1 has a solution magnetic moment[13] of 5.11 μ_B consistent with a high spin ($S = 2$) center. The spectrum of 1 in MeCN in the presence of some excess HIm shows bands at 415 (sh, 2940), 450 (2760), and 500 nm (2500).[14]

$FeCl_3$, thiosalH_2, NEt_3, and 2-methylimidazole (2-MeIm) in EtOH in a 1:2:4:2 ratio yield a blue precipitate. Recrystallization from DMF/ether yields blue-black crystals of $(HNEt_3)$[Fe(thiosal)$_2$(2-MeIm)] (2) in 25% yield. The metal is again five-coordinate (Figure 2)[16] but trigonal bipyramidal, no doubt due to the 2-methyl group,[17] with axial oxygen atoms. Complex 2 has a solution moment[13] of 5.93 μ_B consistent with a high-spin ($S = {}^5/_2$) center. In DMF, 2 shows maxima at 290 (13,090), 363 (5775), and 565 nm (5070).

Complexes 1 and 2 are not proposed as perfect models for the native and Fe(III)-substituted enzymes. Tyrosine and cysteine contain phenoxide and alkylthiolate groups, respectively, while thiosal contains carboxylate and arylthiolate functions. This ligand, however, does suppress reduction of the Mn(III), the primary problem in the preparation of Mn(III) thiolates. The conclusions of this work are that spectral properties of Mn(III) thiolates are a function of the total ligand set and that mixed O,N,S-ligation is necessary before spectral characteristics of the native enzyme are approached. The 500-nm (2500) band in 1 is satisfyingly similar to that of the enzyme, 515 nm (2460); the values for 2 and Fe(III)-substituted enzyme are less similar but both show a red shift vs. the Mn forms. Inversely, our results could be considered supportive of mixed O,N,S-ligation in the enzyme. In addition, five-coordination at Mn(III) when thiolate ligands are present represents an interesting contrast to the usual preference of this oxidation level for six-coordination and may be indicative of five-coordination in the enzyme.[18,20]

We believe the visible bands in the spectrum of 1 to be due to S-to-Mn charge transfer (CT). Support for this comes from studies employing salicylate (sal) rather than thiosal. We have made several Mn(III) complexes with this ligand[21] and none exhibit CT bands at >352 nm. The 515-nm enzyme band must presumably be due to S-to-Mn CT, O-to-Mn CT, or a combination of the two. The current status of our modeling work precludes definitive extrapolations to the enzyme spectrum. However, no complex containing a Mn-O(phenoxide) bond has yet shown a CT band in the 500-nm region, whereas such a band is seen when a Mn-S(thiolate) bond is present; on the basis of this we would support the suggestion that the enzyme 515-nm band contains a S-to-Mn CT contribution.[22]

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(13) Measurements were performed in Me_2SO-d_6 using the Evans NMR method.

(14) The slight excess of HIm was required to suppress DMF-for-HIm exchange on the anion; similar behavior is seen[15] for $[Mn(edt)_2(HIm)]^-$.

(15) Seela, J. L.; Huffman, J. C.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1985**, 58.

(16) Complex 2 crystallizes in space group $P2_1/a$ with (at -158 °C) a = 22.300 (8) Å, b = 12.347 (3) Å, c = 9.419 (2) Å, β = 92.61 (1)°, and Z = 2. 2945 unique reflections with $F > 3\sigma(F)$ were refined to values of R and R_w of 4.76% and 5.31%, respectively.

(17) The change in geometry is undoubtedly due to steric rather than electronic factors associated with the 2-methyl substituent. In TBP geometry, a larger (~120°) N-Fe-S angle is available to accommodate the Me group.

(18) The structure of *T. thermophilus* Mn superoxide dismutase is available[19] and it lends some precedence to the suggestion of similar five-coordination in acid phosphatase.

(19) Stallings, W. C.; Pattridge, K. A.; Strong, R. K.; Ludwig, M. L. *J. Biol. Chem.* **1985**, *260*, 16424-16432.

(20) It is interesting that Mn(III) and Fe(III) form analogous, five-coordinate complexes with mixed O,N,S-ligation. This might explain why Fe can substitute for the Mn with significant (53%) retention of activity.

(21) Products include $[Mn(sal)_2(salH)]^-$ and $[Mn(sal)_2(HIm)_2]^-$. The CT bands of these species in DMF (λ_{max} (ϵ_M)) are 309 (20950), 320 (sh, 19600), 352 (sh, 8730) and 285 (21400), 322 (sh, 12700), respectively.

(22) This assumes the assignment of sweet potato acid phosphatase as being a Mn(III) enzyme is correct. Our modeling work cannot itself resolve this point but does establish that a mixed-O,N,S-ligated Mn(III) center *could* be responsible for the characteristic spectral features of the enzyme.

Registry No. 1, 103225-95-2; **2**, 103225-97-4; $Mn(acac)_3$, 14284-89-0; $[Mn(sal)_2(salH)]^-$, 103225-98-5; $[Mn(sal)_2(HIm)_2]^-$, 103239-84-5; acid phosphatase, 9001-77-8.

Supplementary Material Available: Tables of atomic coordinates and anisotropic thermal parameters for both complexes (7 pages). Ordering information is given on any current masthead page.

Evidence for Reversible Formation of an Intermediate in the "Spontaneous" Hydrolysis Reaction of *p*-Methoxystyrene Oxide

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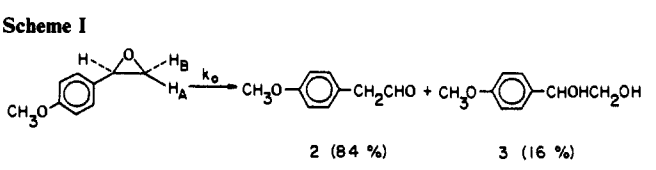
The hydrolysis of epoxides may occur by at least three kinetically distinguishable pathways whose rates are functions of the pH of the solution.[1] At low pH the kinetically dominant reaction is usually the acid-catalyzed hydrolysis, and at high pH hydroxide ion can catalyze the reaction by acting as a nucleophile. Many epoxides also undergo reaction at intermediate pH values by pathways whose rates are independent of pH. This latter reaction has become known as the "spontaneous" or "neutral" reaction and often leads to both carbonyl rearrangement products and diols.

The mechanism of the spontaneous reaction of epoxides varies substantially with the structure of the epoxide. For example, this reaction of propylene oxide in water enriched with ^{18}O yielded glycol in which 60-70% of the label was located at the primary center, and this observation was taken as evidence that water acted as a nucleophilic reagent.[1b] Water also appears to act as a nucleophile in the spontaneous reaction of 1,3-cyclohexadiene oxide.[2] In contrast, benzene oxide and naphthalene oxide rearrange completely to phenols in this reaction process, and rate-limiting carbon-oxygen bond fissure leading to dipolar intermediates was proposed on the basis of isotope effect data.[3] In a related reaction, 6-methoxy-1,2,3,4-tetrahydronaphthalene oxide undergoes a spontaneous reaction with rate-limiting hydrogen migration to yield ca. 75% of 6-methoxy-2-tetralone, along with lesser amounts of cis and trans diols.[4] In this latter case, no distinction could be made between a mechanism that involved an intermediate in the carbonyl-forming reaction and a concerted mechanism in which epoxide yielded ketone in a single step. *We have now examined the hydrolysis reactions of p-methoxystyrene oxide* (1) *and a deuterium-labeled derivative and wish to report* ^1H *NMR data that provide evidence for reversible formation of an intermediate in the spontaneous reaction that yields mainly p-methoxyphenylacetaldehyde.*

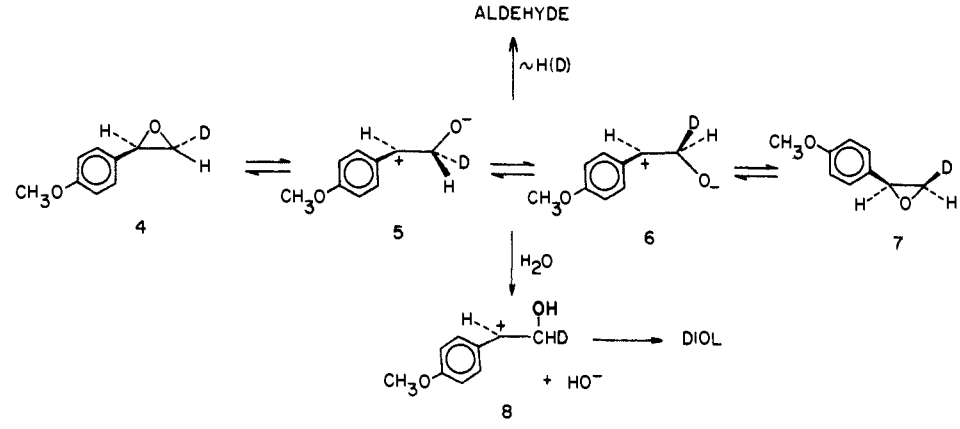
The rates of reaction of 1 in 0.1 M $NaClO_4$ solutions, at 25.0 °C over the pH range 4.7-13, were fit to the equation $k_{obsd} = k_{H^+}a_{H^+} + k_0$. The values of k_{H^+} and k_0 were determined to be $1.1 \pm 0.1 \times 10^4$ M^{-1} s^{-1} and $3.0 \pm 0.2 \times 10^{-3}$ s^{-1}, respectively.[5] Product studies showed that the acid-catalyzed reaction yielded >95% of glycol product 3, whereas the spontaneous (k_0) reaction proceeded mainly to rearranged aldehyde (Scheme I).

p-Methoxy-*trans*-β-deuteriostyrene oxide (4) was also prepared,[6] and its hydrolysis reactions were studied. The kinetic deuterium isotope effects $k_{H^+}(H)/k_{H^+}(D)$ and $k_0(H)/k_0(D)$ were determined

Scheme I



Scheme II



to be 0.97 ± 0.01 and 1.17 ± 0.02, respectively.[5] ^{1}H NMR and mass spectral analyses of the aldehyde product from the k_0 reaction of **4** showed that the ratio of hydrogen migration to deuterium migration was ca. 3:1.[8] The value of this ratio is similar to the kinetic isotope effect for migration of deuterium[9] and suggests that both hydrogens in the methylene position of **1** migrate to similar extents.

When the reaction of **4** was allowed to proceed for 6 min at room temperature (ca. one half-life) and the remaining epoxide isolated by extraction of the reaction solution with ethyl acetate, the ^{1}H NMR spectrum of the recovered epoxide showed that the deuterium was almost equally distributed in both the cis and trans positions. We attribute this scrambling of deuterium to a mechanism in which reversible benzyl C–O bond cleavage yields a stabilized intermediate with a sufficient lifetime for rotation about the C–C bond and ring closure to the cis-labeled isomer **7**, at a rate that exceeds those of product-forming steps.

A number of kinetically equivalent mechanisms can account for the observed results. One possible mechanism is given in Scheme II, in which the intermediate is a dipolar species similar to those proposed for the spontaneous hydrolysis reactions of benzene and naphthalene oxides.[3] This intermediate could serve as a common precursor for both diol and aldehyde products.

In another kinetically equivalent mechanism, water acts as a general acid in converting **4** directly to a benzylic carbocation **8** in a reversible step that would account for the deuterium scrambling. The benzylic carbocation might then be a common precursor for both diol and aldehyde products, or aldehyde could be formed in a parallel, perhaps concerted, reaction. To the extent that aldehyde is a major product, hydrogen migration must be a rate-limiting step.[10]

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Registry No. 1, 6388-72-3; **4**, 103150-00-1; D_2, 7782-39-0.

Supplementary Material Available: Figure containing ^{1}H NMR resonance due to the methylene hydrogens of **1**, **4**, and recovered epoxide from hydrolysis of **4** for ca. 1 half-life at pH 9.10 (1 page). Ordering information is given on any current masthead page.

(1) (a) Bronsted, N. J.; Kilpatrick, M.; Kilpatrick, M. *J. Am. Chem. Soc.* **1929**, *51*, 428. (b) Pritchard, J. G.; Long, F. A. *Ibid.* **1956**, *78*, 2663. (c) Long, F. A.; Pritchard, J. G. *Ibid.* **1956**, *78*, 6008.

(2) Ross, A. M.; Pohl, T. M.; Piazza, K.; Thomas, M.; Fox, B.; Whalen, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 1658.

(3) (a) Kasperek, G. J.; Bruice, T. C.; Yagi, H.; Jerina, D. M. *J. Am. Chem. Soc.* **1972**, *94*, 198. (b) Kasperek, G. J.; Bruice, T. C.; Yagi, H.; Jerina, D. M. *J. Chem. Soc., Chem. Commun.* **1972**, 784.

(4) Gillilan, R. E.; Pohl, T. M.; Whalen, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 4482.

(5) The reactions of **1** and **4** were monitored spectrophotometrically by the change in absorbance at 232 nm in the thermostatted cell compartment of a Perkin-Elmer Model 3840 spectrophotometer.

(6) The labeled epoxide **4** was prepared by the following reaction sequence: (1) bromination of *p*-methoxycinnamic acid followed by decarboxylative debromination of the dibromo acid in $NaHCO_3/CH_2Cl_2$ in a modified procedure of ref 7a to give *p*-methoxy-*trans*-β-bromostyrene; (2) lithiation of the resulting bromide at −110 °C with *tert*-butyllithium and quenching of the organolithium reagent with D_2O[7b] to give *p*-methoxy-*trans*-β-deuteriostyrene; (*4*) careful epoxidation of the deuterium-labeled styrene with CH_3CO_3H/Na_2CO_3 in CH_2Cl_2[7c] at 0 °C to yield **4**. The epoxidation reaction unexpectedly gave **4** with varying amounts of the cis deuterium-labeled epoxide that depended on the reaction conditions and rates of addition of the peracid to the labeled olefin. The mass spectrum of **4** showed that >99% contained deuterium, and the ^{1}H NMR spectrum of the sample used for this experiment showed the presence of ca. 11% of the cis-deuterio isomer.

(7) (a) Cristol, S. J.; Norris, W. P. *J. Am. Chem. Soc.* **1953**, *75*, 2645. (b) Seebach, D.; Newmann, H. *Tetrahedron Lett.* **1976**, 4839. (c) Crandall, J. K.; Conover, W. W.; Komin, J. B.; Machleder, W. H. *J. Org. Chem.* **1974**, *39*, 1723.

(8) The ratio of hydrogen/deuterium migration was determined by analysis of both the methylene absorption and residual aldehydic proton absorption in the ^{1}H NMR spectrum of aldehyde product. The mass spectrum of this material showed that >95% of the aldehyde product contained deuterium.

(9) (a) Collins, C. J.; Rainey, W. T.; Smith, W. B.; Kaye, I. A. *J. Am. Chem. Soc.* **1959**, *81*, 460. (b) Winstein, S.; Takahashi, J. *Tetrahedron* **1958**, *2*, 316.

(10) Both deuterium and hydrogen would be equally disposed geometrically toward migration in the intermediates represented by **5** and **6**, and the ratio of hydrogen vs. deuterium migration would be determined by the kinetic deuterium isotope effect of deuterium migration (with hydrogen remaining) vs. hydrogen migration (with deuterium remaining).