases can accelerate the reaction. Noncatalytic organic additives may retard the hydrolysis of **1b** probably through solvent-polarity effects. Nonionized alcohol must retard the hydrolysis through solvent effects. The conjugate bases, alkoxide ions, of the alcohols of lower pK_a act as nucleophilic catalysts. However, the observed effects seem to result from a composite of catalytic accelerating and solvent decelerating

Table 3. Observed Rate Constants ($10^4 k_{obsd}/s^{-1}$) for the Hydrolysis of **1b** in the Presence of Some Organic Additives in 2-Methoxyethylamine Buffer Solutions at pH 9.80[a)]

Additive (pK_a)	[additive]/M		
	0.05	0.10	0.20
CF_3CH_2OH (12.4)		5.52	6.26
$Me_3N^+CH_2CH_2OH$ (13.9)	5.73		
$ClCH_2CH_2OH$ (14.3)		4.94	5.02
$MeOCH_2CH_2OH$ (14.8)		4.45	4.23
CH_3CH_2OH (16)		4.68	4.46
CH_3CN		4.40 (0.13 M)	4.18 (0.25 M)

a) pH was maintained with 0.10 M buffer at the ionic strength of 0.10 ($NaClO_4$). $10^4 k_{obsd}$=4.84 s^{-1} in the absence of any organic additive.

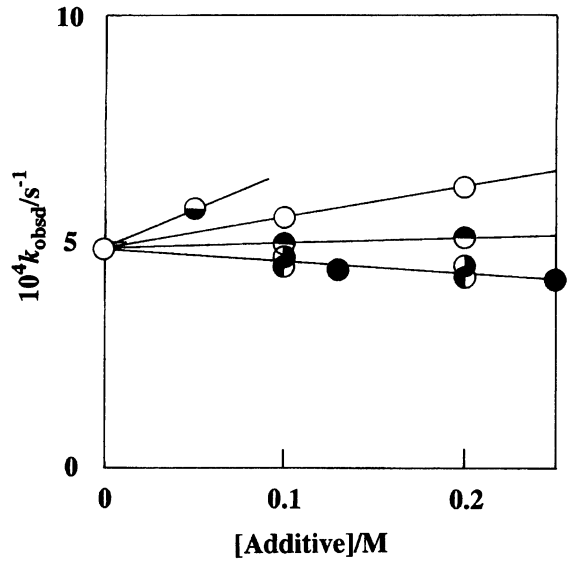
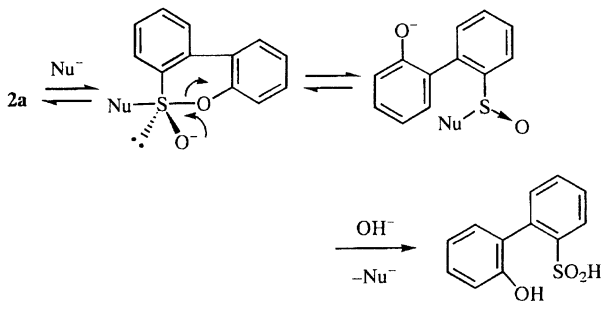


Fig. 10. Effects of some organic additives on the rate of hydrolysis of **1b** in a 2-methoxyethylamine buffer solution at pH=9.80 and 25 °C. $[B]_t$=0.10 M, ionic strength=0.10 ($NaClO_4$). ◒, Choline; ○, 2,2,2-trifluoroethanol; ◓, 2-chloroethanol; ◑, 2-methoxyethanol; ◐ ethanol; ●, acetonitrile.

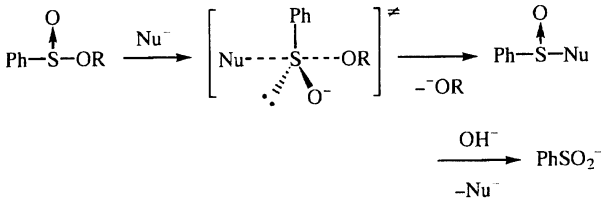
effects, and quantitative treatments are difficult to perform. As choline, $Me_3N^+CH_2CH_2OH$, is a good catalyst in its conjugate base form, 2-hydroxyethylamines must operate as a catalyst in a similar zwitterionic form, $H_3N^+CH_2CH_2O^-$ or $HMe_2N^+CH_2CH_2O^-$. The failure to detect catalysis by amine bases is probably related to the high efficiency of the oxygen bases. At higher pH, the hydroxide ion is the most effective catalyst, and the amine buffer term can hardly be observed experimentally. The observed negative buffer effects must in part arise from solvent effects. At lower pH, the hydroxide term becomes small and amine catalysis becomes observable, as is the case for the more reactive **1a**.

Reaction Mechanism. Similar contrasting observations concerning the buffer catalysis of hydrolysis were recently found for the cyclic sulfinate esters **2a** and **2b**; the former was strongly catalyzed by amine nucleophiles, while the latter underwent only little nucleophilic catalysis. These results are rationalized by a common mechanism involving a hypervalent intermediate but with a different rate-determining step.[12]



(2)

The present reaction of acyclic sulfinates, **1a** and **1b**, undergoes seemingly similar effects of the amine buffers. We were at first tempted to explain the present observations by a similar mechanism with a changing rate-determining step. However, remarkable differences are apparent in the efficiencies of the oxygen nucleophiles. Carboxylates are very effective catalysts of the hydrolysis of **1a**, while they are very weak catalysts for **2a** on the extrapolation of more basic amines. Some alkoxides, including those from hydroxy amines, can accelerate the hydrolysis of **1b**, but not that of **2b**. These observations imply that the mechanism for the nucleophilic catalysis of the reactions of acyclic sulfinate esters is different from that of the cyclic analogs, a stepwise mechanism involving a hypervalent intermediate. A possible alternative for the nucleophilic reaction at the sulfur atom may be a concerted S_N2-like mechanism for the acyclic esters.



(3)

Two questions may thus arise: (1) Why can the hypervalent species be an intermediate for cyclic sulfinates while it is a transition state of the S_N2-like process for the acyclic analogs? (2) Why are the oxygen nucleophiles effective in the S_N2-like reaction, but not in the formation of the hypervalent intermediate? The first question may be answered from the viewpoint of the lifetime of a potential hypervalent intermediate. A cyclic structure can be a stabilizing factor of the hypervalent species[16] and those derived from cyclic sulfinates may have a sufficiently long lifetime to be a real reaction intermediate. However, those derived from acyclic sulfinates must be too short in their lifetime to exist as a real intermediate, and the concerted occurrence of nucleophilic attack and bond breaking of the leaving group must be enforced. Similar considerations of stepwise and enforced concerted mechanisms are made for the nucleophilic substitution at the saturated carbon from the viewpoint of the lifetime of a potential carbocation intermediate.[17,18]

A possible explanation regarding the second question may be provided by the stability of the sulfinate ester compared with the sulfinamide. The latter is less stable than the former.[19] In the transition state for the S_N2-like process, the bonding nature of the product sulfinic species develops so as to contribute to its stability, and the oxygen nucleophiles to provide sulfinate esters must be more effective in this stabilization than the nitrogen nucleophiles to form sulfinic amides. By contrast, the transition state for the formation of hypervalent species cannot merit a contribution from the product state. Some induction period observed in the hydrolysis of **1b** involving alkoxide catalysis must reflect the stability of the sulfinate ester intermediate (PhS(O)Nu) in this reaction; the intermediate ester would accumulate to

some extent during the reaction.

In conclusion, a nucleophilic catalysis of the hydrolysis of acyclic sulfinate ester may take place by a concerted S_N2-like mechanism, while that of cyclic sulfinate may take place by a stepwise addition-elimination mechanism involving a hypervalent intermediate. The acid catalyzed hydrolysis of both acyclic and cyclic sulfinate esters was previously concluded to proceed via an S_N2-like mechanism.[9,10]

Experimental

Materials. Although phenyl benzenesulfinate **1a** was prepared from phenol by a previously described method,[20] purification by distillation was unsuccessful. Analytical and kinetic samples were obtained by preparative HPLC (FineSIL-C_{18} 20 cm column with 1 : 1 (v/v) acetonitrile–water as an eluent). Methyl benzenesulfinate **1b** was obtained as previously described.[8] The carboxylic acids, salts and solid amines used for the buffer preparations were of the best grade commercially available. Liquid amines were distilled from pottasium hydroxide immediately before use.

Kinetic Measurements. The rates of the hydrolysis of **1a** and **1b** were determined at 25 °C spectrophotometrically on a Shimadzu UV-2200 spectrometer by monitoring the absorbance decrease at 245 and 240 nm, respectively. Details concerning the procedure were described previously.[8,10]

The author thanks Hideki Takano for his technical assistance.

References

1) a) T. Okuyama, *Phosphorus, Sulfur, Silicon*, **95/96**, 113 (1994); b) T. Okuyama, in "The Chemistry of Sulphinic Acids, Esters, and Their Derivatives," ed by S. Patai, Wiley, Chichester (1990), pp. 623—637; c) M. Mikolajczyk, in "Organic Sulfur Chemistry," ed by B. Zwanenburg and A. J. H. Klunder, Elsevier, Amsterdam (1987), pp. 23—40; d) M. Mikolajczyk, *Phosphorus Sulfur*, **27**, 31 (1986); e) M. Mikolajczyk and J. Drabowicz, *Top. Stereochem.*, **13**, 333 (1982).

2) C. A. Bunton and B. N. Hendy, *J. Chem. Soc.*, **1962**, 2562.

3) C. A. Bunton and B. N. Hendy, *J. Chem. Soc.*, **1963**, 627.

4) D. Darwish and R. McLaren, *Tetrahedron Lett.*, **1962**, 1231.

5) M. Kobayashi, R. Nishi, and H. Minato, *Bull. Chem. Soc. Jpn.*, **47**, 888 (1974).

6) A. A. Najam and J. G. Tillett, *J. Chem. Soc., Perkin Trans. 2*, **1975**, 858.

7) X. Creary, *J. Org. Chem.*, **50**, 5080 (1985).

8) T. Okuyama, *Heteroatom Chem.*, **4**, 459 (1993).

9) T. Okuyama and S. Nagase, *J. Chem. Soc., Perkin Trans. 2*, **1994**, 1011.

10) T. Okuyama, H. Takano, K. Ohnishi, and S. Nagase, *J. Org. Chem.*, **59**, 472 (1994).

11) J. L. Kice and C. A. Waters, *J. Am. Chem. Soc.*, **94**, 590 (1972).

12) T. Okuyama, *Chem. Lett.*, **1995**, 997; T. Okuyama, H. Takano, and K. Senda, *Bull. Chem. Soc. Jpn.*, **69**, 2639 (1996).

13) Y. Ogata, Y. Sawaki, and M. Isono, *Tetrahedron*, **26**, 731 (1970).

14) 1 M=1 mol dm^{-3}.

15) R. N. Goldberg and L. G. Hepler, *J. Phys. Chem.*, **72**, 4654 (1968).

16) R. A. Hayes and J. C. Martin, in "Organic Sulfur Chemistry," ed by F. Bernardi, I. G. Csizmadia, and A. Mangini, Elsevier, Amsterdam (1985), Chap. 8.

17) W. P. Jencks, *Acc. Chem. Res.*, **13**, 161 (1980); *Chem. Soc. Rev.*, **10**, 345 (1981).

18) J. P. Richard, in "Advances in Carbocation Chemistry," ed by X. Creary, JAI Press, Greenwich, Conn. (1989), Vol. 1, pp. 121—169.

19) J. G. Tillett, in "The Chemistry of Sulphinic Acids, Esters and Their Derivatives," ed by S. Patai, Wiley, Chichester (1990), pp. 603—622.

20) Y. Noguchi, M. Isoda, K. Kuroi, and M. Furukawa, *Chem. Pharm. Bull. (Tokyo)*, **30**, 1646 (1982).