CHEMISTRY LETTERS, pp. 273-276, 1990.

Mechanism of Second-Order Buffer Catalysis in the Hydrolysis of Methoxymethyl Benzenesulfenate

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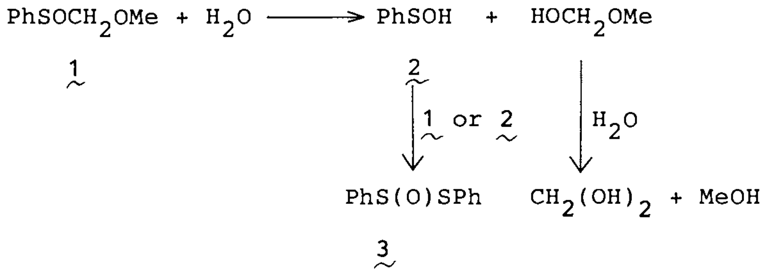
Hydrolysis of methoxymethyl benzenesulfenate is catalyzed by both acid and base. Rates depend on a second order of buffer concentration, which results from general acid-promoted nucleophilic attack by the base at the proformyl carbon.

We found that the hydrolysis of methoxymethyl benzenesulfenate (1) is strongly catalyzed by nucleophiles and occurs through attack at the proformyl carbon by a nucleophilic catalyst.[1)] The hydrolysis depends also strongly on a second order term of buffer concentration: acid and base components of the buffer simultaneously catalyze the hydrolysis. We suggest possible mechanisms for this simultaneous catalysis and present a rationale for its enforcement.

Compound 1 reacted in water to give S-phenyl benzenethiosulfinate (3) as a final product (Eq. 1). The product obtained from the labelled substrate $\mathrm{PhS^{18}OCH_2OMe}$ in buffer solutions showed that bond cleavage occurs mostly (ca. 90 %) at SO-C.[1)]



$$\begin{tikzcd} \underset{1}{\mathrm{PhSOCH_2OMe}} + \mathrm{H_2O} \arrow[r] & \underset{2}{\mathrm{PhSOH}} \arrow[d, "1 \text{ or } 2"] & + \ \mathrm{HOCH_2OMe} \arrow[d, "\mathrm{H_2O}"] \\ & \underset{3}{\mathrm{PhS(O)SPh}} & \mathrm{CH_2(OH)_2} + \mathrm{MeOH} \end{tikzcd}$$

(1)

The rate constants determined for the formation of **3** at 25 °C and an ionic strength 0.5 ($NaClO_4$) are catalyzed by both acid and base in the pH range 1-7, and are strongly buffer-dependent, where

$$k_{obsd} = k_0 + k_1[B]_t + k_2[B]_t^2 \qquad (2)$$

Apparent second- and third-order rate constants, k_1 and k_2, determined from plots of $(k_{obsd} - k_0)/[B]_t$ vs. $[B]_t$ ($[B]_t = [HA] + [A^-]$), are plotted against the base fraction in Fig. 1 to show the correlation of Eq. 3. The catalytic constants obtained are summarized in Table 1.

$$k_{obsd} = k_0 + k_A[HA] + k_B[A^-] + k_{AB}[HA][A^-] \qquad (3)$$

Data in Table 1 show that k_B and k_{AB} are greatly dependent on basicities of the base catalysts ($\beta \simeq 1$) while k_{HA} is little affected by acidities of the acid catalysts ($\alpha \simeq 0$). The base component of buffer must be operating as a nucleophilic catalyst in accord with the catalytic effects observed for less basic nucleophiles in this reaction.1) The reaction (k_{AB}) must involve general acid-promoted nucleophilic catalysis. Furthermore, a sterically hindered amine buffer, Bis-Tris [bis(2-hydroxyethyl)aminotris(hydroxymethyl)methane] seems to show only small second-order catalysis (k_1).

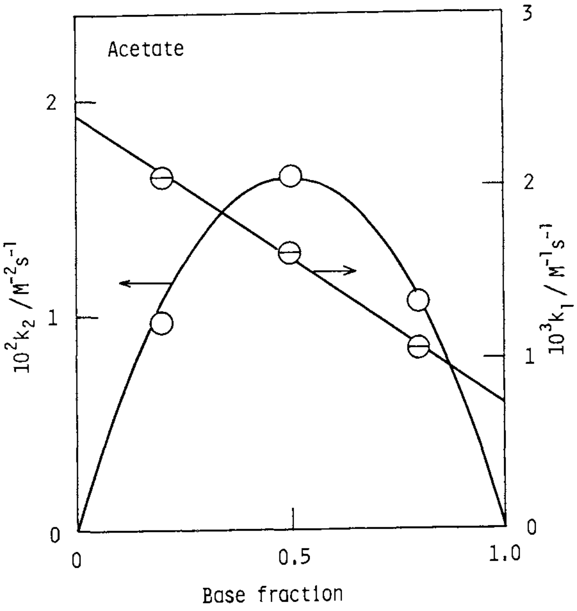


Fig. 1. Plots of apparent catalytic constants, k_1 (⊖) and k_2 (○), against the base fraction of acetate buffer.

Although acid-catalyzed nucleophilic reactions are not uncommon, a case that the base component of buffer acts as a nucleophilic catalyst with assistance of the acid component to show second-order buffer dependence is rare. The only example that definitely shows the second-order dependence on buffer is enolization of carbonyl compounds.2) Nonetheless, the third-order term is only

Table 1. Buffer Catalytic Constants for the Hydrolysis of **1** at 25 °C[a]

HA(pK_a[b])	$10^3k_A/M^{-1}s^{-1}$ [c]	$10^3k_B/M^{-1}s^{-1}$ [c]	$k_{AB}/M^{-2}s^{-1}$ [c]
H_3O^+	390		
$MeOCH_2CO_2H$(3.4)	7.1	0.1	0.064
CH_3CO_2H(4.6)	2.8	0.75	0.066
Me_3CCO_2H(4.9)	1.6	1.6	0.12
MES[d](6.3)	7	50	8.0
MOPS[e](7.2)	2	450	15
$NCCH_2CH_2NMe_2H^+$(7.35)	0	6700	660
H_2O		5.0×10^7	

a) Ionic strength was maintained at 0.50 with $NaClO_4$. b) Observed pH of the buffer solution at [HA] = [A^-]. c) 1 M = 1 mol dm^{-3}. d) 2-Morpholinoethanesulfonic acid. e) 3-Morpholinopropanesulfonic acid.

a minor contributor to the whole rate of enolization and has been the subject of much controversy.[2] By contrast, the present reaction is mainly due to the third-order term in usual buffer solutions; e. g., 97% of the catalysis results from k_2 in 0.5 M MES buffer of [HA] = [A^-].

The progress of the present reaction involving proton transfer to the O and nucleophilic attack at the C atom of the sulfenate to lead to cleavage of the C-O bond may be depicted conveniently by the reaction cube in Fig. 2. Each corner of the cube represents a potential intermediate, but the corners designated by triangles should be avoided because species involving a pentavalent carbon and methoxymethyl cation[3] are too unstable to be discrete intermediates. Thus, the two edges must be avoided to force the nucleophilic attack concerted with the C-O bond cleavage. Because the sulfenate is a mild base[4] and presumably a moderate nucleofuge, a general acid should only be effective if there is considerable C-O bond cleavage in the transition state. The small value of α suggests a preassociation mechanism.[6] The reaction path in the cube may be close to the corner of P^- with little developement of the O-H bond at the transition state. These results are quite different from those observed for formaldehyde acetals of phenols.[7]

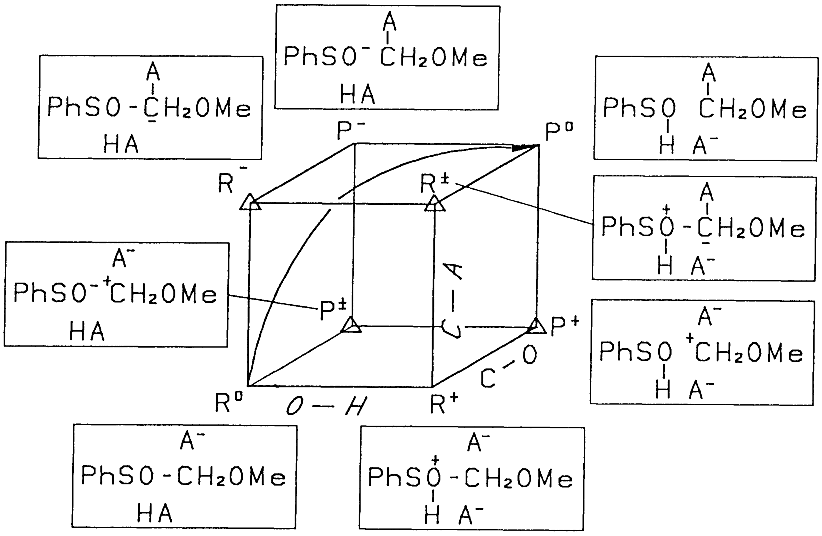


Fig. 2. Reaction cube for acid-promoted nucleophilic attack at carbon. The curved arrow represents a possible path for the simultaneous catalysis, $\underline{k}_{AB}$.

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(Received November 4, 1989)