Electrochemical behavior of the oxo complex of Ru(IV), *trans*-$[RuCl(O)(py)_4]^+$, in both non-aqueous and aqueous solvents

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Abstract

The electrochemical behavior of *trans*-$[Ru^{IV}Cl(O)(py)_4]^+$, and that of its related complexes, *trans*-$[Ru^{III}Cl(OH)(py)_4]^+$ and *trans*-$[Ru^{II}Cl(H_2O)(py)_4]^+$, were investigated in both acetonitrile and aqueous solvents. The reduction process of *trans*-$[Ru^{IV}Cl(O)(py)_4]^+$ was an irreversible one; it converted into *trans*-$[Ru^{II}Cl(OH)(py)_4]^0$ in CH_3CN and *trans*-$[Ru^{II}Cl(H_2O)(py)_4]^+$ in aqueous solvent by a one-step two-electron reduction. The oxo complex undergoes a one-electron oxidation to give a reactive *trans*-$[Ru^{V}Cl(O)(py)_4]^{2+}$, which is the species capable of oxidizing organic substances.

Introduction

The complex of tetrakis(pyridine)ruthenium(IV) with a monooxygen ligand, *trans*-$[RuCl(O)(py)_4]^+$, is peculiar for the following reasons.

(i) The $(Ru^{IV}{=}O^{2-})$ entity of the oxo complex is generated by a rare reaction, in which a coordinated nitro (or nitrosyl) ligand in *trans*-$[RuCl(NO_2)(py)_4]$ (or *trans*-$[RuCl(NO)(py)_4]^{2+}$) is oxidized by NaClO (under basic conditions) to give the oxo complex of Ru(IV) [1–4]. Oxo complexes of Ru(IV), reported by other researchers, and some relevant to the present investigation, including those of Ru(V), have been synthesized by the oxidation of the corresponding aqua (or hydroxo) complexes with a lower formal oxidation state of ruthenium atom [5–17]. The oxygen source of each complex has been proved to be different. We assumed that such different processes exert effects upon the characteristics of the $(Ru^{IV}{=}O^{2-})$ entity. Actually, the former oxo complex, reported by us, can be prepared in a basic medium without decomposition of the entity [2], while the latter is generally unstable at basic conditions [12].

(ii) Another marked difference is the structural parameter. The former is the complex with the longest Ru–O(oxo) bond distance (1.862(8) Å) ever reported for the monooxygen ruthenium(IV) system [1, 2]. Available data of the latter case are within 1.739(2) and 1.765(5) Å [14, 18]. In the present work, the electrochemical behavior of *trans*-$[RuCl(O)(py)_4]^+$ is investigated in both aqueous and non-aqueous solvents, as the extension of a comparative study of the oxo complex of Ru(IV). An electrochemical study is essential to evaluate the characteristics of high-valent metal complexes, and to obtain fundamental knowledge for this type of research. A considerable difference can be observed between the electrochemical behavior of *trans*-$[RuCl(O)(py)_4]^+$ and that of others in the literature [5–10, 13–15, 19–25]: while the reported complex in aqueous solution exhibited a reversible two-step reduction, the present oxo complex undergoes an irreversible one-step two-electron reduction which results in the formation of *trans*-$[RuCl(OH)(py)_4]$ in CH_3CN and *trans*-$[RuCl(H_2O)(py)_4]^+$ in aqueous solvent as the final reduction species. The results clarify the mutual relations of the electrochemical behavior of *trans*-$[RuCl(O)(py)_4]^+$, *trans*-$[RuCl(OH)(py)_4]^+$ and *trans*-$[RuCl(OH_2)(py)_4]^+$ in both acetonitrile and aqueous solvents. The oxo complex in CH_3CN also undergoes a one-electron oxidation to give *trans*-$[Ru^{V}Cl(O)(py)_4]^{2+}$, which is the species capable of oxidizing organic substances.

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Experimental

Materials

All chemicals used for the present syntheses were described in a previous report [4]. Water used in electrochemical experiments was deionized and distilled with a Kinoshita Rika Co. KR-70-C type distillation apparatus. $HClO_4$, NaH_2PO_4, Na_2HPO_4 and NaOH used as supporting electrolyte (buffer salts) were of special grade purchased from Wako Chemical Co. and were used without further purification. Other chemicals were the same as those described in the previous report [4]. The oxo complexes and relevant complexes, *trans*-$[RuCl(O)(py)_4]ClO_4$, *trans*-$[RuCl(O)(py\text{-}4Me)_4]PF_6$, *trans*-$[RuCl(OH)(py)_4]ClO_4$ and *trans*-$[RuCl(H_2O)(py)_4]PF_6$, were prepared according to the methods described previously [26].

Measurements

All electrochemical measurements were carried out using the system which was described in the previous paper [4]. The working electrode of the measurements in aqueous solution was a glassy carbon disk electrode ($\phi = 3$ mm). The reference electrode in aqueous solution was a Ag/AgCl(KCl saturated) electrode, connected to the test solution through a salt bridge containing saturated KCl solution.

Results and discussion

Electrochemical behavior of trans-$[RuCl(O)(py)_4]^+$ in acetonitrile

Reduction process

Cyclic voltammograms (CV) of *trans*-$[RuCl(O)(py)_4]ClO_4$ in CH_3CN, with 0.1 mol dm^{-3} tetraethylammonium perchlorate (TEAP) as supporting electrolyte, are shown in Fig. 1. The CV of *trans*-$[RuCl(O)(py\text{-}4Me)_4]PF_6$ is very similar to that of *trans*-$[RuCl(O)(py)_4]ClO_4$ and is therefore not shown. Their electrochemical data, along with those of relevant complexes, are summarized in Table 1. Six waves (i–vi in Fig. 1) are observed in the potential region -1.5 to 1.6 V*. Three small oxidation waves

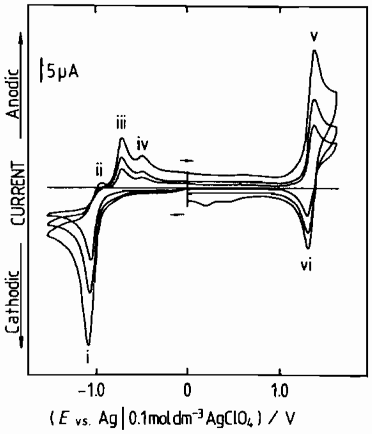

Fig. 1. Cyclic voltammograms of *trans*-$[RuCl(O)(py)_4]ClO_4$ (1.0 mmol dm^{-3}) in 0.1 mol dm^{-3} TEAP–CH_3CN on Pt-disk electrode ($\phi = 3$ mm) at 25 °C (scan rate: 50, 100, 200 mV s^{-1}).

(ii, iii and iv) are associated with the reduction wave i. This reduction wave was shown to be irreversible from the cyclic voltammograms measured at various scan rates: -0.99 V (50 mV s^{-1})~ -1.03 V (200 mV s^{-1}). The limiting current of normal pulse voltammograms (NPV) corresponding to wave i was diffusion-controlled, according to the plot of the limiting current against $t^{-1/2}$ (t: sampling time; 30, 50, 70 ms). The magnitude of the limiting currents of normal pulse voltammograms suggests that i is a two-electron reduction wave, by comparison with the known one-electron process. On the multiple scan at potential regions between -0.2 and -1.4 V, a new reduction wave vii appeared which is associated with the oxidation wave of iii (Fig. 2). The redox couple (iii and vii) was able to be identified as due to *trans*-$[RuCl(OH)(py)_4]^{+/0}$ by a comparison of authentic sample data (Table 1). Another small wave, iv at -0.5 V (Fig. 2), is always observed in the CV of *trans*-$[RuCl(O)(py)_4]^+$ (for both PF_6 or ClO_4 salt); it was ignored since it did not change during the bulk electrolysis described below.

Controlled potential electrolysis performed at -1.2 V indicated that *trans*-$[RuCl(O)(py)_4]ClO_4$ underwent 2e reduction to give *trans*-$[RuCl(OH)(py)_4]$. Figures 3, 4 and 5, which show the change of both hydrodynamic voltammograms with rotating disk electrode and CV with a stationary disk electrode, show that the reduction process of *trans*-$[RuCl(O)(py)_4]^+$ is not simple, and that at least two different reductions proceed successively during the electrolysis. Before the electrolysis, only cathodic cathodic current i (reduction wave of *trans*-$[Ru^{IV}Cl(O)(py)_4]^+$) is observed (a in Figs. 3 and 4). When the electrolysis was initiated, the cathodic current of i decreased and that of vii (reduction wave of *trans*-$[Ru^{III}$-

*At times, *trans*-$[RuCl(O)(py)_4]^+$ showed different cyclic voltammograms than those depicted in Fig. 1. A remarkable difference is observed in the coupled wave of i–ii, where the current height of ii is nearly the same as that of i (see Fig. 4(a), also see the Fig. depicted in a preliminary report [2]). In addition, iv of the previous work is observed as only a faint wave, compared to those of Figs. 1 and 2. Electrochemical investigation was carried out using the complex which showed the same CVs as that mentioned above. The results obtained were the same in each oxo complex of Ru(IV).

TABLE 1. Electrochemical data of oxo complexes of ruthenium(IV) and related complexes in acetonitrile solution[a]

Complex	Ep_c(IV/II)[b] (V)	Ep_a(V/IV)[c] (V)	$E_{1/2}$(III/II) (V)	$E_{1/2}$(IV/III) (V)
trans-[RuCl(O)(py)$_4$]ClO$_4$	−1.03	1.39		
trans-[RuCl(OH)(py)$_4$]ClO$_4$			−0.71	1.34
trans-[RuCl(H$_2$O)(py)$_4$]PF$_6$			0.25[d]	
trans-[RuCl(O)(py-4Me)$_4$]PF$_6$	−1.09	1.31		

[a]V vs. Ag/AgClO$_4$ (0.1 mol dm^{-3} in CH$_3$CN) at 25 °C. [b]Wave i in Fig. 1. [c]Wave v in Fig. 1. [d]Measured at −40 °C.

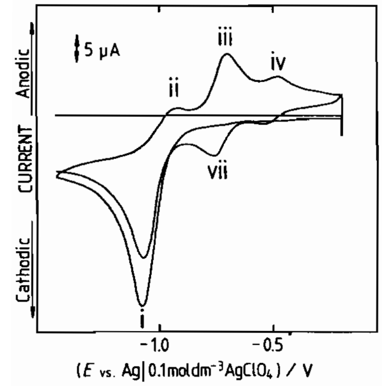

Fig. 2. Cyclic voltammograms of *trans*-[RuCl(O)(py)$_4$]ClO$_4$ on multiple scan between −0.2 and −1.4 V.

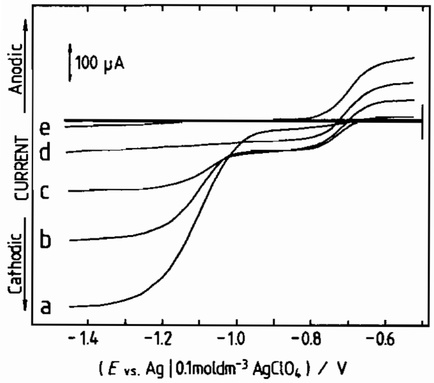

Fig. 3. Hydrodynamic voltammograms at a Pt rotating desk electrode (1600 rpm) monitoring the course of controlled-potential reduction (−1.2 V) of *trans*-[RuCl(O)(py)$_4$]ClO$_4$ (1.0 mmol dm^{-3}) in CH$_3$CN (0.1 mol dm^{-3} TEAP): a, prior to electrolysis; b, c, d, during electrolysis; e, at the end of electrolysis.

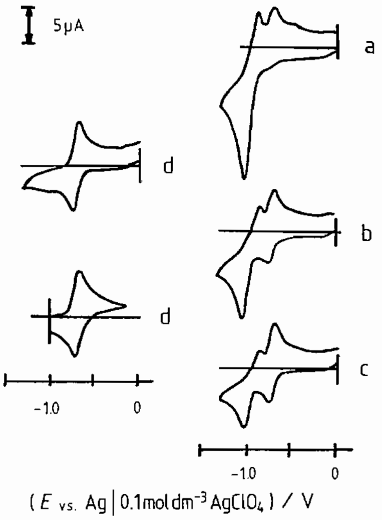

Fig. 4. Changes of cyclic voltammograms of *trans*-[RuCl(O)(py)$_4$]ClO$_4$ during the course of controlled-potential reduction at −1.2 V (in CH$_3$CN). Notations (a, b, c, d (cathodic scan), and d (anodic scan)) correspond to those described in Fig. 3.

Cl(OH)(py)$_4$]$^+$) developed gradually (b and c in Figs. 3, 4 and 5). In the continuous electrolysis, the cathodic current of i disappeared (d in Figs. 3 and 5), and further increasing of both the anodic current of iii (oxidation wave of *trans*-[Ru^{II}Cl(OH)(py)$_4$]^0) and its coupled cathodic current vii was found by the reductive scanning. In the final stage, only iii remained (e in Figs. 3 and 4): no cathodic current, neither i nor vii, is any longer detectable by the reductive scanning. (Note that the potential of the electrolysis (−1.2 V) is located more negative side than those of i and vii.) Nearly 2 moles of electrons per mole of [RuCl(O)(py)$_4$]$^+$ were consumed during the electrolysis.

This observation allows us to understand that, when *trans*-[Ru^{IV}Cl(O)(py)$_4$]$^+$ undergoes reduction, *trans*-[Ru^{III}Cl(OH)(py)$_4$]$^+$ is formed, prior to generation of *trans*-[Ru^{II}Cl(OH)(py)$_4$]^0, which is the final product of the reduction (eqn. (1)).

$$[Ru^{IV}Cl(O)(py)_4]^+ + H^+ + 2e^- \longrightarrow [Ru^{II}Cl(OH)(py)_4] \quad (1)$$

The origin of the H atom in *trans*-[RuCl(OH)(py)$_4$]$^+$ is presently unknown*. However, if we assume that

*The water content of the MeCN solvent, as determined by Karl Fisher titration, was about 10^{-3} mol dm^{-3} (10 times the concentration of the complex) [4].

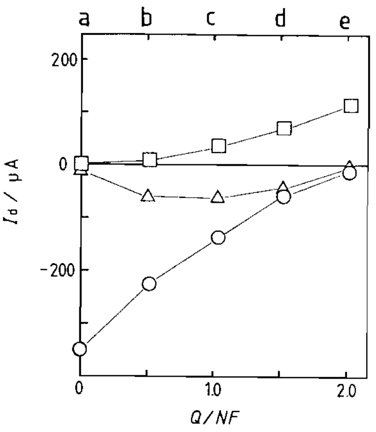

Fig. 5. I_d (estimated from Fig. 3) vs. Q/NF plot for the reduction of *trans*-[RuCl(O)(py)$_4$]ClO$_4$. ○: I_d at −1.4 V (this indicates a change of the sum of the amounts of *trans*-[Ru^{IV}Cl(O)(py)$_4$]$^+$ and *trans*-[Ru^{III}Cl(OH)(py)$_4$]$^+$ generated during the electrolysis); △: I_d at −0.9 V(this indicates a change of the amount of *trans*-[Ru^{III}-Cl(OH)(py)$_4$]$^+$ which is generated during the electrolysis); □: I_d at −0.5 V (this indicates a change of the amount of *trans*-[Ru^{II}Cl(OH)(py)$_4$]^0 which is generated during the electrolysis). The notations (a, b,...e) correspond to those described in Fig. 3.

the H atom is from an avoidable water of CH_3CN, the following two pathways ((a) and (b)) can be considered.

(a) *trans*-[Ru^{IV}Cl(O)(py)$_4$]$^+$ undergoes first a one-electron reduction; it gives *trans*-[Ru^{III}Cl(O)(py)$_4$]$^+$ (eqn. (2)) which will undergo a protonation to generate *trans*-[Ru^{III}Cl(OH)(py)$_4$]$^+$ (eqn. (3)).

$$[\mathrm{Ru^{IV}Cl(O)(py)_4}]^+ + e^- \longrightarrow [\mathrm{Ru^{III}Cl(O)(py)_4}] \quad (2)$$

$$[\mathrm{Ru^{III}Cl(O)(py)_4}] + \mathrm{H}^+ \longrightarrow [\mathrm{Ru^{III}Cl(OH)(py)_4}]^+ \quad (3)$$

The generated species, *trans*-[Ru^{III}Cl(OH)(py)$_4$]$^+$, undergoes a one-electron reduction to give *trans*-[Ru^{II}Cl(OH)(py)$_4$]^0 (eqn. (4)).

$$[\mathrm{Ru^{III}Cl(OH)(py)_4}]^+ + e^- \longrightarrow [\mathrm{Ru^{II}Cl(OH)(py)_4}] \quad (4)$$

(b) An alternative, however, is possible if we can assume that *trans*-[Ru^{IV}Cl(O)(py)$_4$]$^+$ undergoes a one-step two-electron reduction first at the surface of the electrode to give *trans*-[Ru^{II}Cl(O)(py)$_4$]$^-$ (eqn. (5)). The reduction species would be unstable chemically, and so it would rapidly undergo a protonation to give *trans*-[Ru^{II}Cl(OH)(py)$_4$]^0 (eqn. (6)).

$$[\mathrm{Ru^{IV}Cl(O)(py)_4}]^+ + 2e^- \longrightarrow [\mathrm{Ru^{II}Cl(O)(py)_4}]^- \quad (5)$$

$$[\mathrm{Ru^{II}Cl(O)(py)_4}]^- + \mathrm{H}^+ \longrightarrow [\mathrm{Ru^{II}Cl(OH)(py)_4}] \quad (6)$$

The generated species, *trans*-[Ru^{II}Cl(OH)(py)$_4$]^0, is also very reactive toward *trans*-[Ru^{IV}Cl(O)(py)$_4$]$^+$, and so the chemical reaction to give *trans*-[Ru^{III}-Cl(OH)(py)$_4$]$^+$ (eqn. (7)) will follow rapidly.

$$[\mathrm{Ru^{II}Cl(OH)(py)_4}] + [\mathrm{Ru^{IV}Cl(O)(py)_4}]^+ + \mathrm{H}^+ \longrightarrow 2[\mathrm{Ru^{III}Cl(OH)(py)_4}]^+ \quad (7)$$

A conproportionation reaction, similar to eqn. (7), has been found to occur in the reaction between *trans*-[RuCl(O)(py)$_4$]$^+$ and *trans*-[RuCl(H$_2$O)(py)$_4$] under the same conditions [4]. The reaction expressed in eqn. (7) will continue until [Ru^{IV}Cl(O)(py)$_4$]$^+$ is consumed completely. As the experiment of the controlled potential electrolysis shows (Figs. 3–5), a further one-electron reduction to give *trans*-[Ru^{II}-Cl(OH)(py)$_4$]^0, as a final product (eqn. (4)), occurs in the species of *trans*-[Ru^{III}Cl(OH)(py)$_4$]$^+$ which is accumulated by the conproportionation reaction (eqn. (7)).

It should be mentioned that the conproportionation reaction (eqn. (7)) is expected to occur only when the reduction of *trans*-[Ru^{IV}Cl(O)(py)$_4$]$^+$ takes place at higher potential values than those required for the oxidation of *trans*-[Ru^{II}Cl(OH)(py)$_4$]. This is, however, not the case, since the oxidation potential of *trans*-[Ru^{II}Cl(OH)(py)$_4$] (iii) is located at more positive potential than the reduction potential of *trans*-[Ru^{IV}Cl(O)(py)$_4$]$^+$ (i). Such a contradiction might be overcome by considering that an irreversible process is involved in wave i. As described earlier, the irreversible character of the reduction process of *trans*-[Ru^{IV}Cl(O)(py)$_4$]$^+$, which is due to a slow charge transfer, was proved by the observation that the peak potential of the reduction wave of i shifts when the scan rate is altered.

Oxidation process

In the oxidative scanning, CVs of *trans*-[Ru^{IV}-Cl(O)(py)$_4$]$^+$ showed that the redox couple (waves v and vi) appeared at 1.34 V (Fig. 1). The oxidation process (eqn. (8)) was firmly established to be a Nernstian one-electron process by the analysis of normal pulse voltammograms.

$$[\mathrm{Ru^{IV}Cl(O)(py)_4}]^+ \rightleftharpoons [\mathrm{Ru^{V}Cl(O)(py)_4}]^{2+} + e^- \quad (8)$$

When 2-propanol was added to the test solution, the values of both anodic and cathodic currents of the redox couple changed remarkably (Fig. 6); the anodic current increased as the cathodic current disappeared, and a new cathodic wave appeared at

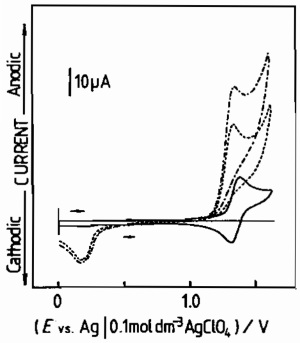

Fig. 6. Cyclic voltammograms of *trans*-$[RuCl(O)(py)_4]ClO_4$ in CH_3CN with 2-propanol. —— in the absence of 2-propanol, - - - in the presence of 2-propanol (42 mmol dm^{-3}), — · — in the presence of 2-propanol (84 mmol dm^{-3}).

TABLE 2. Electrochemical data of oxo complex of ruthenium(IV), hydroxo complex of ruthenium(III), and aqua complex of ruthenium(II) in aqueous solution (pH = 4.4)[a]

Complex	Ep_c (V)	Ep_a (V)
trans-$[RuCl(O)(py)_4]ClO_4$	0.20	0.28
trans-$[RuCl(OH)(py)_4]ClO_4$	0.22	0.29[b]
trans-$[RuCl(H_2O)(py)_4]PF_6$	0.22[b]	0.30

[a]V vs. $Ag/AgClO_4$, KCl(sat.). [b]These two steps are confirmed to be a reversible one-electron process by analysis of normal pulse voltammograms.

around 0.2 V. These results suggest that 2-propanol is oxidized by *trans*-$[Ru^VCl(O)(py)_4]^{2+}$ at the electrode surface during the electrochemical oxidation. An example using the oxo complex for the catalysis of the oxidation of benzyl alcohol has been reported recently [27].

Electrochemical behavior of trans-$[RuCl(O)(py)_4]^+$ in aqueous solvent

The electrochemical behavior of both *trans*-$[RuCl(OH)(py)_4]ClO_4$ and *trans*-$[RuCl(H_2O)(py)_4]PF_6$ was investigated first because their electrochemical behavior was expected to relate to that of *trans*-$[RuCl(O)(py)_4]ClO_4$. Their electrochemical data, measured at pH 4.4, are summarized in Table 2. Both hydroxo and aqua complexes exhibit the same cyclic voltammetrical profile; a redox couple appeared around 0.25 V ($E_{1/2}$), which was confirmed to be a reversible one-electron process from the cyclic voltammograms (ΔEp and ip_c/ip_a) and by the analysis of normal pulse voltammograms. The potential of the couple is pH-dependent; the plot of $E_{1/2}$ against the pH values of the test solution is linear over the pH region from 1.5 to 10.5. The slope of the line of the plots (59 mV/pH) indicates that a one-electron-one-protonation process (eqn. (9)) occurs in this pH region.

$$[Ru^{III}Cl(OH)(py)_4]^+ + H^+ + e^- \rightleftharpoons [Ru^{II}Cl(H_2O)(py)_4]^+ \quad (9)$$

The occurrence of a one-electron-one-protonation reaction (eqns. (10) and (11) was also confirmed for both *trans*-$[RuCl(OH)(py)_4]^+$ and *trans*-$[RuCl(H_2O)(py)_4]^+$ from the curve fittings which were calculated based on a known method [28].

$$[Ru^{III}Cl(H_2O)(py)_4]^{2+} \xrightleftharpoons{K(III)} [Ru^{III}Cl(OH)(py)_4]^+ + H^+ \quad (10)$$

$$[Ru^{II}Cl(H_2O)(py)_4]^+ \xrightleftharpoons{K(II)} [Ru^{II}Cl(OH)(py)_4] + H^+ \quad (11)$$

The values of K(III) (1.5×10^{-2} mol dm^{-3}) and K(II) (1.5×10^{-11} mol dm^{-3}) of these aqua complexes are almost the same as those reported for aqua complexes with polypyridine ligands [7–20, 21].

Under the same experimental conditions, however, *trans*-$[RuCl(O)(py)_4]^+$ shows different cyclic voltammograms from those of both *trans*-$[RuCl(OH)(py)_4]^+$ and *trans*-$[RuCl(H_2O)(py)_4]^+$ (Fig. 7): the redox couple ($E_{1/2}$ = 0.24 V, (Ep_c = 0.20, Ep_a = 0.28 V)) was not reversible (ip_a/ip_c was smaller than unity), while the potential is the same as that of *trans*-$[RuCl(OH)(py)_4]^+$. The values of both the peak current in the cyclic voltammogram and the limiting current in the normal pulse voltammogram, observed in the reduction wave at 0.20 V of *trans*-$[RuCl(O)(py)_4]^+$, were greater than those of *trans*-$[RuCl(OH)(py)_4]^+$, when the experiment were carried out at the same concentration. The irreversibility was also confirmed by the analysis of normal pulse voltammograms.

The irreversibility of the two-electron reduction wave of *trans*-$[RuCl(O)(py)_4]^+$ can be explained if

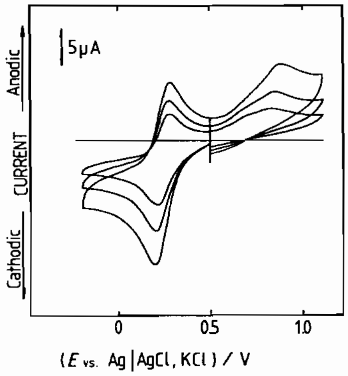

Fig. 7. Cyclic voltammograms of *trans*-$[RuCl(O)(py)_4]ClO_4$ (0.63 mmol dm^{-3}) in 0.1 mol dm^{-3} NaH_2PO_4 (aqueous solvent, pH = 4.40) with glassy carbon disk electrode at 25 °C (scan rate:50, 100, 200 mV s^{-1}).

the following two reductions occur successively at the same potential

$$[Ru^{IV}Cl(O)(py)_4]^+ + H^+ + e^- \longrightarrow [Ru^{III}Cl(OH)(py)_4]^+ \quad (12)$$

$$[Ru^{III}Cl(OH)(py)_4]^+ + H^+ + e^- \rightleftarrows [Ru^{II}Cl(H_2O)(py)_4]^+ \quad (9)$$

where *trans*-$[Ru^{IV}Cl(O)(py)_4]^+$ will undergo a one-electron reduction followed by a rapid chemical reaction to give *trans*-$[Ru^{III}Cl(OH)(py)_4]^+$. The generated species, *trans*-$[Ru^{III}Cl(OH)(py)_4]^+$, is reduced further to *trans*-$[Ru^{II}Cl(H_2O)(py)_4]^+$ reversibly, as described earlier (eqn. (9)). Thus the overall reduction is expressed by eqn. (13).

$$[Ru^{IV}Cl(O)(py)_4]^+ + 2H^+ + 2e^- \longrightarrow [Ru^{II}Cl(H_2O)(py)_4]^+ \quad (13)$$

Two-proton participation in eqn. (13) cannot be confirmed from the observation of pH dependence of the peak potential (as has been done in the case of eqn. (9)), since the method used above to estimate the number of protons in eqns. (10) and (11) is only applicable for a reversible process.

Some evidence which supports the occurring of both reactions (eqns. (12) and (9)) at the same potential is obtained from a controlled potential electrolysis of *trans*-$[Ru^{IV}Cl(O)(py)_4]^+$ which was carried out at pH 4.6. Figure 8 shows changes of the voltammograms with a rotating disk electrode and the plots of the convective diffusion currents (I_d) against the quantity of electricity of the electrolysis (Q/NF). In the early stage of the reduction of *trans*-$[RuCl(O)(py)_4]^+$ (Fig. 8, a–c), the cathodic I_d (of *trans*-$[RuCl(O)(py)_4]^+$) decreases without any oxidation wave appearing. Nearly 1 mole of electron was consumed per mole of *trans*-$[RuCl(O)(py)_4]^+$ until the voltammogram reached c. In the latter half

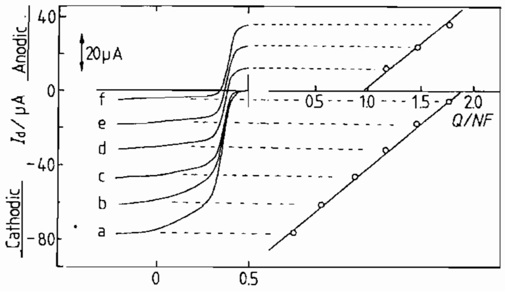

Fig. 8. Hydrodynamic voltammograms at Pt rotating disk electrode (1600 rpm) monitoring the course of the controlled-potential reduction (−0.1 V vs. Ag/AgCl·KCl) of *trans*-$[RuCl(O)(py)_4]ClO_4$ (1.0 mmol dm^{-3}) in buffered (pH = 4.59) solution: a, prior to electrolysis; b–e, during electrolysis; f, at the end of electrolysis.

stage, the reduction wave (of *trans*-$[RuCl(O)(py)_4]^+$) decreased further by the continuous electrolysis (Fig. 8, d–f), as the oxidation wave (of *trans*-$[RuCl(H_2O)(py)_4]^+$) appeared and increased. Totally, two moles of electrons were consumed per mole of the oxo complex to give the voltammogram f in Fig. 8. Such results can reasonably be understood by showing that the reduction to give *trans*-$[Ru^{III}Cl(OH)(py)_4]^+$ (eqn. (12)) occurred mainly at the steps of a–c, while the further reaction to afford *trans*-$[Ru^{II}Cl(H_2O)(py)_4]^+$ (eqn. (9)) proceeded at d–f. The results observed by coulometry are rather simple, compared to those found in acetonitrile solution (Figs. 3 and 4), due to a plentiful supply of protons, which take part in the reaction of the chemically generated species. It appears that essentially the same reduction occurs in *trans*-$[RuCl(O)(py)_4]^+$ of both aqueous and non-aqueous solvents.

The electrochemical behavior of *trans*-$[RuCl(O)(py)_4]^+$ in aqueous solution is unique, not like those of the reported complexes containing the same ($Ru^{IV}{=}O^{2-}$) unit, since the present oxo complex undergoes simultaneously the irreversible two-electron reduction at the same potential (0.20 V at pH = 4.4) throughout the pH region measured (pH 0.7–13). The majority of the oxo complexes of Ru(IV) reported by other researchers display two reversible one-electron redox couples at different potential regions [5, 6, 9, 10, 13, 19, 20, 22, 23, 29]. Some of the examples, however, have shown that the two reversible couples approach each other when the cyclic voltammetry is carried out at high pH conditions, and only a single reversible two-electron redox couple is observed at pH = 13 [7, 20, 21]. Another feature observed in the present oxo complex is that the reduction potential of the wave (*trans*-$[Ru^{IV}Cl(O)(py)_4]^+ + 2e^- \rightarrow$ *trans*-$[Ru^{II}Cl(O)(py)_4]^+$) appeared at a potential region negative compared with that of *trans*-$[Ru^{II}Cl_2(py)_4]^{+/0}$ where no oxo ligand exists. The redox potential is also close to that of *trans*-$[Ru^{III}Cl(OH)(py)_4]^{+/0}$, even to that of *trans*-$[Ru^{II}Cl(H_2O)(py)_4]^{2+/+}$. This is not unusual, since it is known that the value of potentials for the $(Ru^{IV}{=}O^{2-})^{2+}/(Ru^{III}{-}OH)^{2+}$ and $(Ru^{III}{-}OH)^{2+}/(Ru^{II}{-}OH_2)^{2+}$ couples are close in value (0.52 V for $(trpy)(bpy)Ru(O)^{2+} \rightarrow (trpy)(bpy)Ru(OH)^{2+}$ and 0.49 V for $(trpy)(bpy)Ru(OH)^{2+} \rightarrow (trpy)(bpy)Ru(OH_2)^{2+}$) [6, 20]. The lower reduction potential of oxo complexes is believed to be due to a proton loss and donation of the freed p–π oxygen electron density to the metal to form the Ru=O double bond [20, 30].

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References

1 Y. Yukawa, K. Aoyagi, M. Kurihara, K. Shirai, K. Shimizu, M. Mukaida, T. Takeuchi and H. Kakihana, *Chem. Lett.*, (1985) 283.
2 K. Aoyagi, Y. Yukawa, K. Shimizu, M. Mukaida, T. Takeuchi and H. Kakihana, *Bull. Chem. Soc. Jpn.*, *59* (1986) 1493.
3 H. Nishimura, H. Nagao, F. S. Howell, M. Mukaida and H. Kakihana, *Chem. Lett.*, (1988) 491.
4 H. Nagao, H. Nishimura, F. S. Howell, M. Mukaida and H. Kakihana, *Inorg. Chem.*, *29* (1990) 1693.
5 B. A. Moyer and T. J. Meyer, *J. Am. Chem. Soc.*, *100* (1978) 3601.
6 B. A. Moyer, M. S. Thompson and T. J. Meyer, *J. Am. Chem. Soc.*, *102* (1980) 2310.
7 S. Goswami, A. R. Chakravarty and A. Chakravorty, *J. Chem. Soc., Chem. Commun.*, (1982) 1288.
8 C.-M. Che, T.-W. Tang and C.-K. Poon, *J. Chem. Soc., Chem. Commun.*, (1984) 641.
9 A. A. Diamantis, W. R. Murphy, Jr. and T. J. Meyer, *Inorg. Chem.*, *23* (1984) 3230.
10 M. E. Marmion and K. J. Takeuchi, *J. Am. Chem. Soc.*, *110* (1988) 1472.
11 C.-M. Che, K.-Y. Wong and T. C. Mak, *J. Chem. Soc., Chem. Commun.*, (1985) 546.
12 L. Rocker, W. Kutuor, J. A. Gilbert, M. Simmons, R. W. Murry and T. J. Meyer, *Inorg. Chem.*, *24* (1985) 3784.
13 M. E. Marmion and K. J. Takeuchi, *J. Am. Chem. Soc.*, *108* (1986) 510.
14 C.-M. Che, T.-F. Lai and K.-Y. Wong, *Inorg. Chem.*, *26* (1987) 2289.
15 A. Liobet, P. Doppelt and T. J. Meyer, *Inorg. Chem.*, *27* (1988) 514.
16 V. W.-M. Yan, C.-M. Che and W.-T. Tang, *J. Chem. Soc., Chem. Commun.*, (1988) 100.
17 C.-M. Che, V. W.-M. Yan and T. C. W. Mak, *J. Am. Chem. Soc.*, *112* (1990) 2284.
18 C.-M. Che, W.-T. Tang, W.-T. Wong and T.-F. Lai, *J. Am. Chem. Soc.*, *111* (1989) 9048.
19 K. J. Takeuchi, G. J. Samuels, S. W. Gersten, J. A. Gilbert and T. J. Meyer, *Inorg. Chem.*, *22* (1983) 1407.
20 K. J. Takeuchi, M. S. Thompson, D. W. Pipes and T. J. Meyer, *Inorg. Chem.*, *23* (1984) 1845.
21 B. A. Moyer and T. J. Meyer, *Inorg. Chem.*, *20* (1981) 436.
22 C. D. Ellis, J. A. Gilbert, W. R. Murphy, Jr. and T. J. Meyer, *J. Am. Chem. Soc.*, *105* (1983) 4842.
23 G. E. Cabaniss, A. A. Diamantis, W. R. Murphy, Jr., R. W. Lintor and T. J. Meyer, *J. Am. Chem. Soc.*, *107* (1985) 1845.
24 R. A. Binstead and T. J. Meyer, *J. Am. Chem. Soc.*, *109* (1987) 3287.
25 J. C. Dobson and T. J. Meyer, *Inorg. Chem.*, *27* (1988) 3283.
26 H. Nagao, K. Aoyagi, Y. Yukawa, F. S. Howell, M. Mukaida and H. Kakihana, *Bull. Chem. Soc. Jpn.*, *60* (1987) 3247.
27 A. C. Dengel, A. M. El-Hendawy, W. P. Griffith, C. A. O'Mahoney and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, (1990) 737.
28 J. Heyrovsky, *Principles of Polarography*, Academic Press, New York, 1966, p. 161.
29 R. A. Binstead, B. A. Moyer, G. J. Samuels and T. J. Meyer, *J. Am. Chem., Soc.*, *103* (1981) 2897.
30 T. J. Meyer, *J. Electrochem. Soc., Rev. News*, *131* (1984) 221c.