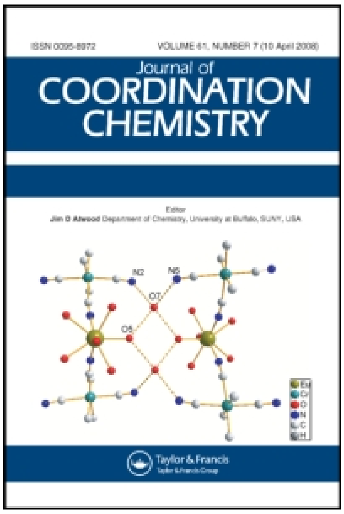

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SHORT COMMUNICATION

Kinetics of the Oxidation of Dithionite ($S_2O_4^{2-}$) by Manganese (III) - Hematoporphyrin

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Manganese porphyrins were first prepared by Zaleski over sixty years ago,[1] and can exist in the plus two, three, and four oxidation states. Calvin[2] has suggested that the manganese required for the oxygen evolution step in plant photosynthesis is bound in a porphyrin type ligand. The synthetic, electrochemical and theoretical studies on manganese porphyrins have been recently reviewed in detail by Boucher.[3] The kinetics of oxidation of Cr^{2+} and V^{2+} by Mn(III)-tetrapyridylporphin have been studied in acid solution,[4] the main result being that such reactions are halide catalyzed, but much less so than their Fe(III) counterparts. The dithionite ion ($S_2O_4{}^{2-}$) is the most common reductant used to produce Mn(II) porphyrins in basic solution,[5] presumably by the overall stoichiometry:

$$4\,OH^- + 2\,Mn(III)\,P + S_2O_4^{=} \xrightarrow{\qquad} 2\,Mn(II)\,P + 2\,H_2O + 2\,SO_3^{2-} \quad (1)$$

We report the kinetics of oxidation of dithionite by Mn(III) hematoporphyrin with a view of establishing the mechanism of such metalloporphyrin reduction and to further explore the chemistry of dithionite.

Manganese hematoporphyrin-IX-dimethylester chloride monohydrate, $MnC_{36}H_{42}O_7N_4Cl$(% Mn: Calc. 7.0, Obs. 6.91) and then the free acid derivative were synthesized by literature methods.[5] The absorption spectra of the trivalent and reduced (by dithionate) forms were as reported,[5] and no destruction of the macrocycle was observed upon reoxidation of Mn(II)P with O_2. At 460 nm, Mn(III)P followed Beers Law from 4.8×10^{-5} M to 3.6×10^{-7} M in 9.1×10^{-2} M NaOH at an ionic strength of 0.5 with NaCl, and over the same concentration range at the same pH in 25% methanol. The kinetics of reduction of Mn(III)P were followed at 25°, 460 nm on a Durrum-Gibson stopped flow apparatus, using a hundred fold excess of dithionite to Mn(III)P. Dithionite was analyzed by the reduction of methylene blue.[6] In the absence of ethanol, the initial rates increased with a decrease in total Mn(III)P, while in 25% methanol, the observed rate constant, k_0, was first order in Mn(III)P over three half-lives and independent of total porphyrin. The results reported here were obtained in 25% methanol.

Table I shows that a constant pH, k_0 varies as the *one-half* order in total dithionite over an eleven fold range. With constant dithionite, Table II shows that k_0 decreases with an increase in hydroxide concentration. Loach and Calvin[5] found a pK_A of 11.95 (24°) for a one proton loss from a coordinated water on $[Mn(III)P{-}(OH_2)_2$ to form $[Mn(III)P{-}(OH_2)(OH)]$, while Davis[7] and Montalvo ascribe this pK to the $[Mn(III)P{-}(OH_2)(OH)]$, $[Mn(III)P\ (OH)_2]$ transformation. Dithionite is known to be in equilibrium[8-10] with two sulphoxylate radical anions ($SO_2^{\cdot-}$), with dissociation constant K_D, at 25° of 6.225×10^{-10} M/l. Since Co(III) porphyrins have a mono-dihydroxide equilibria[11] in the same range as found by Davis for Mn(III)P, a reasonable mechanism for this electron transfer reaction is

$$S_2O_4{}^{2-} = 2\,SO_2^{\cdot-}\ K_D \quad (2)$$

$$Mn(III)P(OH_2)(OH) = Mn(III)P(OH)_2 + H^+ \quad K_A \quad (3)$$

$$SO_2^{\cdot-} + Mn(III)P(OH_2)(OH) \xrightarrow{\qquad} SO_2 + Mn(II)P \quad k_1 \quad (4)$$

$$SO_2^{\cdot-} + Mn(III)P(OH)_2 \xrightarrow{\qquad} SO_2 + Mn(II)P \quad k_2 \quad (5)$$

$$SO_2 + OH^- \xrightarrow{\qquad} SO_3{}^{2-} + H^+\ (\text{Fast}) \quad (6)$$

It is readily shown that

$$k_0 = \frac{(k_1 + k_2K_A[OH^-]/K_w)[S_2O_4{}^{2-}]^{1/2}K_D{}^{1/2}}{(1 + K_A/K_w[OH^-])} \quad (7)$$

Using the data in Table II, a plot of $k_0(1 + (K_A/K_w)[OH^-])/K_D{}^{1/2}[S_2O_4{}^{2-}]^{1/2}$ *versus*

TABLE I
The dependence of k_0 on total dithionite, 25°

$10^2 k_0$ [a,b] (sec^{-1})	$[S_2O_4^{=}]$ (M)	$10^1 k_0 [S_2O_4^{2-}]^{1/2}$ ($M^{-1/2}\ sec^{-1}$)
8.86	1.58×10^{-2}	7.03
5.72	7.57×10^{-3}	6.57
4.43	3.97×10^{-3}	7.03
3.19	2.24×10^{-3}	6.74
2.51	1.42×10^{-3}	6.66

Average $(6.8 \pm 0.2) \times 10^{-1}$

[a] [Mn(III)P] $= 2.58 \times 10^{-5}$ M. $[OH^-] = 4.9 \times 10^{-2}$ M.
[b] $\mu = 0.5$ (NaCl, NaOH), 25% Methanol.

$(K_A/K_W)[OH^-]$ gave k_2 as the slope and k_1 as the intercept. From a least-squares analysis, $k_1 = (7.37 \pm 0.37) \times 10^4\ M^{-1}\ sec^{-1}$ and $k_2 = (2.16 \pm 0.05) \times 10^4\ M^{-1}\ sec^{-1}$. The excellent agreement between the calculated and observed values of k_0, over a forty fold range in hydroxide, is noted in Table II.

TABLE II
The dependence of k_0 on hydroxide and total porphyrin concentration, 25°

	k_0 (sec^{-1})		$[OH^-]$
[Mn(III)P] [a,b] $= 2.37 \times 10^{-5}$ M	*Exptl.*	*Calc.* [c]	
	1.82×10^{-1}	1.83×10^{-1}	3.31×10^{-3}
	1.36×10^{-1}	1.36×10^{-1}	1.15×10^{-2}
	1.24×10^{-1}	1.12×10^{-1}	2.23×10^{-2}
	9.15×10^{-2}	9.33×10^{-1}	4.37×10^{-2}
	8.15×10^{-2}	8.11×10^{-1}	8.66×10^{-2}
	7.39×10^{-2}	7.40×10^{-2}	1.72×10^{-1}

[a] $[S_2O_4^{=}] = 1.50 \times 10^{-2}$ M.
[b] $\mu = 0.5$ (NaCl, NaOH), 25% methanol.
[c] Calculated from the parameters in Equation 7.

k_0 was shown to be insensitive to chloride ion concentration. At a given pH and dithionite concentration, the half-life was 4.1 seconds with 10^{-1} M Cl^-, and 3.7 seconds with 10^{-5} M Cl^-.

The chemistry of dithionite was first explored by Jellinek,[12] and several reviews[13,14] have appeared. The first and second acid dissociation constants are 0.45 and 3.5×10^{-3} M/l respectively. The dithionite ion is a strong reductant in basic solution with $E^0 = 1.12$ volts. The potential of Mn(III)P/Mn(II)P in molar hydroxide[5] is approximately –0.4 volts, giving Reaction 1 an equilibrium constant of ca. 10^{24}. The half order dependence on total dithionite can be understood as due to the sulphoxylate radical anion ($SO_2^{-}\cdot$) being the reactant. The crystal structure[15] of $Na_2S_2O_4$ shows a S–S distance much larger than that of a typical disulfide, and was interpreted as indicating two SO_2^{-}. units linked by a weak S–S bond. The reduction of molecular oxygen by dithionite[6] also apparently proceeds through $SO_2^{-}\cdot$, whose existence has been confirmed by ESR spectroscopy.[8]

Under vigorous conditions dimers of Mn(III) porphyrins have been isolated in basic solution.[16] It has been noted[7] that Mn(III)P shows peculiar potentiometric behaviour in basic solution that could be due to porphyrin aggregation, and such phenomena disappear in the presence of ethanol, which tends to monomerize porphyrins. Our kinetic results in the absence of methanol indicate the existence of a concentration dependent equilibra, which is not apparent from the Beers Law behavior of the absorption spectra.

However the fact that the hyperfine structure in the ESR spectra of Mn(II) porphyrins disappear upon repeated freeze-drying cycles,[17] whereas the visible absorption spectra remains unchanged suggest that changes in the porphyrins's properties are not necessarily sensitive to the absorption spectra.

In the present system, the rates of reduction by $S_2O_4^{2-}$ of $[Mn(III)P(OH_2)(OH)]$ and $[Mn(III)P(OH)_2]$ are very similar. While the reaction could proceed through a hydroxy bridged intermediate, the extreme covalency shown by Mn(III) porphyrins[3] does not exclude a cis type, through-the-porphyrin electron transfer mechanism. The lack of chloride catalysis with $S_2O_4^{2-}$, and the presence of an anion dependent term with the V^{2+} and Cr^{2+} (which incorporates chloride into Cr^{3+}) reductions of Mn(III)-tetrapyridylporphin[4] could be due to the stabilization of the oxidized forms of the metal ion reductants by anions, which is not possible with dithionite. Further studies are underway with dithionite and other reducable metal ions complexed to various macrocyclic ligands.

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