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# Synthesis and Oxidative Demetalation of Two New Tungsten Porphyrins[1a]

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Syntheses and spectral characteristics are reported for two new tungsten porphyrins, (5,10,15,20-tetraphenylporphinato)tungstyl(V) methoxide, W(TPP), and [5,10,15,20-tetrakis(*p*-sulfonatophenyl)porphinato]aquooxotungstate(V), W(TPPS). These two porphyrins are shown to undergo slow demetalation in the presence of air, preceded by oxidation to W(VI) by molecular oxygen. The oxidative demetalation of W(TPPS) exhibits kinetics second order in [W(TPPS)] at pH $\gtrsim 2$ and $\mu = 0.10$ M, with the pseudo-second-order rate constant $k = 4.09 \times 10^{-2}$ $\mathrm{M^{-1}\ s^{-1}}$ in a buffered solution of pH 3.97 saturated with air. A medium effect on the rate constant causes only a slight change in $k_{\mathrm{obsd}}$ over a $>10^4$-fold change in $[\mathrm{H^+}]$. A mechanism is proposed for the demetalation, involving replacement of $H_2O$ by $O_2$ coordinated to W(TPPS), then subsequent oxidation of W(V) to W(VI) within this $O_2$ complex and loss of the porphyrin ligand from W(VI). At pH <2, the kinetics anomalously, but clearly, appear to be *−1 order* in [W(TPPS)], with $k \approx 3.2 \times 10^{-13}$ $\mathrm{M^2\ s^{-1}}$ at pH 1.00 ($HClO_4$).

## Introduction

Some biological applications of tungsten chemistry have been mentioned,[2–4] predominantly related to nitrogen fixation, but such synthetic models incorporating tungsten have been scarce. Also, relatively few tungsten porphyrins have been reported in the literature.[5–7] Reported here are convenient syntheses of two new tungsten porphyrins, (5,10,15,20-tetraphenylporphinato)tungstyl(V) methoxide, W(TPP) (Figure 1), and [5,10,15,20-tetrakis(*p*-sulfonatophenyl)porphinato]aquooxotungstate(V), W(TPPS), the first water-soluble tungsten porphyrin yet described. A previously reported attempt[8] of the synthesis of a tungsten porphyrin by using tungsten hexacarbonyl—the source of tungsten used here—proved unsuccessful, but a more recent report[7] indicates that another synthesis was successful, though both were presumably performed by the standard method.[9] The latter report gave no mention of compositional or spectral characterization except for one erroneous reference.

Also shown here is the first example of oxidative demetalation exhibited by a metalloporphyrin. Systems have been studied in which demetalation is preceded by a reduction in the oxidation state of a coordinated metal,[10] but this is the first example, to our knowledge, of a metalloporphyrin demetalation via oxidation of the coordinated metal, viz., W(V) to W(VI) by molecular oxygen.

## Experimental Section

**Syntheses.** All chemicals were analytical reagent grade unless otherwise stated and were used as obtained. *N*,*N*-Dimethylformamide (DMF) was stored over KOH for 2 days, redistilled under reduced pressure (~11 torr), and then stored over 4A molecular sieves.

Tetraphenylporphine (TPP) was synthesized by the method of Adler et al.[11] The sodium salt of tetrakis(*p*-sulfonatophenyl)porphine (TPPS) was made and purified by the method previously reported.[12]

**Synthesis of W(TPP).** TPP (1 g) and a slight stoichiometric excess (0.6 g) of tungsten hexacarbonyl, $W(CO)_6$ (Strem Chemicals), were refluxed in 100 mL of DMF for 2–3 days. The reaction mixture was cooled and poured with stirring into a beaker containing 100 mL of cold water. The solid which separated was filtered, washed with water, and dried under vacuum. The crude complex was purified by chromatography on a column of activated alumina (ICN Woelm neutral, activity grade I) by using benzene as eluant until no further free TPP was detected in the effluent. Methanol–chloroform (4:1) was then used to elute the tungsten porphyrin from the column. The solvent was evaporated and the solid W(TPP) was dried under vacuum. Elemental analysis was by Chemalytics, Inc. (Tempe, AZ). Anal. Calcd for $C_{44}H_{28}N_4WO(OCH_3)\cdot CH_3OH$:[13] C, 63.10; H, 4.03; N, 6.40. Found: C, 62.68; H, 3.89; N, 6.44.

**Synthesis of W(TPPS).** A slight stoichiometric excess (0.6 g) of $W(CO)_6$ (Strem Chemicals) was added to 1 g of TPPS in 100 mL of refluxing DMF. After 2–3 days, the mixture was cooled, and about half of the DMF solvent was removed with a rotary evaporator. This was then rediluted to 100 mL with water.

The resulting solution was added to a chromatography column packed with several grams of (diethylamino)ethylcellulose ((DEAE)cellulose) anion exchanger (Sigma Chemical Co.) in deionized water. The column was eluted first with deionized water and then with 1 M aqueous sodium perchlorate (Alfa-Ventron 95%). Deaeration of all solvents used here helps reduce oxidation by oxygen, but since the oxidation is very slow, this is not absolutely necessary. With water as eluant, both the W(TPPS) and the free-base TPPS are retained; but with aqueous 1 M perchlorate, only the W(TPPS) comes off in the eluate. The elution by $NaClO_4$ was continued until the W(TPPS) solution appeared visibly low in concentration (pale yellow-green). The volume of the eluate—which is now a solution of pure W(TPPS) in 1 M $NaClO_4$—was reduced about tenfold with a rotary evaporator, and a volume of dry acetone equivalent to about a 20-fold excess over this volume was slowly added to the same flask. Digestion of this mixture results in dissolution of the sodium perchlorate but not of the W(TPPS). It was sometimes observed that this precipitation step resulted in occlusion of some sodium perchlorate in the W(TPPS) solid, as shown by elemental analysis and by the strong 1100-$\mathrm{cm^{-1}}$ IR absorption of $NaClO_4$. Repetition of the precipitation from pure water alleviates this problem. The W(TPPS) was filtered from the mixture and stored in a vacuum desiccator. Yield is usually 50–60%.

**Physical Measurements.** pH measurements were made with a Radiometer Type TTT2 Titrator-pH meter. Infrared spectra were taken with a Beckman Acculab 2 IR spectrophotometer, both as Nujol mulls and KBr pellets. The EPR spectrum of W(TPP) in benzene was determined at 77 K and at room temperature with a Varian E-3 EPR spectrometer. Magnetic susceptibility measurements of W(TPP) were made by the Faraday method from room temperature down to 90 K with an Alpha Model 1402 magnetic susceptibility system with an Alpha Model 1424 variable-temperature accessory.

Visible spectra were taken with a Beckman ACTA-III UV–visible spectrophotometer in 1.00-cm quartz cells at a temperature of 25.5 ± 0.2 °C. Kinetic data were obtained by utilization of an Automatic Sampling System accessory to the ACTA-III, including a Beckman Model 3115 digital printer. Kinetics of the W(TPPS) decomposition were monitored by the appearance of the TPPS diacid ($H_4(\mathrm{TPPS})^{2-}$) peak at 644 nm or the TPPS free-base peak at 515 nm. Pseudo-second-order rate constants were obtained from plots of $(A_\infty - A_t)^{-1}$ vs. time, where $A_t$ is the absorbance of the solution at any time $t$ and $A_\infty$ is the expected final absorbance of the product of each reaction (TPPS free-base or diacid), as determined by the product of the initial absorbance and the ratio of the extinction coefficients for the product and reactant species. The integrated rate expression for the pseudo-second-order reaction is

$$[\mathrm{W(TPPS)}]^{-1} = 2kt + [\mathrm{W(TPPS)}]_0^{-1} \qquad \text{(i)}$$

In terms of absorbances and extinction coefficients

$$b(\epsilon_{\mathrm{TPPS}} - \epsilon_{\mathrm{W(TPPS)}})(A_\infty - A_t)^{-1} = 2kt + b(\epsilon_{\mathrm{TPPS}} - \epsilon_{\mathrm{W(TPPS)}})(A_\infty - A_0)^{-1} \qquad \text{(ii)}$$

where $b$ is the light path length in cm. Thus, from the plot of $(A_\infty - A_t)^{-1}$ vs. $t$, the actual pseudo-second-order rate constant is related to the slope of the plot by (iii). The values of $\epsilon_{\mathrm{TPPS}}$ were taken from

$$2k_{\mathrm{obsd}} = (\mathrm{slope})(b)(\epsilon_{\mathrm{TPPS}} - \epsilon_{\mathrm{W(TPPS)}}) \qquad \text{(iii)}$$

the literature[14] and $\epsilon_{\mathrm{W(TPPS)}}$, which was pH dependent, was measured accurately at pH 3.97,[15] and then values for other pHs were determined

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**Table I.** Buffer Systems Used for Kinetic Measurements

| pH | system | source | concn, M | ionic strength, M |
|---|---|---|---|---|
| 1.00 | $HClO_4$ | Mallinckrodt | 0.100 | $[ClO_4^-] = 0.10$ |
| 1.30 | $HClO_4$-$NaClO_4$ | Mallinckrodt/Alfa-Ventron | 0.100 | $[ClO_4^-] = 0.10$ |
| 2.42 | cyanoacetic acid–sodium cyanoacetate[a] | J. T. Baker | 0.206 | $[CNCH_2COO^-] = 0.10$ |
| 3.97 | potassium hydrogen phthalate-HCl | J. T. Baker primary std. | 0.100 | $[C_6H_4(COO)_2H^-] = 0.10$ |
| 7.01 | TRIS-TRIS·HCl[a] | Fisher | 0.108 | $[(CH_2OH)_3NH^+] = 0.10$ |

[a] Conjugate base or acid was made by quantitative addition of 0.100 N NaOH or HCl.

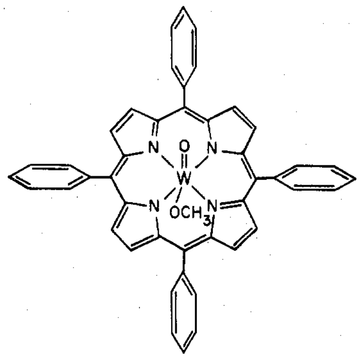

**Figure 1.** (5,10,15,20-Tetraphenylporphinato)tungstyl(V) methoxide, W(TPP).

by a spectrophotometric pH titration of the W(TPPS) in the range of pH 1–6.

Apparent negative first-order rate constants were obtained from plots of $(A_\infty - A_t)^2$ vs $t$.[16]

All kinetic measurements of oxidations by oxygen were made in solutions saturated with air, with the cuvettes either open to the air or in a closed cell with an air reservoir. On the basis of the solubility of air in water[17] and the relatively small change in this solubility up to an ionic strength of 0.10 M,[18] it is estimated that there was at least a 30-fold molar excess of $O_2$ over [W(TPPS)] present during any run.

The fact that the reactions observed actually did require oxygen was checked by performing the same experiments at both pH 1.00 and pH 3.97 in solutions which were flushed with deoxygenated nitrogen gas. There were no changes observed in these spectra over periods equivalent to those in which appreciable changes occurred in the presence of oxygen.

**Buffers for Kinetics.** Five different buffer systems were used, depending on the pH. These systems are listed in Table I. In all cases ionic strength was constant at 0.10 M. As will be seen in the results, the differing types of buffers have little effect on the results observed.

## Results and Discussion

**Syntheses.** In the syntheses of both W(TPP) and W(TPPS), it was noted that shorter reaction times than 2–3 days resulted in a markedly decreased yield of metalloporphyrin. These results are similar to those obtained by Buchler and coworkers,[6] who reported longer reaction times for tungstyl(V) octaethylporphine that for any other metal in their studies. This may explain the difficulty encountered by Ostfeld and Tsutsui,[8] since required reaction times for the corresponding syntheses of $Cr^{III}(OCH_3)TPP$ and $Mo^VO(OCH_3)TPP$ were only 6–7 h.[9]

The purification step of the W(TPPS) procedure is unique, to our knowledge, in that the differing negative charges of the W(TPPS) and the unreacted TPPS free-base were taken advantage of, allowing the two species to be separated very cleanly and efficiently by a synthetic anion exchanger.

One caution that should be made is that if a moderately strong base (e.g., NaOH or $Na_2CO_3$) is present during the synthesis, the tungsten carbonyl reacts with this base to form anionic tungsten species similar to those observed by Hieber et al.[19] Species such as $Na_3[W_2(CO)_6(OH)_3]$ would be eluted from the anion exchange column by 1 M perchlorate and would be difficult to separate from the W(TPPS) product.

**Physical Characterizations.** The visible spectra for both tungsten porphyrins, with their wavelengths and extinction coefficients for the Soret and visible peaks, are listed in Table II.

**Table II.** Absorption Peaks and Extinction Coefficients for $W^V$(TPP) and $W^V$(TPPS)

| species | $\lambda_{max}$, nm | $10^3\epsilon$, $M^{-1}$ $cm^{-1}$ |
|---|---|---|
| $W^VO(OCH_3)(TPP)$[a] | 450 | 254 |
| | 580 | 14 |
| | 625 | 9.9 |
| | 662 sh | ~7 |
| $(W^VOTPP)_2O$[b] | 446 | 215 |
| | 580 | 9.78 |
| | 625 | 7.53 |
| $W^VO(H_2O)(TPPS)$[c] | 451 | 156 |
| | 582 | 13 |
| | 626 | 7.6 |
| $[W^VO(TPPS)]_2O$[d] | 441 | 76 |
| | 581 | 4.7 |
| | 626 | 4.9 |
| | 675 sh | 3.4 |

[a] In methanol + ~1% concentrated aqueous HCl. [b] In alkaline methanol; $\epsilon$ based on absorbance per monomeric W(TPP) unit. [c] In aqueous $HClO_4$ (pH 2). [d] In aqueous NaOH (pH 9); $\epsilon$ based on absorbance per monomeric W(TPPS) unit

Depending on the prevailing acidity or basicity, definite differences in the species present are seen from the spectra. The trend in these changes is quite similar to the trend shown by other metalloporphyrins under the same conditions, namely, an acid dissociation occurs.[20] On the basis of results found for $Mo^V(TPP)$,[21] it is most likely that the tungsten porphyrins form $\mu$-oxo dimers in basic media. The smaller extinction coefficients for the basic species are consistent with this assumption.

A qualitative pH titration followed spectrophotometrically for a $5.4 \times 10^{-6}$ M aqueous W(TPPS) solution produced a plot of absorbance vs. pH with an inflection around pH 4–5.

The infrared spectrum of $W^VO(OCH_3)(TPP)$ shows two strong absorptions in addition to the normal metalloporphyrin absorptions; one is at ~941 $cm^{-1}$ and another at ~906 $cm^{-1}$, which is close to the 901-$cm^{-1}$ absorption observed by Buchler et al.[6] for $W^VO(OCH_3)(OEP)$, and are assigned to the tungstyl (W=O) stretch. In the $W^VO(H_2O)(TPPS)$ spectrum, these absorptions appear at ~851 and ~803 $cm^{-1}$, respectively. We attribute this shift to hydrogen bonding between the hydrated water in the compound and the tungstyl oxygen, resulting in a slight weakening of the bond.

The room-temperature EPR spectrum of W(TPP) contains a set of broad lines. At 77 K, the resolution was very good and $g_\parallel$ and $g_\perp$ values determined were 1.904 and 1.868, respectively. The hyperfine splitting parameter, $A$, due to $^{183}W$ ($I = {}^1/_2$, 14.3% abundant) was calculated to be $95 \times 10^{-4}$ $cm^{-1}$. The unusual reversal in $g_\parallel$ and $g_\perp$ has been noted earlier for oxochlorotungstates.[22] This reversal has been ascribed to spin–orbit interaction of the ligand by Manoharan and Rogers.[23]

Magnetic susceptibility of the W(TPP) obeyed the Curie–Weiss law with a Weiss constant of 3.0 K. The effective moment found was 1.52 $\mu_B$, indicative of one unpaired electron for W(V).

**Oxidation Kinetics.** It was first realized that there was some unusual behavior of these porphyrins when it was observed that

**Table III.** Pseudo-Second-Order Rate Constants for W(TPPS) Demetalation

| pH[a] | $k_{\mathrm{obsd}}$, $M^{-1}$ $s^{-1}$ | $r$[b] |
|---|---|---|
| 2.42 | 0.0501 | 0.998 |
| 3.97 | 0.0409 | >0.999 |
| 7.01 | 0.0142 | 0.995 |

[a] Buffer systems used are listed in Table I. [W(TPPS)] = $2.4 \times 10^{-5}$–$5.5 \times 10^{-5}$ M. [b] Linear correlation coefficient for second-order plots.

W(TPPS) solutions in water or methanol were unstable with respect to demetalation if kept for several days in the presence of air. The cause of this demetalation was finally attributed to oxidation by molecular oxygen.

Buchler et al.[6] discussed the relationship between ionic radii of transition metals in certain oxidation states, including those of tungsten, and the "optimum" radius compatible with the porphyrin ligand. This optimum radius is assumed to be approximately 0.64 Å, while the ionic radii for the higher oxidation states of tungsten are 0.65, 0.62, and 0.58 Å for W(IV), W(V), and W(VI), respectively. From this information, it is surmised that either W(IV) or W(V) is a possible state for metalloporphyrins but that W(VI) is most likely too small to remain coordinated. It is probable, therefore, that simple oxidation of W(V) to W(VI) would bring about demetalation of the tungsten porphyrin. Our observed results bear out this assumption.

The W(VI) species formed are most likely the tungstates. Indeed, the state of tungsten which has the most appreciable aqueous solution chemistry is W(VI),[24] other than in special circumstances such as coordination to a water-soluble porphyrin. The particular tungstate formed depends highly on the prevailing acidity of the solution.[25] In basic aqueous solution, the predominant species is monomeric $WO_4^{2-}$, but at lower pHs, isopolytungstates form (e.g., species such as $H_3W_6O_{21}^{3-}$ at pH ~4).

W(TPPS) was chosen for the kinetics study because of the greater ease of handling aqueous solutions and for quantification of factors such as pH. W(TPP) solutions have been observed to exhibit the same behavior, however. W(TPP) became demetalated in acidic methanol, though this fact was not noticed originally until several months after the solution was prepared.

Kinetics for the aqueous W(TPPS) systems were very well-behaved at pH ≳2, except for a slight deviation from linearity in the integrated rate expression plots during the initial few minutes of some runs. The pseudo-second-order rate constants for this pH range, determined as described in the experimental section, are summarized in Table III.

The run at pH 3.97 was the most extensive and covered a total time span of 99 h, bringing about 63% demetalation. The second-order plot obtained from this run is shown in Figure 2.

The results obtained at pH <2 are anomalous, however. Second-order plots showed relatively poor linearity. It was found that consistent results were obtained when the assumption of −1 order was made. The −1 order plot for $[H^+]$ = 0.100 M ($HClO_4$) is shown in Figure 3. Another reaction performed at $[H^+]$ = 0.050 M with a different lot of $HClO_4$ showed the same behavior. Although such negative-order kinetics behavior is possible,[27] it strongly suggests that the mechanism involved is rather complex and different from that causing the pseudo-second-order kinetics at higher pH. Though inexplicable, such behavior is unprecedented in the literature of porphyrin reaction kinetics, so the observation is noted here.

Concerning the second-order results, it can be seen that there is relatively slight hydrogen ion dependence for these rates. From a plot of log $k_{\mathrm{obsd}}$ vs. −pH, it was found that, *empirically*, $k_{\mathrm{obsd}} \propto [H^+]^{0.12}$ with a linear correlation coefficient $r > 0.98$. Also, the data were *not* well described by a sum of rate expressions of zero and first order in $[H^+]$ (i.e., $k_{\mathrm{obsd}} \propto k_0 + k_1[H^+]$). This behavior is very similar to that observed by George[28] in the oxidation of ferrous ion by molecular oxygen in aqueous perchlorate medium. George explained this slight effect in terms of the ionization of one of the waters of hydration of the reacting ferrous ion.

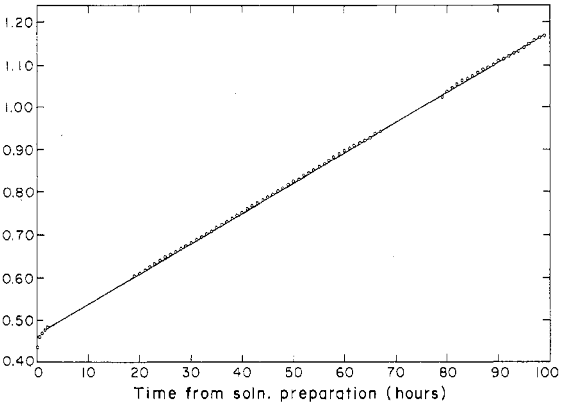

**Figure 2.** Integrated rate expression plot for pseudo-second-order W(TPPS) demetalation at pH 3.97. $A_\infty$(644 nm) = 2.55. All of the 386 data points, spanning 80.6 h, were used for analysis, yielding a linear correlation coefficient $r > 0.999$.

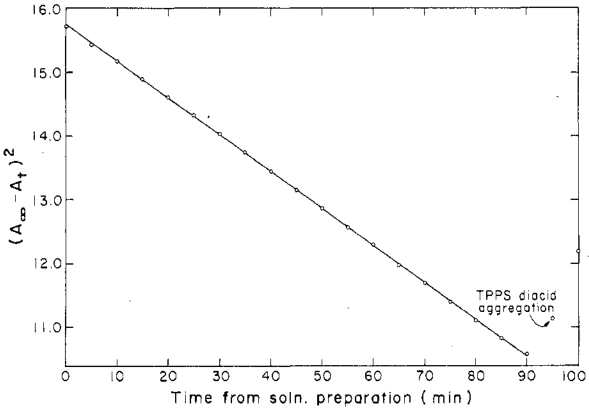

**Figure 3.** Integrated rate expression plot for −1 order W(TPPS) demetalation at pH 1.00. $A_\infty$(644 nm) = 4.46. Nineteen data points, spanning 90 min, yielded a linear correlation coefficient $r > 0.999$. The sudden decrease in absorbance at the 90-min point is caused by the start of the TPPS diacid aggregation.[14,26] The "pseudo-negative-one-order" rate constants calculated for $[H^+]$ = 0.100 and 0.050 M were approximately $32 \times 10^{-14}$ and $5.9 \times 10^{-14}$ $M^2$ $s^{-1}$, respectively.

The oxidation by molecular oxygen of ferrous porphyrins has, in fact, been studied in detail by Castro and co-workers[29] and by Caughey and co-workers[30,31] and has also been observed to be second-order in metalloporphyrin. On the basis of these results, we propose for this oxidative demetalation a mechanism similar to that given by Caughey for the ferrous porphyrins. The following scheme (eq 1–5)

$$\overset{\vee}{\underset{\wedge}{W}}{}^{V}O(H_2O)^{3+} + O_2 \underset{\text{equil}}{\overset{\text{fast}}{\rightleftharpoons}} \overset{\vee}{\underset{\wedge}{W}}{}^{V}O(O_2)^{3+} + H_2O \tag{1}$$

$$\overset{\vee}{\underset{\wedge}{W}}{}^{V}O(O_2)^{3+} + \overset{\vee}{\underset{\wedge}{W}}{}^{V}O(H_2O)^{3+} + H_2O \xrightarrow{\text{slow}} 2\overset{\vee}{\underset{\wedge}{W}}{}^{VI}O(OH)^{3+} + H_2O_2 \tag{2}$$

$$2\overset{\vee}{\underset{\wedge}{W}}{}^{VI}O(OH)^{3+} + 2H^+ \xrightarrow{\text{fast}} 2\overset{\vee}{\underset{\wedge}{W}}{}^{VI}O(H_2O)^{4+} \tag{3}$$

$$H_2O_2 + 2\overset{\vee}{\underset{\wedge}{W}}{}^{V}O(H_2O)^{3+} \rightarrow 2\overset{\vee}{\underset{\wedge}{W}}{}^{VI}O(H_2O)^{4+} + 2OH^- \tag{4}$$

$$2OH^- + 2H^+ \rightarrow 2H_2O \tag{5}$$

is for aqueous W(TPPS) at pH ~4. The porphyrin ligand is symbolized as

$$\overset{\vee}{\underset{\wedge}{\mathrm{W}}}$$

Its charges are omitted and only those of the coordinated tungstyl are included. This sequence is followed by the rapid demetalation of the $W^{VI}O(H_2O)(TPPS)^{2-}$ intermediate by the reaction

$$2[W^{VI}O(H_2O)(TPPS)]^{2-} + 3H_2O \rightarrow H^+ + 2H_4(TPPS)^{2-} + \tfrac{1}{2}H_3W_6O_{21}{}^{3-} \quad (6)$$

The overall oxidation and demetalation reaction is therefore

$$4[W^{V}O(H_2O)(TPPS)]^{3-} + 2H^+ + 4H_2O + O_2 \rightarrow 4H_4(TPPS)^{2-} + \tfrac{2}{3}H_3W_6O_{21}{}^{3-} \quad (7)$$

The second step in the mechanism above is the rate-determining step and explains the observed second-order kinetics.[32] The expected rate law would be

$$-\mathrm{d}[W^{V}O(H_2O)(TPPS)^{3-}]/\mathrm{d}t = k_2[W^{V}O(O_2)(TPPS)^{3-}] \times [W^{V}O(H_2O)(TPP)S^{3-}] = k_2K[W^{V}O(H_2O)(TPP)S^{3-}]^2[O_2]$$

where $K$ is the equilibrium constant of reaction 1. At pH 2.42, it was determined that $k_{obsd}$ $(=k_2K[O_2]) \approx 0.050\ M^{-1}\ s^{-1}$. Taking $[O_2] \approx 2.0 \times 10^{-4}$ M,[17,18] which was held constant, then $k_2K \approx 2.5 \times 10^2\ M^{-2}\ s^{-1}$.

## Conclusion

The mechanism for demetalation of $Ag^{II}(TPPS)$, involving disproportionation of the silver, has already been reported[33] and was believed to be the only instance of metal disproportionation in a porphyrin aggregate investigated. The mechanism for demetalation of the W(V) porphyrins proposed here, involving oxidation of the tungsten, is probably the only oxidative demetalation of a porphyrin investigated thus far.

The relatively slow oxidation step of this system also suggests other possible studies, since the oxygen-coordinated W(TPPS) complex seems to form faster than the succeeding oxidations occur. Thus, there may be another potential synthetic model for binding of molecular oxygen.

**Registry No.** $W^{V}O(OCH_3)(TPP)$, 70281-22-0; $(W^{V}OTPP)_2O$, 70281-23-1; $W^{V}O(H_2O)(TPPS)$, 70281-24-2; $[W^{V}O(TPPS)]_2O$, 70281-25-3; $W(CO)_6$, 14040-11-0.

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(20) This involves the reaction $2(H_2O{-}W(TPPS){=}O)^{3-} \rightleftharpoons (O{=}W(TPPS){-}O{-}W(TPPS){=}O)^{8-} + 2H^+ + H_2O$; $K_D = [(W(TPPS))_2O]\cdot[H^+]^2/[W(TPPS)]^2$. Cf. Hambright, P. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; Chapter 6.
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(32) The demetalation in aqueous solutions above the $pK_a$ for W(TPPS) can still occur through the monomeric W(TPPS) because of the fast acid-base equilibrium between the monomer and dimer.[20] In buffered solutions, a constant ratio $[W^{V}O(H_2O)(TPPS)^{3-}]^2/[(W^{V}O(TPPS))_2O^{8-}]$ is maintained. The fact that the rate at pH 7.01 is in line with those at the lower pHs is indicative of this.
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