

# Cooperative catalysis and critical decomposition distances in water oxidation by tris(ethylenediamine)ruthenium (III) complex confined in a Nafion membrane

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## Abstract

The activity of tris(ethylenediamine)ruthenium (III) complex,  $[\text{Ru}(\text{en})_3]^{3+}$ , as a water oxidation catalyst was studied in a homogeneous aqueous solution and a heterogeneous Nafion (Nf) membrane. In the aqueous solution, the apparent catalytic activity ( $k_{\text{app}}$  ( $\text{s}^{-1}$ )) decreased monotonously with the concentration due to a bimolecular decomposition of the complex. The bimolecular decomposition of the complex was remarkably suppressed by incorporating it into a Nf membrane. An optimum complex concentration for  $k_{\text{app}}$  in the Nf membrane was exhibited, which was explained both by a cooperative catalysis and a bimolecular decomposition of the complex. The  $k_{\text{app}}$  in the Nf membrane was analyzed in terms of an intrinsic catalytic activity ( $k_{\text{O}_2}$  ( $\text{s}^{-1}$ )) of the complex, a cooperative catalysis distance ( $r_{\text{co}}$  (nm)) and a critical decomposition distance ( $r_{\text{d}}$  (nm)) between them based on intermolecular distance distribution to obtain the  $k_{\text{O}_2} = 8.5 \times 10^{-5} \text{ s}^{-1}$ ,  $r_{\text{co}} = 1.44 \text{ nm}$  and  $r_{\text{d}} = 1.07 \text{ nm}$ . The results in the  $[\text{Ru}(\text{en})_3]^{3+}$  system were compared with those obtained in the  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  system. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Water oxidation catalyst; Ruthenium complex; Nafion membrane

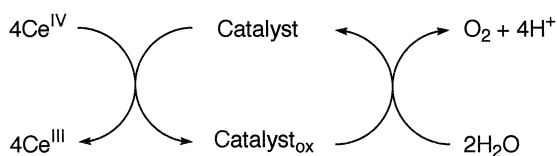
## 1. Introduction

Water oxidation is one of the most important and fundamental catalyses in nature. This process is important not only in the biological activity but also in a photochemical solar energy conversion system which is attracting much attention to obtain a renewable energy resource [1–3]. Many water oxidation catalyst systems have been reported [4–6]. In order to optimize the catalysis, it is important to study factors

affecting the activity and stability of the catalysts and to establish activity models involving these factors. However, there has been no report on an activity model in a water oxidation catalysis except our earlier works on molecule-based water oxidation catalyst confined onto inorganic particles [7] or in a polymer membrane [8–11].

We have already reported four-electron water oxidation catalyses to evolve dioxygen ( $\text{O}_2$ ) by ammine-coordinated mononuclear ruthenium complexes [10,11]. These complexes work as a two-electron oxidation catalyst and catalyze four-electron water oxidation by two complex

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molecules. There has been an essential problem as to stabilization of these ammine-coordinated complex, i.e., these complexes undergo a bimolecular decomposition by the oxidation of their ammine-ligands to yield dinitrogen ( $N_2$ ).

We considered that the complex possessing ammine-chelate-ligands such as ethylenediamine (en) instead of ammine-ligand could suppress or avoid their bimolecular decomposition. The water oxidation catalysis by the ruthenium complex with ammine-chelate-ligands has not been reported. In the present paper, water oxidation catalysis (see Scheme 1) by tris(ethylenediamine)ruthenium (III) complex,  $[Ru(en)_3]^{3+}$ , in an aqueous solution and a Nafion (Nf) membrane will be studied and compared with those by  $[Ru(NH_3)_6]^{3+}$  to estimate chelating effect on its activity and stability.

## 2. Experimental

### 2.1. Materials

Tris(ethylenediamine)ruthenium (III) chloride,  $[Ru(en)_3]Cl_3$ , was synthesized and purified as described previously [12]. A Nafion 117 (Nf) membrane (thickness 180  $\mu m$ ) was purchased from Aldrich Chemical. Cerium(IV) diammonium nitrate,  $Ce(NH_4)_2(NO_3)_6$ , was purchased from Wako. All the materials were of commercially available purest grade and used as received.

### 2.2. Preparation of a Nf membrane incorporating $[Ru(en)_3]^{3+}$

Nf membrane was swollen sufficiently by soaking in pure water for ca. 24 h. The mem-

brane was immersed in a  $2.4 \times 10^{-4}$ – $8.0 \times 10^{-3}$  mol  $dm^{-3}$  (M) complex aqueous solution ( $5.0 \times 10^{-3}$   $dm^3$ ) for ca. 5 h so that the complex is incorporated into the membrane by cation exchange. The complex amount in the membrane was estimated from the decrease of the complex concentration in its aqueous solution before and after adsorption of the complex. The complex concentration in the membrane was calculated from the complex amount and the membrane volume.

### 2.3. Dioxygen evolution

In an aqueous solution system, excess  $Ce(NH_4)_2(NO_3)_6$  oxidant ( $6.0 \times 10^{-3}$  mol) was added quickly to  $0$ – $1.0 \times 10^{-2}$  M complex aqueous solution ( $5.0 \times 10^{-3}$   $dm^3$ ) in a reaction vessel. In a Nf membrane system, the membrane (volume:  $2.0 \times 10^{-4}$   $dm^3$ ) that incorporated  $0$ – $4.0 \times 10^{-5}$  mol complex was put into pure water in a reaction vessel, and an excess  $Ce^{IV}$  oxidant ( $6.0 \times 10^{-3}$  mol) was added quickly. In both the systems, the atmosphere in the reaction vessel was replaced with argon gas before adding the  $Ce^{IV}$  oxidant. For all the experiments, the vessel was kept at  $25^\circ C$ . The pH was 0.43 without any buffer under the whole complex concentration range, and the pH change was less than 0.03 before and after the  $O_2$  evolution experiment. The  $O_2$  evolved was analyzed on a gas chromatograph equipped with a 5 Å molecular sieve column using argon carrier gas (flow rate is  $40$   $cm^3$   $min^{-1}$ ) at  $50^\circ C$ .

## 3. Results and discussion

The amount of  $O_2$  evolved increased with time after adding an excess  $Ce^{IV}$  oxidant in the aqueous solution and Nf membrane. It was saturated at ca. 10 h in the aqueous solution, but not saturated even at 20 h in the Nf membrane under the same complex amount conditions ( $1 \times 10^{-5}$  mol) as shown in Fig. 1a and b. The amount of  $O_2$  evolution ( $2.5 \times 10^{-4}$   $dm^3$ ) after

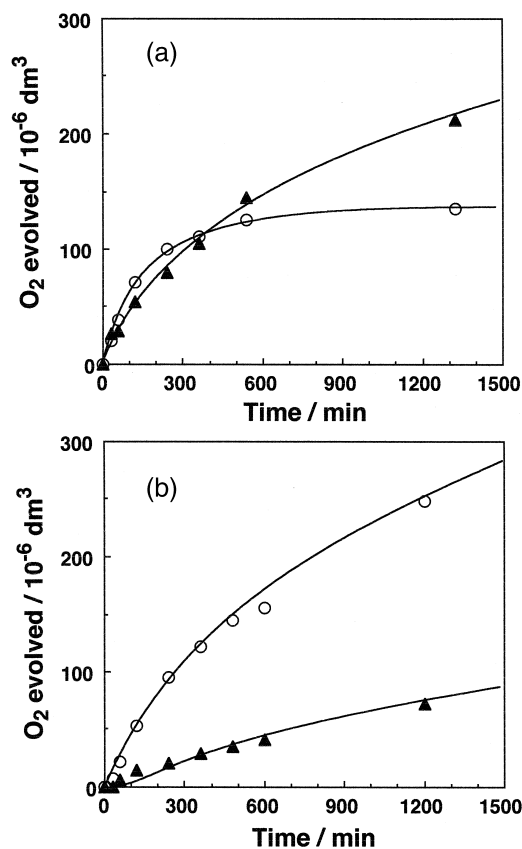


Fig. 1. (a) Changes of the amounts of  $O_2$  ( $\circ$ ) and  $N_2$  ( $\blacktriangle$ ) evolved with reaction time in the aqueous solution. The amount of a  $Ce^{IV}$  oxidant,  $6 \times 10^{-3}$  mol; the amount of the complex,  $1 \times 10^{-5}$  mol; solution volume,  $5 \times 10^{-3}$  dm<sup>3</sup>. (b) Changes of the amounts of  $O_2$  ( $\circ$ ) and  $N_2$  ( $\blacktriangle$ ) evolved with reaction time in the Nf membrane. The amount of a  $Ce^{IV}$  oxidant,  $6 \times 10^{-3}$  mol; the amount of the complex,  $1 \times 10^{-5}$  mol; membrane volume,  $2.0 \times 10^{-4}$  dm<sup>3</sup>; liquid phase volume,  $5 \times 10^{-3}$  dm<sup>3</sup>.

20 h in the Nf membrane was 1.8 times larger than the saturated value ( $1.3 \times 10^{-4}$  dm<sup>3</sup>) in aqueous solution.  $N_2$  was also evolved, and the  $N_2$  can result only from the decomposition by the oxidation of the en-ligands of the complex since no  $N_2$  was detected in an aqueous solution containing the same amount  $Ce^{IV}$  without the complex. The amount of  $N_2$  evolved in the Nf membrane was much smaller than that in the aqueous solution.

The initial  $O_2$  evolution rate ( $V_{O_2}$  (mol s<sup>-1</sup>)) was obtained from the initial slope at time zero

of the plots of  $O_2$  evolved vs. time, and the relationship between  $V_{O_2}$  and the complex concentration in the aqueous solution is shown in Fig. 2a.  $V_{O_2}$  increased with the complex concentration and then decreased after passing a maximum  $V_{O_2}$  at  $1.0 \times 10^{-3}$  M. The initial  $N_2$  evolution rate ( $V_{N_2}$  (mol s<sup>-1</sup>)) was second order

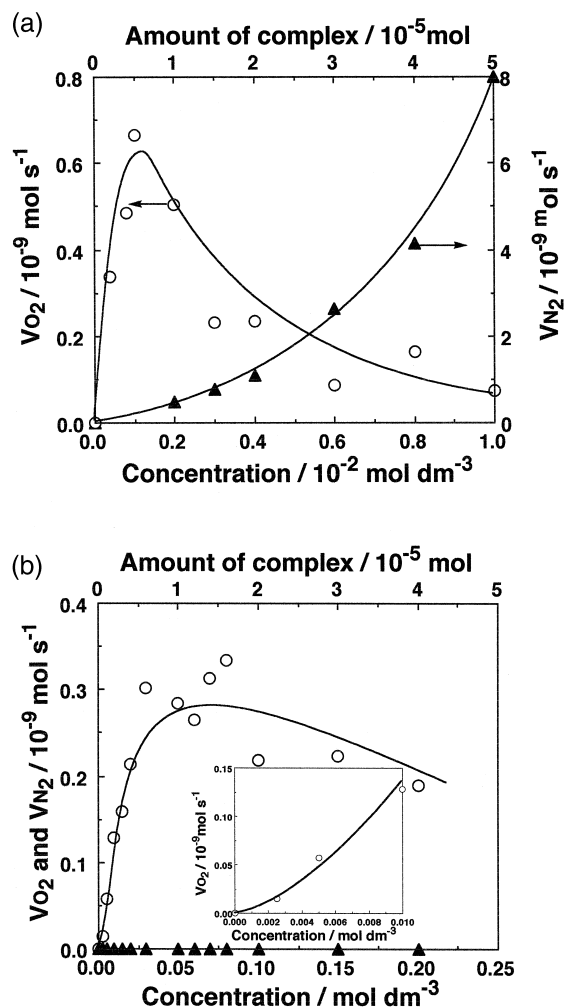


Fig. 2. (a) Plots of the initial rates of  $O_2$  ( $V_{O_2}$  ( $\circ$ )) and  $N_2$  ( $V_{N_2}$  ( $\blacktriangle$ )) evolution vs. complex concentration and complex amount in the aqueous solution. The amount of a  $Ce^{IV}$  oxidant,  $6 \times 10^{-3}$  mol; solution volume,  $5 \times 10^{-3}$  dm<sup>3</sup>. (b) Plots of the initial rates of  $O_2$  ( $V_{O_2}$  ( $\circ$ )) and  $N_2$  ( $V_{N_2}$  ( $\blacktriangle$ )) evolution vs. complex concentration and complex amount in the Nf membrane. The inset illustrates the plots at low concentrations. The amount of  $Ce^{IV}$  oxidant,  $6 \times 10^{-3}$  mol; membrane volume,  $2.0 \times 10^{-4}$  dm<sup>3</sup>; liquid phase volume,  $5 \times 10^{-3}$  dm<sup>3</sup>.

with respect to the complex concentration, showing that the decomposition of  $[\text{Ru}(\text{en})_3]^{3+}$  is a bimolecular reaction in the aqueous solution. The catalytic water oxidation by the high oxidation state complexes is in competition with their bimolecular decomposition, so that  $V_{\text{O}_2}$  decreased at high concentrations.

Fig. 2b shows the plots of  $V_{\text{O}_2}$  vs. complex concentration in the Nf membrane. The plots at low concentrations were second-order with respect to the complex concentration as shown in the inset of Fig. 2b, indicating that  $\text{O}_2$  evolution is a bimolecular reaction of the complex. The complex can work only as a two-electron oxidation catalyst. Therefore, two molecules of the complex are required for four-electron water oxidation catalysis and work cooperatively. The  $V_{\text{O}_2}$  decrease at more than 0.1 M in Fig. 2b is ascribed to a bimolecular decomposition of the complex. However, the complex concentration ( $8.0 \times 10^{-2}$  M) for the maximum  $V_{\text{O}_2}$  in the Nf membrane is much higher than that ( $1 \times 10^{-3}$  M) in the aqueous solution. The  $V_{\text{N}_2}$  was almost zero in the whole concentration range. These results show that the bimolecular decomposition was suppressed by incorporating it into the membrane.

In order to study the catalysis by  $[\text{Ru}(\text{en})_3]^{3+}$ , the apparent catalyst activity ( $k_{\text{app}}$  ( $\text{s}^{-1}$ )), which means turnover number of the catalyst, was defined as,

$$k_{\text{app}} = V_{\text{O}_2} / n_{\text{Ru}} \quad (1)$$

where  $n_{\text{Ru}}$  (mol) is the amount of the complex present in the reaction system either in the aqueous solution or Nf membrane. The dependence of  $k_{\text{app}}$  on the complex concentration in the aqueous solution are shown in Fig. 3a including our earlier data of  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  [11] which has very a structure similar to  $[\text{Ru}(\text{en})_3]^{3+}$ . The  $k_{\text{app}}$  values of  $[\text{Ru}(\text{en})_3]^{3+}$  are much higher than those of  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  at low concentrations (less than  $4 \times 10^{-3}$  M). The  $k_{\text{app}}$  decreased monotonously with the concentration in both the complex systems, which is caused

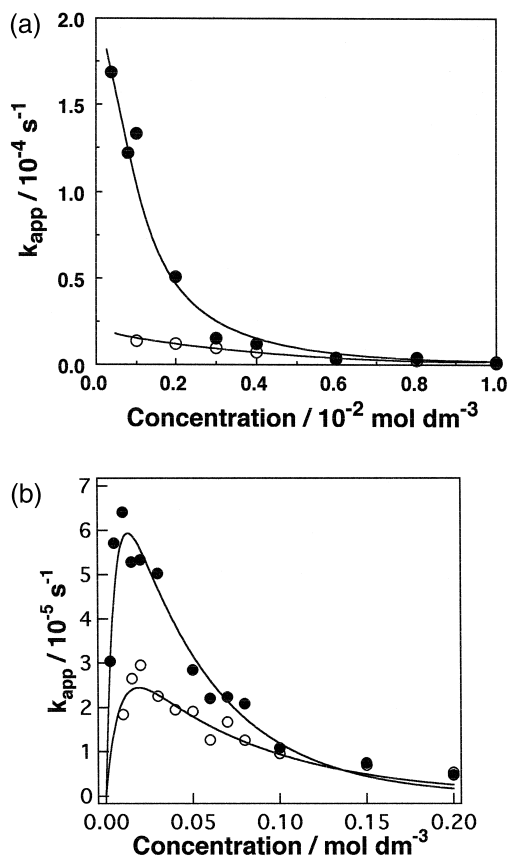


Fig. 3. (a) Relationships between the apparent catalyst activity ( $k_{\text{app}}$ ) and complex concentration in the aqueous solution. (●)  $[\text{Ru}(\text{en})_3]^{3+}$ ; (○)  $[\text{Ru}(\text{NH}_3)_6]^{3+}$ . (b) Relationships between the apparent catalyst activity ( $k_{\text{app}}$ ) and complex concentration in the Nf membrane. The lines show calculated curves based on Eq. (2). (●)  $[\text{Ru}(\text{en})_3]^{3+}$ ; (○)  $[\text{Ru}(\text{NH}_3)_6]^{3+}$ .

by the bimolecular decomposition of these complexes. The  $k_{\text{app}}$  of  $[\text{Ru}(\text{en})_3]^{3+}$  decreased much more drastically than that of  $[\text{Ru}(\text{NH}_3)_6]^{3+}$ , showing that the bimolecular decomposition is much more marked for  $[\text{Ru}(\text{en})_3]^{3+}$  than  $[\text{Ru}(\text{NH}_3)_6]^{3+}$ . This is supported by the much higher  $V_{\text{N}_2}$  values ( $8.0 \times 10^{-9}$  mol  $\text{s}^{-1}$  at  $1.0 \times 10^{-2}$  M) of  $[\text{Ru}(\text{en})_3]^{3+}$  than those ( $1.8 \times 10^{-10}$  mol  $\text{s}^{-1}$  at  $1.0 \times 10^{-2}$  M) [11] of  $[\text{Ru}(\text{NH}_3)_6]^{3+}$ . Thus, any chelating effect of  $[\text{Ru}(\text{en})_3]^{3+}$  on the inhibition of its bimolecular decomposition could not be observed. A chelate effect on a stability constant of metal complexes is generally known. It is at least inferred from

these results that the dissociation equilibrium of donation groups of the ligand does not affect the bimolecular decomposition of ammine–ruthenium complexes.

The relationship between  $k_{\text{app}}$  and the complex concentration in the Nf membrane for  $[\text{Ru}(\text{en})_3]^{3+}$  is shown in Fig. 3b together with  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  data [11]. The  $k_{\text{app}}$  increased with the concentration at low concentrations, and then decreased with the concentration after passing a maximum value around  $1.0 \times 10^{-2}$  M in both the complex system. The increase of  $k_{\text{app}}$  at the low concentration region (less than  $1.0 \times 10^{-2}$  M) can be explained by a cooperative catalysis by two molecules of the complexes, and the decrease of  $k_{\text{app}}$  at the high concentration region (more than  $1.0 \times 10^{-2}$  M) by their bimolecular decomposition. An isolated complex in the membrane could not work for this cooperative catalysis. As the complex concentration increases, the fraction of the adjacent complexes capable of a cooperative catalysis increases to result in the  $k_{\text{app}}$  increase. When the concentration increases further, the fraction of the complex which undergoes a bimolecular decomposition would increase to result in the  $k_{\text{app}}$  decrease. The  $k_{\text{app}}$  values of  $[\text{Ru}(\text{en})_3]^{3+}$  in the Nf membrane are larger than those of  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  at low concentrations, and for instance the maximum  $k_{\text{app}}$  ( $6.4 \times 10^{-5} \text{ s}^{-1}$ ) in the former is 2.2 times larger than that ( $2.9 \times 10^{-5} \text{ s}^{-1}$ ) in the latter. This is ascribable to the higher intrinsic activity of the  $[\text{Ru}(\text{en})_3]^{3+}$  than that of  $[\text{Ru}(\text{NH}_3)_6]^{3+}$ , which is supported by the activity analysis described later.

The  $k_{\text{app}}$  values in the Nf membrane were higher than those in the aqueous solution at the same complex concentration ( $1.0 \times 10^{-2}$  M) by 20 times for  $[\text{Ru}(\text{NH}_3)_6]^{3+}$ , and by 43 times for  $[\text{Ru}(\text{en})_3]^{3+}$  (compare Fig. 3a and b). The diffusion of the complexes is suppressed by incorporating them into the membrane, which favors a cooperative catalysis and which suppresses the bimolecular decomposition, leading to the higher  $k_{\text{app}}$  values in the Nf membrane. The higher degree (43 times) of the  $k_{\text{app}}$  increase for the

$[\text{Ru}(\text{en})_3]^{3+}$  by the incorporation than that (20 times) for the  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  would be caused by the much higher bimolecular decomposition in the aqueous solution for the former than the latter system (vide supra).

Both the cooperative catalysis and the bimolecular decomposition in the membrane depend on the intermolecular distance between the complexes. It is important to take intermolecular distance distribution of the complex into account rather than average intermolecular distance. We have reported the analysis of the catalytic activities of molecule-based water oxidation catalysts which work as a two-electron oxidation catalyst in a polymer membrane based on intermolecular distance distribution [10]. When assuming that the cooperative catalysis can take place only within a cooperative catalysis distance ( $r_{\text{co}}$  (nm)), and that the complexes present within a critical decomposition distance ( $r_{\text{d}}$  (nm)) undergo a bimolecular decomposition,  $k_{\text{app}}$  is represented by Eq. (2) [10],

$$k_{\text{app}} = k_{\text{O}_2} \left[ \exp\{-4\pi(r_{\text{d}}^3 - s^3)\alpha c N_{\text{A}} \times 10^{-24}/3\} - \exp\{-4\pi(r_{\text{co}}^3 - s^3)\alpha c N_{\text{A}} \times 10^{-24}/3\} \right] \quad (2)$$

where  $k_{\text{O}_2}$  ( $\text{s}^{-1}$ ),  $N_{\text{A}}$  ( $\text{mol}^{-1}$ ),  $c$  ( $\text{mol dm}^{-3}$ ),  $s$  (nm) and  $\alpha$  are an intrinsic catalytic activity of the complex for the cooperative catalysis, Avogadro's number, complex concentration in the membrane, contact distance between them and the degree ( $\alpha = 40$ ) [8] of localization of the complex in the membrane, respectively. As for the  $s$  value, the  $[\text{Ru}(\text{en})_3]^{3+}$  was approximated as a sphere, and its diameter was calculated to be  $s = 1.01$  nm from the distance and the angle of the atoms (Ru–N, 0.210 nm; N–H, 0.101 nm,  $\langle \text{H–N–Ru} \rangle$ ,  $110^\circ$ ; C–H, 0.147 nm; C–H, 0.111 nm;  $\langle \text{Ru–N–C} \rangle$ ,  $119^\circ$ ;  $\langle \text{H–C–H} \rangle$ ,  $109^\circ$ ) [13] as well as the van der Waals radius (0.12 nm) of hydrogen. The first exponential term in the large brackets of Eq. (2) expresses the fraction of the complex which does not undergo the bimolecular decomposition (the intermolecular distance,  $r$ , is longer than  $r_{\text{d}}$ ), and the second

Table 1  
Summary of  $k_{\text{O}_2}$ ,  $s$ ,  $r_{\text{co}}$  and  $r_{\text{d}}$  values in water oxidation catalysis by mononuclear ruthenium complexes in a Nafion membrane

System	$k_{\text{O}_2}$ ( $10^{-5} \text{ s}^{-1}$ )	$s$ (nm)	$r_{\text{co}}$ (nm)	$r_{\text{d}}$ (nm)
Nf/ [Ru(en) <sub>3</sub> ] <sup>3+</sup>	8.5 ± 0.5	1.01	1.44 ± 0.06	1.07 ± 0.005
Nf/ [Ru(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> <sup>a</sup>	3.5 ± 0.5	0.75	1.21 ± 0.1	0.82 ± 0.01

<sup>a</sup>Cited from Ref. [11].

exponential term expressing the fraction of the complex which can not work as a cooperative catalyst ( $r$  is longer than  $r_{\text{co}}$ ). Namely, the first term minus second one in Eq. (2) represents the fraction of the complex which can work as a cooperative catalyst without bimolecular decomposition ( $r$  is between  $r_{\text{d}}$  and  $r_{\text{co}}$ ).

The Eq. (2) was applied to the relationship between  $k_{\text{app}}$  and concentration for [Ru(en)<sub>3</sub>]<sup>3+</sup> in Fig. 3b using the nonlinear least-square method. The best fittings were obtained as shown in the curve of Fig. 3b when  $k_{\text{O}_2} = 8.5 \times 10^{-5} \text{ s}^{-1}$ ,  $r_{\text{co}} = 1.44 \text{ nm}$  and  $r_{\text{d}} = 1.07 \text{ nm}$ . The good fitting of the Eq. (2) supports that this treatment is reasonable. The fitting parameters obtained are summarized in Table 1 including analysis results for [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>. The  $k_{\text{O}_2}$  ( $8.5 \times 10^{-5} \text{ s}^{-1}$ ) for [Ru(en)<sub>3</sub>]<sup>3+</sup> is 2.4 times higher than that for [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>, showing that intrinsic catalytic activity of a ruthenium complex increased by the coordination of en-chelate-ligands instead of ammine-ligands. The  $r_{\text{d}}$  (1.07 nm) is close to the  $s$  value (1.01 nm) showing that the bimolecular decomposition takes place between the complexes in close proximity with each other. The  $r_{\text{co}}$  value (1.44 nm) is reasonable considering that (1.21 nm) of [Ru(en)<sub>3</sub>]<sup>3+</sup>, but is longer than the calculated distance (0.58 nm) between the Ru centers in a presumed Ru–O–O–Ru intermediate binding for the catalysis (Ru–O, 0.214 nm [14]; O–O, 0.148 nm [13]). The  $r_{\text{co}}$  value obtained can be explained by a possible mechanism of a cooperative catalysis by [Ru(en)<sub>3</sub>]<sup>3+</sup>, i.e., intermediate is formed through hydrogen bonds between wa-

ter and –NH<sub>2</sub>– protons of en ligands (Ru–N–H ··· O–O ··· H–N–Ru), whose calculated distance between Ru centers is ca 1.1 nm.

#### 4. Conclusion

The activity of [Ru(en)<sub>3</sub>]<sup>3+</sup> as a water oxidation catalyst was studied and compared with that of [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> in a homogeneous aqueous solution and a heterogeneous Nf membrane. It was found that [Ru(en)<sub>3</sub>]<sup>3+</sup> works as a cooperative catalysis and undergoes a bimolecular decomposition at high concentrations in the aqueous solution. Any chelating effect of [Ru(en)<sub>3</sub>]<sup>3+</sup> on the inhibition of its bimolecular decomposition could not be observed. However, the intrinsic activity of the complex increased by the coordination of en-chelate-ligands instead of ammine-ligands. The dependence of the apparent catalytic activity ( $k_{\text{app}}$  (s<sup>-1</sup>)) on the concentration in Nf membrane was analyzed in terms of an intrinsic catalytic activity ( $k_{\text{O}_2}$  (s<sup>-1</sup>)) of the complex, a cooperative catalysis distance ( $r_{\text{co}}$  (nm)) and a critical decomposition distance ( $r_{\text{d}}$  (nm)) between them based on intermolecular distance distribution to obtain the  $k_{\text{O}_2} = 8.5 \times 10^{-5} \text{ s}^{-1}$ ,  $r_{\text{co}} = 1.44 \text{ nm}$  and  $r_{\text{d}} = 1.07 \text{ nm}$ . The  $k_{\text{O}_2}$  for [Ru(en)<sub>3</sub>]<sup>3+</sup> is 2.4 times higher than that for [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>. The  $r_{\text{d}}$  (1.07 nm) are close to the  $s$  value showing that the bimolecular decomposition takes place between the complexes in close proximity with each other. It was suggested from the  $r_{\text{co}}$  value (1.44 nm) that the cooperative catalysis by the [Ru(en)<sub>3</sub>]<sup>3+</sup> takes place through hydrogen bonds between water and –NH<sub>2</sub>– protons of en-ligands (Ru–N–H ··· O–O ··· H–N–Ru).

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