coordinated ability than THF, \(k_1\) at 40 °C was \((7.0 \pm 0.4) \times 10^{-3} \text{s}^{-1}\), the rate decreased to 28 times slower than the corresponding rate in THF \((k_2 = 2.0 \pm 0.1) \times 10^{-3} \text{s}^{-1}\) at 40 °C.

There is precedent for this solvent dependence in the reductive elimination of anions from bis(phosphine)dimethylcadmium (II).\(^{10}\) The low activation enthalpy barriers and large negative entropies in polar solvents were also attributed to a late transition state that permits coordination of solvent molecules.

Theoretical studies of \(H_2\) reductive elimination from \(c\text{-PtH}_2(P\text{Me}_3)_2\) by the GVB,\(^4\) GVB-Cl,\(^4\) RHF,\(^6\) and SD-Cl\(^6\) methods have appeared. Calculated activation barriers for \(H_2\) elimination are 18.2, 24.1, 42.1, and 109.7 kcal/mol with endothermicities of +15.9, +6.7, +36.9, and +21.5 kcal/mol, respectively. A SCF calculation for \(c\text{-PtH}_2(P\text{Me}_3)_2\) yielded a kinetic barrier of 18.9 kcal/mol,\(^{14}\) close to that we observe for the Pt–H dissociation energy. Data reported here should provide a benchmark for future theoretical work.

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Synthetic Model Approach to the Manganese(III) Acid Phosphatase and Its Iron(III)-Substituted Form

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Several reports have described the isolation of red-violet acid phosphatases from plants such as soybean,\(^1\) spinach,\(^2\) and sweet potato.\(^3\) The latter enzyme appears to contain a mononuclear Mn(III) site with thiolate (cysteine) and phenoxide (tyrosine) ligation;\(^4\) histidine residues essential for activity possibly indicate coordination of solvent molecules.

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I has a solution magnetic moment\(^1\) of 5.11 \(\mu_B\) consistent with a high spin \((S = 2)\) center. The spectrum of I in MeCN in the presence of some excess HIm shows bands at 415 (sh, 2940), 450 (2760), and 500 nm (2500).\(^{14}\) FeCl\(_3\), thiosal\(_2\)H\(_2\), NEt\(_3\), and 2-methylimidazolide (2-Melm) in EtOH in a 1:2:4:2 ratio yield a blue precipitate. Recrystallization from DMF/ether yields blue-black crystals of \((\text{HNET})_2\text{Fe(thiosal)}_2(2-	ext{Melm})\) (2) in 25% yield. The metal is again five-coordinate (Figure 2)\(^8\) but trigonal bipyramidal, not doubt due to the 2-methyl group,\(^7\) with axial oxygen atoms. Complex 2 has a solution moment\(^11\) of 5.93 \(\mu_B\) 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 phenoxo and alkylthiolate groups, respectively, while thiolate 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 I is satisfactorily 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 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.\(^{12,20}\)

We believe the visible bands in the spectrum of I to be due to S-to-Mn charge transfer (CT). Support for this comes from studies employing salicylaldehyde (sal) rather than thioal. We have made several Mn(III) complexes with this ligand\(^{21}\) and none exhibit CT bands at \(\geq 552\) nm. The 515-nm enzyme band must presumably be due to S-to-Mn CT, \(\epsilon_{\text{Sp}}\text{H}\). Water also appears to act 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 carboxyl rearrangement products and diols. The mechanism of the spontaneous reaction of epoxides varies substantially with the structure of the epoxye. 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 nucleophile reagent.\(^{22}\) Water also appears to act as a nucleophile in the spontaneous reaction of 1,3-cyclohexadiene oxide.\(^{23}\) In contrast, benzene oxide and naphthalene oxide rearrange completely to phenols in this reaction process, and rate-limiting carbon–oxygen bond fission leading to dipolar intermediates was proposed on the basis of isotope effect data.\(^{23}\) 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.\(^{24}\) 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 epoxye 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 \(^1\)H NMR data that provide evidence for reversible formation of an intermediate in the spontaneous reaction that yields mainly p-methoxyphenylacetaldheyde.

The rates of reaction of I in 0.1 M NaClO\(_4\) solutions, at 25.0 °C over the pH range 4.7-13, were fit to the equation

\[
\log k_{\text{obsd}} = k_{\text{H}+} + k_0.
\]

The values of \(k_{\text{H}+}\) and \(k_0\) were determined to be 1.1 \(\pm 0.1 \times 10^6\) 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 aldeyde (Scheme 1). p-Methoxy-trans-\(\beta\)-deuteriostyrene oxide (4) was also prepared and its hydrolysis reactions were studied. The kinetic deuterium isotope effects \(k_{H+}(H)/k_{H+}(D)\) and \(k(H)/k(D)\) were determined

\[
\text{Scheme I}
\]