Hexaammineruthenium Complex as Two-Electron Catalyst for Oxygen Evolution by Homogeneous and Heterogeneous Water Oxidation

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(Received October 16, 1990)

Synopsis. The $[Ru(NH_3)_6]^{3+}$ complex is shown to be a two-electron catalyst for homogeneous as well as heterogeneous water oxidation to evolve dioxygen. The oxygen evolution is proposed to proceed by two molecules of the complex through a peroxo-bridged intermediate involving higher oxidation state $[Ru^V(NH_3)_6]^{5+}$.

The mechanism of oxygen evolution in plant photosynthesis still remains unsolved. According to the present knowledge, dioxygen evolves as a result of water photooxidation in the active center of photosystem II (PS II) with the participation of Mn ions which are weakly bound to the protein part of PS II.[1,2] Since oxygen evolution by water oxidation is a four-electron process (Eq. 1) only few artificial catalysts have been

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \qquad (1)$$

known, because of the difficulty to couple an one-electron reaction with a four-electron process.[3] It is now known that $[Ru(bpy)_3]^{3+}$ is capable of bringing about a four-electron oxidation of water to oxygen if it is coupled with a solid catalyst such as RuO_2, PtO_2, and MnO_2.[4-6] However, these catalysts can not be used as models to elucidate photosynthetic oxygen evolution, since the redox chemistry on their surface is difficult to study.[7] Therefore, the design and synthesis of chemical models of PS II and the study of water oxidation in nonbiological systems by utilizing metal complexes are the best ways to elucidate the mechanism of the photosynthetic oxygen evolution.

The present authors could show that oxygen evolution by water oxidation can be achieved by four-electron oxidation catalysts, in both homogeneous and heterogeneous media.[9-13] Oxygen evolution could be realized, even by two-electron oxidation catalysts, if two molecules of the catalyst can interact with each other under homogeneous as well as heterogeneous conditions to enable four-electron oxidation of two water molecules.[8-13] These catalysts have been successfully applied in a photoelectrochemical system to photolyze water for simultaneous oxygen and hydrogen evolution which mimics PS II.[14] We have already reported[10,12] the catalytic activity of water-coordinated dinuclear ($[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$) and mononuclear ($[Ru(NH_3)_5(H_2O)]^{3+}$) ruthenium complexes where the coordinated water molecules are involved in the water oxidation to evolve dioxygen. It is interesting and important to study whether a mononuclear metal complex, whose coordination sites are entirely occupied by ligands other than water, is active as a water oxidation catalyst. From this point of view we studied the catalytic activity of the $[Ru(NH_3)_6]^{3+}$ complex. Although the solution chemistry of ruthenium–ammine complexes has been studied extensively,[15,16] attention has not been focused on redox chemistry involving the higher oxidation states (e.g., Ru(IV) and Ru(V)). In this paper we report on both the homogeneous and heterogeneous catalytic activities of hexaammineruthenium(III) towards water oxidation to evolve dioxygen.

Experimental

Materials. $Ru(NH_3)_6Cl_3$ (Aldrich), ammonium cerium(IV) nitrate (Wako Pure Chemicals Co.) and kaolin clay (Nakarai Chemicals Ltd.) were used as received. The $[Ru(NH_3)_6]^{3+}$ complex was adsorbed into clay by mixing known amounts of clay and the ruthenium complex in deionized water. The mixture was stirred until complete adsorption was indicated by the disappearance of the solution color. The clay was filtered after adsorption, washed with deionized water and dried at 25 °C in air.

Instruments. Uv-visible spectra were recorded using a Hitachi 330 spectrometer. Cyclic voltammograms were run using a function generator (model HB-104) and a potentiostat/galvanostat (model HA-301) from Hokuto Denko Ltd. The electrode used to record the cyclic voltammograms was Nafion-coated basal plane pyrolytic graphite (BPG). Platinum wire was used as a counter electrode and a saturated calomel electrode (SCE) as reference electrode.

Oxygen Evolution. Oxygen evolution by water oxidation catalyzed by $[Ru(NH_3)_6]^{3+}$ was investigated by adding excess Ce(IV) as oxidant to an aqueous solution of $[Ru(NH_3)_6]^{3+}$ in a closed, deaerated vessel. The gas evolved by the reaction was analyzed by a gas chromatograph (Shimadzu GC-4C) as described earlier.[11] Repeated experiments showed that the results are reproducible with a 5% difference in the turnover values.

Results and Discussion

Although the uncoated BPG electrode gave a large catalytic current due to water oxidation, the Nafion-coated BPG electrode gave a better cyclic voltammogram for the $[Ru(NH_3)_6]^{3+}$ complex, probably because of the complex concentration into the coated Nafion film. The $[Ru(NH_3)_6]^{3+/2+}$ couple was observed in the potential region from −0.6 to 0.2 V vs. SCE and in the positive potential region (+0.6 to 1.5 V vs. SCE) two oxidative waves are observed, while their reduction waves were not clear (Fig. 1). These irreversible oxidations in the anodic region must be due to a reduction of the higher oxidation state of ruthenium (Ru(V)) by water rather than by electrochemical reduction. Based on the present results, the various redox processes occurring in $[Ru(NH_3)_6]^{3+}$ would be given by

$$[\mathrm{Ru^{V}(NH_3)_6}]^{5} \underset{+e^-}{\overset{+e^-}{\rightleftharpoons}} [\mathrm{Ru^{IV}(NH_3)_6}]^{4+} \underset{+e^-}{\overset{+e^-}{\rightleftharpoons}}$$

$$+1.32\ \mathrm{V} \qquad\qquad +1.04\ \mathrm{V}$$

$$[\mathrm{Ru^{III}(NH_3)_6}]^{3+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\mathrm{Ru^{II}(NH_3)_6}]^{2+}. \qquad (2)$$

$$-0.22\ \mathrm{V}$$

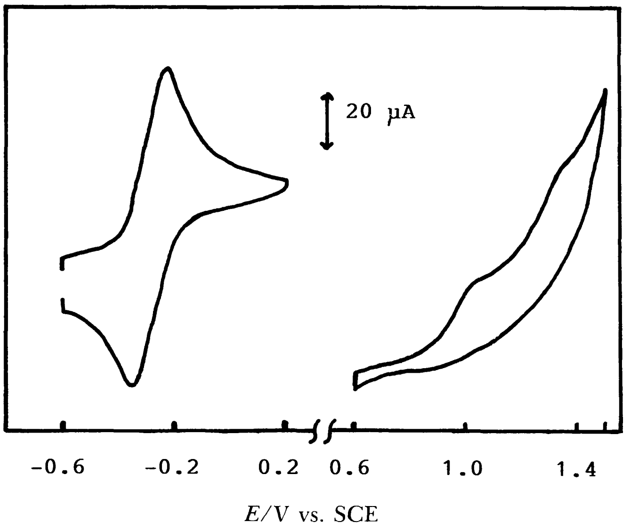

Fig. 1. Cyclic voltammogram of $[\mathrm{Ru(NH_3)_6}]^{3+}$ in 0.1 M $\mathrm{KNO_3}$ at Nafion coated BPG at a scan rate of 50 mV s⁻.

The $[\mathrm{Ru(NH_3)_6}]^{3+}$ complex easily forms Ru(V) upon oxidation, and the redox potentials of the complex show that it can be used as a two-electron oxidant for water oxidation. Water oxidation to evolve oxygen was investigated by adding excess ammonium cerium (IV) nitrate as an oxidant to an aqueous solution containing the ruthenium complex. Gas bubbles were readily observed in solution upon the addition of excess (Ce(IV) ion. The experimental results regarding a homogeneous catalysis of water oxidation by the monomeric ruthenium complex was treated with great caution, since decomposition of the complex may produce ruthenium oxide, which is catalytically active for water oxidation.[4,6,7] No ruthenium oxide deposition, however, could be observed after the water oxidation experiment. Though the complex turned over after oxygen evolution, the complex lost catalytic activity after 8—9 turnovers, possibly due to a slow formation of colorless Ru(III) ions from $[\mathrm{Ru(NH_3)_6}]^{3+}$ by decomposition during the process.[12]

The amount oxygen evolved with various concentrations of $[\mathrm{Ru(NH_3)_6}]^{3+}$ and Ce(IV) in homogeneous and heterogeneous clay-adsorbed states and the turnover numbers of the catalysts towards water oxidation are given in Tables 1 and 2. In both the homogeneous and heterogeneous systems, $[\mathrm{Ru(NH_3)_6}]^{3+}$ worked as a catalyst to evolve oxygen by water oxidation. A maximum turnover number of 8.3 was obtained for a homogeneous catalysis and 8.7 for a heterogeneous catalysis.

The higher oxidation state ruthenium-ammine complex ($[\mathrm{Ru^{V}(NH_3)_6}]^{5+}$) produced upon the addition of excess Ce(IV) would oxidize water to oxygen (Eqs. 3

Table 1. Oxygen Evolution by Water Oxidation Using $[\mathrm{Ru(NH_3)_6}]^{3+}$ under Homogeneous and Heterogeneous Conditions at 25 °C[a)]

$[\mathrm{Ru(NH_3)_6}]^{3+}$	$[\mathrm{Ru(NH_3)_6}]^{3+}$ in water		$[\mathrm{Ru(NH_3)_6}]^{3+}$ in kaolin clay	
mole (M)	$\mathrm{O_2}$[b)] / 10^{-6} dm³	Turnover number	$\mathrm{O_2}$[c)] / 10^{-6} dm³	Turnover number
2×10^{-6} (2×10^{-4})	162	6.7	209	8.7
4×10^{-6} (4×10^{-4})	332	6.8	340	7.0
6×10^{-6} (6×10^{-4})	405	5.7	324	4.5

a) Ru: Ce$^{\mathrm{IV}}$, 1: 300 (molar ratio) (Ru=$[\mathrm{Ru(NH_3)_6}]^{3+}$); kaolin clay, 300 mg; solution volume, 10 cm³. b) Reaction time, 60 min. c) Reaction time, 90 min.

Table 2. Oxygen Evolution by Water Oxidation Using $[\mathrm{Ru(NH_3)_6}]^{3+}$ under Homogeneous and Heterogeneous Conditions at 25 °C[a)]

Ru: Ce$^{\mathrm{IV}}$	$[\mathrm{Ru(NH_3)_6}]^{3+}$ in water		$[\mathrm{Ru(NH_3)_6}]^{3+}$ in kaolin clay	
Molar ratio	$\mathrm{O_2}$ / 10^{-6} dm^{-3}	Turnover number	$\mathrm{O_2}$ / 10^{-6} dm^{-3}	Turnover number
1: 50	117	2.4	—	—
1:100	281	5.8	—	—
1:200	400	8.3	326	6.7
1:300	386	8.0	340	7.0
1:400	—	—	370	7.6

a) Ru=$[\mathrm{Ru(NH_3)_6}]^{3+}$, 4×10^{-6} mole (4×10^{-4} M); kaolin clay, 300 mg; solution volume, 10 cm³; reaction time, 90 min.

and 4):

$$[\mathrm{Ru^{III}(NH_3)_6}]^{3+} + 2\mathrm{Ce(IV)} \longrightarrow [\mathrm{Ru^{V}(NH_3)_6}]^{5+} + 2\mathrm{Ce(III)} \qquad (3)$$

$$2[\mathrm{Ru^{V}(NH_3)_6}]^{5+} + 2\mathrm{H_2O} \longrightarrow 2\begin{array}{c}[\mathrm{Ru^{V}(NH_3)_6}]^{5+}\\ \vdots \\ \mathrm{H_2O}\end{array}$$

$$\xrightarrow{-4\mathrm{H^+}} [(\mathrm{NH_3})_6\mathrm{Ru^{V}\text{-}O\text{-}O\text{-}Ru^{V}(NH_3)_6}]^{8+}$$

$$\longrightarrow 2[\mathrm{Ru^{III}(NH_3)_6}]^{3+} + \mathrm{O_2} \qquad (4)$$

Endicott and Taube, who studied[17] the oxidation-reduction reactions of mononuclear ruthenium-ammine complexes, suggested that a spin-paired d^4 ion (Ru(IV)) is well-suited to accommodate seven groups in the coordination sphere of the complex. Ru(III) also forms seven-coordinated species as kinetic intermediates.[18,19] Earley and Fealey have studied[20] the kinetics of the reduction of the trinuclear ruthenium-ammine complex, and showed that Ru(III) and Ru(IV) can accommodate the seventh coordination site in the intermediate step. Such a seven-coordinated intermediate has already been proposed for oxygen evolution by water oxidation using di- and trinuclear ruthenium complexes.[11] Taking these facts into consideration, the involvement of two water molecules in the catalytic water oxidation process to evolve one molecule of oxygen in the absence of any other external catalyst can be explained as follows. The water molecule would form a loose coordination bond with the $[\mathrm{Ru^{V}(NH_3)_6}]^{5+}$ complex, and two such intermediates of the water-coordinated monomeric Ru(V) complex would interact to form a Ru–O–O–Ru bonded intermediate upon the removal of 4 protons, which could release one molecule of oxygen. Although such a peroxo-bridged Ru–O–O–Ru intermediate complex is not known, an oxo-bridged stable dinuclear ruthenium complex, $[(\mathrm{NH_3})_5\mathrm{Ru\text{-}O\text{-}Ru(NH_3)_5}]^{4+}$, is known.[21] Renger has proposed a model for the water splitting complex that is in better agreement with the reported experimental findings,[22] postulating a dinuclear manganese complex in which water ligands are finally oxidized to oxygen via the stage of a bridging peroxo ligand. The formation of an O–O bond in an intermediate has already been proposed to explain oxygen evolution by water oxidation using other metal complex systems.[8,12]

Our earlier studies[9,12] and the present observations show that one-electron oxidants can mediate oxygen evolution from water only in the heterogeneous state,[9,23] whereas two- and four-electron oxidants can catalyze oxygen evolution from water in the homogeneous state itself.[10–12] This leads to the conclusion that the two molecules of a two-electron oxidant, such as monomeric Ru(V), upon water coordination, can easily interact to form Ru–O–O–Ru with the removal of 4 protons which can spontaneously liberate oxygen. This scheme is supported by the fact that such an interaction was hindered by increasing the ionic strength of the reaction medium.[12,24]

Ramasamy Ramaraj acknowledges The Institute of Physical and Chemical Research (RIKEN) for providing the financial support for a three months stay at RIKEN.

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