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MANGANESE DIOXIDE AS SPECIFIC REDOX CATALYST IN THE PHOTOSENSITIZED OXYGEN GENERATION FROM WATER

Yohmei OKUNO,* Osamu YONEMITSU, and Yukihiro CHIBA
Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060

Catalytic formation of oxygen from water was observed in the photosensitized reaction by trisbipyridineruthenium(II) using manganese dioxide as a redox catalyst and pentaammine chlorocobalt(III) as an electron acceptor in acidic solution. The β- and "activated" materials are found to be the most efficient and specific redox catalysts, and a 230% of O_2 yield based on MnO_2 is obtained.

The interest in constructing photochemical devices that are competent to capture and store light energy originates in the yet unresolved primary photoconversion processes of photosynthesis.1) Water decomposition into its elements initiated by visible light absorption is one of the most attractive means of solar energy storage.

We have recently developed2) a system for hydrogen evolution from water by visible light irradiation of aqueous solution containing $[Ru(bpy)]Cl_2$ and $(Et_4N)_2[Fe_4S_4(SBzl)_4]$, a synthetic analogue3) of ferredoxin which is known to play a very important role at the terminal end of photosystem I in green plant photosynthesis.1)

To realize a complete water photolysis system, the development of tetraelectronic water oxidation reaction using specific and efficient redox catalyst that can facilitate oxygen formation is a key step. Though oxygen generation remains obscure part in the mechanism of plant photosynthesis, molecular oxygen evolves as a result of water photooxidation in the active center of photosystem II with participation of manganese ions.1,4-7) Earlier investigators have employed mainly $RuO_2 \cdot nH_2O$8) and zeolite supported $RuO_2/IrO_2$9) as mediators for O_2 evolution. However, these catalysts are non-specific and highly active for H_2 generation as well.10,11) We now report on the utilization of manganese dioxide as specific and efficient redox catalyst for O_2 formation.12)

The materials A-G tested here are prepared by literature methods [A:(β-form),13) B:(γ-II),14) C:(activated)15)], or purchased ones [D:(Alfa, lot# 032476), E:(Kanto, lot# 709B3034), F:(Wako, lot# LTG4746), G:(Nakarai, lot# V2K4246)] which are used as recieved. Catalyst D is an activated form.

Continuous oxygen evolution was observed when a mixture of $Ru(bpy)_3Cl_2$ (540 μM), $[Co(NH_3)_5Cl]Cl_2$ (22 mM) and MnO_2 in 20 ml of 0.5M acetate buffer was illuminated with halogen lamp equipped with Toshiba cut-off filter L-39 (light intensity; 8.5 x 10^2 $J \cdot m^{-2} \cdot s^{-1}$ measured by 65A Radiometer from Yellow Springs Instrument, $\lambda > 390$nm) And the evolved gas was analyzed by glc as described previously.2)

M= $mol \cdot l^{-1}$.

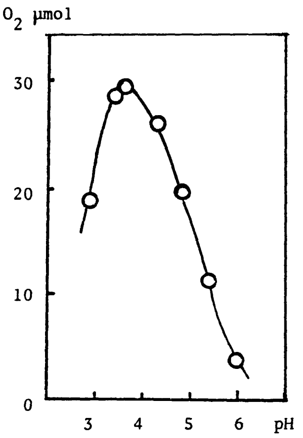

Fig. 1. Effect of pH on the oxygen yield by 1 H irradiation; 20ml of 0.5M acetate buffer, $[Ru(bpy)_3]Cl_2$ (540uM), $[Co(NH_3)_5Cl]Cl_2$ (22mM), Catalyst D(5.7mM), (see text).

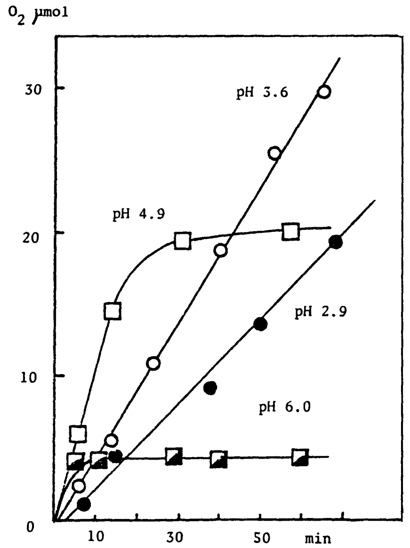

Fig.2. Time dependence of oxygen production at different pH's using catalyst D(5.7 mM).

Effect of pH

The optimum pH of 3.6 was revealed by a pH profile of the amount of oxygen produced (V_{O_2}) after illumination for 1 h using catalyst D (5.7 mM), which is shown in Fig. 1. This result was somewhat surprising, since the optimum for O_2 generation at pH 8.5 by chemically prepared $[Ru(bpy)_3]^{3+}$ and RuO_2/IrO_2/zeolite in the non-photochemical process is already described.16) Actually, above pH 4, oxygen evolves more rapidly (fastest at pH 5.4), but the amount produced reached a plateau very soon. And the yield at the plateau depends largely upon the pH (Fig. 2). This may involve the influence of decreased efficiency of the catalyst, pH effect on the other reactions occuring in the system9) and back electron transfer reaction between $[Ru(bpy)_3]^{3+}$ and $[Co(NH_3)_5Cl]^{+}$.16) On the other hand, below pH 4, a plot of V_{O_2} vs. time gave a straight line (Fig. 2). At pH 3.6, the amount of O_2 produced reached at its best under the conditions. The decreased O_2 yield in the lower pH may be due to higher oxidation potential of water.

Effect of manganese ions

Figure 3 shows the results of a study of oxygen production as a function of amount of added catalyst D by 2 h irradiation at the optimum pH. The amount of O_2 produced is roughly proportional to the amount of the catalyst added, giving the highest O_2 yield (1.19 ml, 53 μmol) with 8.6 mM of MnO_2, and then decreases gradually above that concentration. Little amount of O_2 (4.4 μmol) is formed in the absence of MnO_2 after 2 h illumination with an induction time of approximately 40 min. at pH 3.6.17)

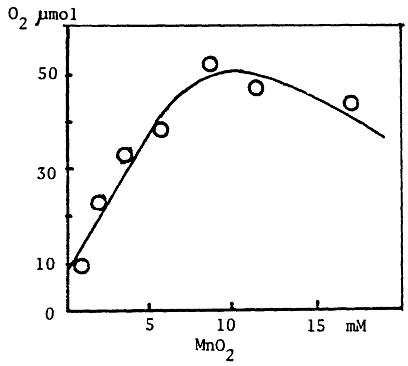

Fig.3. Oxygen formation as a function of the amount of added catalyst D after 2 h irradiation at pH 3.6.

The numbers of cycle with respect to $Ru(bpy)_3Cl_2$ and $[Co(NH_3)_5Cl]Cl_2$ arrived at saturation over around 8.6 mM of MnO_2, and are 20 and 0.48, respectively, in the conditions used. A yield of 230% in regard to MnO_2 is observed at the concentration of 2 mM. Very little amount of oxygen was produced when illuminated with divalent manganese ions (5 μmol each with the acetate and sulfate), which is close to the result in the absence of the catalyst (cf. ref. 17). No oxygen is detected using $Mn(acac)_3$ or $Mn(acac)_3$ plus catalyst D, or without $[Co(NH_3)_5Cl]Cl_2$.

Effect of the nature of manganese dioxide

The oxygen yield appears to depend notably on the nature of the manganese dioxide used. A series of the materials from different sources as specified before have been examined.

The results are summarized in Fig. 4, where the amount of oxygen produced after 2 h irradiation is schematically illustrated using 8.6 mM of different sources of the catalyst.18)

A marked effect of the nature of MnO_2 has been found. When the activated and β-manganese dioxide catalysts are used, oxygen generation is very efficient at pH 3.6; 1189μl, 569μl and 807μl with catalysts D,C and A, respectively, for 2h.

The catalysts employed here are all fine powders, and the exact effect revealed above is not well understood at present.

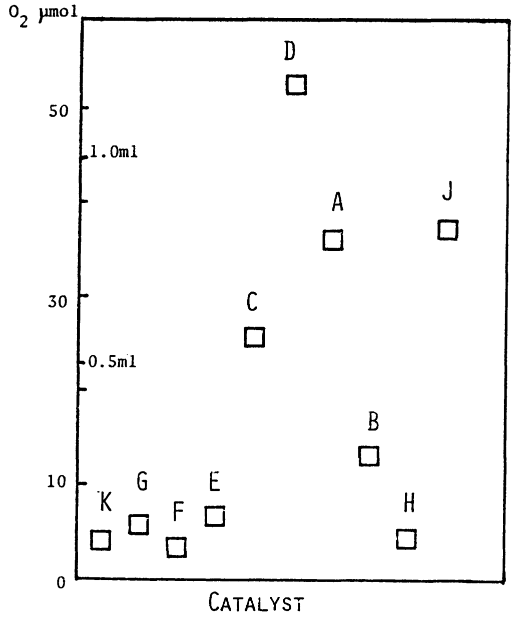

Fig.4. Schematic representation of efficiency of the different sources of MnO_2(8.6mM unless otherwise stated); A(β), B(γ), C(activated, D(Alfa, activated), E(Kanto), F(Wako), G(Nakarai), H(50mg of MnO_2/zeolite), J(15mg of RuO_2/IrO_2/zeolite), K(without catalyst, cf. ref.17), see text for further details.

It should be noted that manganese dioxide is specific redox catalyst for oxygen evolution. Zeolite supported RuO_2/IrO_2 (10 mg)9) catalyzes also hydrogen production efficiently, and a large quantity (2.1 ml during 1 h) of H_2 is formed by a model system containing $Ru(bpy)_3Cl_2$, methyl viologen and EDTA as an electron donor.10) However, in contrast with RuO_2/IrO_2/zeolite, only a trace of amount of hydrogen (0.07 ml) is produced in the presence of catalyst D (3.3 mM) under the same conditions.

The results described here may lead complete water dissociation, generating hydrogen and oxygen at separate parts. Experiments to these goals as well as towards artificial photosynthesis by connecting water reduction system using Fe-S complexes developed earlier by us2) are being pursued.

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12) During our study, oxygen evolution with a system containing $Ru(bpy)_3Cl_2$, Mn(IV) pyrophosphate and MnO_2 at pH 7 has been reported, which gave 7.5×10^{-7} mol of O_2 (17μl) at its best by 2 h irradiation (cf. 1189 μl in our case): V.Ya.Shafirovich, N.K.Khannanov, and A.E.Shilov, J.Inorg.Biochem., 15,113 (1981).
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18) For the comparison, zeolite supported MnO_2 (catalyst H) and RuO_2/IrO_2 (catalyst J) which were prepared by a reported method[9] are included.

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