Mononuclear Ruthenium–Ammine Complexes as Catalysts for Water Oxidation

Ramasamy Ramaraj, Akira Kira, and Masao Kaneko*

Solar Energy Science Research Group, The Institute of Physical and Chemical Research, Wako, Saitama, 351-01, Japan

Mononuclear ruthenium complexes catalyse water oxidation with evolution of oxygen under homogeneous as well as heterogeneous conditions.

Water oxidation to give molecular oxygen is of great importance and many laboratory models have been put forward to mimic the photosystem II of photosynthesis. The difficulty in oxygen evolution by water oxidation lies in the need to couple the four-electron oxidation of water with the one-electron chemistry of the photoredox process (equation 1).[1] Kiwi and Grätzel[2] have shown that many metal oxides (*e.g.* PtO_2 and RuO_2) are able to catalyse the oxidation of water by strong one-electron oxidants. These catalysts are far from ideal and many problems are associated with their use in model systems. The heterogeneous catalysts have been inadequately characterized[3] and they suffer anodic corrosion.[4] In recent reports, it has been shown that polynuclear metal complexes act as homogeneous[5—7] as well as heterogeneous[7,8] catalysts for oxidation of water to oxygen. Collin and Sauvage[9] prepared a number of mononuclear ruthenium complexes of sterically hindered di-imine chelates, but obtained negative results for their catalytic activity for water oxidation. They concluded that a multimetallic system is required to promote water oxidation to oxygen. We have now found, however, that mononuclear metal complexes can catalyse oxygen evolution by water oxidation, and report our results.

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

$Ru(NH_3)_5Cl^{2+}$ was purchased from Aldrich; $Ru(NH_3)_5(H_2O)^{3+}$ was prepared by a modification of the reported procedure.[10] The kaolin clay-adsorbed $Ru(NH_3)_5(H_2O)^{2+}$ complex was prepared by mixing known amounts of the clay and an aqueous solution of the ruthenium complex. Cyclic voltammetric studies were carried out using basal plane pyrolytic graphite (B.P.G.) electrodes coated with poly(styrene sulphonate), nafion, or kaolin clay. Water oxidation studies were carried out under argon by mixing the mononuclear ruthenium complex and excess of ammonium cerium(IV) nitrate. The evolved gas was analysed by gas chromatography (1.5 m column of molecular sieve 5 Å and argon carrier). Mass spectral studies were carried out using water containing $H_2{}^{18}O$ and the evolved $^{16}O_2$ and $^{16}O^{18}O$ were identified at m/z 32 and 34. The ionic strength was adjusted using KNO_3.

The solution chemistry of ruthenium–ammine complexes has been studied extensively;[11,12] however, attention has not been focused on redox chemistry involving the higher oxidation states (for *e.g.* Ru^{IV} and Ru^{V}). The uncoated B.P.G. gave a large catalytic current due to water oxidation at higher potentials in water. However, polymer coated-B.P.G. electrodes gave much better cyclic voltammograms for the ruthenium complexes. For both the complexes, three oxidative waves were observed in the potential region −0.5 to 1.4 V *vs.* standard calomel electrode (S.C.E.) which are reversible on the reductive scan with a peak separation of 60—80 mV. These waves are observed at 1.28, 1.06, and −0 25 V *vs.* S.C.E. The $Ru(NH_3)_5Cl^{2+/3+}$ couple appears at −0.25 V *vs.* S.C.E., and the other two peaks clearly indicate the formation of $Ru^V(NH_3)_5Cl^{4+}$ by a series of one-electron oxidations of $Ru^{III}(NH_3)_5Cl^{2+}$ (equation 2). Similar results were obtained for the $Ru(NH_3)_5(H_2O)^{3+}$ complex. However, the peak potentials are shifted to less positive values than for the $Ru(NH_3)_5Cl^{2+}$ complex.

$$Ru^{II}(NH_3)_5Cl^{+} \underset{\substack{e^- \\ -0.25\ V}}{\overset{-e^-}{\rightleftharpoons}} Ru^{III}(NH_3)_5Cl^{2+} \underset{\substack{+e^- \\ 1.06\ V}}{\overset{-e^-}{\rightleftharpoons}}$$

$$Ru^{IV}(NH_3)_5Cl^{3+} \underset{\substack{+e^- \\ 1.28\ V}}{\overset{-e^-}{\rightleftharpoons}} Ru^{V}(NH_3)_5Cl^{4+} \qquad (2)$$

Water oxidation experiments were carried out with the mononuclear ruthenium complexes using ammonium cerium(IV) nitrate as oxidant. An aqueous mixture containing 2 µmol of $Ru(NH_3)_5Cl^{2+}$ was deaerated by bubbling argon gas for 2 h and then excess (<100 equiv.) of Ce^{IV} was added. Gas evolution was clearly observed within 1 min after mixing. The amounts of oxygen evolved in 90 min are given in Table 1. Repeated experiments showed that the results are reproducible. The presence of acid or alkali in the reaction medium does not affect significantly the water oxidation process. When the ionic strength of the solution was varied from 0.5 to 2.5 M, the amount of oxygen evolution was reduced to one third, showing that ion-pair formation in the intermediate stage hinders the water oxidation process. Table 1 shows that $Ru(NH_3)_5(H_2O)^{3+}$ is a better catalyst for water oxidation both in homogeneous and heterogeneous (clay adsorbed) systems, possibly owing to the presence of water molecules in the co-ordination sphere. These mononuclear ruthenium–ammine complexes seem to be chemically resistant, even under acidic and oxidizing conditions, since no ruthenium oxide deposit could be seen after the water oxidation experiment. This shows that no intermediate RuO_4 was formed during the water oxidation process. However, the monomeric ruthenium–ammine complexes lost catalytic activity after >16 turnovers possibly owing to the slow formation of colourless Ru^{III} ions from the penta-ammine ruthenium complexes during the process.

From the electrochemical data, it is clear that the ruthenium–ammine complexes can act as a two-electron oxidant for water oxidation. For evolution of one molecule of oxygen by water oxidation two molecules of ruthenium complex are needed. The addition of excess of Ce^{IV} to a solution of a mononuclear ruthenium–ammine complex should lead to the oxidation of the complex to give a Ru^V complex, and two molecules of the Ru^V complex formed should then oxidize water to oxygen produce oxygen (equations 3 and 4, X = Cl^- or H_2O).

$$2\,Ru^{III}(NH_3)X + 4\,Ce^{IV} \longrightarrow 2\,Ru^{V}(NH_3)_5X + 4\,Ce^{III} \qquad (3)$$

$$2\,Ru^{V}(NH_3)_5X + 2\,H_2O \longrightarrow 2\,Ru^{III}(NH_3)_5X + O_2 + 4\,H^{+} \qquad (4)$$

Endicott and Taube[13] studied the redox reactions of monomeric ruthenium complexes, and suggested that a spin-paired d^4 ion (Ru^{IV}) may be well suited for accommodating seven co-ordinating groups in the co-ordination sphere of the complex. Ruthenium(III) also forms seven-co-ordinated species as kinetic intermediates.[14] Taking these facts into consideration the involvement of two monomeric ruthenium–ammine complexes in the catalytic water oxidation process to evolve one molecule of oxygen in the absence of external catalyst can be explained as follows. Two molecules of the water-co-ordinated monomeric Ru^V complex will lead to the formation of a Ru–O–O–Ru bonded intermediate with the removal of $4H^+$, which will release one molecule of oxygen. Such a peroxy-bridged Ru–O–O–Ru intermediate complex is not known; however, an oxo-bridged dinuclear ruthenium complex, $[(NH_3)_5Ru{-}O{-}Ru(NH_3)_5]^{4+}$, is known.[15] Recently, the formation of O–O bonds in an intermediate has been proposed to explain oxygen evolution by water oxidation using multimetal complex systems,[5,8] lending support to formation of the above mentioned intermediate.

Received, 22nd September 1986; Com. 1357

Table 1. Oxygen evolution by water oxidation using mononuclear ruthenium–ammine complexes at 25 °C.[a]

Complex	O_2, µl	O_2, µmol
$Ru(NH_3)_5Cl^{2+}$	166	6.68
$Ru(NH_3)_5(H_2O)^{3+}$	287	11.85
	378[b]	15.58

[a] $Ru(NH_3)_5Cl^{2+}$, 2 µmol; $Ru(NH_3)_5(H_2O)^{3+}$, 2 µmol; Ru:Ce^{IV}, 1:200 (molar ratio); reaction volume, 10 ml; reaction time, 90 min.
[b] Kaolin clay (100 mg)-adsorbed $Ru(NH_3)_5(H_2O)^{3+}$ (1 µmol) in the heterogeneous state.

References

1 A. Harriman, *J. Photochem.*, 1984, **25**, 33.
2 J. Kiwi and M. Grätzel, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 860; 1979, **18**, 624.
3 G. Blondeel, A. Harriman, G. Porter, D. Urvin, and J. Kiwi, *J. Phys. Chem.*, 1983, **87**, 2629.
4 A. Mills and M. L. Zeeman, *J. Chem. Soc., Chem. Commun.*, 1981, 948.
5 J. A. Gilbert, D. S. Eggleston, W. R. Murphy, Jr., D. A. Geselowitz, S. W. Gersten, D. J. Hodgson, and T. J. Meyer, *J. Am. Chem. Soc.*, 1985, **107**, 3855.
6 R. Ramaraj, A. Kira, and M. Kaneko, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 3515.
7 R. Ramaraj, A. Kira, and M. Kaneko, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, in the press.
8 R. Ramaraj, A. Kira, and M. Kaneko, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 825.
9 J. P. Collin and J. P. Sauvage, *Inorg. Chem.*, 1986, **25**, 135.
10 C. G. Kuehn and H. Taube, *J. Am. Chem. Soc.*, 1976, **98**, 689.
11 P. C. Ford, *Coord. Chem. Rev.*, 1970, **5**, 75.
12 H. S. Lim, D. J. Barclay, and F. C. Anson, *Inorg. Chem.*, 1972, **11**, 1460.
13 J. F. Endicott and H. Taube, *Inorg. Chem.*, 1965, **4**, 437.
14 H. Scheiddizer, J. Armor, and H. Taube, *J. Am. Chem. Soc.*, 1968, **90**, 5828.
15 J. A. Baumann and T. J. Meyer, *Inorg. Chem.*, 1980, **19**, 345.