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OXYGEN EVOLUTION BY WATER OXIDATION WITH TRIS(2,2'-BIPYRIDYL)RUTHENIUM(III) COMPLEX

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Oxygen evolution by water oxidation with tris(2,2'-bipyridyl)-ruthenium(III) complex was studied by mass spectrum, gas chromatography, visible spectrum, and volumetric method. It was confirmed that water is oxidized to give dioxygen. A model for water oxidation through $Ru(bpy)_3^{2+}$ was studied.

Tris(2,2'-bipyridyl)ruthenium(II) complex ($Ru(bpy)_3^{2+}$) is attracting much attention as a sensitizer to decompose water by solar irradiation to produce hydrogen and oxygen.[1-8] Intensive studies have been made on photochemical hydrogen evolution with this complex in the presence of methylviologen and sacrificial reducing agent such as EDTA and triethanolamine, but very few studies on the O_2 evolution with trivalent Ru complex.[9-11] In the present paper, the O_2 evolution by water oxidation with $Ru(bpy)_3^{3+}$ as well as a model for oxidation site of water photolysis are described. Although O_2 evolution by $Ru(bpy)_3^{3+}$ with PtO_2 catalyst was reported,[10] the details such as the origin of the O_2 and its yield were not studied. It was reported that O_2 was evolved with $Ru(bpy)_3^{3+}$ at pH 8 without catalyst,[9] but the present study described later showed no O_2 evolution at this pH. The O_2 evolution by water oxidation with $Ru(bpy)_3^{3+}$ thus remains ambiguous. It is important to study it in detail for designing water photolysis system, because water oxidation to give O_2 is an essential reaction to use water as reducing agent for H_2 evolution.

$Ru(bpy)_3^{3+}(ClO_4^-)_3$ was prepared by oxidation of $Ru(bpy)_3^{2+}(ClO_4^-)_2$ with suspended PbO_2 in 60 % $HClO_4$ aqueous solution and recrystallized in 3 M $HClO_4$ to give green crystal (77 % yield). It was identified with visible spectrum (Fig. 1), elemental analyses, ESR spectrum (6 hyperfine structures at g = 2.0414), and magnetic measurement (number of spin was equal to 1 per molecule, measured by magnetometer, Model 155 of Princeton Applied Research Corp.). The aqueous solution of $Ru(bpy)_3^{3+}(Cl^-)_3$ was prepared by chlorine oxidation of $Ru(bpy)_3^{2+}(Cl^-)_2$ in water.

Fig. 2 shows the gas chromatogram of the gas evolved by reaction of 10 mM $Ru(bpy)_3^{3+}(ClO_4^-)_3$ in water at pH 3 containing 100 mg RuO_2 powder as catalyst under argon at room temperature. The gas was identified to be O_2 from the retention time. The O_2 evolved was calculated by subtracting the O_2 content coming from the air that was contained in the reaction vessel, from the total O_2. The amount of O_2 measured by gas chromatography almost agreed with that measured volumetrically by Warburg apparatus. Fig. 3 shows the mass spectrum of the gas evolved by reaction in water containing 1.67 % $H_2{}^{18}O$ under the same condition as above. Oxygen was confirmed by the peaks at m/e = 32, 34, and 36, which correspond to ${}^{16}O_2^+$, ${}^{18}O{}^{16}O^+$, and ${}^{18}O_2^+$, respectively. The ratio of ${}^{18}O{}^{16}O^+$ to ${}^{16}O_2^+$ was found to be 3.2 %, which is in good agreement with the calculated value of 3.3 %. It is therefore concluded that O_2 was evolved by oxidation of water. The visible spectrum of the solution changed

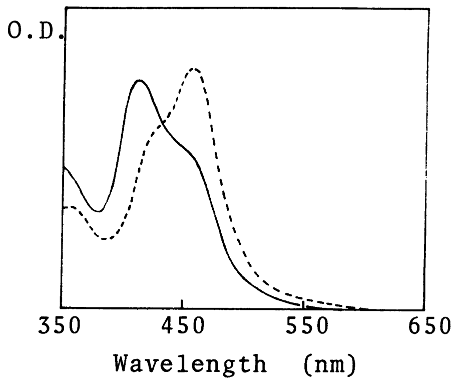


Fig. 1 Visible spectra of $Ru(bpy)_3^{3+}$-$(ClO_4^-)_3$ (——) and $Ru(bpy)_3^{2+}(ClO_4^-)_2$ (---) in H_2O.

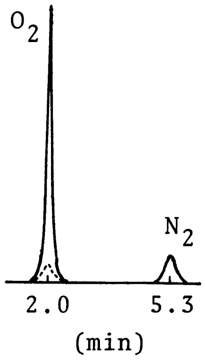


Fig. 2 Gas chromatogram of the gas evolved by reaction of $Ru(bpy)_3^{3+}$-$(ClO_4^-)_3$ in water in the presence of RuO_2. Carrier; argon, 20 ml/min, Column; Molecular Sieve 5A (1.5 m), at room temperature. ---; O_2 peak corresponding to the air contained.

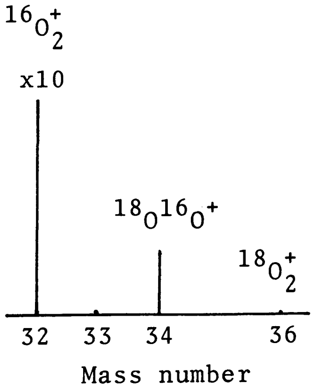


Fig. 3 Mass spectrum of O_2 evolved by oxidation of water containing 1.67 % $H_2{}^{18}O$ with $Ru(bpy)_3^{3+}(ClO_4^-)_3$ and RuO_2.

from that of trivalent complex (λ_{max} = 422 nm) to the divalent one (λ_{max} = 456 nm) after the reaction.

The pH dependence of the O_2 evolution was shown in Table 1. The optimum pH condition is around 3, giving the O_2 yield of 90 %. In pH 1 the trivalent complex suffered no change and O_2 was not detected. In neutral and alkaline media the trivalent complex was reduced rapidly to give the divalent one, however, no O_2 was evolved. This result indicates that spectrum change does not always accompany O_2 evolution. Some other oxidation besides O_2 evolution would occur in the neutral and alkaline conditions. The effect of catalyst on the O_2 evolution was shown in Table 2. Although O_2 was evolved without catalyst, its yield was very low. PtO_2 worked as catalyst, but the O_2 yield was not high. RuO_2 was an efficient catalyst to give O_2 yield of 90 %.

In a water photolysis system containing $Ru(bpy)_3^{2+}$ as sensitizer, the divalent Ru complex has to at first be oxidized to trivalent one, which oxidizes water to O_2. Turnover of the Ru complex is important for this catalytic reaction. In order to construct one model of oxidation site in water photolysis, a reaction system was studied composed of excess oxidizing agent, $Ru(bpy)_3^{2+}$, and RuO_2. Among the oxidizing agents of MnO_2, $K_2Cr_2O_7$, PbO_2, $Ce(SO_4)_2$, and $K_2S_2O_8$ studied, PbO_2 gave the best result for O_2 evolution. An aqueous solution containing 10 mM PbO_2 as suspension, 20 μM $Ru(bpy)_3^{2+}$, 50 mg of RuO_2 powder, and 1.67 % $H_2{}^{18}O$ was treated

Table 1. Effect of pH on O_2 evolution by water oxidation with 10 mM $Ru(bpy)_3^{3+}$-$(ClO_4^-)_3$ in the presence of 100 mg RuO_2 under argon. Solution:10 ml, Reaction; 2 h., 25°C.

pH	O_2 evolved (μl)	(Yield %)
1	0	0
3	552	90.3
4	445*	72.8
7	~0	~0
8	0	0

*) $Ru(bpy)_3^{3+}(Cl^-)_3$ used

Table 2. Effect of catalyst on O_2 evolution by water oxidation with 10 mM $Ru(bpy)_3^{3+}(ClO_4^-)_3$ at pH 3 under argon at 25°C. Solution;10 ml, Reaction;2 h.

Catalyst	O_2 evolved (μl)	(Yield %)
None	~10	~1.6
PtO_2	62	10.1
RuO_2	552	90.3

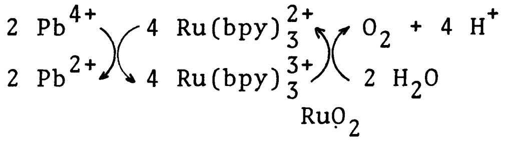
under argon at 20°C for 1 h. The mass spectrum (3.2 % $^{18}O^{16}O^+$ with respect to $^{16}O_2^+$) and gas chromatogram of the gas evolved showed that O_2 was evolved by oxidation of water. Since O_2 was formed also by the two component system of PbO_2/RuO_2, the O_2 evolved through $Ru(bpy)_3^{2+}$ was calculated by subtracting the amount of O_2 through PbO_2/RuO_2 from the total O_2 evolved. The results were shown in Table 3. About 40 to 60 % of the O_2 was formed through $Ru(bpy)_3^{2+}$, and the turnover number of the Ru complex was around 2 to 9 under this reaction condition.

Table 3. O_2 evolution by $PbO_2/Ru(bpy)_3^{2+}/RuO_2$ system under argon at 20°C. PbO_2;10 mM(suspended), $Ru(bpy)_3^{2+}$; 20 μM, RuO_2; 50 mg, Reaction;1 h.

		pH 2*	pH 3**
O_2(μl) evolved by	$PbO_2/Ru(bpy)_3^{2+}/RuO_2$	17.1	6.7
	PbO_2/RuO_2	6.5	3.9
O_2 evolved through $Ru(bpy)_3^{2+}$	(μl)	10.6	2.8
	(%)	62	42
Turnover number of $Ru(bpy)_3^{2+}$		8.8	2.3

*) HCl-KCl buffer, **) $HCl-CH_3COONa$ buffer

The O_2 evolution through the Ru complex can be represented by scheme 1. The visible spectrum of the mixture showed the oxidation of the Ru complex to a trivalent one on addition of PbO_2.



Scheme 1

In conclusion, these results described above warrant the use of $Ru(bpy)_3^{2+}$ as catalyst for oxidation site to evolve O_2 in a water photolysis system.

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