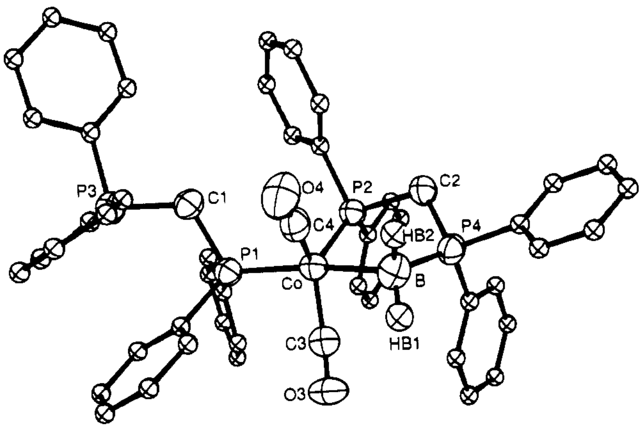

Figure 1. ORTEP diagram of $[(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})(BH_2)]$ (**2**), showing the atom-labeling scheme. Selected bond distances (Å) and angles (deg) are as follows: Co–B, 2.227 (6); Co–P(1), 2.193 (1); Co–P(2), 2.198 (1); Co–C(3), 1.745 (1); Co-C(4), 1.738 (1); P(4)–B, 1.912 (6); P(1)–Co–B, 164.3 (2); P(1)–Co–P(2), 101.91 (3); P(2)–Co–B, 93.1 (2); C(3)–Co–B, 82.4 (2); C(4)–Co–B, 75.5 (2); Co–B–P(4), 103.9 (3).

The other unusual feature of the structure of **2** is the long Co–B bond of 2.227 (6) Å. Most cobalt–boron bonds in cobaltaboranes fall in the range 2.00–2.15 Å.[7] The two hydrogen atoms on boron were located by difference Fourier techniques and were refined successfully, leading to approximately tetrahedral geometry around boron.

The detailed structure of **2** is significantly different from the square-pyramidal (SP) structure at cobalt deduced for **1** on the basis of spectroscopic data,[2] but it is well-known that the TBP and SP structures have similar energies. The long and presumably weak Co–B bond, now established for **2**, is probably a result of the weak nucleophilic character of $[Co(CO)_4]^-$, and the ease of decomposition or dissociation of unbridged complexes with Co–B bonds such as **1** and $[(CO)_4CoBH_3]^-$ can be rationalized on this basis.[2,8] Our molecular orbital calculations on the latter molecule, which may be considered a model for **2**, predict that the charges on the BH_3 and $Co(CO)_4$ fragments are −0.55 and −0.45 e, respectively, and the optimized Co–B bond distance is 2.43 Å.[9] The μ-dppm ligand may stabilize **2** not only by providing its well-known binucleating ability but also by providing steric shielding and by increasing the electron density on cobalt and hence giving greater covalency to the Co–B bond.[9] Complex **2** and related compounds with $M{-}BH_2$ bonds have great potential in synthesis if high-yield synthetic methods can be realized. Further work to this end is in progress.

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Supplementary Material Available: Tables of crystal data, atomic positional and thermal parameters, anisotropic thermal parameters, and atomic distances and angles (10 pages); a listing of the observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

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(9) The Co–B bond in **2** is a 2c–2e bond, probably polarized in the sense $Co^{\delta-}{-}B^{\delta+}$. Evidence for this is seen in the low values of ν(CO) for **2**[5] compared to related Co(O) complexes such as $[Co_2(CO)_4(\mu\text{-dppm})_2]$.[4] In the extreme case, the Co–B bond could be considered as a donor–acceptor bond with $Co(CO)_2L_2^-$ as donor and BH_2L^+ as acceptor. In the MO calculations on the model compound $[(CO)_4Co{-}BH_3]$, the angles around the B and Co atoms were the tetrahedral and trigonal-bipyramidal angles, respectively, and distances were from literature values. The basis set for the ab initio calculation was STO-3G. An extended Huckel calculation gave good agreement on the charges on the fragments [−0.54 and −0.46 e on BH_3 and $Co(CO)_4$, respectively]: McNeill, E. A.; Scholer, F. R. *J. Am. Chem. Soc.* **1977**, *99*, 6243.

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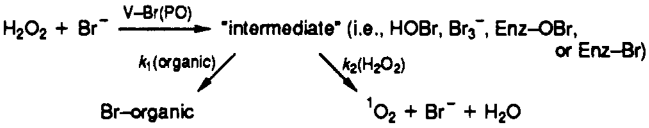
Chlorination Catalyzed by Vanadium Bromoperoxidase

Vanadium bromoperoxidase (V–Br(PO)) isolated from marine algae catalyzes the oxidation of bromide, which results in the bromination of certain organic compounds[1-3] or the production of singlet oxygen from the bromide-assisted disproportionation of hydrogen peroxide.[4]



The marine environment is a very rich source of halogenated natural products. Rhodophyta (red algae) produce the most diverse array of brominated and chlorinated compounds (e.g., terpenes, phenols, β-keto acids, etc.),[5,6] and phaeophyta (brown algae) produce large quantities (e.g., ca. 10^4 tons/year) of volatile brominated and chlorinated hydrocarbons (e.g., $CHBr_3$, $CHBr_2Cl$, etc.).[7] The biosynthesis of the brominated compounds is likely to be mediated by bromoperoxidase through electrophilic bromination by oxidized bromine species. By contrast, the origin of the marine chlorinated natural products has not been elucidated. It has been reported that chloride is neither a substrate nor an inhibitor of V–Br(PO),[8] whereas bromide and iodide are substrates and fluoride is an inhibitor of V–Br(PO).[9] In our investigations of the halide selectivity of V–Br(PO), we have reinvestigated the reactivity of V–Br(PO) with chloride. We report the first observation that vanadium bromoperoxidase *does* catalyze the oxidation of chloride by hydrogen peroxide *and* the chloride-assisted disproportionation of hydrogen peroxide.

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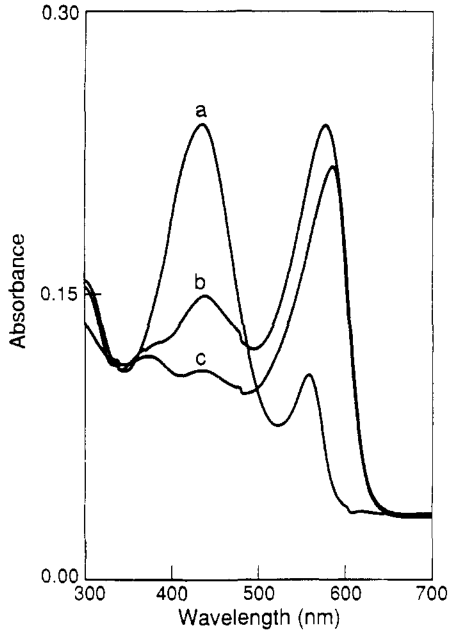
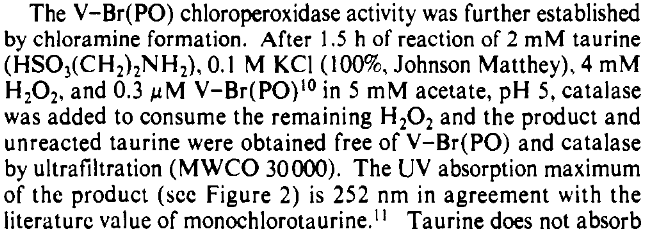


Figure 1. UV-vis spectra of the V-Br(PO)-catalyzed chlorination of phenolsulfonephthalein: (a) phenolsulfonephthalein; (b) solution mixture after reaction for 1 h; (c) solution mixture after reaction for 2 h. The reaction conditions are described in the text. The spectra shown are 1/10 dilutions of the reaction mixture in 0.1 M phosphate, pH 7. V-Br(PO) used through out all experiments was isolated from *A. nodosum* as previously reported[4,9] and stored in water.[10]

V-Br(PO), isolated from the brown alga *Ascophyllum nodosum*, catalyzes the conversion of 0.1 mM phenolsulfonephthalein (i.e., phenol red) to the tetrachlorinated derivative, as identified by electron-impact mass spectral analysis (i.e., for M,$^+$ *m/e* 490, 492, and 494 at the correct relative intensities; *m/e* 496 was too weak to detect), under conditions of 0.1 M potassium chloride, 2 mM hydrogen peroxide, and 0.3 μM V-Br(PO) in 0.1 M citrate buffer pH 5. The UV-vis spectrum of this product is consistent with the formation of 3′,3″,5′,5″-tetrachlorophenolsulfonephthalein (i.e., λ_{max} 589 nm, pH 7),[6] as shown in Figure 1c. Phenol red (i.e., λ_{max} 428 nm, pH 7) (Figure 1a) chlorination proceeds through the formation of an intermediate with a λ_{max} of 575 nm (Figure 1b), consistent with the formation of 3′,3″-dichlorophenolsulfonephthalein:[6]



In addition, V-Br(PO) catalyzes the chlorination of an authentic sample of 3′,3″-dichlorophenolsulfonephthalein, forming the tetrachloro derivative as identified spectrophotometrically. In the absence of V-Br(PO), hydrogen peroxide does not oxidize chloride; consequently, chlorinated products are not formed.

The V-Br(PO) chloroperoxidase activity was further established by chloramine formation. After 1.5 h of reaction of 2 mM taurine ($HSO_3(CH_2)_2NH_2$), 0.1 M KCl (100%, Johnson Matthey), 4 mM H_2O_2, and 0.3 μM V-Br(PO)[10] in 5 mM acetate, pH 5, catalase was added to consume the remaining H_2O_2 and the product and unreacted taurine were obtained free of V-Br(PO) and catalase by ultrafiltration (MWCO 30000). The UV absorption maximum of the product (see Figure 2) is 252 nm in agreement with the literature value of monochlorotaurine.[11] Taurine does not absorb in this region. If excess H_2O_2 is not removed, the UV spectrum does not have a definite absorption maximum but only a shoulder at ca. 250 nm due to the absorption of hydrogen peroxide. The reactivity of the product is also consistent with standard analytical methods to identify and quantify chloramines,[12] including the oxidation of iodide to triiodide (λ_{max} 353 nm), bromide to tribromide (λ_{max} 267 nm), and 5-thio-2-nitrobenzoic acid[13] (λ_{max} 412 nm) to 5,5′-dithiobis(2-nitrobenzoic acid). The extinction coefficient of the V-Br(PO)-catalyzed monochlorotaurine product, 398 M^{-1} cm^{-1}, is identical with the literature value of monochlorotaurine,[11] further confirming the formation of monochlorotaurine.[14]

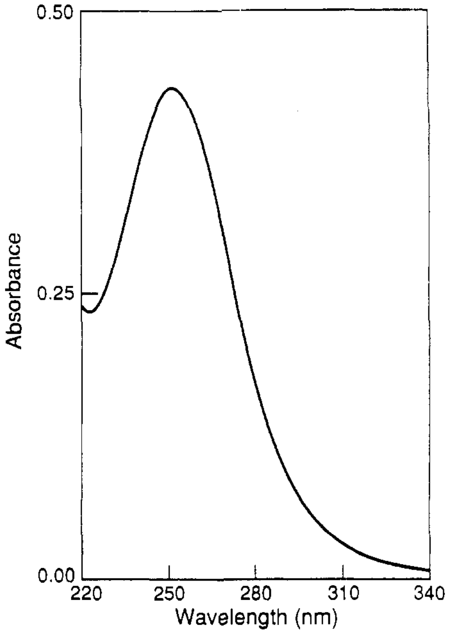


Figure 2. UV spectrum of the V-Br(PO)-catalyzed formation of monochlorotaurine from taurine, chloride, and hydrogen peroxide, isolated as described in the text.

Table I. Comparison of the Rates of Dioxygen Formation and MCD Chlorination[a]

[Cl$^-$], mM	-d[MCD]/d*t*,[b] μM/min	d[O_2]/d*t*, μM/min	[taurine], mM
50	1.94 (0.04)[c]	1.96 (0.05)	0
100	3.05 (0.18)	3.00 (0.05)	0
200	4.62 (0.10)	4.61 (0.01)	0
400	6.48 (0.35)	7.08 (0.06)	0
200	4.62 (0.07)	1.31 (0.09)	1.0

[a] Reactions conditions: 0.1 M citrate pH 5, 0.75 mM H_2O_2, 0.27 μM V-Br(PO),[10] μ 3.14 M adjusted with Na_2SO_4. The reactions were initiated by the addition of V-Br(PO). Potassium chloride was obtained from Johnson Matthey and certified as free from contamination by bromide or iodide (i.e., Puratronic, 100%, CAS No. 7447-40-7). Above 0.4 M Cl$^-$, the rate of dioxygen formation is faster than MCD chlorination; the rate difference is under investigation. [b] 50 μM MCD. [c] Value in parentheses is standard deviation of 2–4 determinations.

In addition, V-Br(PO) catalyzes the chlorination of monochlorodimedone (2-chloro-5,5-dimethyl-1,3-dimedone, MCD), the substrate commonly used to measure the specific activity of haloperoxidases.[15] The specific activity of MCD chlorination was found to be 0.49 U/mg (1.5 M KCl (100%, Johnson Matthey), 1.0 mM H_2O_2, 50 μM MCD in 0.1 M citrate, pH 5), which is approximately 500 times lower than the specific bromoper-

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(10) The stock solutions of V-Br(PO) used throughout all experiments were washed with water by ultrafiltration (Centricon 30) to remove all amine contaminants (i.e., Tris buffer, etc.).

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(14) The monochloramine derivatives of ammonia,[20] valine,[21] serine,[21] and leucine[21] were also prepared as described for taurine and identified spectrophotometrically with λ_{max} at 240, 256, 256, and 255 nm, respectively, consistent with literature values.

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oxidase activity.[8,9] The value of K_m^{Cl}, which was determined to be 344 mM at pH 5, indicates that V–Br(PO) has a much lower affinity for chloride than bromide (i.e., K_m^{Br} = 10 mM at pH 5[9]). The V–Br(PO) pH optima for chloroperoxidase activity was found to be pH 5, which is the same for bromoperoxidase activity.[9,16] In contrast, the Fe heme bromoperoxidase isolated from the marine green alga *Penicillus capitatus* catalyzes the oxidation of bromide with optimum activity at pH 6 and the oxidation of chloride with optimum activity at pH 4,[17] although like the case for the vanadium enzyme, the chloroperoxidase activity is much less than the bromoperoxidase activity.[17,18] The substantially lower chloroperoxidase activity of V–Br(PO) reflects, in part, the smaller driving force for chloride oxidation by hydrogen peroxide than bromide oxidation but also the difference in K_m values for the halides.

In the absence of an organic substrate, V–Br(PO) catalyzes the chloride-assisted disproportionation of hydrogen peroxide, forming dioxygen as measured by an oxygen electrode. The rate of dioxygen formation is equal to the rate of MCD chlorination (Table I), suggesting that the rate-limiting step for both reactions is the formation of a common intermediate (e.g., the oxidized chloride species) analogous to the reactions with bromide (see scheme, above).[9] The rate of the chloride-assisted dioxygen formation is inhibited by amines (e.g., taurine; Table I), which is consistent with chloramine formation, since hydrogen peroxide cannot reduce chloramine to form dioxygen and chloride.[19] By contrast, the bromide-assisted disproportionation of hydrogen peroxide is not inhibited by amines because hydrogen peroxide rapidly reduces bromamine compounds, forming singlet oxygen.[3,19] Consequently, the rates of MCD bromination and bromide-assisted disproportionation of hydrogen peroxide (in the absence of MCD) are equal independent of the presence of amine.[3,9] The rate of MCD chlorination is not inhibited by taurine (Table I).

Previously proposed mechanisms of the biosynthesis of certain chlorinated compounds have invoked electrophilic bromination of alkenes followed by passive chloride attack.[6] While this mechanism could explain the origin of adjacent brominated and chlorinated carbons, it does not readily account for chlorine-only-containing compounds. Thus, with the discovery of chloroperoxidase activity of the vanadium enzyme, the origin of specific chlorinated marine natural products can now be addressed. We are continuing to investigate the mechanism and substrate selectivity of chlorination catalyzed by V–Br(PO) to ascertain whether this abundant marine vanadoenzyme should be termed *vanadium chloroperoxidase*.

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Articles

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"Pressure-Testing" Marcus–Hush Theories of Outer-Sphere Electron-Transfer Kinetics

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Predictions of the effect of pressure *P* on rate constants *k* of outer-sphere electron-transfer reactions in solution have been made on the basis of Marcus–Hush theory, with adjustments for medium compression, ion pairing, dielectric saturation, solvent electrostriction, nonadiabaticity, and solvent dynamics. A method of estimating the pressure dependence of the solvent refractive index, required by the theory, is given. For solvents of very low dielectric constant *D*, such as chloroform, the calculations are unrealistic because of large opposing Coulombic and Debye–Hückel contributions, as well as extensive ion pairing. For more polar solvents, the theoretical volumes ΔV^* and compressibilities $\Delta\beta^*$ of activation vary strongly and non-linearly with *P*, especially for nonaqueous solvents at low *P*, so that comparison with corresponding experimental quantities cannot be made, except perhaps approximately at the midpoint of the pressure range. Instead, comparisons are made between theoretical and experimental plots of ln (k/k_0) vs *P* ($k = k_0$ at $P = 0$) for 14 self-exchange reactions of metal complexes in aqueous and nonaqueous solvents. The correlations are good for water (except that nonadiabaticity is indicated for $Co(en)_3^{3+/2+}$ and possibility $MnO_4^{2-/-}$), good to poor for polar organic solvents, and unrealistic for solvents of very low *D*. In no case could behavior expected for rate control by solvent dynamics be found.

Introduction

In recent years, several experimental studies of the effects of pressure *P* on the rate constants *k* of symmetrical outer-sphere electron-transfer (self-exchange) reactions of metal complexes ML_x^{z+} and $ML_x^{(z+1)+}$ in various solvents have been reported together with attempts to rationalize the results in terms of adaptations of the Marcus–Hush theory.[1-12] These rationalizations have suffered in some cases from the lack of the necessary physical data for some of the nonaqueous solvents, notably the pressure

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