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PHOTO-INDUCED ELECTRON-TRANSFER REACTIONS OF DI-μ-OXO-BINUCLEAR MANGANESE COMPLEXES

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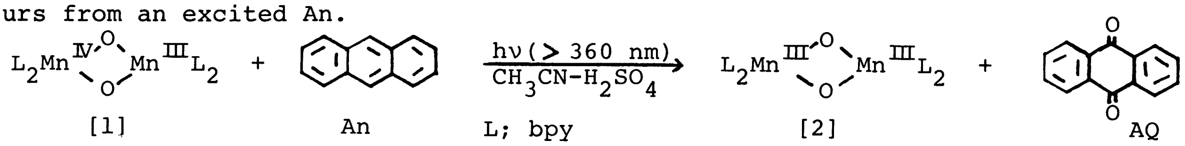
Photo-induced redox reactions of di-μ-oxo-binuclear manganese complex $[Mn_2^{IV,III}O_2(bpy)_4]^{3+}(ClO_4)_3$[1] were studied in the presence of organic compounds. Irradiation of a CH_3CN-1.0 M H_2SO_4(3:1) solution of [1] in the presence of anthracene gave anthraquinone with the reduction of [1]. On the other hand, similar irradiation of [1] in the presence of 9,10-dicyanoanthracene promoted the photochemical oxidation of water.

The chemical behavior of di-μ-oxo-binuclear manganese complexes has received much attention because of their ability to model phenomena in photosynthetic systems.$^{1-3)}$ We have previously demonstrated that di-μ-oxo-binuclear manganese complexes, $[Mn_2^{IV,III}O_2L_4]^{3+}$ (L:bpy or phen), are reduced to $[Mn_2^{III,III}O_2L_4]^{2+}$ with the oxidation of water to hydroxyl radical upon irradiation of their aqueous acidic solutions with 313 nm light.$^{4)}$ There is, however, little known about the electron-transfer ability of these complexes to organic compounds. We now report the results of photo-induced redox reactions of a binuclear manganese complex $[Mn_2^{IV,III}O_2(bpy)_4]^{3+}(ClO_4)_3$[1] in the presence of electron-donating and accepting aromatic compounds.

Irradiation of a CH_3CN-1.0 M H_2SO_4(3:1) solution containing [1](2.0 mM) and anthracene(An)(4.0 mM) with > 360 nm light gave anthraquinone(AQ) in 50-60% yield based on the used An accompanying the reduction of [1], and An was recovered in 30-40% yield. The spectral change of the reaction mixture during this photoreaction is shown in Fig. 1. Absorbance of the absorption maximum at 620 nm due to [1] decreased gradually with irradiation time, indicating that [1] is reduced to a lower valent manganese complex[2].$^{4)}$ Since irradiation with > 360 nm light excites mainly An, the photoreaction likely occurs from an excited An.



[1] An L; bpy [2] AQ

On the other hand, irradiation of an acidic solution of [1] in the presence of electron-accepting compounds such as 9,10-dicyanoanthracene(DCA) or 1,10-phenanthroline (phen) with > 360 nm light and even with 313 nm light caused no reduction of [1]. Indeed, no spectral change of [1] at 620 nm was observed upon these irradiations. However, irradiation of an acidic solution of [1] and DCA in the presence of phenylacetic acid with > 360 nm light produced benzyl alcohol and benzaldehyde in a total yield of 300-400% based on [1] used. Similar irradiation of DCA and phenylacetic acid in the absence of [1] gave no benzyl alcohol at all. The formation of benzyl alcohol in the former system implies that hydroxyl radical is generated by the one-electron oxidation of water.$^{4,6)}$

These results can be explained in terms of the electron-transfer mechanism illustrated in scheme 1. In the presence of electron-donating molecules(D) such as An, an electron-transfer from the excited D(D*) to [1] leads to the formation of the cation radicals of D($D^{+\cdot}$) and the reduced manganese complex[2]. The cation radicals($D^{+\cdot}$) thus formed are converted into AQ through anthrone by the reaction with water.5) On the other hand, in the presence of electron-accepting molecules(A) such as DCA and phen, an electron-transfer from [1] to the excited A(A*) leads to the formation of the anion radicals of A($A^{-\cdot}$) and a high-valent manganese complex$[Mn_2^{IV,IV}O_2(bpy)_4]^{4+}$[3]. It is known that the high valent complexes of this sort, $[Mn_2^{IV,IV}O_2L_4]^{4+}$, in aqueous acidic solutions oxidize water in their ground state to give hydroxyl radical and lower valent complexes$[Mn_2^{IV,III}O_2L_4]^{3+}$, and the reaction of phenylacetic acid with hydroxyl radical in acidic solutions gives benzyl alcohol.4) Thus, our mechanism that the photo-induced electron-transfer occurs from [1] to A* is consistent with all of the experimental observations.

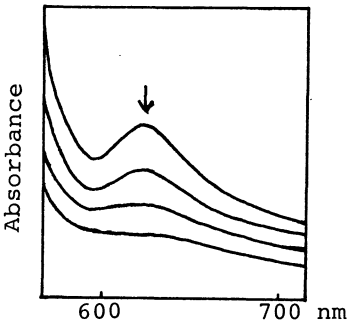
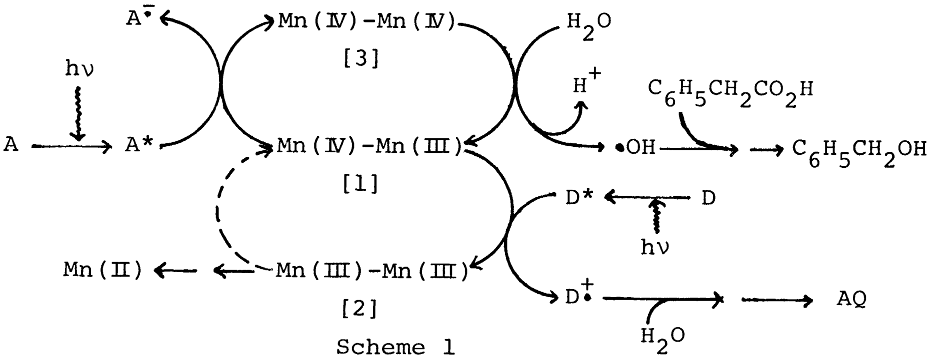


Fig. 1. Change in absorption spectrum of [1] in a CH_3CN-1.0 M H_2SO_4(3:1) solution in the presence of An upon irradiation with >360 nm light.

It must be noted here that if the photo-induced oxidation of water takes place by the above mechanism, the manganese complex[1] would serve as a catalyst for the photochemical decomposition of water. Indeed, the preliminary study indicated that several cycles of the sequential electron-transfer reactions take place as shown in scheme 1. However, longer irradiation brought about complex reactions induced by hydroxyl radical and resulted in the decomposition of [1].



Scheme 1

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References and Footnote

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