Ligand Effect on the Electrochemical Oxidation of *trans*-$[Ru(NO_2)X(py)_4]^n$ (n=0 for X=NO_2, n=+ for X=NH_3). Reactivity of Coordinated Nitro (Ru^{II}–NO_2) to Give Monooxygen Moiety (Ru^{IV}=O) Depends on the Ambient Ligand (X)

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The electrochemical behavior of *trans*-$[Ru(NO_2)X(py)_4]^n$ (n=0 for X=NO_2 and n=+ for NH_3) in CH_3CN was investigated at various temperatures. *trans*-$[Ru^{II}(NO_2)_2(py)_4]$ undergoes a one-electron oxidation to give *trans*-$[Ru^{III}(NO_2)_2(py)_4]^+$. Rapid chemical reactions (nitro–nitrito isomerization, dimeric intermediate formation, and its disintegration) follow in succession until nearly equal amounts of *trans*-$[Ru(NO)(NO_2)(py)_4]^{2+}$ and *trans*-$[Ru^{II}(NO_2)(solvent)(py)_4]^+$ are generated as the final products. Essentially the same result was found in *trans*-$[Ru(NO_2)(NH_3)(py)_4]^+$. These results were quite different from those observed previously in the electrochemical oxidation of *trans*-$[Ru^{II}Cl(NO_2)(py)_4]$, where both *trans*-$[Ru^{IV}Cl(O)(py)_4]^+$ and *trans*-$[Ru(NO)Cl(py)_4]^{2+}$ were generated directly by one-electron oxidation. We conclude that the different electrochemical behavior between *trans*-$[RuCl(NO_2)(py)_4]$ and *trans*-$[Ru(NO_2)X(py)_4]^n$ (X=NO_2 and NH_3) stems primarily from a different disintegration mode of the above-mentioned dimeric intermediate species.

The study of high-valent ruthenium complexes with monooxygen ligands (Ru^n=O^{2-}, n=IV. V. VI) as active electrocatalysts is a matter of current interest.[1—11] While investigating redox characteristics of the nitrosyl complex of ruthenium(II), we have found a reaction in which either nitro complex of Ru(II) (*trans*-$[RuCl(NO_2)(py)_4]$) or nitrosyl complex of Ru(II) (*trans*-$[Ru(NO)Cl(py)_4]^{2+}$) is convertible to monooxygen complex of Ru(IV) (*trans*-$[RuCl(O)(py)_4]^+$).[12—16] Electrochemical investigation had shown that the reaction is initiated by the oxidation of *trans*-$[RuCl(NO_2)(py)_4]$ to *trans*-$[RuCl(NO_2)(py)_4]^+$; the oxidized species undergoes a facile isomerization to give nitrito complex of Ru(III) (*trans*-$[RuCl(ONO)(py)_4]^+$), which results in the formation of a transient dimeric intermediate species ($\{Cl(py)_4Ru\text{–}N(O)O\text{–}N(O)O\text{–}Ru(py)_4Cl\}^{2+}$).[14,16] Bonding rupture might occur in the intermediate to give three product species (*trans*-$[Ru(NO)Cl(py)_4]^{2+}$, *trans*-$[RuCl(O)(py)_4]^+$, and *trans*-$[RuCl(OH)(py)_4]^+$). When the oxidation of *trans*-$[RuCl(NO_2)(py)_4]$ (and also *trans*-$[Ru(NO)Cl(py)_4]^{2+}$) is carried out chemically under an basic condition, the reaction progresses, in principle, until all of the *trans*-$[RuCl(NO_2)(py)_4]$ is converted into *trans*-$[RuCl(O)(py)_4]^+$.[17]

We have also reported that such reactions to afford a monooxygen ligand occur selectively.[16] When *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$ undergoes two-electron oxidation, *trans*-$[Ru(ONO)(O)(py)_4]^+$ can be obtained, via the formation of *trans*-$[Ru(ONO)(OH)(py)_4]^+$, but without passing through the intermediate process that is observed in *trans*-$[RuCl(NO_2)(py)_4]$. A ^{15}N labeling experiment has proved that the original nitro nitrogen of *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$ is retained in *trans*-$[Ru(ONO)(O)(py)_4]^+$.[15] The source of the oxo ligand in the two complexes (*trans*-$[RuCl(O)(py)_4]^+$ and *trans*-$[Ru(ONO)(O)(py)_4]^+$) is therefore clearly different.

This paper reports that *trans*-$[Ru^{II}(NO_2)_2(py)_4]$ undergoes one-electron oxidation to give *trans*-$[Ru^{II}(NO_2)(solvent)(py)_4]^+$, via an intermediate process consisting of nitro and nitrito moieties. No complex containing (Ru^{IV}=O^{2-}) moiety was generated. The solvolysis product is, however, capable of changing to a precursor species, *trans*-$[Ru^{II}(NO_2)(H_2O)(py)_4]^+$, of the reported oxo complex of Ru(IV) with nitrito ligand, *trans*-$[Ru^{IV}(ONO)(O)(py)_4]^+$.[15,16] *trans*-$[Ru^{II}(NH_3)(NO_2)(py)_4]^+$ also shows essentially the same electrochemical behavior.

As described above, the oxidation reactions of *trans*-$[Ru(NO_2)X(py)_4]^n$ (n=0 for Cl, NO_2. n=+ for OH_2, NH_3) type of complexes depend strongly on the ambient ligand. For the illustration of the discrepancy due to X ligand, a new mechanistic pathway that is related partly to the previous oxidation scheme of *trans*-$[RuCl(NO_2)(py)_4]$ is proposed for the title complexes. Part of the present electrochemical results has been included in a preliminary report.[18]

Experimental

Material. All the complexes: *trans*-$[Ru(NO_2)_2(py)_4]$, *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$, *trans*-$[Ru(NO)(OH)(py)_4]^{2+}$, *trans*-$[Ru(NH_3)(H_2O)(py)_4]^+$, *trans*-$[Ru(NO)(NH_3)(py)_4]^{3+}$, and *trans*-$[Ru(NO_2)(NH_3)(py)_4]^+$ were prepared by the methods reported previously.[16,19,20] Other chemicals were obtained as reagent grade and were used without further purification, unless otherwise noted.

Electrochemical Measurements. All measurements were carried out using the same instruments and the same conditions as reported for *trans*-$[RuCl(NO_2)(py)_4]$:[16] Tetraethylammonium perchlorate (TEAP), used as the sup-

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porting electrolyte, was special polarographic grade (Nakai Chem. Co.). Acetonitrile solvent was carefully purified according to the procedure reported previously.[16] Measurements were performed on either a Husoh polarograph (Model 321) or a Husoh coulometer (Model 343B) instrument. A platinum-disk electrode (ϕ=2 mm), a platinum-wire counter electrode, and an SCE reference electrode separated from the solution by a bridge comprised the three-electrode system. All potentials were measured vs. SCE electrode and vs. the $Ag/AgClO_4$ couple as an internal standard.

Results and Discussion

Electrochemical Oxidation of *trans*-$[Ru(NO_2)_2(py)_4]$: *(I) Both trans-$[Ru(NO)(NO_2)(py)_4]^{2+}$ and trans-$[Ru(NO_2)(solv)(py)_4]^+$ are generated by one-electron oxidation at 25° C.* Cyclic voltammetry and coulometry were carried out at various temperatures, for comparison of oxidative behavior between *trans*-$[Ru(NO_2)_2(py)_4]$ and *trans*-$[RuCl(NO_2)(py)_4]$, including *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$, that had been investigated under the same conditions.[16] The results obtained allow us to discuss the influence of ambient ligand (X) on the reactivity of coordinated NO_2 in *trans*-$[Ru(NO_2)X(py)_4]^n$ (X=Cl, NO_2, OH_2). As shown in Fig. 1A and Table 1, the cyclic voltammograms of *trans*-$[Ru(NO_2)_2(py)_4]$ in CH_3CN at 25°C exhibit a single irreversible oxidation wave (i) at 0.52 V (E_{pa}, vs. $Ag/AgClO_4$ (0.1 mol dm^{-3} in CH_3CN)) within the potential region expected for the Ru(II)/Ru(III) oxidation. The electron transfer process is diffusion-controlled with $ip/\sqrt{v}$ constant over the range of scan rates used, 50—200 mV s^{-1}. On scan reversal, small reduction waves (ii) and (iii), associated with the irreversible oxidation wave (i), were observed at −0.17 and −0.98 V. The lack of any cathodic response and the appearance of new cathodic waves, (ii) and (iii), are evidently due to a rapid decomposition of the oxidized species, *trans*-$[Ru^{III}(NO_2)_2(py)_4]^+$. We concluded that both reduction waves (ii and iii) can be ascribed to *trans*-$[Ru(NO)(NO_2)(py)_4]^{2+/+/0}$, based on the observations to be described later.

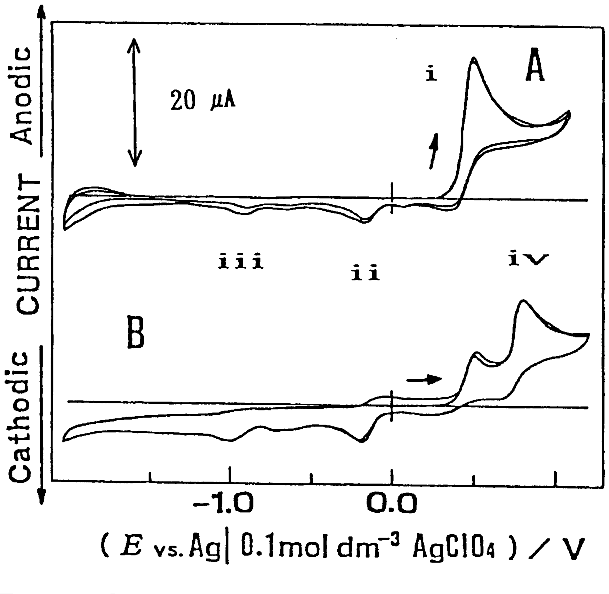

Fig. 1. Cyclic voltammograms of *trans*-$[Ru(NO_2)_2(py)_4]$ (0.08 mmol dm^{-3} in CH_3CN) at 25°C, stationary Pt electrode, Et_4NClO_4 (0.1 mol dm^{-3}): (A) before electrolysis (100 mV s^{-1}); (B) after controlled-potential electrolysis (n=0.65) at 0.52 V (100 mV s^{-1}). i, $[Ru(NO_2)_2(py)_4]^{+/0}$; ii, $[Ru(NO)(NO_2)(py)_4]^{2+/+}$; iii, $[Ru(NO)(NO_2)(py)_4]^{+/0}$; iv, $[Ru(NO_2)(solv)(py)_4]^{2+/+}$.

The controlled potential electrolysis of the solution beyond 0.55 V at 25°C (n=1 by coulometry, Table 1) showed that the shapes of the two waves (ii) and (iii) developed as the electrolysis progressed. We assigned those waves as due to *trans*-$[Ru(NO)(NO_2)(py)_4]^{2+/+/0}$ (See later). The current height examination by normal pulse voltammetry showed that nearly one mole quantity of *trans*-$[Ru(NO)(NO_2)(py)_4]^{2+}$ was generated from 2 moles of *trans*-$[Ru(NO_2)_2(py)_4]$. The oxidation wave which appeared at −0.10 V is coupled to the reduction wave (ii) at −0.17 V.

A further new anodic wave ((iv) in Fig. 1B, E_{pa}=0.79 V) appeared, and it developed during the period of the electrolysis. The potential of the second new wave (iv) is the same value as that measured for the authentic sample of *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$ in CH_3CN solvent at 25°C. Since aqua complexes of Ru(II) undergo a facile solvation in CH_3CN solvent,[21] the wave ((iv) in Fig. 1B, E_{pa}=0.79 V) is reasonably explained as that of *trans*-$[Ru(NO_2)(CH_3CN)(py)_4]^+$. (Our initial report on this wave,[16,18] as that of *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$, is thought to be a mis-assignment,[22] although exact data of the complex are still not available because it is difficult to synthesize).

The results observed in both cyclic voltammetry and coulometry were clearly different from those in the electrochemical oxidation of *trans*-$[Ru^{II}Cl(NO_2)(py)_4]$ (Scheme 1),[15,16] in which *trans*-$[Ru^{IV}Cl(O)(py)_4]^+$ is generated directly by one-electron oxidation, along with *trans*-$[Ru^{II}Cl(OH)(py)_4]^+$ and *trans*-$[Ru^{II}(NO^+)Cl(py)_4]^{2+}$. In the present work, however, no wave

$$2[Ru^{II}Cl(NO_2)(py)_4] \rightarrow 2[Ru^{III}Cl(NO_2)(py)_4]^+ + 2e^- \quad (1)$$

$$2[Ru^{III}Cl(NO_2)(py)_4]^+ \rightleftarrows [Ru^{III}Cl(NO_2)(py)_4]^+ + [Ru^{III}Cl(ONO)(py)_4]^+ \quad (2)$$

$$[Ru^{III}Cl(NO_2)(py)_4]^+ + [Ru^{III}Cl(ONO)(py)_4]^+ \rightarrow \{(py)_4ClRuN(O)O\text{-}N(O)ORuCl(py)_4\}^{2+} \quad (3)$$

$$\rightarrow [Ru^{II}(NO^+)Cl(py)_4]^{2+} + 1/2[RuCl(O)(py)_4]^+ + 1/2[RuCl(OH)(py)_4]^+ + NO_2^- \quad (4)$$

Scheme 1.

Table 1. Electrochemical Data of *trans*-$[Ru(NO_2)_2(py)_4]$ and Related Species That Were Generated by the Oxidation of the Dinitro Complex of Ru(II)

Complex	E/V		n (Q/NF)
	at 25°C	at −40°C	
trans-$[Ru(NO_2)_2(py)_4]$	$0.52^{c)}$	$0.52^{c)}$	1.0 (25°C) 1.3 (−40°C)
trans-$[Ru(ONO)(NO_2)(py)_4]^{+\ a)}$		$-0.05^{d)}$	
trans-$[Ru(ONO)_2(py)_4]^{+\ a)}$		$0.34^{d)}$	
trans-$[Ru(NO_2)(ONO_2)(py)_4]^{a)}$		$0.06^{e)}$	
trans-$[Ru(NO)(NO_2)(py)_4]^{2+\ b)}$	$-0.17^{e)}$ $-0.98^{d)}$	$-0.17^{e)}$ $-0.99^{d)}$	
trans-$[Ru(NO)(OH)(py)_4]^{2+}$	$-0.69^{d)}$		
trans-$[Ru(NO_2)(CH_3CN)(py)_4]^{+}$	$0.79^{c)}$		

a) Tentatively assigned. b) The species undergoes the decomposition to give *trans*-$[Ru(NO)(OH)(py)_4]^{2+}$. c) E_{pa}. d) E_{pc}. e) $E_{1/2}$.

which indicates the formation of $(Ru^{IV}{=}O^{2-})$ moiety can be observed.

Regardless of the different results for *trans*-$[Ru^{II}(NO_2)_2(py)_4]$ and for *trans*-$[Ru^{II}Cl(NO_2)(py)_4]$, we can assume that the generation of the nitrosyl species (waves ii and iii, *trans*-$[Ru(NO)(NO_2)(py)_4]^{2+}$) is informative for understanding that the electrochemical oxidation of *trans*-$[Ru(NO_2)_2(py)_4]$ does occur through the dimeric intermediate process described in Scheme 1, Eq. 3. Based on this assumption, the formation of either *trans*-$[Ru(NO)(NO_2)(py)_4]^{2+}$ or *trans*-$[Ru(NO_2)(CH_3CN)(py)_4]^{+}$ can easily be explained by an oxidation process which is similar to that proposed for *trans*-$[RuCl(NO_2)(py)_4]$ (Scheme 1). In conjunction with the reaction sequences from Eqs. 1, 2, and 3 (Scheme 1), a new Scheme 2 can be proposed for the oxidation process of *trans*-$[Ru(NO_2)_2(py)_4]$. Eqs. 5, 6, and 7 (Scheme 2) are virtually the same as Eqs. 1, 2, and 3 in Scheme 1. When the dimeric intermediate described in Eq. 7 (Scheme 2) disintegrates at (i) and (ii) (see Figure in Ref. 23), the conversion reaction proceeds through Eqs. 1, 2, 3, and 4 (Scheme 1), while Eqs. 5, 6, 7, 8, and 9 (Scheme 2) can be assumed to occur when the bonds break at (i) and (iii). Some evidence which supports the generation of the $(O_2NORu^{II}\text{–})^{+}$ species in Eq. 8 (Scheme 2) (*trans*-$[Ru(NO_2)(ONO_2)(py)_4]$) could be observed in the low temperature experiment (See (*II*); the experiment at −40°C). The disintegration species, *trans*-$[Ru(NO_2)(ONO_2)(py)_4]$, will decompose rapidly to give a solvolized species, *trans*-$[Ru(NO_2)(CH_3CN)(py)_4]^{+}$, under the same conditions: Previous work on the oxidation of *cis*-$[RuCl(NO_2)(bpy)_2]$ has proved that this solvolysis actually occurs.[24)]

$$2(\text{-}Ru^{II}NO_2)^{+} \rightarrow 2(\text{-}Ru^{III}NO_2)^{2+} + 2e^{-} \qquad (5)$$

$$2(\text{-}Ru^{III}NO_2)^{2+} \rightleftarrows (\text{-}Ru^{III}NO_2)^{2+} + (\text{-}Ru^{III}ONO)^{2+} \qquad (6)$$

$$\rightarrow \{\text{-}RuNO(O)N(O)ORu\text{-}\}^{4+} \qquad (7)$$

$$\rightarrow (\text{-}Ru^{III}NO^{0})^{3+} + (O_2NORu^{II}\text{-})^{+} \qquad (8)$$

$$\rightarrow (\text{-}Ru^{II}NO^{+})^{3+} + (\text{solv-}Ru^{II}\text{-})^{2+} + NO_3^{-} \qquad (9)$$

(both pyridine ligands and one NO_2^{-} ligand, which do not undergo chemical reactions, are omitted for clarity)
Scheme 2.

Another species, $(\text{-}Ru^{II}NO^{+})^{3+}$ in Eq. 9 (Scheme 2) (*trans*-$[Ru(NO)(NO_2)(py)_4]^{2+}$), was indicated to exist by the following observation: The cyclic voltammogram of the electrolysed solution described above was measured again after the solution was kept for 12 h; the waves (−0.17 (ii) and −0.98 V (iii)) that were assigned to those of *trans*-$[Ru(NO)(NO_2)(py)_4]^{2+/+/0}$ disappeared and, instead of these waves, a new intense wave was formed at −0.69 V. The potential value of the new wave agrees well with that of the known *trans*-$[Ru(NO)(OH)(py)_4]^{2+}$.[20)] The cyclic voltammogram of *trans*-$[Ru(NO)(OH)(py)_4]^{2+}$ is characteristic in its shape, because the complex undergoes only one-electron reduction at the site of $(Ru^{II}NO^{+})^{3+}$ moiety in the measurable potential region, as reported previously,[20)] while the analogue $\{RuNO\}^{6}$ type of complexes exhibit an additional one-electron reduction to generate $(RuNO)^{+}$ moiety.[25—29)]

The change observed above in cyclic voltammograms can best be explained as indicating that *trans*-$[Ru(NO)(NO_2)(py)_4]^{2+}$ is decomposed gradually to give a *trans*-$[Ru(NO)(OH)(py)_4]^{2+}$ species, which is the most stable complex with regard to a substitution of the ligand trans to nitrosyl, under the conditions. The source of the OH ligand in *trans*-$[Ru(NO)(OH)(py)_4]^{2+}$ is expected to come from an impurity water of the CH_3CN solvent.[30)] All our efforts to synthesize a nitrosyl complex that has a π-acceptor ligand (such as the nitro) at the trans position of a nitrosyl (*trans*-$[Ru(NO)(NO_2)(py)_4]^{2+}$) have so far been unsuccessful.

(II) Further species are generated at low temperature (ca. −40°C). The cyclic voltammetry of *trans*-$[Ru(NO_2)_2(py)_4]$ was also carried out near −40°C. The oxidation wave (i) due to $[Ru(NO_2)_2(py)_4]^{0/+}$

(observed at 0.52 V (E_{pa}) in the 25°C experiment) was still irreversible even at this low temperature (Fig. 2).

In addition to the waves (−0.17 and −0.98 V in Fig. 1A) due to $[Ru(NO)(NO_2)(py)_4]^{2+/+/0}$, small new peaks were observed at about 0.34 and −0.05 V (both E_{pc}). This observation can be understood if a nitro–nitrito rearrangement occurs at (Ru^{III}–NO_2) moiety: Such isomerization was actually found in the electrochemical oxidation of both *trans*-$[RuCl(NO_2)(py)_4]$ and *cis*-$[RuCl(NO_2)(bpy)_2]$.[16,31] Thus, both peaks can best be explained as due to the isomerized nitrito species, $[Ru(NO_2)(ONO)(py)_4]^{+/0}$ and $[Ru(ONO)_2(py)_4]^{+/0}$, which are essential species for the intermediate process (Eqs. 6, and 7 in Scheme 2). It was difficult to determine unambiguously which species gave rise to those peaks, but the reduction of $[Ru(NO_2)(ONO)(py)_4]^+$ is likely to occur initially.

The nitro group is known to act with a metal atom as a ligand that coordinates by both σ-donor and π-acceptor abilities. As the π-bonding nature between nitro ligand and metal is reduced when the formal oxidation state of a central metal increases, the Ru–N(nitro) bond is weakened and thus an electron-rich oxygen atom will come to prefer to bind with the higher-valent form of the ruthenium atom.

A further small coupled wave (iii), which was tentatively assigned to $[Ru(NO_2)(O_2NO)(py)_4]^{0/+}$ in Eq. 8 (Scheme 2), appeared at 0.06 V ($E_{1/2}$) when the electrolysis was performed at low temperature. If we assume that both reactions, the formation of a transient intermediate (Eq. 7 in Scheme 2) and the decomposition of $[Ru^{II}(NO_2)(O_2NO)(py)_4]$ species (from Eq. 8 to Eq. 9 in Scheme 2), are suppressed at the low temperature, the following five species would be found in the progression from Eq. 5 to Eq. 8 in Scheme 2: $[Ru^{III}(NO_2)_2(py)_4]^+$, $[Ru^{III}(NO_2)(ONO)(py)_4]^+$, $[Ru^{III}(ONO)_2(py)_4]^+$, $[Ru^{II}(NO_2)(O_2NO)(py)_4]$, and $[Ru(NO)(NO_2)(py)_4]^{2+}$. Actually, we were able to find the same number of species generated at low temperature (Table 1). Since $[Ru^{II}(NO_2)(O_2NO)(py)_4]$ can exist for only a short lifetime, *trans*-$[Ru^{II}(NO_2)(solv)(py)_4]^+$ is detected as its decomposition product when the experiment is carried out at room temperature.

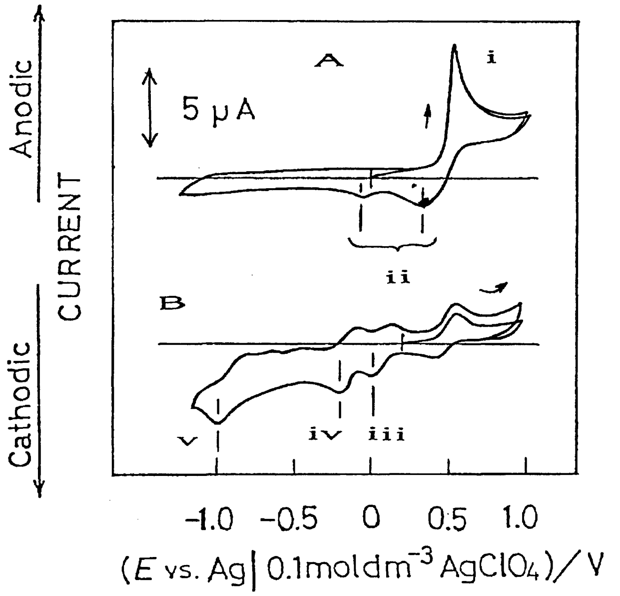

Fig. 2. Cyclic voltammograms of *trans*-$[Ru(NO_2)_2(py)_4]$ (1 mmol dm^{-3}) in CH_3CN at low temperature (ca. −40°C) (100 mV s^{-1}): (A) voltammograms prior to electrolysis; (B) voltammograms at the stage after partial electrolysis ($n = 0.7$). i, $[Ru(NO_2)_2(py)_4]^{+/0}$; ii, $[Ru(NO_2)(ONO)(py)_4]^{+/0}$ and $[Ru(ONO)_2(py)_4]^{+/0}$; iii, $[Ru(NO_2)(ONO_2)(py)_4]^{+/0}$; iv and v, $[Ru(NO)(NO_2)(py)_4]^{3+/2+/0}$.

Electrochemical Oxidation of *trans*-$[Ru(NO_2)(NH_3)(py)_4]^+$. The analogous nitro complex of Ru(II), *trans*-$[Ru(NO_2)(NH_3)(py)_4]^+$, shows essentially the same electrochemical behavior as that of *trans*-$[Ru(NO_2)_2(py)_4]$ over the region from 25°C to −40°C. It undergoes a 1-electron oxidation at 25°C as shown in Table 2 and Fig. 3. The one-electron oxidation of *trans*-$[Ru(NO_2)(NH_3)(py)_4]^+$ ((i), $E_{pa}=0.57$ V) gave two species as the final oxidation products. One set of reduction waves, appearing at 0.08 V ((ii), $E_{1/2}$) and −0.76 V ((iii), E_{pc}), had the same values as those reported in *trans*-$[Ru(NO)(NH_3)(py)_4]^{3+}$.[20] Another oxidation wave can be observed at 0.82 V ((v), E_{pa}): This is the same potential as that of the authentic sample of *trans*-$[Ru(NH_3)(H_2O)(py)_4]^+$ measured at 25°C in CH_3CN solvent. As described earlier in the characterization of the wave (iv) of *trans*-$[Ru(NO_2)(CH_3CN)(py)_4]^+$ (Table 1 and Fig. 1), we assume again that the wave at 0.82 V can be ascribed to the solvation species of *trans*-$[Ru(NH_3)(H_2O)(py)_4]^+$, *trans*-$[Ru(NH_3)(CH_3CN)(py)_4]^+$, not to that of *trans*-$[Ru(NH_3)(H_2O)(py)_4]^+$.

During the exhaustive electrolysis at low temperature, a wave which was best assigned to $[Ru(O_2NO)(NH_3)(py)_4]^+$ could be observed at 0.38 V (the wave is not shown in Fig. 3), in addition to the waves of $[Ru(NO)(NH_3)(py)_4]^{3+/2+/+}$ ($E_{1/2}=0.05$ V and $E_{pc}=-0.79$ V).

While the experiment carried out at room temperature showed that the one-electron oxidation reaction occurred exclusively, the electrolysis at −40°C indicated that a nearly 1.3-electron oxidation reaction is operating (see Table 1). The different number of electrons released at different temperatures (25°C and −40°C) can be explained if the oxidation of the short-lived $[Ru^{II}(NO_2)(ONO_2)(py)_4]$ into $[Ru^{III}(NO_2)(ONO_2)(py)_4]^+$ occurs partly at the low temperature. Another explanation is also possible if we assume that the dimeric intermediate is decomposed to give an oxo complex of Ru(IV), in the same way as in Eqs. 3, and 4 (Scheme 1); for this a re-oxidation pathway of the generated hydroxo

Table 2. Electrochemical Data of *trans*-$[Ru(NO_2)(NH_3)(py)_4]ClO_4$ and Related Species That are Generated by the Oxidation of the Ammine–Nitro Complex of Ru(II)

Complex	*E*/V at 25°C	*E*/V at −40°C	*n* (*Q*/*NF*)
trans-$[Ru(NO_2)(NH_3)(py)_4]^+$	0.57[b)]	0.57[b)]	1.0 (25°C) 1.3 (−40°C)
trans-$[Ru(ONO)(NH_3)(py)_4]^+$ [a)]		0.25[c)]	
trans-$[Ru(ONO_2)(NH_3)(py)_4]^+$ [a)]		0.38[d)]	
trans-$[Ru(NO)(NH_3)(py)_4]^{3+}$	0.08[d)]	0.05[d)]	
	−0.76[c)]	−0.79[c)]	
trans-$[Ru(CH_3CN)(NH_3)(py)_4]^{2+}$	0.82[b)]		

a) Tentatively assigned. b) E_{pa}. c) E_{pc}. d) $E_{1/2}$.

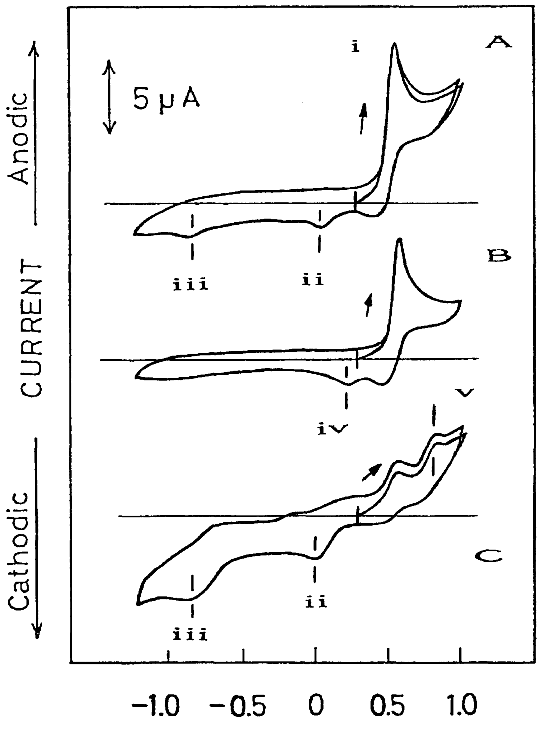

Fig. 3. Cyclic voltammograms of *trans*-$[Ru(NO_2)(NH_3)(py)_4]ClO_4$ (1 mmol dm^{-3}) in CH_3CN at 25°C and −40°C (stationary Pt electrode), Et_4NClO_4 (0.1 mol dm^{-3}): (A) at 25°C, before electrolysis (100 mV s^{-1}); (B) at −40°C, before electrolysis (100 mV s^{-1}); (C) at 25°C, after controlled potential electrolysis (n=0.8) at 0.55 V (100 mV s^{-1}). i, $[Ru(NO_2)(NH_3)(py)_4]^{2+/+}$; ii, $[Ru(NO)(NH_3)(py)_4]^{3+/2+}$; iii, $[Ru(NO)(NH_3)(py)_4]^{2+/+}$; iv, $[Ru(ONO)(NH_3)(py)_4]^{2+/+}$; v, $[Ru(NH_3)(solv)(py)_4]^{3+/2+}$.

complex of Ru(II) is needed.[15,16] However, no evidence which supports such an oxo complex formation reaction is presently available.

Ligand Effect due to the Ambient Ligands. The oxidation reactions of *trans*-nitrotetrakis(pyridine) complexes of Ru(II), *trans*-$[Ru(NO_2)X(py)_4]^n$, can be divided into three categories, based on the conversion pathways which depend on whether the X ligands (Cl, H_2O, NO_2, NH_3) exist trans to nitro ligands: Scheme 1 for *trans*-$[Ru(NO_2)Cl(py)_4]$,[16] Scheme 2 for *trans*-$[Ru(NO_2)X(py)_4]^n$ (X=NO_2, NH_3), and Scheme 3 for *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$ as described above.[16]

$$[(H_2O)(py)_4Ru^{II}(NO_2)]^+ \rightarrow [(HO)(py)_4Ru^{III}(NO_2)]^+ + e^- + H^+ \quad (10)$$

$$[(HO)(py)_4Ru^{III}(NO_2)]^+ \rightarrow [(HO)(py)_4Ru^{III}(ONO)]^+ \quad (11)$$

$$[(HO)(py)_4Ru^{III}(ONO)]^+ \rightarrow [(O)(py)_4Ru^{IV}(ONO)]^+ + e^- + H^+ \quad (12)$$

Scheme 3.

Schemes 1 and 2 both involve the same type dimeric intermediate species ($\{X-(py)_4Ru-NO(O)N(O)ORu-(py)_4-X\}^{2+}$), but their net processes are quite different: While *trans*-$[RuCl(NO_2)(py)_4]$ undergoes one-electron oxidation to produce directly *trans*-$[RuCl(O)(py)_4]^+$, whose oxygen atom comes from original nitro ligand (Eqs. 1, 2, 3, and 4 in Scheme 1), *trans*-$[Ru(NO_2)_2(py)_4]$ gives *trans*-$[Ru(NO_2)(CH_3CN)(py)_4]^+$, along with *trans*-$[Ru(NO)(NO_2)(py)_4]^{2+}$ (Eqs. 7, 8, and 9 in Scheme 2), under the same conditions. The solvolysis product generated in Scheme 2, *trans*-$[Ru(NO_2)(CH_3CN)(py)_4]^+$, can easily be changed in aqueous solution to *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$, a precursor species of *trans*-$[Ru(ONO)(O)(py)_4]^+$.[16] Chemically reversible interconversion between ($Ru^{II}-OH_2$) and ($Ru^{IV}=O^{2-}$) moieties, via ($Ru^{III}-OH^-$), has been investigated in detail.[32] Synthetic efforts to obtain the complex with ($Ru^{IV}=O^{2-}$) moiety from the dinitro complex of Ru(II), by chemical oxidation, are in progress.

We conclude that the difference observed in the oxidative behavior of *trans*-$[Ru(NO_2)X(py)_4]$ (X=Cl, NO_2, NH_3 (Schemes 1 and 2)) stems primarily from the different disintegration modes of the dimeric intermediate species. As described earlier, the existence of NO_2 (or NH_3) at the terminal position of the intermediate species affects the desintegration mode so as to give a final product with a lower oxidation state, while a Cl ligand allows a transient "$(Cl–Ru–O)^+$" moiety with a higher oxidation state to be generated[14,16] The ligand effect, which allows such different disintegration modes of intermediates, is a problem for further study.

Another nitro complex of Ru(II) with aqua ligand (*trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$) does not form such an intermediate, at least in a chemical oxidation, though occurrence of a nitro–nitrito isomerization was suggested when *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$ undergoes an electrochemical one-electron oxidation.[33]

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17) See Scheme 1 (Eqs. 1, 2, 3, and 4): $[Ru(NO)Cl(py)_4]^{2+}$ generated in Eq. 4 can be converted to the original $[RuCl(NO_2)(py)_4]$, on the basis of the well-known nitro–nitrosyl reactions:[19,34]

$$[Ru(NO)Cl(py)_4]^{2+} + 2OH^- \rightarrow [RuCl(NO_2)(py)_4] + H_2O$$

The resultant nitro complex undergoes again the oxidation in Eq. 1. Then, the oxidized species undergoes the subsequent chemical reactions, Eqs. 1, 2, 3, and 4, to give $[RuCl(O)(py)_4]^+$.[16] Another product, $[RuCl(OH)(py)_4]^+$ in Eq. 4, is also convertible to $[RuCl(O)(py)_4]^+$ under the same conditions.[35,36]

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22) The redox potential data of *trans*-$[RuCl(H_2O)(py)_4]^+$ is obtainable without a solvation, even in CH_3CN solvent, when the experiment is carried out at a low temperature (−40°C);[16] $[RuCl(H_2O)(py)_4]^{2+/+}$ exhibited the oxidation wave at 0.25 V, but this value moved to 0.50 V when the same experiment was carried out at 25°C. The potential value measured at 25°C is the same as that of an authentic sample of *trans*-$[RuCl(CH_3CN)(py)_4]^+$.[16] No such temperature dependence is detected in *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$, suggesting that the solvolysis by CH_3CN solvent occurs in *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$ in a moment, even at this low temperature.

23) (Fig. 4 quoted from Ref. 16).

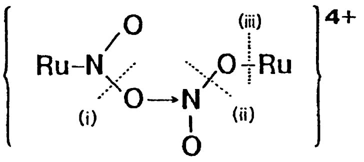

Fig. 4.

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