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THE PHOTOCHEMICAL BEHAVIOR OF DI-μ-OXO-BINUCLEAR MANGANESE COMPLEXES IN ACIDIC SOLUTION[1)]

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Di-μ-oxo-dimanganese complex $[\mathrm{Mn_2}^{\mathrm{IV,III}}\mathrm{O_2(bpy)_4}](\mathrm{ClO_4})_3$, which is stable in the ground state, is reduced by irradiation of 313 nm light in acidic solutions. On the other hand, $[\mathrm{Mn_2}^{\mathrm{IV,IV}}\mathrm{O_2(phen)_4}](\mathrm{ClO_4})_4$ is reduced in the dark to the $\mathrm{Mn^{IV}}$-$\mathrm{Mn^{III}}$ complex and then further reduced upon irradiation. The photoreductions of the complexes are accompanied by the one-electron oxidation of water to generate hydroxyl radical.

Manganese is essential for the generation of oxygen from water in photosynthesis.[2)] However, the chemical role of manganese and even the chemical environment around this metal ion in the photosynthetic system remain uncertain. Various mono- and bi-nuclear manganese complexes have been proposed as a model for a reaction center of the oxygen generation processes.[3,4)] Calvin has pointed out that if a binuclear manganese complex containing two Mn(IV) ions is employed, then one molecule of oxygen could be generated from two molecules of water by their four-electron oxidation.[3a)] On these backgrounds, we have undertaken to study the chemical and photochemical behavior of tetrakis(2,2'-bipyridyl)-di-μ-oxo-dimanganese(IV,III) perchlorate[1] and tetrakis(1,10-phenanthroline)-di-μ-oxo-dimanganese(IV,IV) perchlorate[2], in a hope to gain a more information on the redox chemistry of manganese complexes. This communication reports the results of our investigations.

The cyclic voltammograms of [1] and [2] in acetonitrile are shown in Fig. 1. The redox reactions of these complexes deduced from the above results are outlined in Scheme 1. Recently, Morrison and Sawyer[5)] have independently studied the electrochemical redox reactions of the same complexes also by means of cyclic voltammetry and

$$[\mathrm{Mn_2}^{\mathrm{IV,IV}}\mathrm{O_2(bpy)_4}]^{4+} \underset{\substack{E_{1/2} = +0.96\mathrm{V} \\ \mathrm{vs.\ Ag/Ag^+}}}{\overset{e^-}{\rightleftharpoons}} [\mathrm{Mn}^{\mathrm{IV,III}}\mathrm{O_2(bpy)_4}]^{3+} \underset{E_{pc} = -0.02\mathrm{V}}{\overset{e^-}{\rightleftharpoons}} [\mathrm{Mn_2}^{\mathrm{III,III}}\mathrm{O_2(bpy)_4}]^{2+}$$

$$[\mathrm{Mn_2}^{\mathrm{IV,IV}}\mathrm{O_2(phen)_4}]^{4+} \underset{\substack{E_{1/2} = +0.97\mathrm{V} \\ \mathrm{vs.\ Ag/Ag^+}}}{\overset{e^-}{\rightleftharpoons}} [\mathrm{Mn_2}^{\mathrm{IV,III}}\mathrm{O_2(phen)_4}]^{3+} \underset{E_{1/2} = +0.09\mathrm{V}}{\overset{e^-}{\rightleftharpoons}} [\mathrm{Mn_2}^{\mathrm{III,III}}\mathrm{O_2(phen)_4}]^{2+}$$

bpy; bipyridyl, phen; phenanthroline

Scheme 1

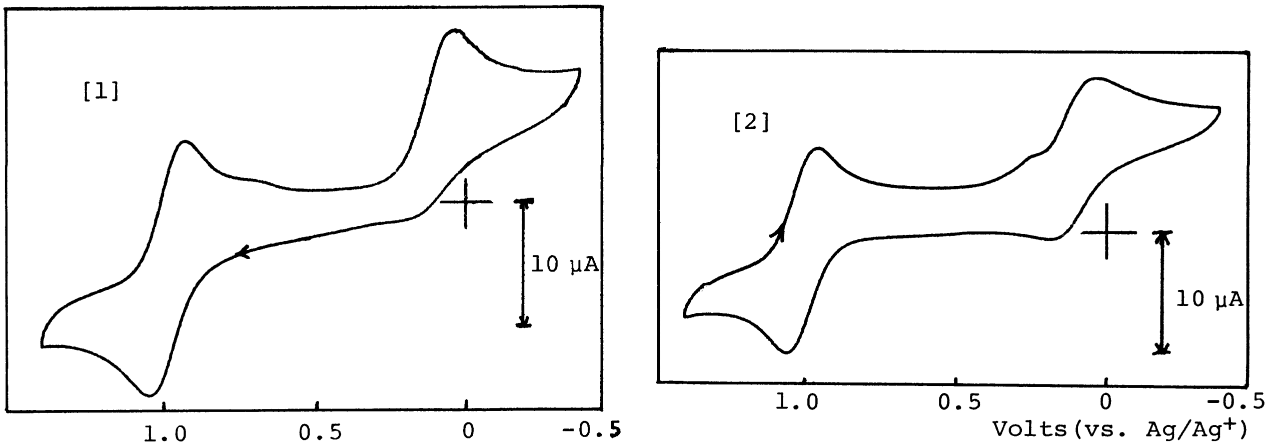


Fig. 1. Cyclic voltammograms of 1.0 x 10^{-3} M solutions of [1] and [2] in 0.1 M Et_4NClO_4-CH_3CN: Scan rate = 0.2 v/s.

obtained essentially the same conclusions as those represented in Scheme 1.

A striking feature of these redox reactions is that both of the complexes had the positive high potentials around at 0.96 V(vs. Ag/Ag^+), which corresponds to 1.3 V(vs. S.C.E.), for the reversible one-electron Mn^{IV}-Mn^{IV}/Mn^{IV}-Mn^{III} couples; the potentials are high enough to oxidize water. On the other hand, the potentials for the Mn^{IV}-Mn^{III}/Mn^{III}-Mn^{III} couples were relatively low and below the potentials for water decomposition.

In accordance with these results, an acidic solution of the reddish-brown Mn^{IV}-Mn^{IV} complex[2] was gradually reduced to the dark-green Mn^{IV}-Mn^{III} complex[3] upon standing in the dark. That this reduction actually occurred was also confirmed by the fact that the spectrum of [2] recorded after standing for several hours in 1.0 M H_2SO_4 in the dark was very similar to that of [1] under the similar conditions (Figs. 2 and 3). In addition, neutral or acidic solutions of the dark-green Mn^{IV}-Mn^{III} complex[1] were stable on standing even for a few days in the dark.[6]

Although [1] and [3] were stable in the dark, they were reduced to the Mn(II)

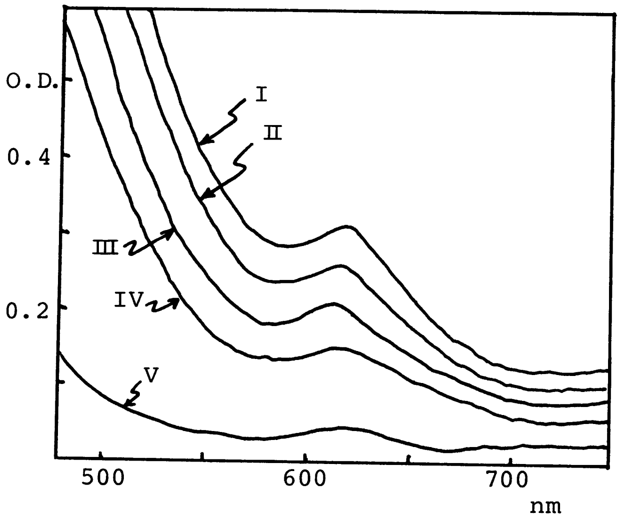


Fig. 2. Change in absorption spectrum of 2.0 x 10^{-3} M solutions of [1] in 1.0 M H_2SO_4: 313 nm irradiation for 0(I), 20(II), 40(III), 60(IV), 120 min(V).

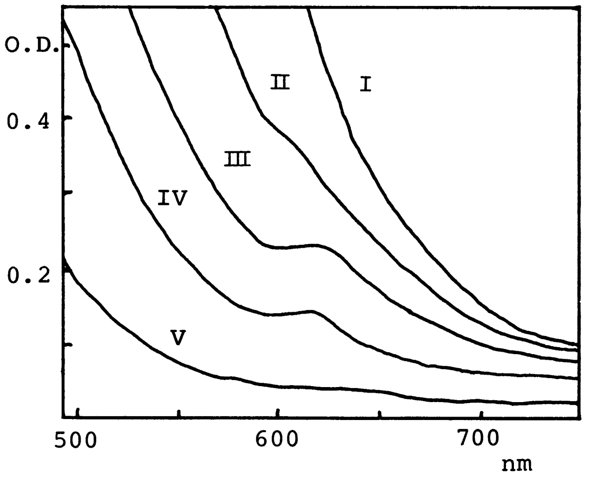


Fig. 3. Change in absorption spectrum of 2.0 x 10^{-3} M solutions of [2] in 1.0 M H_2SO_4: in the dark for 0(I), 180(II), 360 min(III), 313 nm irradiation for 0(III), 50 (IV), 100 min(V).

complexes via the Mn^{III}-Mn^{III} complexes upon irradiation through a Pyrex filter by a high-pressure mercury arc. However, no reactions occurred upon irradiation through a UV-35 filter($>$ 320 nm). This result suggests that the excitation at the metal-ligand charge-transfer bands of [1] and [3] is effective for the photoreduction of these complexes.7) The spectral changes during the photoreduction of [1] and [3] in 1.0 M H_2SO_4 are depicted in Figs. 2 and 3, respectively. The rates of disappearance of [1] in various concentrations of H_2SO_4 were measured from decrease in the absorbance at 620 nm. At the initial stage of the photoreduction where the photoreduction of Mn^{IV}-Mn^{III} to Mn^{III}-Mn^{III} has taken place, the reaction proceeded at the constant rates and the rates increased with increasing the acid concentrations(Fig. 4). A similar results was also obtained in aqueous H_3PO_4 solutions.

A simplified mechanism of the reactions are shown in Scheme 2. From this scheme, the rate equation (i) for the photoreduction of [1] and [3] to the Mn^{III}-Mn^{III} complex [6] can be derived. Straight lines were obtained when the values of $1/\phi'$ are plotted against those of $1/[H^+]$(Fig. 5), where ϕ' is the relative quantum yield of disappearance of [1] calculated from the slopes of straight lines of Fig. 4. These results suggest that an active species of the photoreduction is the excited protonated manganese complex[5]. From the ratios of intercepts to slopes obtained from Fig. 5, k_1/k_d values are calculated to be 1.25 and 0.72 in H_2SO_4 and H_3PO_4, respectively. This means that the rate constants for protonation to the excited complex are approximately equal to those for the decay in both acid solutions.

Hydrogen peroxide as a photoreduction product was detected by the polarographic analysis of the reaction mixture. Moreover, benzyl alcohol was obtained as a main product along with a small amount of benzaldehyde8) when the photoreactions of [1] and

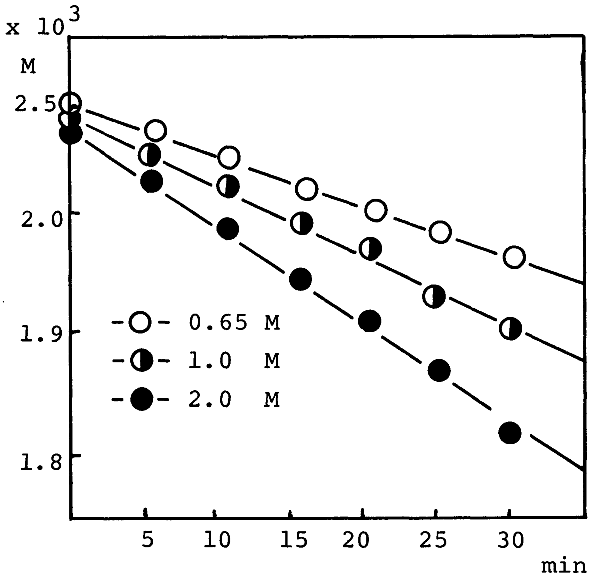


Fig. 4. Plots of concentrations of [1] in H_2SO_4 solutions vs. irradiation time. The concentrations were estimated using the data of Fig. 2 and the appropriate molar absorption coefficients.

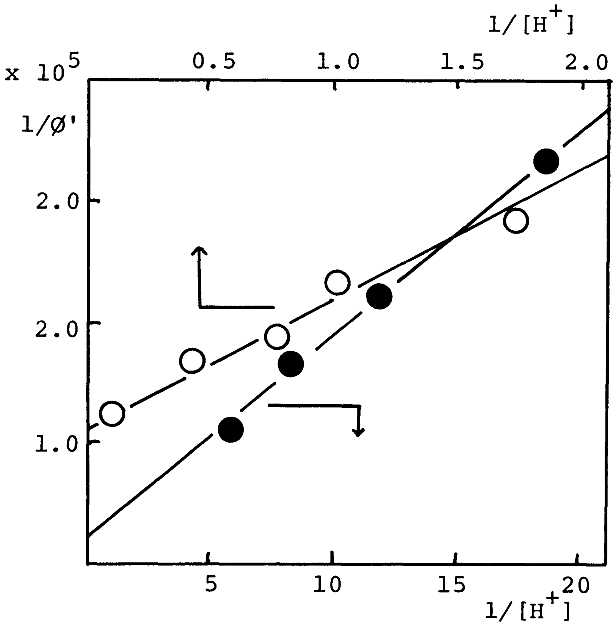
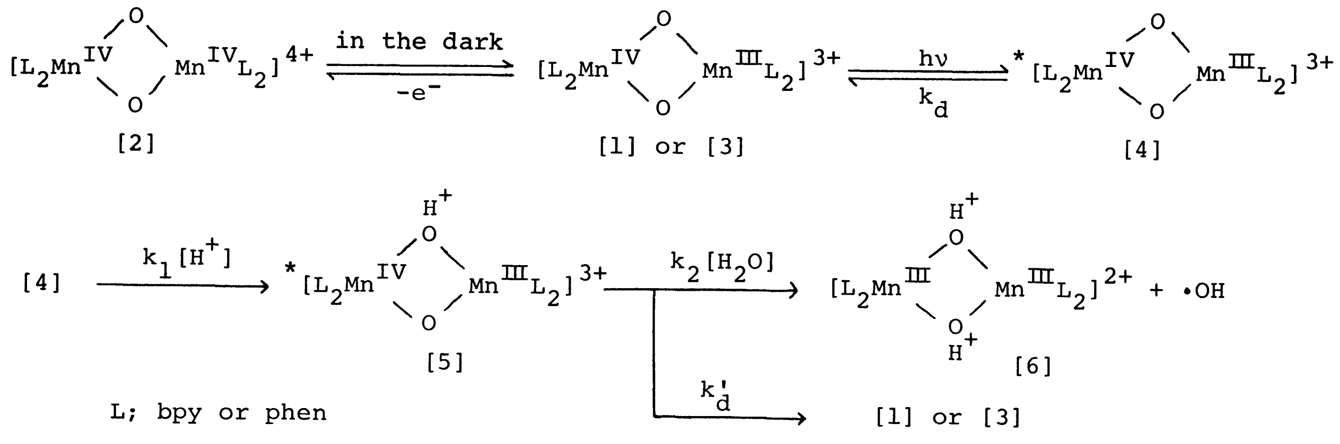


Fig. 5. Plots of $1/\phi'$ vs. $1/[H^+]$ in the photoreduction of [1] in H_2SO_4 (-○-) and H_3PO_4(-●-) solutions.



L; bpy or phen

Scheme 2

$$1/\text{Ø}' = a\left(1 + \frac{k'_d}{k_2[H_2O]}\right)\left(\frac{k_d}{k_1}\frac{1}{[H^+]} + 1\right) \qquad \ldots\ldots\ldots \quad (i)$$

[3] were conducted in acidic solutions in the presence of phenylacetic acid.[9) The formation of benzyl alcohol implies that hydroxyl radical is generated by the one-electron oxidation of water.[9)

In conclusion, the present results indicate that (1) the Mn^{IV}-Mn^{IV} complex is reduced to the Mn^{IV}-Mn^{III} state in the dark, (2) the Mn^{IV}-Mn^{III} complex is reduced to the Mn^{II} state via the Mn^{III}-Mn^{III} state only by the photoexcitation, (3) the photoreduction of the Mn^{IV}-Mn^{III} complex proceeds through the protonated excited complex which possesses a high redox potential, and (4) the reduction of the complexes is always accompanied by the one-electron oxidation of water to generate hydroxyl radical.

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