Buffer Effects on the Ring Opening of Cyclic Sulfinate Esters as Evidence for the Hypervalent Intermediate[1]

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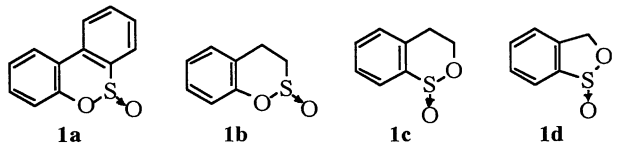
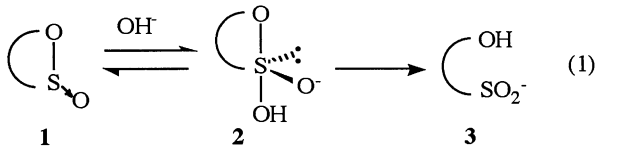
Ring opening of dibenzo-1,2-oxathiin 2-oxide (**1a**) and 3,4-dihydro-1,2-benzoxathiin 2-oxide (**1b**) is accelerated by buffer bases while that of 3*H*-2,1-benzoxathiole 1-oxide (**1d**) is essentially independent of buffer concentrations in tertiary amine buffers or decelerated in some buffers. These results are taken as evidence for the hypervalent intermediate of this reaction.

Nucleophilic substitution at sulfur may proceed stepwise with a hypervalent addition intermediate or in a single step without any intermediate.[2] We have recently presented evidence for the intermediate in the acid hydrolysis of some sulfinamides,[3] while a single-step SN2 mechanism was suggested for the acid hydrolysis of sulfinate esters.[4] We now present buffer effect observations in the base-catalyzed ring opening of some cyclic sulfinate esters (**1a-d**), which support strongly involvement of the hypervalent intermediate (**2**) in the reaction pathway (Eq. 1).





Reactions of the cyclic sulfinate esters **1** (prepared as described previously[5,6]) were carried out in aqueous solution (ionic strength, 0.10 M, maintained with $NaClO_4$) at 25 °C, and were monitored spectrophotometrically on a Shimadzu UV 1200 spectrometer.[4] The reaction observed above pH 6 is hydroxide-catalyzed ring opening for all the substrates. The phenolic esters, **1a** (k_{OH^-} = 7.0 x 10^3 $dm^3mol^{-1}s^{-1}$) and **1b** (k_{OH^-} = 2.8 x 10^4 $dm^3mol^{-1}s^{-1}$), are much more reactive than the esters of aliphatic alcohols, **1c** (k_{OH^-} = 0.52 $dm^3mol^{-1}s^{-1}$) and **1d** (k_{OH^-} = 79.5 $dm^3mol^{-1}s^{-1}$).

The reactions of **1a** and **1b** were examined in buffer solutions usually of tertiary amines. They are accelerated by the buffer (Figure 1). The buffer effects observed arise completely from the base components, and catalytic constants are dependent on pK_a of the conjugate acid of the catalyst as shown in Figure 2 for **1a**. Although the plots show a considerable scattering, a line of the unit slope is drawn to constitute an approximate regression line. This strong dependence on the buffer base must be ascribed to the nucleophilic catalysis rather than to the general base catalysis. Sterically hindered 2,6-lutidine is a much less effective catalyst than 3,4-lutidine.

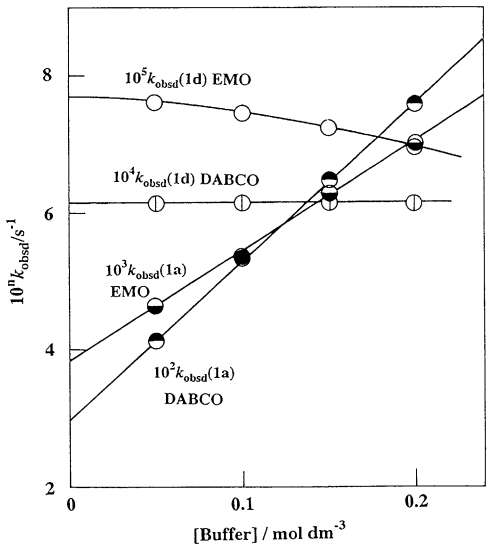
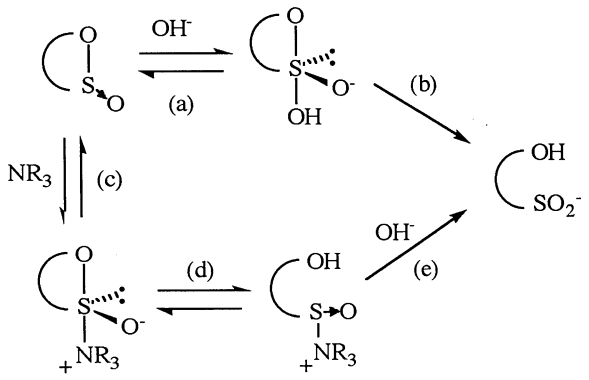


Figure 1. Buffer dependences of rate constants for the ring opening of **1a** and **1d** in *N*-ethylmorpholine (EMO) (pH 7.8) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (pH 8.8) buffers.

In contrast to the strong buffer dependence of ring opening of **1a** and **1b**, buffer catalysis of the reaction of **1d** could not be detected in many of the teriary amine buffers, while the negative effects were observed in *N*-ethylmorpholine (EMO) (Figure 1) and *N*-methylpiperidine (MPI) buffers. No acceleration of the reaction of **1d** (or **1c**) was observed in tertiary amine buffers examined.

The contrasting observations in buffer catalysis of ring opening reactions of phenolic sulfinates (**1a** and **1b**) and alcoholic sulfinate (**1d**) may be accommodated by a mechanism involving a hypervalent addition intermediate (Scheme 1) but



Scheme 1.

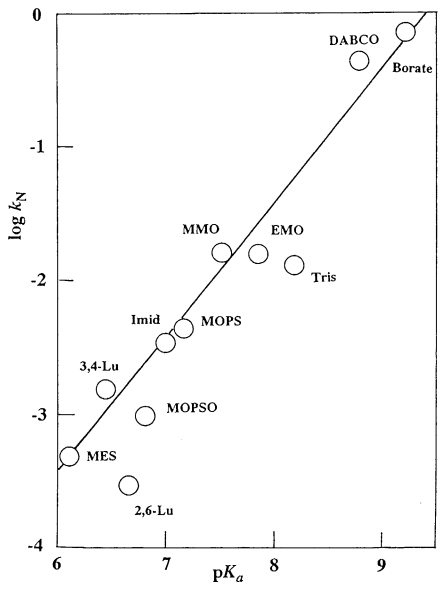


Figure 2. Dependences of catalytic constants for the ring opening of **1a** on the pK_a of the conjugate acids. MES, 2-(*N*-morpholino)ethanesulfonic acid; Lu, lutidine; MOPSO, 2-hydroxy-3-(*N*-morpholino)propanesulfonic acid; Imid, imidazole; MOPS, 3-(*N*-morpholino)propanesulfonic acid; MMO, *N*-methylmorpholine; Tris, tris(hydroxymethyl)aminomethane.

with different rate-determining step for the respective substrates. Phenolate ion is much better nucleofuge than the alkoxide.

The ring opening of **1a** (and **1b**) may proceed with rate-determining formation of the intermediate (step a or c) owing to the high nucleofugality of phenolate (fast decay of the intermediate, step b or d), while that of **1d** may take place with the fast equilibrium formation of the intermediate (step a) followed by its slow decay (departure of the poor nucleofuge, alkoxide, step b). In the former reaction, the buffer nucleophile can act as a catalyst since it can compete with hydroxide ion to form a hypervalent intermediate which then gives rapidly the sulfinyl intermediate (step d). The nucleofugality of NR_3 of the intermediate (sulfinamide) must be still better than the phenolate, and step e should be very fast.

By contrast, the equilibrium participation of the nucleophile in the reaction of **1d** may result in essentially the specific hydroxide ion catalysis.[7] Observed negative effects of the EMO and MPI buffers are difficult to account for, but accumulation of the intermediate might occur to retard the overall reaction.

Preliminary experiments of this work were carried out by Koji Senda and Hideki Takano, and the substrates used were prepared by the coworkers appeared in Reference 6.

References and Notes

1 This paper is dedicated to Professor Shigeru Oae on the occasion of his seventy-fifth birthday.
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7 Since the leaving ability of the $-N^+R_3$ group is better than -OH group, the equilibrium step c may be negligible as compared with the equilibrium a. This makes a difference in catalytic behavior from the case where the nucleophiles participate in the rate-determining step. However, if the equilibrium constant for step c is large, the intermediate accumulates and the retardation may result.