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COMMUNICATION

Electrocatalytic oxidation of alcohols by a carbon-supported Rh porphyrin†‡

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A Rh porphyrin on carbon black was shown to catalyze the electro-oxidation of several aliphatic alcohols (ethanol, 1-propanol, and 2-propanol) and benzyl alcohols. The overpotentials for alcohol oxidation were very low. The reaction mechanism and substrate specificity are discussed.

The electrochemical oxidation of alcohols is an important process with regard to direct alcohol fuel cells, alcohol sensing, and the electrochemical conversion of alcohols to aldehydes and ketones. While Pt or Pt alloys have mainly been studied as electrocatalysts for this electrochemical reaction,¹ some metallocomplex-based catalysts have also been examined for alcohol oxidation.^{2–5}

Metallocomplexes are widely used as homogenous catalysts for oxidation. These homogenous oxidation catalysts offer several advantages: (1) only a small amount of metal is used, (2) the reaction mechanism is simpler than with heterogenous catalysts, and (3) the activity can be controlled to some extent by manipulating the ligand structure. For alcohol oxidation, Ru complex- or Ni complex-based electrocatalysts have been investigated.^{2–5} Although metallocomplex-based electrocatalysts for the electro-reduction of O₂ (cathode catalysts) have been substantially investigated for the development of non-platinum cathode catalysts in fuel cells,^{6–8} there are few examples of catalysts for electro-oxidation (anode catalysts) that include metallocomplexes,^{2–5} since the overpotentials are high and the maximum reaction rate is slow.

Against this background, we have tried to develop metallocomplex-based electro-oxidation catalysts that oxidize alcohols at low overpotentials. In this study, we paid special attention to Rh porphyrins as a potential component of metallocomplex-based electrocatalysts. It has been shown that Rh porphyrins have good catalytic activity for the electrooxidation of inorganic compounds (CO, ⁹ NaBH₄, ¹⁰ and N₂H₄¹¹) and organic compounds (oxalic acid¹² and glucose¹³). In addition to electrochemical reactions, the reaction of Rh porphyrins and alcohols has been extensively studied.^{14–18} Recently, Liu *et al.* reported that a Rh porphyrin can catalyze the oxidation of various alcohols by O₂.¹⁴ It is reasonable to expect that alcohols might undergo electro-oxidation by Rh porphyrins.

In this report, we show that Rh porphyrins can catalyze the electro-oxidation of aliphatic and benzyl alcohols at much lower overpotentials than with other metallocomplex-based catalysts. Several reaction properties such as substrate specificity and pH-dependence were examined, and a reaction mechanism is discussed based on these properties.

2,3,7,8,12,13,17,18-Octaethylporphyrinato rhodium(III) chloride ([Rh^{III}(OEP)(Cl)]) was synthesized as described in the literature¹⁹ with some modifications. The Rh porphyrins were adsorbed on carbon black by an evaporation-to-dryness method. The amount of Rh porphyrin was fixed at 30 µmol g_{carbon black}⁻¹. The activity of electrochemical alcohol oxidation was evaluated by hydro-dynamic voltammetry using a rotating disk electrode modified with a carbon-supported [Rh^{III}(OEP)(Cl)] ([Rh^{III}(OEP)(Cl)]/C²⁰). Electrochemical measurements were performed using this electrode in 1 M NaOH. The products of this reaction were examined by HPLC. Experimental details are described in ESI.[‡]

Fig. 1A shows voltammograms of [Rh^{III}(OEP)(Cl)]/C, which exhibit ethanol oxidation in a 1 M NaOH solution. Line (a) is a voltammogram of this catalyst under an argon atmosphere without ethanol. A clear Faradaic current was not observed. Upon the addition of ethanol (0.48 M), the oxidation current significantly increased (line b). The results clearly show that [Rh^{III}(OEP)(Cl)]/C catalyzes ethanol oxidation at low overpotentials. When the electrode was rotated at 3600 rpm, the current increased due to enhanced mass transfer of ethanol (line c). A further increase in the electrode rotation rate from 3600 rpm to 6400 rpm did not increase the oxidation current (line d). Above at least 3600 rpm, the current was limited by the kinetics of ethanol oxidation. The current controlled by the kinetic process reached 3.5 mA cm^{-2} at 0.55 V (vs. a reversible hydrogen electrode (RHE)). The results clearly indicate that carbon-supported [Rh^{III}(OEP)(Cl)] catalyzes ethanol oxidation.

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[‡] Electronic supplementary information (ESI) available: pH-dependence (Fig. S1), inhibitory effects of aldehydes and ketones (Fig. S2), a kinetic isotope effect (Fig. S3), and experimental details for the synthesis of Rh porphyrins, catalyst preparation, electrochemical measurements, and product analysis. See DOI: 10.1039/c2cc30888f



Fig. 1 (A) Voltammograms of Rh-OEP/C (a) in the absence of ethanol, (b) in the presence of ethanol (0.48 M), (c) in the presence of ethanol (0.48 M) with electrode rotation (3600 rpm), and (d) in the presence of ethanol (0.48 M) with electrode rotation (6400 rpm). (B) Voltammograms of Rh-OEP/C in the presence of alcohol (0.48 M) with electrode rotation (6400 rpm); (a) 2-propanol, (b) ethanol, (c) 1-propanol, and (d) methanol. Measurements were performed in a 1 M NaOH solution at 25 °C (scan rate = 10 mV s⁻¹) under an argon atmosphere.

The onset potential (*ca.* 0.28 V *vs.* RHE) was much lower than those with previous Ru complex- or Ni complex-based electrocatalysts (above 1.0 V *vs.* RHE).^{4,5} The onset potential was also much lower than those for O₂ electro-reduction by Pt catalysts (*ca.* 0.7 V–1.0 V *vs.* RHE). Thus, a combination of [Rh^{III}(OEP)(Cl)]/C-catalyzed alcohol oxidation and Pt-catalyzed O₂ reduction can generate electric power. This corresponds to the result that the oxidation of alcohols by O₂ proceeds rapidly when catalyzed by Rh porphyrin.¹⁴

Ethanol oxidation by [Rh^{III}(OEP)(Cl)]/C was also examined in neutral solutions as well as basic solutions by voltammetry. Ethanol oxidation sharply decreased with a decrease in pH. Below pH 12, oxidation current was hardly observed (Fig. S1, ESI‡). This strongly suggests that OH⁻ is required for ethanol oxidation.

Fig. 1B shows linear sweep voltammograms of the electrooxidation of several aliphatic alcohols by $[Rh^{III}(OEP)(CI)]/C$. The results showed that all of the alcohols tested here undergo electro-oxidation by $[Rh^{III}(OEP)(CI)]/C$ at low overpotentials. For all of these alcohols, an increase in the rate of electrode rotation from 3600 rpm to 6400 rpm did not affect alcohol oxidation, as observed in ethanol oxidation. The intrinsic activity of alcohol oxidation controls the current under these conditions. This activity significantly depends on the alcohol used. The current increased in the order 2-propanol (line a) > ethanol (line b) > 1-propanol (line c) \gg methanol (line d). While the oxidation of ethanol and 2-propanol gave high current, the oxidation of methanol gave only slight current.

To investigate the difference in activity according to alcohol used in detail, the oxidation of low-concentration (10 mM) alcohols by [Rh^{III}(OEP)(Cl)]/C was also examined. Fig. 2A shows the results. Interestingly, [Rh^{III}(OEP)(Cl)]/C exhibited significantly high activity toward 1-propanol (line c), while 1-propanol was much less reactive than 2-propanol at a higher concentration (0.48 M, Fig. 1B).

Fig. 3 shows the dependence of the oxidation current at 0.6 V on the concentrations of alcohols. The profile of 1-propanol is totally different from those of 2-propanol and ethanol. It exhibited a bell-shaped curve with a peak at 20 mM. This strongly suggests that the product of the reaction had a kind of inhibitory effect. Next, we examined inhibition of



Fig. 2 Voltammograms of Rh-OEP/C in the presence of alcohol (10 mM) with electrode rotation (6400 rpm); (a) 2-propanol, (b) ethanol, (c) 1-propanol, (d) methanol, (e) benzylalcohol, (f) 4-fluorobenzylalcohol, and (g) 4-methoxybenzylalcohol. Measurements were performed in a 1 M NaOH solution at 25 °C (scan rate = 10 mV s⁻¹) under an argon atmosphere.



Fig. 3 A plot of the oxidation current at 0.6 V vs. concentrations of (a) 2-propanol, (b) ethanol, and (c) 1-propanol. The conditions are the same as those in Fig. 2.

2-propanol oxidation by a possible product. The results clearly showed that propionaldehyde strongly inhibits 2-propanol oxidation even at a low concentration (1 mM), while acetone and acetaldehyde have mild effects (Fig. S2, ESI[‡]). The low activity of 1-propanol at high concentrations can be explained by the inhibitory effect of the product.

At low concentrations, the current reflects the intrinsic activity without inhibition by products. The oxidation current of methanol was also very low at 10 mM (Fig. 2A). The intrinsic activity of [Rh^{III}(OEP)(Cl)]/C toward methanol was low. The current increased in the order 1-propanol (line c) > 2-propanol (line a) > ethanol (line b) \gg methanol (line d). This order suggests two possibilities: one is that electron donation to α -carbon is favorable for this reaction and the other is that the presence of a hydrogen atom on β -carbon is key for this reaction.

Fig. S3 (ESI[‡]) shows a comparison of 2-propanol and 2-propanol-2-d₁. A large kinetic isotope effect is apparent. The rate-determining step involves the extraction of a hydrogen atom on the α -carbon.

Here, we discuss a possible reaction mechanism for alcohol oxidation. It has been reported that alcohol coordinates on a water-soluble Rh porphyrin.^{14,17} Alcohols should also coordinate on Rh porphyrins during the electro-oxidation of alcohols.

The coordinated alcohol (alkoxide in basic solutions) undergoes electrochemical oxidation. Since ethanol oxidation occurs only in basic solution (Fig. S1, ESI‡), the extraction of a hydrogen atom by OH⁻ is needed for alcohol oxidation. The kinetic isotope effect observed in Fig. S3 (ESI‡) indicates that the elimination of an α -hydrogen atom occurs in the rate-determining step. As well as the extraction of a hydrogen atom, electron transfer to the electrode *via* a Rh porphyrin molecule occurs to generate ketones or aldehydes. The generation of Rh(1) or Rh–H species has been observed in the oxidation of alcohols by O₂.¹⁴ It is unknown whether these species participate in the electro-oxidation of alcohols, since they would be easily oxidized by the electrode.

We also examined the electro-oxidation of benzyl alcohol derivatives. Since benzyl alcohols exhibit low solubility, the reactivity was examined at a low concentration (10 mM). The results are shown in Fig. 2B. Carbon-supported [Rh^{III}(OEP)(Cl)] also oxidized benzyl alcohols at low overpotentials. The reactivity significantly depended on the *p*-substituent. An electron-donating substituent was favorable. Liu *et al.* reported that the aerobic oxidation of benzyl alcohols containing electron-donating groups proceeds faster than that of benzyl alcohols containing electron-withdrawing groups.¹⁴ The order of overpotentials observed in electrochemical oxidation coincides with the order observed in alcohol oxidation by O_2 .

We determined the product of the oxidation of benzyl alcohol. The oxidation of benzyl alcohol gave benzoic acid (3.9 μ mol) as well as benzaldehyde (2.2 μ mol). The amount of electrons (20 μ mol) calculated from the amounts of benzaldehyde and benzoic acid almost coincides with the amount of electrons (23 μ mol) calculated from coulometry.²¹ The generation of carboxy acid is favorable in terms of fuel cell applications, but is undesirable with respect to the chemical conversion of alcohol to aldehyde. Regulation of the product is now being studied.

In conclusion, our results showed that carbon-supported [Rh^{III}(OEP)(Cl)] catalyzed the oxidation of aliphatic and benzyl alcohols at low overpotentials. The potential regions are much lower than those for alcohol oxidation by other metallocomplexes. The rate of alcohol oxidation significantly depends on the alcohol used. Among aliphatic alcohols, 2-propanol exhibited the highest activity at a high concentration (0.48 M), and methanol gave the lowest activity. 1-Propanol gave the highest activity at a low concentration (10 mM), while the activity was low at a high concentration. The unusual concentration-dependence of 1-propanol can be explained by the inhibition by the product. For the oxidation of benzyl alcohols, substrate specificity is correlated with electronic properties of substituents. The results of experiments on pH-dependence and a kinetic isotope effect suggest that alcohols coordinated on a Rh atom undergo the extraction of a hydrogen atom on the α -carbon atom that is attached to a hydroxy group. The oxidation of benzyl alcohols gave benzoic acid as well as benzaldehyde. Thus, the electro-oxidation of alcohols by

metallocomplexes at such low overpotentials might lead to the development of an anode catalyst for not only direct alcohol fuel cells, but also the electrochemical conversion of alcohols to ketones and aldehydes.

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- 20 It should be noted that this denotation is the initial state, since the axial ligand (Cl) and the oxidation number of the central metal during the catalytic cycle are unclear.
- 21 The difference should be attributed to the instability of benzaldehyde in the basic solution.