butions will also furnish very useful information on both collision-induced dissociation and dissociative trapping. For instance, as pointed out in section III, comparison of the high with the low velocity peak yields the contribution of dissociative trapping and provides information on the magnitude of the potential well that leads to the trapping.

In conclusion, molecular dissociation in high-energy collision from surfaces is predicted here to result in some pronounced features in observable quantities: a rainbow peak in the fragment angular distribution; doubly peaked energy distribution; and the formation of rotational predissociation states in a fraction of nondissociated molecules. The existence of such well-defined features is useful for successful application of molecular beam scattering to the study of these processes.

Acknowledgment. We thank Dr. A. Amirav and Dr. E. Kolodney for helpful discussions. The Fritz Haber Center at the Hebrew University is supported by the Minerval Gesellschaft fur die Forschung, GmbH, Munich, FRG. This research was supported by a grant from the Foundation for Basic Research of the Israel Academy of Sciences.

Registry No. I₂, 7553-56-2; I, 14362-44-8.

Redox Reactions of Manganese Porphyrins in Aqueous Solutions. Steady-State and Pulse Radiolysis Spectrophotometric Studles¹

K. M. Morehouse[†] and P. Neta^{*}

Radiation Laboratory and Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556, and National Bureau of Standards, Washington, D.C. 20234 (Received: June 27, 1983)

The redox reactions of manganese porphyrins in aqueous solutions were studied by steady-state and pulse radiolysis. Mn^{III}P was reduced to Mn^{II}P or oxidized to Mn^{IV}P by chemical and radiolytic methods and the various species were characterized by spectrophotometry. The reduction of $Mn^{II}\dot{P}$ to $Mn^{II}\dot{P}$ was studied only by pulse radiolysis since the product is short-lived. Pulse radiolysis also permitted determination of the rate constants for the various redox reactions. Reduction of Mn^{III}P and Mn^{II}P by e_{aq}^{-} took place with $k \sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ while their reduction by the radicals from *i*-PrOH was generally 1 order of magnitude slower. Mn^{II}P was rapidly oxidized by Cl_2^- and Br_2^- by an inner-sphere mechanism involving initial addition of these radicals to the Mn. The $CH_2C(CH_3)_2OH$ radical from t-BuOH was also found to oxidize Mn^{IIP} to Mn^{IIP} via an intermediate adduct formation. Oxidation of Mn^{IIP} to Mn^{IVP} was rapid and quantitative at high pH, using Br_2^- or CH_2CHO radicals as the oxidants. The reaction was also monitored in neutral solutions using Br_2^- and in acidic solutions using $Cl_2^$ as the oxidants. In these cases the products are unstable but appear to be the Mn^{IVP} forms.

Introduction

Photosynthetic oxidation of water is believed to involve some manganese complex as a charge accumulator. Therefore, it has been proposed²⁻⁵ that a manganese complex may be used as the foundation for the photooxidation of water. The most promising model compounds are the manganese porphyrins and phthalocyanines,⁵ since they undergo facile redox reactions on the Mn. We have, therefore, decided to study the redox behavior of water-soluble manganese porphyrins in order to establish the kinetic and thermodynamic basis for their possible eventual application.

One-electron-transfer reactions of porphyrins (P) can be conveniently studied by pulse radiolysis (see, e.g., ref 6 and references therein). These compounds can be reduced by e_{aq} or various organic radicals, e.g., (CH₃)₂COH, and oxidized by Cl₂⁻, Br₂⁻, or CH₂CHO radicals. In the present paper we report spectrophotometric and kinetic studies on the reduction of Mn^{III}P to Mn^{II}P and further to Mn^{II}P⁻ and on the oxidation of Mn^{II}P to Mn^{III}P and of Mn^{III}P to Mn^{IV}P under various experimental conditions.

Experimental Section

[†]University of Notre Dame.

The metalloporphyrins were obtained from Midcentury Chemical Co. in the form of $Mn^{III}_{III}TPPS$ (tetrakis(4-sulfonatophenyl)porphyrin, Na⁺ salt), Mn^{III}TMPyP (tetrakis(N-methyl-4-pyridyl)porphyrin, Cl⁻ salt), and Mn^{III}TPyP (tetra-4pyridyl)porphyrin). They are all monomeric in dilute aqueous solutions,⁷⁻¹⁰ and their concentrations were determined spectrophotometrically on the basis of the reported extinction coeffi-

* University of Notre Dame and National Bureau of Standards. Address correspondence to this author at the National Bureau of Standards.

cients.9-11 The other chemicals used as buffers or scavengers were Baker Analyzed reagents, except for ethylene glycol, which was from Fisher. Water was purified by a Millipore Milli-Q system.

Solutions were prepared freshly before each experiment and were kept in the dark to minimize photolysis. They were deoxygenate by bubbling with pure N_2 or N_2O ; the latter serves as an electron scavenger ($N_2O + e_{aq} \rightarrow N_2 + OH + OH^-$). Spectra were monitored in a Cary 219 spectrophotometer interfaced with a PDP-11/55 computer for storage and manipulation of spectra.

Steady-state irradiations were carried out in a ⁶⁰Co source (Gammacell 220) with a dose rate of 2×10^{17} eV g⁻¹ min⁻¹. Pulse radiolysis experiments utilized the computer-controlled apparatus described previously.¹² Pulses of 8-MeV electrons from an ARCO-LP-7 linear accelerator were usually of 10-ns duration with doses (300-600 rd) that produce 2-4 μ M of radicals from water. An electronic shutter and the proper interference filters were used to minimize photolytic effects by the analyzing light. Dosimetry was performed by N₂O-saturated KSCN solutions

- (2) Loach, P. A.; Calvin, M. Biochemistry 1963, 2, 361.
- (3) Calvin, M. Science 1974, 184, 375.
- (4) Porter, G. Proc. R. Soc. London, Ser. A 1978, 362, 281.
- (5) Harriman, A. Coord. Chem. Rev. 1979, 28, 147.
- (6) Neta, P. J. Phys. Chem. 1981, 85, 3678.
- (7) Krishnamurthy, M.; Sutter, J. R.; Hambright, P. J. Chem. Soc., Chem. Commun. 1975, 13.

(8) Pasternack, R. F.; Huber, P. R.; Boyd, P.; Engasser, G.; Francesconi, L.; Gibbs, E.; Fasella, P.; Venturo, G. C.; Hinds, L. de C. J. Am. Chem. Soc. 1972. 94. 4511.

(9) Harriman, A.; Porter, G. J. Chem. Soc., Faraday Trans. 2 1979, 75, 1532.

⁽¹⁾ The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2481 from the Notre Dame Radiation Laboratory.

⁽¹⁰⁾ Kalyanasundaram, K.; Neumann-Spallart, M. J. Phys. Chem. 1982, 86, 5163.

 ⁽¹¹⁾ Hambright, P., private communication.
 (12) Patterson, L. K.; Lilie, J. Int. J. Radiat. Phys. Chem. 1974, 6, 129.



Figure 1. Absorption spectra of $Mn^{III}P$'s (—) and their reduction products, the $Mn^{II}P$'s (---). Solutions containing 3.9×10^{-5} M $Mn^{III}TPPS$ or 6.4×10^{-5} M $Mn^{III}TMPyP$ and 0.1 M *i*-PrOH at pH 6.8 were saturated with N₂O and irradiated in the γ -cell. Dose rate = 2.4×10^{17} eV g⁻¹ min⁻¹, optical path length = 2 mm. Dotted lines were spectra recorded after 30-s irradiation each for MnTPPS and after 60-s irradiation each for MnTMPyP. The Mn^{II}P's were reoxidized by air to yield the corresponding Mn^{III}P's nearly quantitatively.

assuming $G[(SCN)_2^-] = 6.0$ and $\epsilon = 7600 \text{ M}^{-1} \text{ cm}^{-1}$ at 480 nm.¹³

Results and Discussion

N

Radiolytic reduction was done with either e_{aq}^{-} (in the presence of *t*-BuOH as an OH scavenger)

$$H_2O \longrightarrow e_{ao}, OH, H$$
 (1)

$$Mn^{III}P + e_{n0}^{-} \rightarrow Mn^{II}P$$
 (2)

or the hydroxyisopropyl radical produced in N_2O -saturated *i*-**PrOH** solutions.

$$e_{aq}^{-} + N_2 O \rightarrow OH + OH^{-} + N_2$$
(3)

$$OH + (CH_3)_2 CHOH \rightarrow H_2 O + (CH_3)_2 COH$$
(4)

$$Mn^{III}P + (CH_3)_2\dot{C}OH \rightarrow Mn^{II}P + (CH_3)_2CO + H^+ (5)$$

In order to carry out one-electron reduction of the $Mn^{II}P$, solutions of $Mn^{III}P$ were bubbled with N_2O , the porphyrin was reduced stoichiometrically with $Na_2S_4O_4$,¹⁴ and then the solution was irradiated.

$$An^{II}P + (CH_3)_2\dot{C}OH \rightarrow Mn^{II}\dot{P} + (CH_3)_2CO + H^+ (6)$$

Radiolytic oxidation of the Mn^{IIP} and Mn^{IIIP} was attempted with Br_2^- , Cl_2^- , and CH_2CHO in N_2O -saturated solutions containing Br^- at pH 7-13, Cl^- at pH 4, or ethylene glycol at pH >11.6 Reaction with OH is not expected to give quantitative oxidation because this radical preferentially adds to the ligand.

because this radical preferentially adds to the ligand. Reduction of $Mn^{III}P$ to $Mn^{II}P$. Steady-state radiolysis of N₂O-saturated neutral and alkaline solutions of $Mn^{III}P$ containing *i*-PrOH leads to quantitative reduction to the $Mn^{II}P$. This is evident from a comparison of the spectra obtained in the radiolysis with those recorded with dithionite-reduced substrates. The spectral changes upon γ -radiolysis exhibit good isosbestic points (Figure 1), thus indicating clean reduction. The G values for



Figure 2. Differential absorption spectra observed upon pulse radiolysis reduction of $Mn^{III}P^{*}s$. Solutions containing (5-8) × 10⁻⁵ M porphyrins and 0.1 M *i*-PrOH were saturated with N₂O and then irradiated with pulses of electrons. The spectra were monitored after completion of the formation reaction (20-80 μ s after the pulse). (A) Mn^{III}TPPS, pH 6.8. (B) Mn^{III}TPPS, pH 11.9. (C) Mn^{III}TMPyP, pH 6.8. (D) Mn^{III}TPyP, pH 6.8. The solid lines were calculated from the spectra recorded in the γ -irradiation experiment as in Figure 1. One unit on the relative absorbance scale corresponds to $\epsilon = 1000 \text{ M}^{-1} \text{ s}^{-1}$ for species produced with a yield of G = 6.

reduction of Mn^{III}TPPS and Mn^{III}TMPyP at pH 7 and 13 are in the range of 6.8 ± 0.4 , i.e., equal to the total yield of radicals, indicating quantitative reduction.

Pulse radiolysis experiments gave differential spectra (Figure 2, experimental points) which are in good agreement with those calculated (Figure 2, solid lines) from the steady-state radiolysis or the chemical reduction experiments. Similar spectra were observed in the presence of t-BuOH, but with half the yield, owing to reduction by e_{aq}^{-} only. Results similar to those of Figure 2 were obtained under other conditions (concentrations, pH, scavengers). The example shown for MnTPyP (Figure 2D) exhibits a considerable difference between the results of the pulse radiolysis and the γ -radiolysis experiments. This difference results from the low solubility of the uncharged Mn^{II}TPyP in neutral solutions, which apparently dimerizes under these conditions and causes a spectral shift. The difference spectrum in the pulse radiolysis is taken at short times, before dimerization of the product could occur. In fact, the spectrum monitored 70–80 ms after the pulse is shifted and is in good agreement with the γ -radiolysis experiments. Furthermore, experiments at higher concentrations show clearly that the Mn^{II}TPyP product precipitates out of the solution. At pH 3, on the other hand, where the Mn^{II}TPyP is more soluble, no discrepancy in the spectrum and no precipitate were observed.

The kinetics of reduction were followed at various wavelengths, usually at the maxima and minima, and as a function of porphyrin concentration. The second-order rate constants derived are summarized in Table I. All forms of the manganese porphyrin studied are reduced with $(CH_3)_2\dot{C}O^-$ with $k \sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Reduction by $(CH_3)_2\dot{C}O^-$ is generally faster than that by its acid form $(CH_3)_2\dot{C}OH$ ($pK_a = 12.0$),¹⁵ which is in fact observed with the Mn^{III}TMPyP. However, with Mn^{III}TPPS this trend is not evident, probably because it is compensated by the electrostatic effect of the negatively charged reactants on the rate of reaction. The hydrated electrons reduce most porphyrins with diffusion-controlled rates ($k \sim 10^{10} \text{ M}^{-1} \text{ s}^{1}$, Table I).

Reduction of $Mn^{II}P$. The transient absorption spectra recorded upon radiolytic reduction of $Mn^{II}TPPS$ and $Mn^{II}TMPyP$ (Figure 3) exhibit broad absorptions around 770 nm which are characteristic of the ligand π -radical anions produced by reaction 6. These species decay by second-order reactions ($2k = 7.8 \times 10^7$ $M^{-1} s^{-1}$ for $Mn^{II}TPPS^-$ and $7.4 \times 10^8 M^{-1} s^{-1}$ for $Mn^{II}TMPyP^-$),

⁽¹³⁾ Schuler, R. H.; Patterson, L. K.; Janata, E. J. Phys. Chem. 1980, 84, 2088.

⁽¹⁴⁾ Duncan, I. A.; Harriman, A.; Porter, G. J. Chem. Soc., Faraday Trans. 2 1980, 76, 1415.

TABLE I:	Rate Constants for Reduction of Manganese
Porphyrins	by Radicals in Aqueous Solutions

porphyrin	radical	pН	k, M ⁻¹ s ⁻¹
$\frac{[(H_2O)_2Mn^{III}TPPS]^{3-}}{[(H_2O)_2Mn^{III}TPPS]^{3-}}$	e _{aq} (CH₃)₂ĆOH	6.8 3.1,	$\sim 1 \times 10^{10}$ 1.5 × 10 ⁹
[(H ₂ O)(OH)Mn ^{III} TPPS] ⁴⁻	(CH ₃), ĊOH	8.9	$1.7 imes 10^9$
[(OH) ₂ Mn ^{III} TPPS] ⁵⁻	(CH ₃) ₂ CO	11.9, 12.6	1.7×10^{9}
$[(H_2O)_2Mn^{III}TMPyP]^{5+}$	eag	6.8	$\sim 3 \times 10^{10}$
$[(H_2O)_2Mn^{III}TMPyP]^{s+}$	(CH ₃) ₂ ĊOH	3.1, 6.8	1.4 × 10°
$[(H, O)(OH)Mn^{III}TMPyP]^{4+}$	(CH ₃),ĊOH	8.9	1.6×10^{9}
$[(OH), Mn^{III}TMPyP]^{3+}$	$(CH_3), \dot{CO}^-(H^+)$	11.9	2.3×10^{9}
[(OH), Mn ^{III} TMPyP] ³⁺	(CH,),ĊO⁻	12.4	2.2×10^{9}
$[(H_2O)_2Mn^{III}TPyP]^+$	eag	6.8	$\sim 1 \times 10^{10}$
$[(H_2O)_2Mn^{III}TPyP]^+$	(CH ₃) ₂ COH	4.0,	1.6×10^{9}
•••		6.8	
$[(H_2O)Mn^{11}TPPS]^{4-}$	eaq	6.8	$\sim 1 \times 10^{10}$
$[(H_2O)Mn^{II}TPPS]^{4-}$	(CH ₃) ₂ ĊOH	6.8	1.8×10^{8}
$[(H_2O)Mn^{II}TPPS]^{4-}$	(CH ₃),ĊO ⁻	12.4	$8.4 imes 10^8$
$[(H_2O)Mn^{II}TMPyP]^{4+}$	e _{ag}	6.8	$\sim 3 \times 10^{10}$
$[(H_2O)Mn^{II}TMPyP]^{4+}$	(CH ₃) ₂ ĊOH	6.8	1.8×10^{9}
$[(H,O)Mn^{II}TMPyP]^{4+}$	(CH,),ĊO-	12.4	$2.2 imes 10^{9}$



Figure 3. Differential absorption spectra observed upon one-electron reduction of $Mn^{II}P$'s. The corresponding $Mn^{III}P$'s were first reduced with sodium dithionite and then irradiated with pulses of electrons. (A) 6 × 10⁻⁵ M $Mn^{II}TPPS$ in 0.1 M *i*-PrOH at pH 6.8, saturated with N₂O. Spectrum recorded 300-500 μ s after the pulse. (B) 1 × 10⁻⁴ M $Mn^{II}TMPyP$ in 0.1 M *i*-PrOH at pH 6.8, saturated with N₂O, 30-50 μ s after the pulse.

to give chlorins and phlorins, as discussed previously.¹⁶

Oxidation of $Mn^{II}P$. The reaction of $Mn^{II}P$ with OH radicals is not expected to yield the $Mn^{III}P$ quantiatively since OH radicals are known to add rapidly to unsaturated systems¹⁷ and are likely to add to various positions on the porphyrin ligand. We have, therefore, used one-electron oxidants which do not tend to add to double bonds, i.e., Cl_2^- , Br_2^- , and CH_2CHO . Although these radicals are known to react in many cases by a simple electron transfer, oxidation of certain metal complexes by Cl_2^- and $Br_2^$ has been shown¹⁸ to occur by an inner-sphere mechanism. Therefore, the reactions in the present case may follow the sequence 7–9. The experiments confirm this assumption. The

$$Br_2^- + Mn^{II}P \rightarrow [Br_2 - Mn^{III}P]$$
(7)

$$[Br_2 - Mn^{III}P] \rightarrow Br^- + Br - Mn^{III}P$$
(8)

$$Br-Mn^{III}P + H_2O \rightleftharpoons H_2O-Mn^{III}P + Br^{-}$$
(9)

 TABLE II:
 Rate Constants for Oxidation of Manganese

 Porphyrins by Radicals in Aqueous Solutions

porphyrin	radical	pН	k, M ⁻¹ s ⁻¹
[(H ₂ O)Mn ^{II} TPPS] ⁴⁻	Br ₂ ⁻ .	6.8	$1.8 \times 10^{9} a$
[(OH)Mn ¹¹ TPPS] ⁵⁻	Br_2^{-b}	12.9	$2.5 \times 10^{9} a$
$[(H_2O)Mn^{II}TMPyP]^{4-}$	Br ₂ ⁻	6.8	8.5 × 10 ⁹ a
[(OH)Mn ¹¹ TMPyP] ³⁺	Br ₂ - <i>b</i>	12.9	1.4×10^{10} a
$[(H_2O)Mn^{11}TMPyP]^{4+}$	Cl ₂ ⁻	4.0	1.5×10^{10}
$[(H,O)Mn^{II}TPPS]^{4-}$	ĊH ₂ C(CH ₂),OH	9.4,	$\sim 9.5 \times 10^{8}$
	2 0.2	12.6	
$[(H_2O)Mn^{II}TMPyP]^{4+}$	ĊH,C(CH,),OH	9.0	$\sim 1.8 \times 10^{9}$
$[(H,O), Mn^{III}TPPS]^{3-}$	Cl,	3.0	2.1×10^{9}
$[(H_2O)_2Mn^{III}TMPyP]^{s+}$	Cl,~	3.0	1.5×10^{9}
$[(H_2O), Mn^{III}TPyP]^+$	C1,-	3.0	1.0×10^{10}
$[(H_2O)_2Mn^{III}TPPS]^{3-}$	Br ₂	6.8,	6.7×10^{7}
		8.9	
[(OH) ₂ Mn ^{III} TPPS] ^{5~}	Br,	12.9	9.2×10^{8}
$[(H_2O)_2Mn^{111}TMPyP]^{5+}$	Br ₂	6.8	$6.8 imes 10^{8}$
$[(OH)_2 Mn^{III}TMPyP]^{3+}$	$Br_2 - b$	12.9	4.6×10^{9}
$[(H_2O)_2Mn^{III}TPyP]^+$	Br ₂	6.8	1×10^8
[(OH) ₂ Mn ^{III} TPPS] ⁵⁻	CH ₂ CHO	12.4	$6.2 imes10^8$
$[(OH)_2 Mn^{III}TMPyP]^{3+}$	ĊH₂CHO	12.4	2.2×10^8
[(OH), Mn ^{III} TPyP] ⁻	ĊH,CHO	11.9	$\sim 4 \times 10^{8}$
[(OH), Mn ^{III} TPPS] ⁵⁻	OH	12.4	8×10^9
[(OH), Mn ^{III} TPPS] ⁵⁻	0^	14	3.4×10^{8}
[(OH), Mn ^{III} TMPyP] ³⁺	OH	12.4	3.5×10^{9}
$[(H_2O)_2Mn^{III}TPyP]^+$	OH	6.8	6×10^{9}

^a k for initial addition step; see text for details. ^b At pH 12.9 $\sim 10\%$ of the radicals are in the form of BrOH⁻, based on the equilibria given in ref 20.



Figure 4. Differential absorption spectra observed upon one-electron oxidation of $Mn^{II}P$'s, by oxidizing radicals. (A) 6×10^{-5} M $Mn^{II}TPPS$, 0.1 M ethylene glycol, pH 12.4, saturated with N₂O, recorded 100–140 μ s after the pulse. (B) 5.5×10^{-5} M $Mn^{II}TPPS$, 0.01 M KBr, pH 12.9, saturated with N₂O, 200–300 μ s. (C) 6×10^{-5} M $Mn^{II}TPPS$, 0.01 M KBr, pH 6.8, saturated with N₂O, 60–80 μ s after the pulse. (D) 8×10^{-5} M $Mn^{II}TMPY$, 0.01 M KBr at pH 6.8, saturated with N₂O, recorded (Δ) 4–8 and (O) 50–80 μ s after the pulse. The corresponding $Mn^{II}P'$ s were reduced with sodium dithionite to the $Mn^{II}P$'s and then irradiated with pulses of electrons. The solid lines are from similar steady-state γ -radiolysis experiments as described in the text.

kinetics of the reaction of Br_2^- with $Mn^{II}TPPS$ and $Mn^{II}TMPyP$, measured by following the decay of Br_2^- absorption at 360 nm and the buildup of the Mn^{III} species at various other wavelengths, conform to second-order processes with $k_7 \sim 10^9 M^{-1} s^{-1}$ (Table II). The spectra observed after the completion of the first reactions (7 and 8) were clearly different from those of the final products. For $Mn^{II}TMPyP$ the spectral difference is clearly seen in Figure 4D, whereas for $Mn^{II}TPPS$ this difference, although real, is much smaller. Reaction 9 was observed on a time scale about 1 order of magnitude longer than that of the initial $Br_2^$ reaction, and the first-order rate constants were found to be $4 \times 10^3 s^{-1}$ for MnTPPS and $6 \times 10^4 s^{-1}$ for MnTMPyP, i.e., similar to those observed with vitamin B_{12r} .^{18a} The actual k_9 and k_{-9} were not calculated because the equilibrium constant K_9 is unknown, although the final products appear from the spectra to be pre-

⁽¹⁶⁾ Baral, S.; Neta, P.; Hambright, P. Radiat. Phys. Chem., in press.
(17) Farhataziz; Ross, A. B. Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.) 1977, No. 59.

⁽¹⁸⁾ See, e.g.: (a) Meyerstein, D.; Espenson, J. H.; Ryan, D. A.; Mulac,
W. A. *Inorg. Chem.* 1979, 18, 863. (b) Morliere, P.; Patterson, L. K. *Ibid.*1982, 21, 1837 and references therein.



Figure 5. Differential absorption spectra observed upon reaction of $CH_2(OH)(CH_3)_2$ with $Mn^{II}P$'s, showing the initial and final spectra. The solid line was obtained from a similar γ -irradiation experiment. (A) 6 $\times 10^{-5}$ M $Mn^{II}TPPS$, 0.1 M *t*-BuOH, pH 6.8, saturated with N₂O, spectra recorded (\diamond) 40-80 μ s and (O) 50-80 ms after the pulse. (B) 1×10^{-4} M $Mn^{II}TMPyP$, 0.1 M *t*-BuOH, pH 6.8, saturated with N₂O, spectra recorded (\Box) 10-15 μ s and (O) 15-30 ms after the pulse. (C) γ -irradiation of 8 $\times 10^{-5}$ M $Mn^{II}TMPyP$, 0.1 M *t*-BuOH pH 6.8, in 0.2-cm cell, N₂O saturated.

dominantly in the aquo form.¹⁹

Parallel experiments at pH 12.9 showed a similar behavior. At this pH the oxidizing radical is still mostly $Br_2^{-,20}$ However, the values of k_7 are slightly higher and the exchange reaction 9 is also somewhate faster, 9×10^3 s⁻¹ for MnTPPS and 1.5×10^5 s⁻¹ for MnTMPyP. The differences in rate constants are probably owing to the different protonation state of the MnP.

Oxidation by Cl_2^- can be studied in acidic solutions. Since $Mn^{II}TPPS$ demetallates in acid,²¹ we studied only the more stable $Mn^{II}TMPyP$. Oxidation of this porphyrin by Cl_2^- at pH 4 was found to take place with $k = 1.5 \times 10^{10} M^{-1} s^{-1}$ (Table II), slightly faster than in the case of Br_2^- .

Another oxidizing radical studied is $\dot{C}H_2CHO$, which is produced from ethylene glycol by.²²

$$OH + HOCH_2CH_2OH \rightarrow HOCHCH_2OH + H_2O$$
 (10)

$$HO\dot{C}HCH_2OH \xrightarrow{OH} \dot{C}H_2CHO + H_2O$$
 (11)

Oxidation of $Mn^{II}TPPS$ by CH_2CHO took place with only 60% efficiency. The remaining 40% appeared as reduction by HOCHCH₂OH, which took place in competition with reaction 11, as evident from the absorption at 750 nm (Figure 4A). With $Mn^{II}TMPyP$ the reduction was predominant and, therefore, the kinetics and mechanisms of the CH_2CHO reactions were not studied in detail.

Another radical which may react with Mn^{II}P by an inner-sphere mechanism is that formed by reaction of OH with *t*-BuOH, i.e., $\dot{C}H_2C(CH_3)_2OH$, as found in the case of $Co^{II}P^{.23}$ The spectra shown in Figure 5 indicate that $\dot{C}H_2C(CH_3)_2OH$ forms an adduct



Figure 6. Chemical oxidation of a solution containing 4.3×10^{-5} M Mn^{III}TPPS, 0.01 M KBr, pH 12.9, N₂O saturated with gradual addition of Br₂.



Figure 7. Transient differential absorption spectra observed upon oneelectron oxidation of $Mn^{III}TPPS$ by several oxidizing radicals. The solid lines in A and B were obtained from the difference between the spectra of the product and the starting material in Figure 6. (A) 6×10^{-5} M $Mn^{III}TPPS$, 0.1 M ethylene glycol, pH 12.4, saturated with N₂O, spectra recorded 100-200 μ s after the pulse. (B) 6×10^{-5} M $Mn^{III}TPPS$, 0.01 M KBr, pH 12.9, N₂O, 200-300 μ s after the pulse. (C) 8×10^{-5} M $Mn^{III}TPPS$, 0.01 M KBr, pH 6.8, N₂O, 500-800 μ s. (D) 7×10^{-5} M $Mn^{III}TPPS$, 0.01 M NaCl, pH 3.3, N₂O, 30-50 μ s.

with $Mn^{II}P$, but, unlike the case of the $Co^{II}P$, this adduct is unstable and forms $Mn^{III}P$ as the final product.

 $Mn^{II}P + \dot{C}H_2C(CH_3)_2OH \rightarrow HOC(CH_3)_2CH_2 - Mn^{III}P \quad (12)$

 $HOC(CH_3)_2CH_2-Mn^{III}P \rightarrow HOC(CH_3)_3 + Mn^{III}P$ (13)

The rate constants were $k_{12} \sim 10^9$ M⁻¹ s⁻¹ (Table II) and $k_{13} \sim 4 \times 10^2$ s⁻¹ for MnTPPS and $\sim 7 \times 10^3$ s⁻¹ for MnTMPyP. However, the overall yields of oxidation were relatively low, indicating the occurrence of side reactions which may affect the observed kinetics.

The reaction of OH with $Mn^{II}P$ was examined at pH 11–12. Both $Mn^{II}TPPS$ and $Mn^{II}TMPyP$ give a partial yield of the $Mn^{III}P$ form (~60% and 30%, respectively) but the kinetics were complex and the nature of the other products was unclear; probably OH attacks several sites.

Oxidation of $Mn^{III}P$. The question of whether $Mn^{III}P$ is oxidized to $Mn^{IV}P$ or $Mn^{III}P^+$ has been raised in the past. It appears from the results of Calvin and co-workers^{2,24} and from the results of Harriman and Porter⁹ that in most cases oxidation takes place on the metal rather than on the ligand. Several manganese(IV) porphyrins have been prepared by oxidation of the corresponding $Mn^{III}P$ with hypochlorite, H_2O_2 , or Br_2 at high pH, while in neutral and acidic solutions $Mn^{IV}P$ is generally unstable. In a similar fashion, we have oxidized $Mn^{III}TPPS$ and $Mn^{III}TMPyP$ with Br_2 and with H_2O_2 at high pH and recorded the spectra of the Mn^{IV} forms (Figure 6), which are found to be in agreement with those

⁽¹⁹⁾ The Br⁻ concentration in these experiments was only 0.01 M and we have added up to 1 M KBr with no observable spectroscopic changes. (20) (a) Since the equilibrium Br⁻ + BrOH⁻ \Rightarrow Br⁻ + OH⁻ has $K \sim 70$

^{(20) (}a) Since the equilibrium $B^{+} + B^{+}OH \Rightarrow Br_{2}^{-} + OH$ has $K \approx 70^{-}$ and $[Br^{-}] = 0.01$ M. Mamou, A.; Rabani, J.; Behar, D. J. Phys. Chem. 1977, 81, 1447. (b) Fessenden, R. W., private communication.

⁽²¹⁾ Morehouse, K. M.; Neta, P. J. Phys. Chem., in press

 ⁽²²⁾ Bansal, K. M.; Grätzel, M.; Henglein, A.; Janata, E. J. Phys. Chem.
 1973, 77, 16. Steenken, S. Ibid. 1979, 83, 595.
 (23) Baral, S.; Neta, P. J. Phys. Chem. 1983, 87, 1502.

⁽²⁴⁾ Loach, P. A.; Calvin, M. Biochim. Biophys. Acta 1964, 79, 379. Wohlgemuth, R.; Otvos, J. W.; Calvin, M. Proc. Natl. Acad. Sci. U.S.A. 1982, 79, 5111.

reported previously.⁹ We have also carried out radiolytic oxidation at high pH using Br_2^- or CH₂CHO as the oxidizing radical. The spectra obtained in these cases are in good agreement with those found in the chemical oxidation experiments. The differential spectra calculated from the above experiments were then used for examination of the pulse radiolysis results (Figure 7). It should be pointed out, however, that in the γ -radiolysis the oxidation could not be carried out quantitatively. Apparently, the product is partially reduced by the Br⁻ or the ethylene glycol present in excess.

Pulse radiolysis experiments at pH 12.9 in the presence of Brshow that Mn^{III}TPPS and Mn^{III}TMPyP are oxidized by Br₂⁻ with $k_{14} = 9.2 \times 10^8$ and 4.6×10^9 M⁻¹ s⁻¹, respectively, to give the manganese(IV) porphyrins (Figure 7 and Table II).

$$Mn^{III}P + Br_2^- \rightarrow 2Br^- + Mn^{IV}P$$
(14)

As the pH is decreased, the rate of reaction decreases to become ~ 10 times lower at pH 7–9 (Table II). The decrease in the rates results from the change of $(HO)_2Mn^{III}P$ into $(H_2O)_2Mn^{III}P$, occurring between pH 7 and 13 with both porphyrins. These acid-base equilibria also cause changes in redox potentials²⁵ which are in line with the observed decrease in reactivity.

The differential spectra recorded upon oxidation by Br_2^- at pH 7 are slightly different from those found at high pH; the shifts may be due to the acid-base equilibria of the Mn^{III}P species. It is suggested, therefore, that oxidation at pH 7 also yields Mn^{IV}P, which at this pH is unstable and could not be confirmed by γ -radiolysis or chemical oxidation experiments. Similarly, pulse radiolytic oxidation by Cl₂⁻ at pH 3.3 occurred very rapidly (Table II) and gave a differential spectrum (Figure 7) which suggests formation of Mn^{IV}P, but again the product is unstable.

Oxidation by $\dot{C}H_2CHO$ at $pH \sim 12$ was somewhat slower than oxidation by Br_2^- at this pH or by Cl_2^- at pH 3 but faster than that by Br_2^- at pH 7 (Table II). The differential spectra (Figure 7) are in very good agreement with those obtained from the chemical oxidation experiments and indicate a clean one-electron oxidation by $\dot{C}H_2CHO$, without any interference by a possible reduction with HOCHCH₂OH (as found in the other cases discussed above).

Since $Mn^{IV}P$ is stable at high pH, we have also made an attempt to oxidize $Mn^{III}P$ by O⁻ at pH 14. Unlike OH, which can add to many sites on the porphyrin, O⁻ (OH + OH⁻ \rightleftharpoons O⁻ + H₂O, $pK_a = 11.8)^{26}$ is known to have extremely slow addition reactions²⁷

(25) Harriman, A. J. Chem. Soc., Dalton Trans., submitted for publication. and may thus react by an electron-transfer oxidation.²⁸ The results indicate that even at pH 14 oxidation of $Mn^{III}P$ to $Mn^{IV}P$ by O⁻ takes place with only ~50% efficiency; the remaining radicals apparently react via other routes.

Summary and Conclusions

Oxidation and reduction of water-soluble manganese porphyrins by various free radicals have been studied. The species involved, $Mn^{IV}P$, $Mn^{II}P$, $Mn^{II}P$, and $Mn^{II}P^-$, were characterized through their absorption spectra. One-electron reductions by e_{aq}^- , $(CH_3)_2COH$, and $(CH_3)_2CO^-$ and oxidations by Cl_2^- , Br_2^- , and CH_2CHO were found in most cases to be clean and efficient reactions with rate constants in the range of 10^9-10^{10} M⁻¹ s⁻¹, nearly diffusion controlled. The reaction of $CH_2C(CH_3)_2OH$ radicals with $Mn^{II}P$ was also found to give partial yield of $Mn^{III}P$. However, the primary radicals of water radiolysis, H and OH, were found to react by processes which do not result in quantitative overall redox reactions and were not studied in detail.

Since these Mn porphyrins undergo such facile redox reactions, they may hold some promise as possible catalysts for oxidation of water. The formation of the Mn^{IV}P even at low pH, as evident from the spectra taken at short times in the pulse radiolysis experiments, is especially promising because Mn^{IV}P can, in principle, accept two electrons from water as has been proposed before^{2,24}

$$(H_2O)Mn^{IV}P \rightarrow OMn^{II}P + 2H^+$$
(15)

and lead to formation of oxygen. Further studies on the production of $Mn^{IV}P$ and its reactions at short times are underway.

Acknowledgment. We thank Drs. P. Hambright, A. Harriman, R. W. Fessenden, and R. H. Schuler for helpful discussions.

Registry No. $[(H_2O)_2Mn^{III}TPPS]^{3-}$, 70288-07-2; $[(H_2O)(OH)-Mn^{III}TPPS]^{4-}$, 89043-40-3; $[(OH)_2Mn^{III}TPPS]^{5-}$, 89043-41-4; $[(H_2O)_2Mn^{III}TMPyP]^{5+}$, 76608-24-7; $[(H_2O)(OH)Mn^{III}TMPyP]^{4+}$, 89043-42-5; $[(OH)_2Mn^{III}TMPyP]^{3+}$, 89043-43-6; $[(H_2O)_2Mn^{III}TPPP]^{+}$, 76608-25-8; $[(H_2O)Mn^{III}TPPS]^{5-}$, 89043-44-7; $[(OH)Mn^{III}TPPS]^{5-}$, 89065-33-8; $[(H_2O)Mn^{III}TPPS]^{4+}$, 89043-44-7; $[(OH)Mn^{III}TPPS]^{5-}$, 89043-46-9; $[(OH)_2Mn^{III}TPPP]^{+}$, 89043-45-8; $[(OH)Mn^{III}TPPS]^{5-}$, 89043-46-9; $[(OH)_2Mn^{III}TPPP]^{-}$, 89043-47-0; $Mn^{IIT}TPPS^{-}$, 89043-48-1; $Mn^{IIT}MPyP^{-}$, 89043-49-2; $Mn^{IIT}TPPS$, 72924-09-5; $(CH_3)_2COH$, 5131-95-3; $(CH_3)_2CO-$, 17836-38-3; Br_2^{-} , 12595-70-9; CI_2^{-} , 12595-89-0; $CH_2C(CH_3)_2OH$, 5723-74-0; CH_2CHO , 4400-01-5; OH, 3352-57-6; O⁻, 14337-01-0; $(CH_3)_2CHOH$, 67-63-0; *t*-BuOH, 75-65-0.

⁽²⁶⁾ Rabani, J.; Matheson, M. S. J. Phys. Chem. 1966, 70, 761. Weeks, J. L.; Rabani, J. Ibid. 1966, 70, 2100.

⁽²⁷⁾ Neta, P.; Hoffman, M. Z.; Simic, M. J. Phys. Chem. 1972, 76, 847. Neta, P.; Schuler, R. H. Ibid. 1975, 79, 1.

⁽²⁸⁾ Neta, P.; Schuler, R. H. J. Am. Chem. Soc. 1975, 97, 912.