Inorg. Chem. **1990**, *29*, 1693–1700 **1693**

Contribution from the Department of Chemistry, Faculty of Science and Technology,
Sophia University, Kioi-cho 7-1, Chiyoda-ku, Tokyo, Japan 102

Selective Formation of Ruthenium(IV) Complexes with a Monooxygen Ligand: *trans*-[RuX(O)(py)$_4$]$^+$ (X = Cl, ONO)

Hirotaka Nagao, Hisatoshi Nishimura, Yoshiko Kitanaka, F. Scott Howell, Masao Mukaida,* and Hidetake Kakihana

Received October 25, 1989

trans-[RuCl(NO$_2$)(py)$_4$] is oxidized chemically to give *trans*-[RuCl(O)(py)$_4$]$^+$, while *trans*-[Ru(NO$_2$)(H$_2$O)(py)$_4$]$^+$ yields the analogous *trans*-[Ru(ONO)(O)(py)$_4$]$^+$ with retention of the nitro nitrogen. The origins of the oxygen ligand in each complex clearly differ. Electrochemical oxidation was also utilized to investigate the following chemical reaction processes: *trans*-[RuCl(NO$_2$)(py)$_4$] generates, at 25 °C, three species, *trans*-[RuCl(NO)(py)$_4$]$^{2+}$, *trans*-[RuCl(OH)(py)$_4$]$^+$, and *trans*-[RuCl(O)(py)$_4$]$^+$, while 1.25 mol of electrons are released per mole of *trans*-[RuCl(NO$_2$)(py)$_4$]. At −40 °C, however, another route where an oxidation of *trans*-[RuCl(NO$_2$)(py)$_4$] by 1.5 mol of electrons yields two species, *trans*-[RuCl(NO)(py)$_4$]$^{2+}$ and *trans*-[RuCl(ONO$_2$)(py)$_4$]$^+$, seems to be operating. The above electrochemical results suggest that the chemical oxidation of *trans*-[RuCl(NO$_2$)(py)$_4$] proceeds via the formation of a transient intermediate consisting of *trans*-[RuCl(NO$_2$)(py)$_4$]$^+$ and its isomer, *trans*-[RuCl(ONO)(py)$_4$]$^+$. The intermediate, {Cl(py)$_4$Ru–N(O)O–N(O)O–Ru(py)$_4$Cl}$^{2+}$, then decomposes into *trans*-[RuCl(O)(py)$_4$]$^+$ and *trans*-[RuCl(NO)(py)$_4$]$^{2+}$, along with NO$_2^-$ ions. Under the chemical conditions, *trans*-[RuCl(NO)(py)$_4$]$^{2+}$, once formed, changes rapidly to *trans*-[RuCl(NO$_2$)(py)$_4$], the original starting material of the reaction, and then follows repeated reoxidation until the oxo complex of Ru(IV), *trans*-[RuCl(O)(py)$_4$]$^+$, is formed as a sole product. Such an intermediate process is not necessary for the chemical oxidation of *trans*-[Ru(NO$_2$)(H$_2$O)(py)$_4$]$^+$, which gives *trans*-[Ru(ONO)(O)(py)$_4$]$^+$.

Introduction

Reaction of a nitrosyl complex of Ru(II) (*trans*-[RuCl(NO)(py)$_4$]$^{2+}$) with an oxidizing agent yields quantitatively an oxo complex of Ru(IV) (*trans*-[RuCl(O)(py)$_4$]$^+$).[1,2] The origin of the oxygen ligand strongly depends on what ligand is trans to nitrosyl.[3] Because the reaction is extremely rare and because its process involves a new insight into the chemistry of inorganic syntheses, especially of complexes with monooxygen ligands,[4-13] we have begun a detailed study of the reaction progress.

In this paper, we report the results of our study on the chemical and electrochemical oxidation of *trans*-[RuX(NO$_2$)(py-Y)$_4$]^n (X = Cl for $n = 0$, H$_2$O for $n = 1+$; Y = H, Me) complexes into oxo complexes of Ru(IV). The nitro complexes of Ru(II) were chosen in the present investigation, instead of nitrosyl complexes of Ru(II), for the following reason: the present rare reaction was found in the study of the chemical oxidation of a nitrosyl complex of Ru(II), *trans*-[RuCl(NO)(py)$_4$]$^{2+}$, using NaClO as oxidant.[1,2] Under the conditions, however, the nitrosyl complex of Ru(II) changes first to the corresponding nitro complex of Ru(II),[14] *trans*-[RuCl(NO$_2$)(py)$_4$], without any oxidation of *trans*-[RuCl(NO)(py)$_4$]$^{2+}$ in either metal or ligands. Direct oxidation of the {RuNO}^{6} moiety can never be expected,[15] while its reduction has been substantiated.[16-19]

Oxidation of a coordinated NO$_2^-$ ligand was first investigated by Keene and Meyer et al.[20] They showed that *cis*-[RuCl(NO$_2$)(bpy)$_2$] was oxidized electrochemically to give both *cis*-[RuCl(NO)(bpy)$_2$]$^{2+}$ and *cis*-[RuCl(ONO$_2$)(bpy)$_2$]$^+$ via the formation of a transient intermediate consisting of *cis*-[RuCl(NO$_2$)(bpy)$_2$]$^+$ and its isomer, *cis*-[RuCl(ONO)(bpy)$_2$]$^+$. Their reaction mechanism is useful to explain the present chemical oxidation of *trans*-[RuCl(NO$_2$)(py)$_4$], which gives *trans*-[RuCl(O)(py)$_4$]$^+$ as a sole product.

The purpose of this article is to clarify the mechanistic process of the novel chemical reaction (from *trans*-[RuCl(NO$_2$)(py-Y)$_4$] to *trans*-[RuCl(O)(py-Y)$_4$]$^+$). The conversion of *trans*-[Ru(NO$_2$)(H$_2$O)(py-Y)$_4$]$^+$ into *trans*-[Ru(ONO)(O)(py-Y)$_4$]$^+$ was studied in this connection; a remarkable influence due to the coligand could be seen. A part of the present investigation has been reported briefly.[21,22]

Experimental Section

Materials. Tetraethylammonium perchlorate (TEAP) and tetrabutylammonium perchlorate (TBAP) were special polarographic grade (Nakarai Chem. Co.). Tetrabutylammonium hexafluorophosphate (TBAH) was prepared by adding NH$_4$PF$_6$ to an aqueous solution of (n-Bu)$_4$NI, and was purified with a mixed solvent of EtOH–H$_2$O. LiClO$_4$ was purified with water. Both recrystallized materials were vacuum-dried in the dark at 60 °C. The CH$_3$CN solvent was carefully purified, as described in the text. C$_6$H$_5$CN was purified by using a vacuum line with P$_2$O$_5$ as a drying agent. CH$_2$Cl$_2$ was dried by a distillation with P$_2$O$_5$. Other common chemicals were obtained as a reagent grade and were used without further purification.

Electrochemical Measurements. All measurements were at a platinum disk electrode (ϕ = 2 mm or 3 mm), with a counter or auxiliary electrode of a spiral of platinum wire. Potentials were measured vs. a Ag/0.1 mol dm^{-3} AgClO$_4$ in CH$_3$CN reference electrode at 25 °C (and also at low temperature (0 to −40 °C) when it was necessary). When CH$_2$Cl$_2$ was used as solvent, the reference electrode was connected to the test solution through a bridge with base solution (TBAP (0.1 mol dm^{-3}) in CH$_2$Cl$_2$). Cyclic and normal-pulse voltammetries and controlled-potential electrolysis (with both a rotating platinum disk electrode and a platinum gauze electrode) were carried out by using a Husō polarograph, Model 321, and Husō coulometer, Model 343B.

Other Measurements. Routine UV spectra were recorded on a Hitachi 200-20 spectrometer. Infrared spectra were measured on a Hitachi EPI G2 spectrometer. ^{1}H and ^{13}C NMR spectra were obtained on JEOL FX-200 and GX-270 spectrometers. Magnetic moments were measured

---

(1) Yukawa, Y.; Aoyagi, K.; Kurihara, M.; Shirai, K.; Shimizu, K.; Mukaida, M.; Takeuchi, T.; Kakihana, H. *Chem. Lett.* **1985**, 283.
(2) Aoyagi, K.; Yukawa, Y.; Shimizu, K.; Mukaida, M.; Takeuchi, T.; Kakihana, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1493.
(3) Nishimura, H.; Nagao, H.; Howell, F. S.; Mukaida, M.; Kakihana, H. *Chem. Lett.* **1988**, 491.
(4) Griffith, W. P.; Pawson, D. J. *J. Chem. Soc., Dalton Trans.* **1973**, 1315.
(5) Moyer, B. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3601.
(6) Moyer, B. A.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 436.
(7) Takeuchi, K. J.; Samuels, G. J.; Gresten, S. W.; Gilbert, J. A.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1407.
(8) Liobet, A.; Doppelt, P.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 514.
(9) Che, C.-M.; Tang, T.-W.; Poon, C.-K. *J. Chem. Soc., Chem. Commun.* **1984**, 641.
(10) Che, C.-M.; Lai, T.-F.; Wong, K.-Y. *Inorg. Chem.* **1987**, *26*, 2289.
(11) Che, C.-M.; Cheng, W.-K.; Mark, T. C. W. *Inorg. Chem.* **1988**, *27*, 250.
(12) Marmion, M. E.; Takeuchi, K. J. *J. Am. Chem. Soc.* **1986**, *108*, 510.
(13) Marmion, M. E.; Takeuchi, K. J. *J. Am. Chem. Soc.* **1988**, *110*, 1472.
(14) Swinehart, J. H. *Coord. Chem. Rev.* **1967**, *2*, 385.
(15) Nitrosyl complexes with formal oxidation state of (Ru$^{\mathrm{II}}$NO$^+$) are abbreviated as {RuNO}^{6}: Enemark, J.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339.
(16) Silverthorn, W.; Feltham, R. D. *Inorg. Chem.* **1976**, *6*, 1662.
(17) Callahan, R. D.; Meyer, T. J. *Inorg. Chem.* **1977**, *16*, 574.
(18) Callahan, R. D.; Brown, G. M.; Meyer, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 894.
(19) Aoyagi, K.; Mukaida, M.; Shimizu, K.; Kakihana, H. *J. Chem. Soc., Dalton Trans.* **1985**, 1733.
(20) Keene, F. R.; Salmon, D. J.; Walsh, J. L.; Abruna, H. D.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 1896.
(21) Nagao, H.; Howell, F. S.; Mukaida, M.; Kakihana, H. *J. Chem. Soc., Chem. Commun.* **1987**, 1618.
(22) Nishimura, H.; Nagao, H.; Howell, F. S.; Mukaida, M.; Kakihana, H. *Chem. Lett.* **1990**, 133.

0020-1669/90/1329-1693$02.50/0 © 1990 American Chemical Society

by the Gouy method using $\mathrm{Hg[Co(SCN)_4]}$ as a calibration standard. Elemental analyses (C, N, H) were performed by the Sophia University Analytical Facility.

Preparations. A deep blue solution ("Ru blue") was first prepared for use in convenient syntheses of the Ru(II) and Ru(III) complexes listed below. Hydrated ruthenium trichloride (1 g) was dissolved in a mixture of 50 $\mathrm{cm^3}$ of water and 50–60 $\mathrm{cm^3}$ of ethanol. The solution was refluxed on a water bath for 4–5 h until the color of the solution turned from dark brown to deep blue, via dark green.

***trans*-$\mathbf{[RuCl_2(py)_4]}$.** The following modification of a previous procedure was employed to give pure product in good yield.[23] To the blue solution was added pyridine (25 $\mathrm{cm^3}$); the resultant mixture was refluxed for 0.5–1 h, and then the volume of the solution was reduced on a rotary evaporator until yellow crystals deposited. The crystals were collected by filtration and washed with water, ethanol, and finally ether. Yield: 80–85% (based on Ru). Anal. Calcd for $\mathrm{RuCl_2C_{20}H_{20}N_4}$: C, 49.18; H, 4.14; N, 11.47. Found: C, 48.83; H, 4.17; N, 11.21.

Preparations of the following complexes using *trans*-$[\mathrm{RuCl_2(py)_4}]$ as a starting material have been reported:[23,24] *trans*-$[\mathrm{Ru(NO_2)_2(py)_4}]$, *trans*-$[\mathrm{RuCl(NO_2)(py)_4}]$, *trans*-$[\mathrm{RuCl(NO)(py)_4}]^{2+}$ ($\mathrm{ClO_4}$ and $\mathrm{PF_6}$ salts), *trans*-$[\mathrm{Ru(OH)(NO)(py)_4}]^{2+}$ ($\mathrm{ClO_4}$ and $\mathrm{PF_6}$ salts), and *trans*-$[\mathrm{Ru(NO_2)(NH_3)(py)_4}]\mathrm{PF_6}$.

***trans*-$\mathbf{[RuCl_2(py\text{-}4Me)_4]}$.** The series of 4-methylpyridine (py-4Me) complexes in this work have not been reported. *trans*-$[\mathrm{RuCl(py\text{-}4Me)_4}]$ was prepared by the procedure used for *trans*-$[\mathrm{RuCl_2(py)_4}]$, except that 4-methylpyridine was used instead of pyridine. Yield: 80–85%. Anal. Calcd for $\mathrm{RuCl_2C_{24}H_{28}N_4}$: C, 52.93; H, 5.19; N, 10.29. Found: C, 52.92; H, 5.08; N, 10.23. The compound is diamagnetic.

***trans*-$\mathbf{[Ru(NO_2)_2(py\text{-}4Me)_4]\cdot 0.5H_2O}$.** This complex was prepared by the procedure for *trans*-$[\mathrm{Ru(NO_2)_2(py)_4}]$, except that mixture of ethanol (250 $\mathrm{cm^3}$) and 4-methylpyridine (25 $\mathrm{cm^3}$) was used instead of pyridine. Yield: 80–85%. Anal. Calcd for $\mathrm{RuC_{24}H_{29}N_6O_{4.5}}$: C, 50.16; H, 5.10; N, 14.63. Found: C, 50.44; H, 4.94; N, 14.33.

***trans*-$\mathbf{[RuCl(NO)(py\text{-}4Me)_4](ClO_4)_2\cdot H_2O}$.** This was prepared by almost the same procedure as that for the corresponding *trans*-$[\mathrm{RuCl(NO)(py)_4](ClO_4)_2\cdot H_2O}$. Yield: 70–80%. Anal. Calcd for $\mathrm{RuCl_3C_{24}H_{30}N_5O_{10}}$: C, 38.12; H, 4.01; N, 9.27. Found: C, 37.85; H, 3.70; N, 9.24. IR: ν(NO), 1916 $\mathrm{cm^{-1}}$. ^{1}H NMR ($\mathrm{CD_3CN}$): δ 8.16 (8 H, d), 7.47 (8 H, d), 2.54 (12 H, s ($\mathrm{CH_3}$)). ^{13}C NMR ($\mathrm{CD_3CN}$): δ 156.9 (s), 154.3 (s), 129.4 (s), 21.4 (s ($\mathrm{CH_3}$)). The compound is diamagnetic.

***trans*-$\mathbf{[RuCl(NO_2)(py\text{-}4Me)_4]\cdot H_2O}$.** This was prepared by the same procedure as that for *trans*-$[\mathrm{RuCl(NO_2)(py)_4}]$. Yield: 80%. Anal. Calcd for $\mathrm{RuClC_{24}H_{30}N_5O_3}$: C, 50.10; H, 4.79; N, 12.21. Found: C, 50.29; H, 5.09; N, 12.22. The compound is diamagnetic.

***trans*-$\mathbf{[RuCl(O)(py)_4]ClO_4}$ and *trans*-$\mathbf{[RuCl(O)(py)_4]PF_6}$.** To a suspension of *trans*-$[\mathrm{RuCl(NO_2)(py)_4}]$ (0.3 g) in water (15 $\mathrm{cm^3}$) was added NaClO solution (5%, 5 $\mathrm{cm^3}$), along with $\mathrm{NaClO_4}$ (1 g) (or $\mathrm{NH_4PF_6}$ (0.3 g)) as a precipitant of the reaction product. The mixed solution was stirred for 3–6 h at 23–26 °C while the yellow suspension became light green. After the mixed solution was kept for an additional 3–6 h without stirring, the precipitate was collected by filtration, washed with cold water, and dried in vacuo. Yield: 90% for $\mathrm{ClO_4}$ salt and 95% for $\mathrm{PF_6}$ salt. Anal. Calcd for $\mathrm{RuCl_2C_{20}H_{20}N_4O_5}$ ($\mathrm{ClO_4}$ salt): C, 42.22; H, 3.52; N, 9.85. Found: C, 42.18; H, 3.50; N, 9.91. Calcd for $\mathrm{RuClC_{20}H_{20}N_4OPF_6}$ ($\mathrm{PF_6}$ salt): C, 39.09; H, 3.26; N, 9.12. Found: C, 38.95; H, 3.17; N, 9.21. The complex can be prepared by the procedure described above by using *trans*-$[\mathrm{RuCl(NO)(py)_4](ClO_4)_2}$ or the $\mathrm{PF_6}$ salt. *Comment*: A purified *trans*-$[\mathrm{RuCl(NO)(py)_4}]^{2+}$ complex is necessary for the preparation. The following procedure is recommended if *trans*-$[\mathrm{RuCl(NO)(py)_4}]^{2+}$ complex is contaminated by the analogous *trans*-$[\mathrm{Ru(OH)(NO)(py)_4}]^{2+}$ (its existence as impurity can easily be judged by IR spectra (ν(NO): 1905–1910 $\mathrm{cm^{-1}}$ for *trans*-$[\mathrm{RuCl(NO)(py)_4}]^{2+}$ and 1865–1870 $\mathrm{cm^{-1}}$ for *trans*-$[\mathrm{Ru(OH)(NO)(py)_4}]^{2+}$). The mixture of the nitrosyl complex ($\mathrm{ClO_4}$ salt) was dissolved in water by heating. Adding a solution of NaOH to the nitrosyl solution (pH 9–10) immediately gave a yellow precipitate (*trans*-$[\mathrm{RuCl(NO_2)(py)_4}]$). The yellow precipitate was collected by filtration and was dissolved in HCl (3 mol $\mathrm{dm^{-3}}$) to give *trans*-$[\mathrm{RuCl(NO)(py)_4}]^{2+}$. The purified *trans*-$[\mathrm{RuCl(NO)(py)_4}]^{2+}$ was precipitated again by adding $\mathrm{NaClO_4}$ or $\mathrm{NH_4PF_6}$.

***trans*-$\mathbf{[RuCl(O)(py\text{-}4Me)_4]ClO_4\cdot 1.5H_2O}$ and *trans*-$\mathbf{[RuBr(O)(py\text{-}4Me)_4]PF_6}$.** These complexes can be prepared by the procedures for *trans*-$[\mathrm{RuCl(O)(py)_4]ClO_4}$ and $\mathrm{PF_6}$ salt, using *trans*-$[\mathrm{RuCl(NO_2)(py\text{-}4Me)}]$, and *trans*-$[\mathrm{RuBr(NO_2)(py\text{-}4Me)_4}]$ as starting materials. Yield: 90–95% for both complexes. Anal. Calcd for $\mathrm{RuCl_2C_{24}H_{31}N_4O_{6.5}}$: C, 44.24; H, 4.81; N, 8.60. Found: C, 44.23; H, 4.64; N, 8.88. Calcd for $\mathrm{RuBrC_{24}H_{28}N_4OPF_6}$: C, 40.34; H, 3.96; N, 7.86. Found: C, 40.25; H, 3.96; N, 7.86.

***trans*-$\mathbf{[Ru(ONO)(O)(py)_4]ClO_4}$ and *trans*-$\mathbf{[Ru(ONO)(O)(py)_4]PF_6}$.** To a solution of *trans*-$[\mathrm{Ru(NO_2)(H_2O)(py)_4]ClO_4}$ (0.1 g) in $\mathrm{H_2O}$ (10 $\mathrm{cm^3}$) solid NaOH (0.06–0.07 g) was added. The pH of the solution was maintained at 12.5–13.0 (pH meter), and then NaClO solution (5 $\mathrm{cm^3}$) was added, along with a minimum amount of solid $\mathrm{NaClO_4}$ (or $\mathrm{NH_4PF_6}$). The mixed solution was stirred for 3 h and then kept in a refrigerator for 1–2 days. The green crystals that deposited were collected by filtration, washed with cold water, and dried. Yield: 75–85% in both. Anal. Calcd for $\mathrm{RuClC_{20}H_{20}N_5O_7}$ ($\mathrm{ClO_4}$ salt): C, 41.49; H, 3.49; N, 12.10. Found: C, 41.13; H, 3.50; N, 12.06. Calcd for $\mathrm{RuC_{20}H_{20}N_5O_3PF_6}$ ($\mathrm{PF_6}$ salt): C, 38.46; H, 3.23; N, 11.22. Found: C, 38.23; H, 3.10; N, 11.03. The complexes can be prepared by the procedure described above, using *trans*-$[\mathrm{Ru(OH)(NO)(py)_4](ClO_4)_2}$ as a starting material.

***trans*-$\mathbf{[Ru(NO_2)(H_2O)(py)_4]ClO_4\cdot 1.5H_2O}$.** To a solution of *trans*-$[\mathrm{Ru(OH)(NO)(py)_4](ClO_4)_2}$ (0.24 g) in water (10 $\mathrm{cm^3}$) was added solid NaOH (0.07 g). The pH of the solution was kept at 12.8 (pH meter), while the solution was stirred for 2–3 h. Solid $\mathrm{NaClO_4}$ was added to the solution from which a yellow crystalline product deposited. The yellow crystals were collected by filtration, washed with cold water, and dried in vacuo. Yield: 50–60%. Anal. Calcd for $\mathrm{RuClC_{20}H_{25}N_5O_{8.5}}$: C, 39.50; H, 4.15; N, 11.52. Found: C, 39.49; H, 3.85; N, 11.89.

***trans*-$\mathbf{[RuCl(CH_3CN)(py)_4]PF_6}$.** To a solution of *trans*-$[\mathrm{RuCl(O)(py)_4]PF_6}$ (0.1 g) in $\mathrm{CH_3CN}$ (dried, 3 $\mathrm{cm^3}$) was added $\mathrm{PPh_3}$ (0.064 g). The solution was bubbled for 2 min with argon. Diethyl ether (12 $\mathrm{cm^3}$) was added to the mixed solution; the resulting solution was set aside for 1 day in a refrigerator. The yellow crystals obtained were collected by filtration, washed with ether, and dried in vacuo. An argon atmosphere and dried reagents were necessary for good yields. Yield: 40–50%. Anal. Calcd for $\mathrm{RuClC_{22}H_{23}N_5PF_6}$: C, 41.32; H, 3.64; N, 10.96. Found: C, 41.42; H, 3.58; N, 10.88. UV–vis ($\mathrm{CH_3CN}$): 355 nm ($\epsilon = 2.3 \times 10^4$ $\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$), 244 nm ($\epsilon = 1.9 \times 10^4$), 226 nm ($\epsilon = 1.8 \times 10^4$). ^{1}H NMR ($\mathrm{CD_3CN}$): δ 8.46 (8 H, d), 7.92 (4 H, t), 7.35 (8 H, t), 2.78 (3 H, s). ^{13}C NMR ($\mathrm{CD_3CN}$): δ 157.7 (s), 137.6 (s), 126 (s), 127.8 (s), 5.21 (s).

***trans*-$\mathbf{[RuCl(H_2O)(py)_4]PF_6\cdot H_2O}$.** To a solution of *trans*-$[\mathrm{RuCl(O)(py)_4]ClO_4}$ (0.2 g) in $\mathrm{HPF_6}$ (0.01 mol $\mathrm{dm^{-3}}$, 15 $\mathrm{cm^3}$) was added zinc as a fine powder (0.4 g) as the reductant. During the reaction, argon gas was bubbled in the solution (24 h). The solution color changed slightly from pale green to orange. A orange color product was obtained by adding $\mathrm{NH_4PF_6}$ (0.15 g) to the solution. The product was collected by filtration, washed with cold water, and dried in vacuo. Yield: 45–50%. Anal. Calcd for $\mathrm{RuClC_{20}H_{24}O_2N_4PF_6}$: C, 37.89; H, 3.82; N, 8.84. Found: C, 37.55; H, 3.95; N, 8.69.

Results

Chemical Oxidation. Isolation and Characterization of Oxo Complexes: *trans*-$\mathbf{[RuCl(O)(py)_4]^+}$ and *trans*-$\mathbf{[Ru(ONO)(O)(py)_4]^+}$. Oxidation of *trans*-$[\mathrm{RuCl(NO_2)(py)_4}]$ by NaClO gave *trans*-$[\mathrm{RuCl(O)(py)_4}]^+$, which was identical with the product obtained in the oxidation of *trans*-$[\mathrm{RuCl(NO)(py)_4}]^{2+}$. A structure determination of the oxo complex has been performed previously.[1] Under the same conditions, *trans*-$[\mathrm{Ru(NO_2)(H_2O)(py)_4}]^+$ changed into *trans*-$[\mathrm{Ru(ONO)(O)(py)_4}]^+$ (Table I), which is analogous to *trans*-$[\mathrm{RuCl(O)(py)_4}]^+$. The nitrito–oxo complex is stable indefinitely when it is stored in the solid state, even when exposed to room light, but X-ray structural work was unsuccessful because partial decomposition occurred during intensity data collection.

The *trans*-$[\mathrm{Ru(ONO)(O)(py)_4}]^+$ complex was identified on the basis of elemental analyses, IR spectra, magnetic properties, and electrochemistry. The IR spectrum of the complex ($\mathrm{PF_6}$ salt) exhibits characteristic absorption bands at 1485, 983, and 798 $\mathrm{cm^{-1}}$. Two absorption bands at 1485 and 983 $\mathrm{cm^{-1}}$ were moved to 1460 and 977 $\mathrm{cm^{-1}}$, respectively, by a ^{15}N labeling experiment, while the last band remained at 798 $\mathrm{cm^{-1}}$. Two bands at 1485 and 983 $\mathrm{cm^{-1}}$ were quite different in frequency from those of a coordinated nitro ligand and are best assignable to the bands due to the nitrito ligand.[25,26] To our knowledge, this appears to be the first example of a nitrito complex of ruthenium isolated as a single compound. The nitrito complexes of ruthenium prepared so far, without any change of the oxidation state, were mixtures

---

(23) Bottomley, F.; Mukaida, M. *J. Chem. Soc., Dalton Trans.* **1982**, 1933.

(24) Bottomley, F.; White, P. S.; Mukaida, M.; Shimura, K.; Kakihana, H. *J. Chem. Soc., Dalton Trans.* **1988**, 2965.

(25) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; John Wiley and Sons: New York, 1978.

(26) Adeymi, S. A.; Millar, F. J.; Meyer, T. J. *Inorg. Chem.* **1972**, *11*, 994.

Table I. Characteristics of Nitro Complexes of Ru(II) (Used for the Present Oxidation Reaction) and Oxo Complexes of Ru(IV) (Obtained as the Oxidation Products)

	IR[a]					CV[b]			
	$-NO_2$		$-ONO$						
	ν_{as}	ν_s	$\nu_{N=O}$	ν_{N-O}	$\nu_{Ru=O}$	E_{pc}	E_{pa}	μ_{eff}[d]	UV–vis[c] λ (ε)
trans-$[RuCl(NO_2)(py)_4]$	1312 (1284)	1292 (1261)[e]				[f]		dia	340 (1.2×10^4) 242 (1.9×10^4)
trans-$[RuCl(NO_2)(py\text{-}4Me)_4]$	1300	1285				[f]		dia	364 (1.8×10^4) 242 (1.6×10^4)
trans-$[Ru(NO_2)(H_2O)(py)_4]PF_6$	1315	1280				[f]		dia	342 (1.8×10^4) 242 (1.5×10^4)
trans-$[RuCl(O)(py)_4]PF_6$					805	~−1.0	1.39	2.92	690 (1.4×10^2), 450 sh 265 (1.4×10^4)
trans-$[RuCl(O)(py)_4]ClO_4$					805				686 (1.3×10^2), 430 (1.1×10^2) 265 (1.0×10^4)
trans-$[RuCl(O)(py\text{-}4Me)_4]PF_6$					800	−1.09	1.31		
trans-$[RuCl(O)(py\text{-}4Me)_4]ClO_4$					800				
trans-$[Ru(ONO)(O)(py)_4]PF_6$			1485 (1460)	983 (977)	798				
trans-$[Ru(ONO)(O)(py)_4]ClO_4$			1476 (1464)	976 (965)	798	−1.00	1.12	2.91	686 (1.2×10^2) 429 (2.2×10^2) 265 (1.6×10^4)

[a] In cm^{-1} (KBr). [b] In V vs Ag|$AgClO_4$ (0.1 mol dm^{-3} in CH_3CN) at 25 °C. E_{pc}, $Ru^{II/IV}$; E_{pa}, $Ru^{IV/V}$. [c] In nm (ε in dm^3 mol^{-1} cm^{-1}) in CH_3CN. [d] In μ_B (22 °C). [e] Figures in parentheses are data obtained by ^{15}N labeling experiments. [f] Cyclic voltammetric data for the nitro complexes of Ru(II) are summarized in Table II.

Table II. Electrochemical Data for Nitro Complexes of Ru(II) and the Complexes Related to Their Oxidation Reaction[a]

	E_{pa}		
complex	at 25 °C	at −40 °C	Q/NF (n)
trans-$[RuCl(NO_2)(py)_4]$	0.28	0.30	1.26–1.34
trans-$[RuCl(NO_2)(py\text{-}4Me)_4]$	0.04[c]		1.16–1.26
trans-$[Ru(NO_2)_2(py)_4]$	0.49		
trans-$[Ru(NO_2)(NH_3)(py)_4]PF_6$	0.56		
trans-$[Ru(NO_2)(H_2O)(py)_4]PF_6$	0.79		
trans-$[RuCl(H_2O)(py)_4]PF_6$		0.25[b]	
trans-$[RuCl(CH_3CN)(py)_4]PF_6$	0.50[b]		
trans-$[RuCl_2(py)_4]$	−0.14[b]		0.98
trans-$[RuCl(OH)(py)_4]PF_6$	−0.67[b,d]		
trans-$[RuCl(NO)(py)_4](PF_6)_2$	−0.11[b] −0.99[e]	−0.14[b] −0.97[b]	

[a] Cyclic voltammetric data for the complexes (1 mmol dm^{-3}) in TEAP (0.1 mol dm^{-3})–CH_3CN. E_{pa} in V. [b] $E_{1/2}$. [c] In TBAP (0.1 mol dm^{-3})–PhCN. [d] Reference 27. [e] E_{pc}.

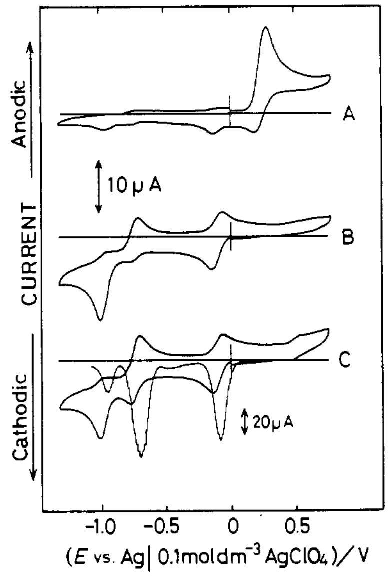


Figure 1. Cyclic voltammograms of *trans*-$[RuCl(NO_2)(py)_4]$ (1.0×10^{-3} mol dm^{-3}) in CH_3CN at 25 °C (stationary Pt electrode, Et_4NClO_4 (0.1 mol dm^{-3})): (A) before electrolysis (100 mV s^{-1}); (B) after controlled-potential electrolysis at 0.4 V (100 mV s^{-1}); (C) after addition of *trans*-$[RuCl(H_2O)(py)_4]PF_6$ (2.50×10^{-4} mol dm^{-3}) to the solution from part B (100 mV s^{-1}), and measurement of differential-pulse polarograms.

of nitro complexes.[26] Another absorption band at 798 cm^{-1} could be assigned to a Ru=O stretching frequency. Reported terminal oxo frequencies for a variety of oxidation states of Ru,[4-7,9,10,12,13] including that of *trans*-$[RuCl(O)(py)_4]^+$, whose Ru=O stretching frequency has been confirmed by an ^{18}O labeling experiment,[27] also occur in this region (Table I).

The effective magnetic moment of *trans*-$[Ru(ONO)(O)(py)_4]^+$ was found to be 2.92 μ_B. This is almost the same as that of the analogous *trans*-$[RuCl(O)(py)_4]^+$ and is close to the spin-only value for two spins unpaired. The observation of two unpaired electrons is consistent with the orbital splitting scheme proposed by Meyer et al., in which the existence of the half-filled $d\pi^*$ orbitals results in an extensive stabilization of the Ru–O bonding through a $p\pi(O^{2-})$–$d\pi(Ru)$ interaction.[6,7]

Cyclic voltammetric data observed for both *trans*-$[RuCl(O)(py)_4]^+$ and *trans*-$[Ru(ONO)(O)(py)_4]^+$ in 0.1 M TEAP–CH_3CN at a platinum stationary electrode are summarized in Table II, along with those of their relative complexes. Both oxo complexes exhibited at 25 °C a single irreversible reduction wave at around −0.99 V, which is a much more negative potential than that expected for $Ru^{2+/3+/4+}$ couples. At a scan rate between 200 and 50 mV s^{-1}, the coupled oxidation wave was very small (for *trans*-$[RuCl(O)(py)_4]^+$) or was completely absent (for *trans*-$[Ru(ONO)(O)(py)_4]^+$), while it appeared with almost the same height as that of the reduction wave at low temperature (−40 °C). The current height, observed by normal-pulse voltammetry under the same experimental conditions, of the reduction wave at −0.99 V corresponds to that of the two-electron redox system.

Cyclic voltammograms of *trans*-$[Ru(ONO)(O)(py)_4]^+$ look virtually the same as those of *trans*-$[RuCl(O)(py)_4]^+$, except for some complexity which arises in *trans*-$[Ru(ONO)(O)(py)_4]^+$ since the two-electron reduction of the complex results in concomitant isomerization of the nitrito ligand into a nitro one (see later). Detailed electrochemical studies of these complexes will be reported separately.

Electrochemical Oxidation of *trans*-$[RuCl(NO_2)(py)_4]$. Generation of Three Species: *trans*-$[RuCl(NO)(py)_4]^{2+}$, *trans*-$[RuCl(OH)(py)_4]^+$, and *trans*-$[RuCl(O)(py)_4]^+$. All of the nitro complexes of Ru(II) studied, except for *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$, give similar voltammetric results; the data are summarized in Table II. The electrochemical behavior of both *trans*-$[RuCl(NO_2)(py)_4]$ and *trans*-$[RuCl(NO_2)(py\text{-}4Me)_4]$ has been investigated in detail because the reactivity of the cations,

---

[27] Nagao, H.; Aoyagi, K.; Yukawa, Y.; Howell, F. S.; Mukaida, M.; Kakihana, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3247.

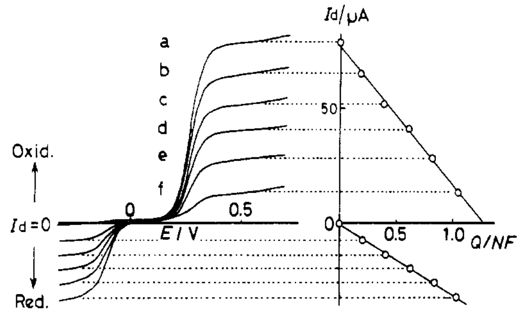


Figure 2. Typical voltammograms at Pt rotating disk electrode monitoring the course of controlled-potential oxidation (0.40 V vs. Ag AgClO$_4$) of a 1.0 × 10^{-3} mol dm^{-3} solution of *trans*-$[RuCl(NO_2)(py)_4]$ in CH_3CN (0.1 mol dm^{-3} Et_4NClO_4), and plots of the *Id* and *Q*/*NF*: (a) prior to electrolysis; (b–e) during the electrolysis; (f) at the end of the electrolysis ($n = 0.94$).

trans-$[RuCl(NO_2)(py)_4]^+$ and *trans*-$[RuCl(NO_2)(py\text{-}4Me)_4]^+$, relates directly to the processes of their chemical oxidation reactions.

Cyclic voltammograms of *trans*-$[RuCl(NO_2)(py)_4]$ at 25 °C display an irreversible oxidation wave at 0.28 V (vs Ag|AgClO$_4$ (0.1 mol dm^{-3} in CH_3CN)) within the potential region expected for the $Ru^{2+/3+}$ couple (Figure 1A).[28] The electron transfer process is diffusion-controlled with $ip/v^{1/2}$ constant over the range of scan rate used. In a multiple-scan cyclic voltammogram from 0 to −1.40 V, three small waves, absent on the initial reductive scan, appeared at −0.1, −0.7, and −1.0 V, which were the same potential values as found for *trans*-$[RuCl(NO)(py)_4]^{2+}$ (first reduction wave), *trans*-$[RuCl(OH)(py)_4]^+$, and *trans*-$[RuCl(O)(py)_4]^+$ (overlapped with the second reduction wave of *trans*-$[RuCl(NO)(py)_4]^{2+}$ (Table II)). Similar electrochemical behavior was observed for the relevant complexes *trans*-$[Ru(NO_2)(NH_3)(py)_4]^+$ and *trans*-$[Ru(NO_2)_2(py)_4]$, but not for *trans*-$[RuCl_2(py)_4]$ where no coordinated nitro ligand exists and only a reversible one-electron redox couple is observed (Table II).

The occurrence of the three oxidation products, *trans*-$[RuCl(O)(py)_4]^+$, *trans*-$[RuCl(OH)(py)_4]^+$, and *trans*-$[RuCl(NO)(py)_4]^{2+}$, was borne out by results of controlled-potential electrolysis (Figure 1B,C). On bulk electrolysis at 0.4 V, a yellow CH_3CN solution of *trans*-$[RuCl(NO_2)(py)_4]$ became green as the waves due to the three species developed; nearly 1.3 mol of electrons were removed per mole of *trans*-$[RuCl(NO_2)(py)_4]$ ($n = 1.26$–1.34 for nine runs).[29] The generation of $^1/_2$ equiv of *trans*-$[RuCl(NO)(py)_4]^{2+}$, based on the original *trans*-$[RuCl(NO_2)(py)_4]$, could be confirmed: monitoring the result by a rotating platinum disk electrode showed the disappearance of the oxidative process and the generation of a reduction wave at −0.10 V (Figure 2). The ratio of an increasing height of the reduction wave (of *trans*-$[RuCl(NO)(py)_4]^{2+}$) to the decreasing height of the oxidation wave (of *trans*-$[RuCl(NO_2)(py)_4]$) was constant at about $^1/_2$. The other half of *trans*-$[RuCl(NO_2)(py)_4]$ changes into *trans*-$[RuCl(OH)(py)_4]^+$ and *trans*-$[RuCl(O)(py)_4]^+$ in nearly equal amounts.

The existence of *trans*-$[RuCl(O)(py)_4]^+$ in the oxidized solution could not be confirmed solely by comparison of the electrochemical data, since E_{pc} of *trans*-$[RuCl(O)(py)_4]^+$ appeared in almost the same potential region as that of the irreversible cathodic wave of *trans*-$[RuCl(NO)(py)_4]^{2+}$ (second reduction wave). Its existence, as one oxidation product, could be proved by the following experiment: when *trans*-$[RuCl(H_2O)(py)_4]^+$ was added to the previously described electrolyzed solution, the small reduction wave of *trans*-$[RuCl(OH)(py)_4]^+$ observed at −0.67 V increased immediately as the height of the irreversible wave at −1.00 V decreased (Figure 1C); $^1/_4$ equiv of *trans*-$[RuCl(H_2O)(py)_4]^+$, based on the original *trans*-$[RuCl(NO_2)(py)_4]$, was consumed to complete the reaction. The observed conproportionation reaction, expressed in eq 1, suggests that $^1/_2$ equiv of *trans*-$[RuCl(NO_2)(py)_4]$ was converted into both *trans*-$[RuCl(O)(py)_4]^+$ and *trans*-$[RuCl(OH)(py)_4]^+$ in nearly equal amounts. Such conproportionation of Ru^{IV} and Ru^{II} complexes generating the corresponding Ru^{III} has been observed for most polypyridyl complexes of ruthenium.[30]

$$[Ru^{IV}Cl(O)(py)_4]^+ + [Ru^{II}Cl(H_2O)(py)_4]^+ \rightarrow 2[Ru^{III}Cl(OH)(py)_4]^+ \quad (1)$$

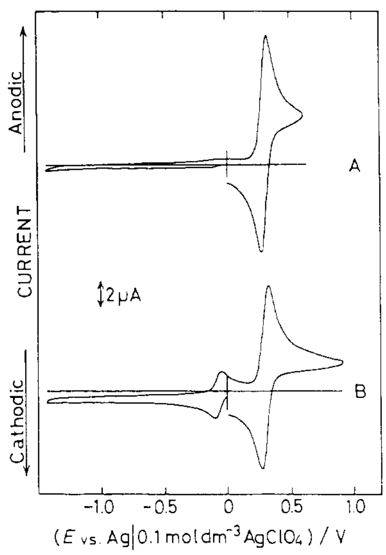


Figure 3. Cyclic voltammograms of *trans*-$[RuCl(NO_2)(py)_4]$ (1 × 10^{-3} mol dm^{-3}) in CH_3CN at low temperature (ca. −40 °C) (100 mV s^{-1}): (A) voltammogram prior to electrolysis; (b) voltammogram at an early stage of the electrolysis at 0.40 V ($n = 0.33$) (continues in Figure 4A).

The electrochemical behavior of *trans*-$[RuCl(NO_2)(py\text{-}4Me)_4]$ is very similar to that of the parent pyridine complex except that the oxidation wave is shifted to more negative potential by 0.18 V (Table II), as expected for the greater σ-electron donation of the methyl group attached to the pyridine skeleton.[31]

While the products generated by the electrochemical oxidation at room temperature were unequivocally shown, the cyclic voltammetry performed at various low temperature indicates that additional oxidation species are involved in the oxidation process. When the solution was cooled to −40 °C, cyclic voltammetry showed first a single reversible couple at 0.33 V (Figure 3A), instead of the irreversible wave of *trans*-$[RuCl(NO_2)(py)_4]^{0/+}$ observed at 25 °C (Figure 1A). At scan rates between 50 and 200 mV s^{-1}, the $E_{1/2}$ value, calculated as $(E_{pc} + E_{pa})/2$, remained constant at 0.30 V; the ratio of i_a and i_c peak current vs (scan rate)$^{1/2}$ was linear for both i_a and i_c. The experiment by controlled-potential electrolysis with $E_{appl} = 0.40$ V verified the existence of a product complex with a reversible couple at $E_{1/2} = -0.07$ V (Figure 3B). The wave height of the redox couple increases by further oxidative electrolysis, while it decreases and finally disappears completely by reductive electrolysis at −0.10 V; then the original *trans*-$[RuCl(NO_2)(py)_4]^{0/+}$ couple is restored. The voltammetry results can best be explained as follows: an electron transfer at the central metal site in *trans*-$[RuCl(NO_2)(py)_4]$ results in a structural rearrangement, nitro–nitrito isomerization:[32] a one-electron oxidation of *trans*-$[RuCl(NO_2)(py)_4]$ gives first chemically unstable *trans*-$[RuCl(NO_2)(py)_4]^+$ (A in Figures 1 and 3), and the oxidation species

---

[28] A second irreversible one-electron oxidation with a peak potential at 1.39 V (100 mV s^{-1}) is observed that is too positive to be observable in CH_3CN solvent. This process represents oxidation of *trans*-$[RuCl(NO_2)(py)_4]^+$ cation and not investigated further.

[29] The determined *n* value of the controlled-potential electrolysis for *trans*-$[RuCl_2(py)_4]$, measured for comparison, was 0.98 electron/mol.

[30] Binstead, R. A.; Moyer, B. A.; Samules, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2897.

[31] *Critical Stability Constants*; Martell, A. E.; Smith, R. M. Eds.; Plenum Press: New York and London, 1982; Vol. 5, First Supplement, pp 223 and 219.

[32] Abruna, H. D.; Walsh, J. L.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1981**, *20*, 1481.

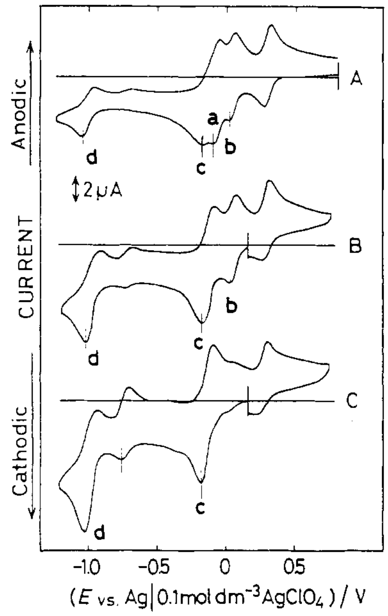


Figure 4. Controlled-potential electrolysis of *trans*-$[RuCl(NO_2)(py)_4]$ at -40 °C. (A) Cyclic voltammograms (CV) of the electrolyzed solution ($n = 1.05$) at -40 °C (continuing from Figure 3B), measured just after the electrolysis was performed: (a) $[RuCl(ONO)(py)_4]^{+/0}$; (b) $[RuCl(ONO_2)(py)_4]^{+/0}$; (c and d) $[RuCl(NO)(py)_4]^{2+/+,+/0}$. (B) CV of the solution from part A, which was kept for 5 h after being allowed to warm to -10 °C. (C) CV of the solution from part B, which was kept for additional 18 h at 0 °C.

is then followed by isomerization to *trans*-$[RuCl(ONO)(py)_4]^+$ (a similar electrochemical behavior is observed in *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$ (see later), which gives a nitrito complex of Ru(IV) as described earlier).

Further continuous oxidative electrolysis of *trans*-$[RuCl(NO_2)(py)_4]$ at -40 °C gave three waves almost simultaneously at +0.04, -0.19, and -1.05 V, which were attributable to *trans*-$[RuCl(ONO_2)(py)_4]^{0/+}$, *trans*-$[RuCl(NO)(py)_4]^{1+/2+}$, and *trans*-$[RuCl(NO)(py)_4]^{0/+}$, respectively (Figure 4A). Electrochemical data of *trans*-$[RuCl(ONO_2)(py)_4]^+$ are presently not available, but the wave at +0.04 V can reasonably be assumed to be due to the nitrato complex, based on the result reported by Meyer et al.[20]

When the solution at -40 °C was allowed to warm, cyclic voltammograms at intermediate temperatures revealed a further new redox system at -0.69 V, corresponding to the redox potential of *trans*-$[RuCl(OH)(py)_4]^{0/+}$ (Figure 4B,C).

Nitro-Nitrito Rearrangement Induced by Transfer of Electrons at the Central Metal Site. All the data reported in the electrochemical experiments are consistent with the following chemistry of *trans*-$[RuCl(NO_2)(py)_4]$. (Scheme I, where dotted lines indicate that intermediate e is decomposed to A or B group products spontaneously). At 25 °C, the isomerized species c exists as a very reactive species; it undergoes a rapid chemical reaction to give *trans*-$[RuCl(NO)(py)_4]^{2+}$, *trans*-$[RuCl(OH)(py)_4]^+$, and *trans*-$[RuCl(O)(py)_4]^+$ via the transient intermediate e. No reductive wave of compound c is observable.

The occurrence of linkage isomerization of *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$ can also be observed by cyclic voltammetry: On the first scan at 25 °C, a one-electron oxidation wave due to the formation of $[Ru(NO_2)(H_2O)(py)_4]^{2+}$ appears at 0.79 V (E_{pa}, wave 1 in Figure 5a). The wave is irreversible as evidenced by the absence of a corresponding cathodic wave in the cyclic voltammograms. Lowering the temperature to -40 °C, however, increases the cathodic wave current (wave i in Figure 5b) though the irreversibility is still observed. Such behavior is characteristic of an oxidation followed by a chemical reaction (EC), the rate of which is decreased by lowering the temperature. In fact, a similar cyclic voltammogram was observed in a one-electron oxidation of *trans*-$[RuCl(NO_2)(py)_4]$, analogous to *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$, in which the linkage isomerization into

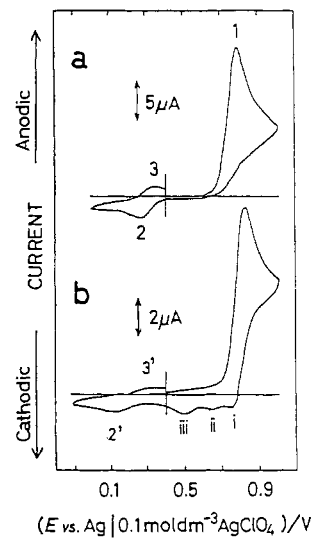
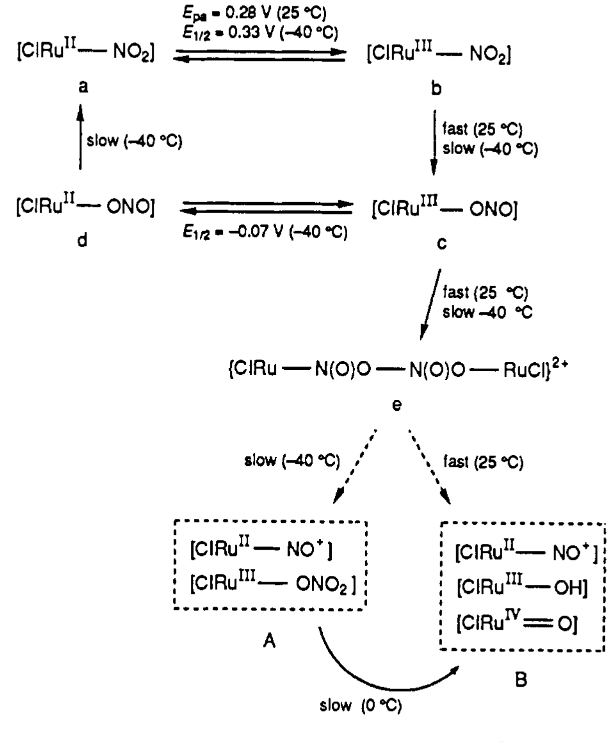


Figure 5. Cyclic voltammograms of *trans*-$[Ru(NO_2)(H_2O)(py)_4]ClO_4$ (1×10^{-3} mol dm^{-3}) in CH_3CN (200 mV s^{-1}, Et_4NClO_4 (1×10^{-3} mol dm^{-3}), stationary Pt electrode). (a) CV at 25 °C: (1) $[Ru(NO_2)(H_2O)(py)_4]^{+/2+}$; (2 and 3) $[Ru(ONO)(OH)(py)_4]^{0/+}$. (b) CV at -40 °C: (i) $[Ru(NO_2)(H_2O)(py)_4]^{+/2+}$; (ii and iii) either $[Ru(NO_2)(OH)(py)_4]^{0/+}$ or $[Ru(ONO)(H_2O)(py)_4]^{+/2+}$; (2' and 3') the same as 2 and 3 at 25 °C.

Scheme I



trans-$[RuCl(ONO)(py)_4]^+$ was believed to occur.[21]

Thus the generated nitro species, $[Ru(NO_2)(H_2O)(py)_4]^{2+}$, will isomerize rapidly to give a nitrito species that undergoes a reduction at 0.27 V (E_{pc}, wave 2 in Figure 5a). The isomerized nitrito species was tentatively identified, on the basis of a low-temperature experiment, as being $[Ru(ONO)(OH)(py)_4]^+$ rather than $[Ru(ONO)(H_2O)(py)_4]^{2+}$, since an aqua ligand in Ru(III) complex releases its proton rapidly to give a hydroxo complex of Ru(III).[33]

Two more waves appeared at 0.65 and 0.45 V (both E_{pc}, Figure 5b) on the reductive scan, but these waves were not observed in the experiment at 25 °C. The splitting observed is best explainable by assuming that either $[Ru(NO_2)(OH)(py)_4]^+$ or [Ru-

---

(33) Takeuchi, K. J.; Thompson, M. S.; Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 1845.

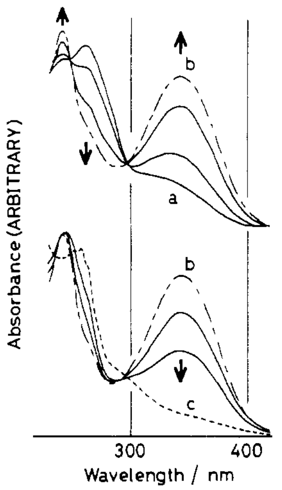


Figure 6. Spectral changes observed in the reaction of MeOH with *trans*-$[\mathrm{Ru(ONO)(O)(py)_4}]\mathrm{ClO_4}$ (2×10^{-5} mol dm^{-3}): (a) initial spectrum of *trans*-$[\mathrm{Ru(ONO)(O)(py)_4}]^+$; (b) spectrum that corresponds to *trans*-$[\mathrm{Ru(NO_2)(H_2O)(py)_4}]^+$ (ca. 42 min after reaction); (c) final spectrum at 72 h after reaction.

$\mathrm{(ONO)(H_2O)(py)_4]^{2+}}$ species exist for a short lifetime at the surface of an electrode, along with $[\mathrm{Ru(ONO)(OH)(py)_4}]^+$, which is reduced at 0.1 V (E_{pc}, wave 2′ in Figure 5b).

At more cathodic potential regions, another small reductive wave is observed at −0.69 V, probably due to *trans*-$[\mathrm{Ru(OH)(NO)(py)_4}]^{2+}$.[34] Appearance of the nitrosyl wave is diagnostic for the existence of a transient intermediate such as e in Scheme I, suggesting that, in MeCN solvent, a process similar to that "from c to e" is likely to occur as a minor reaction. An attempted controlled-potential electrolysis (to estimate the number of electrons that participate in the oxidation) of *trans*-$[\mathrm{Ru(NO_2)(H_2O)(py)_4}]\mathrm{PF_6}$ was unsuccessful.

Thus at 25 °C, a one-electron oxidation of *trans*-$[\mathrm{Ru(NO_2)(H_2O)(py)_4}]^+$ gives predominantly *trans*-$[\mathrm{Ru(ONO)(OH)(py)_4}]^+$, and a further one-electron oxidation results in the formation of *trans*-$[\mathrm{Ru(ONO)(O)(py)_4}]^+$.

There is a clear evidence that such isomerization occurs chemically between *trans*-$[\mathrm{Ru(NO_2)(H_2O)(py)_4}]^+$ and *trans*-$[\mathrm{Ru(ONO)(O)(py)_4}]^+$. The nitrito complex of Ru(IV) can be obtained when the nitro complex of Ru(II) is oxidized by NaClO under aqueous basic conditions (Table I). The reverse reaction, from the nitrito to the nitro complex, does occur when *trans*-$[\mathrm{Ru(ONO)(O)(py)_4}]^+$ undergoes a moderate chemical reduction, where the original *trans*-$[\mathrm{Ru(NO_2)(H_2O)(py)_4}]^+$ is regenerated. The structural rearrangement, with a half-life of ca. 20 min at room temperature, was monitored by the UV spectral change, although quantitative kinetic studies have not been made: a freshly prepared methanol solution of *trans*-$[\mathrm{Ru(ONO)(O)(py)_4}]^+$ exhibits an intense absorption band at 264 nm (curve a in Figure 6). The solution changes from a pale green to yellow while standing at room temperature. In the first stage of the spectral change, the intensity of the band decreases as two new bands appear at around 235 and 335 nm. The wavelengths of maximum absorption of the two bands shift to 242 and 342 nm, respectively; their intensities increase to give spectrum b. Isosbestic points could be seen only an early stage of the spectral change at 248 and 297 nm, but they did not remain throughout the first stage of the reaction. In the second stage, the intensity of the band at 342 nm continued to decrease until spectrum b changed to spectrum c, where no absorption band was found except that at 257 nm. No appreciable rearrangement occurs in MeCN solvent, at least during the first several hours.

Evidence for the nitrito–nitro isomerization (from *trans*-$[\mathrm{Ru(ONO)(O)(py)_4}]^+$ to *trans*-$[\mathrm{Ru(NO_2)(H_2O)(py)_4}]^+$) comes from the fact that the spectrum b is the same as the spectrum of *trans*-$[\mathrm{Ru(NO_2)(H_2O)(py)_4}]^+$ used as an authentic sample. When the experiment was attempted on a preparative scale, the nitro complex of Ru(II) could be isolated from the solution; this complex gave the same spectrum as spectrum b. An occurrence of nitro–nitrito isomerization is generally thermosensitive, and its progress has been investigated by many researchers.[35–38] The present case, however, is the first reported example where isomeric pairs, with different formal oxidation states of their metals ions, could be synthesized.

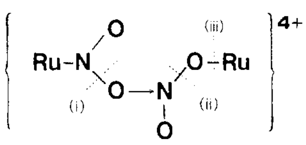


Figure 7. Possible decomposition scheme for the intermediate species.

Discussion

Conversion Process of ($\mathrm{Ru^{II}—NO_2}$) to ($\mathrm{Ru^{IV}{=}O}$) Moieties in Electrochemical Oxidation. At 25 °C, *trans*-$[\mathrm{RuCl(NO_2)(py)_4}]$ in $\mathrm{CH_3CN}$ is oxidized electrochemically to give three species, *trans*-$[\mathrm{RuCl(NO)(py)_4}]^{2+}$, *trans*-$[\mathrm{RuCl(OH)(py)_4}]^+$, and *trans*-$[\mathrm{RuCl(O)(py)_4}]^+$; about 1.25 mol of electrons are released per mole of *trans*-$[\mathrm{RuCl(NO_2)(py)_4}]$. The overall stoichiometry is expressed by eq 2.

$$2[\mathrm{RuCl(NO_2)(py)_4}] \xrightarrow[\mathrm{(H)}]{} [\mathrm{RuCl(NO)(py)_4}]^{2+} + 0.5[\mathrm{RuCl(OH)(py)_4}]^+ + 0.5[\mathrm{RuCl(O)(py)_4}]^+ + \mathrm{NO_2}^- + 2.5\mathrm{e}^- \quad (2)$$

At low temperature (−40 °C), however, the presence of the 1.5e oxidation reaction (eq 3) is suggested by the formation of two

$$2[\mathrm{RuCl(NO_2)(py)_4}] \rightarrow [\mathrm{RuCl(NO)(py)_4}]^{2+} + [\mathrm{RuCl(ONO_2)(py)_4}]^+ + 3\mathrm{e}^- \quad (3)$$

species: *trans*-$[\mathrm{RuCl(NO)(py)_4}]^{2+}$ and *trans*-$[\mathrm{RuCl(ONO_2)(py)_4}]^+$ complexes. Equation 3 is the same as that in the electrochemical oxidation of *cis*-$[\mathrm{RuCl(NO_2)(bpy)_2}]$ at 25 °C reported by Meyer et al.[20] They explained that the reaction proceeds by the transfer of oxygen from one nitro group to another, via a nitro–nitrito isomerization, in which 1.5 mol of electrons/mol of *cis*-$[\mathrm{RuCl(NO_2)(bpy)_2}]$ are released to complete the reaction (Scheme II). Equations 2 and 3 differ in the final products and in the numbers of electrons released during the electrolysis.

Scheme II

$$2[\mathrm{Ru^{II}Cl(NO_2)(bpy)_2}] \rightarrow 2[\mathrm{Ru^{III}Cl(NO_2)(bpy)_2}]^+ + 2\mathrm{e}^-$$

$$[\mathrm{Ru^{III}Cl(NO_2)(bpy)_2}]^+ \rightleftarrows [\mathrm{Ru^{III}Cl(ONO)(bpy)_2}]^+$$

$$[\mathrm{Ru^{III}Cl(NO_2)(bpy)_2}]^+ + [\mathrm{Ru^{III}Cl(ONO)(bpy)_2}]^+ \rightarrow \{\mathrm{Cl(bpy)_2Ru\text{-}N(O)O\text{-}N(O)O\text{-}Ru(bpy)_2Cl}\}^{2+} \rightarrow [\mathrm{Ru^{II}Cl(NO^+)(bpy)_2}]^{2+} + [\mathrm{Ru^{III}Cl(ONO_2)(bpy)_2}]^+ + \mathrm{e}^-$$

A mechanistic explanation is now possible (except for the origin of the H atom in *trans*-$[\mathrm{RuCl(OH)(py)_4}]^+$ (see eq 2)) by combining the results observed at 25 °C and at −40 °C. As has been proved,[21,39] the initial step of the reaction must be a one-electron oxidation of *trans*-$[\mathrm{RuCl(NO_2)(py)_4}]$ to give a transient intermediate, $\{\mathrm{Cl(py)_4Ru\text{-}N(O)O\text{-}N(O)O\text{-}Ru(py)_4Cl}\}^{2+}$, according to the process proposed by Meyer et al.,[20] via the linkage isomerization of *trans*-$[\mathrm{RuCl(NO_2)(py)_4}]^+$ to *trans*-$[\mathrm{RuCl(ONO)(py)_4}]^+$. The occurrence of the isomerization to give the transient intermediate could be proved by both chemical and electrochemical oxidations, as described earlier. The transient intermediate can decompose at low temperature (−40 °C) to allow the oxygen

---

[34] Nishimura, H.; Matsuzawa, H.; Togano, T.; Mukaida, M.; Kakihana, H.; Bottomley, F. *J. Chem. Soc., Dalton Trans* **1990**, 1317. (The wave at −0.69 V was not indicated in Figure 5.)

[35] Burmeister, J. L. *Coord. Chem. Rev.* **1968**, *3*, 225.

[36] Norbury, A. H.; Sinha, A. I. P. *Q. Rev., Chem. Soc.* **1970**, *24*, 69.

[37] Balahura, R. J.; Lewis, N. A. *Coord. Chem. Rev.* **1976**, *20*, 109.

[38] Miyoshi, K.; Katoda, N.; Yoneda, H. *Inorg. Chem.* **1983**, *22*, 1839.

[39] Nagao, H.; Mukaida, M.; Shimizu, K.; Howell, F. S.; Kakihana, H. *Inorg. Chem.* **1986**, *25*, 4312.

transfer from one nitro group to another, producing equal amounts of *trans*-$[RuCl(NO)(py)_4]^{2+}$ and *trans*-$[RuCl(ONO_2)(py)_4]$. This is the case where the intermediate undergoes bond cleavage only at bond i in Figure 7.

At higher temperatures, the transient intermediate would decompose further by bond breaking at bond ii to give NO_2^- and *trans*-$[Ru^{III}Cl(O^-)(py)_4]^+$, along with *trans*-$[RuCl(NO)(py)_4]^{2+}$ (eqs 4 and 5). The $[Ru^{II}Cl(O^0)(py)_4]^+$ is isoelectronic with either

$$\{Cl(py)_4Ru{-}N(O)O{-}N(O)O{-}Ru(py)_4Cl\}^{2+} \rightarrow [Ru^{II}Cl(NO^+)(py)_4]^{2+} + [Ru^{II}Cl(ONO_2)(py)_4] \quad (4)$$

$$[Ru^{II}Cl(ONO_2)(py)_4] \rightarrow [Ru^{II}Cl(O^0)(py)_4]^+ + NO_2^- \quad (5)$$

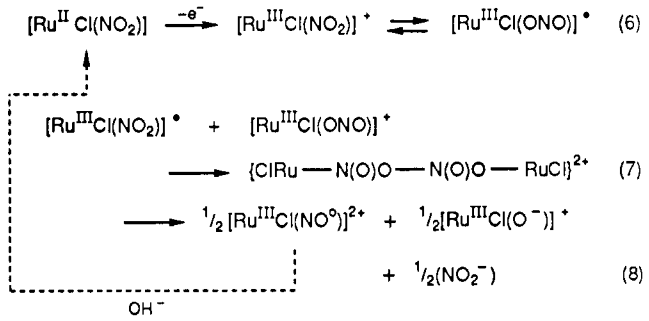
$[Ru^{III}Cl(O^-)(py)_4]^+$ or $[Ru^{IV}Cl(O^{2-})(py)_4]^+$. Equation 5 relates to Meyer's assumption that a polypyridyl complex of Ru(II) is capable of reducing an oxyanion such as NO_3^- by the reaction in which a ($Ru^{IV}{=}O^{2-}$) species is formed transiently:[40]

$$[Ru(bpy)_2(py)(OH_2)]^{2+} + NO_3^- \rightarrow [Ru(bpy)_2(py)(ONO_2)]^+ + H_2O \rightarrow [Ru(bpy)_2(py)(O)]^{2+} + NO_2^-$$

If the bond breaks at point iii in Figure 7, a solvated complex, *trans*-$[RuCl(CH_3CN)(py)_4]^+$, is generated during the electrolysis. It should be emphasized that the existence of such solvated complexes (whose electrochemical data are available in Table II) could not be detected by cyclic voltammetry at any stage of the oxidation.

We can summarize the results of the electrochemical experiments in eqs 6–9, where *trans*-$[RuCl(NO_2)(py)_4]$ changes typically to 0.5 mol of *trans*-$[RuCl(NO)(py)_4]^{2+}$, 0.25 mol of *trans*-$[RuCl(OH)(py)_4]^+$, and 0.25 mol of *trans*-$[RuCl(O)(py)_4]^+$ by 1.25 electron oxidation (Scheme III). Both $[Ru^{III}Cl(NO^0)]^{2+}$ and $[Ru^{III}Cl(O^-)]^+$ can change to the more stable $[Ru^{II}Cl(NO^+)]^{2+}$ and $[Ru^{IV}Cl(O^{2-})]^+$, respectively, by intramolecular electron-transfer reactions. Nearly half of $[Ru^{III}Cl(O^-)]^+$ (or $[Ru^{IV}Cl(O^{2-})]^+$ or $[Ru^{II}Cl(O^0)]^+$) appeared to be converted into $[Ru^{II}Cl(OH)]^0$, although the mechanistic process for the incorporation of the H atom is presently unknown.

Scheme III



$$\tfrac{1}{4}[Ru^{II}Cl(OH)] \rightarrow \tfrac{1}{4}[Ru^{III}Cl(OH)]^+ + \tfrac{1}{4}e^- \quad (9)$$

We assumed previously that *trans*-$[RuCl(OH)(py)_4]$ was formed by a hydride transfer from CH_3CN solvent to *trans*-$[Ru^{III}Cl(O^-)(py)_4]^+$ species which is isoelectronic with *trans*-$[Ru^{IV}Cl(O^{2-})(py)_4]^+$ and *trans*-$[Ru^{II}Cl(O^0)(py)_4]^+$.[21] For the sake of obtaining evidence that supports this speculation, the controlled-potential electrolysis was attempted under various conditions, with the solvent and/or the electrolyte changed, for *trans*-$[RuCl(NO_2)(py)_4]$ and also for *trans*-$[RuCl(NO_2)(py\text{-}4Me)_4]$. The determined *n* values, summarized in Table III, show that all the experiments proceed by essentially the same oxidation progress. If the hydride transfer takes part in this oxidation reaction, at least in the experiment using C_6H_5CN solvent, different results, including *n* values different from those obtained in other solvents, should be obtained, since the usual transfer of a hydride from C_6H_5CN is not expected. Neither H^- transfer (from the solvents) or H^+ transfer (from the electrolytes) could be detected in these electrochemical experiments.

Table III. Controlled-Potential Electrolyses of Nitro Complexes of Ru(II) under Various Conditions

complex	solvent	electrolyte	*Q/NF* (*n*)
trans-$[RuCl(NO_2)(py)_4]$	CH_3CN	TEAP	1.26–1.34 (9)[a]
		TBAP	1.22
		$LiClO_4$	1.21–1.22 (2)
	PhCN	TEAP	1.20
		TBAP	1.16–1.27 (3)
		$LiClO_4$	1.14
	CH_2Cl_2	TBAP	1.16–1.22 (2)
trans-$[RuCl(NO_2)(py\text{-}4Me)_4]$	CH_3CN		(insoluble)
	PhCN	TEAP	1.10
		TBAP	1.16–1.26 (3)
		$LiClO_4$	1.07
	CH_2Cl_2	TBAP	1.18–1.20 (2)

[a] Figures in parentheses are the number of repetitions.

Another possibility for the origin of the H atom is the existence of an avoidable water in the solvent used for the experiment. CH_3CN used for the present work was purified by three distillations with CaH_2, followed by distillation with NaH and then P_2O_5, using a long Widmer type distillation column (ca. 100 cm) under argon. The water content of the solvent, as determined by Karl Fisher titration, was always near 10^{-3} mol dm^{-3} (10 times the concentration of *trans*-$[RuCl(NO_2)(py)_4]$). Under the conditions where the concentration of water was adjusted to 1.3×10^{-2}–5.6×10^{-1} mol dm^{-3}, no marked effect due to added water could be found.

Selective Formation of Oxygen Ligand in the Chemical Oxidation. The above explanation for the electrochemical oxidation enables us to understand the progress of the rare chemical reaction, where *trans*-$[RuCl(O)(py)_4]^+$ is produced as the sole product (yield 95% in usual). Previously, we assumed that a bonding rupture might occur directly in the $[Cl{-}Ru^{III}{-}NO_2]^+$ moiety to give NO_2^- and $[Cl{-}Ru^{III}{-}OH]^+$, which is changeable to $[Ru^{IV}Cl(O^{2-})]^+$ under our experimental conditions. In fact, all nitro complexes of Ru(III) reported previously are chemically unstable,[39] except *trans*-$[Ru(NO_2)(PMe_3)_2(trpy)]^{2+}$ reported recently by Takeuchi et al.[41]

There is, however, some evidence which suggests that both the electrochemical oxidation in CH_3CN solvent and the chemical oxidation in aqueous basic solution proceed along virtually the same mechanistic path: when *trans*-$[RuCl(NO_2)(py)_4]$ in CH_3CN is oxidized by Ce^{4+}, instead of NaClO in aqueous basic solution, *trans*-$[RuCl(NO)(py)_4]^{2+}$ is generated along with *trans*-$[RuCl(O)(py)_4]^+$,[42] as in the case of the electrochemical experiment referred to above.

The nitrosyl complex, *trans*-$[RuCl(NO)(py)_4]^{2+}$, thus generated can be converted rapidly to the original nitro complex of Ru(II), on the basis of a well-known nitrosyl–nitro conversion reaction, when the oxidation is performed under basic conditions. Reoxidation of the nitro complex of Ru(II), which follows the cyclic route in Scheme III through the dotted line (from eq 8 to eq 6), results in an extremely high yield of *trans*-$[RuCl(O)(py)_4]^+$. Another byproduct in the electrochemical oxidation, *trans*-$[RuCl(OH)(py)_4]^+$, would easily be changed to *trans*-$[RuCl(O)(py)_4]^+$ by one-electron oxidation (eq 10), if it existed. The

---

(40) Durhan, B.; Wilson, S. R.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 600.

(41) Leising, R. A.; Takeuchi, K. J. *J. Am. Chem. Soc.* **1988**, *110*, 4079.

(42) To the solution of *trans*-$[RuCl(NO_2)(py)_4]$ in CH_3CN (0.1 g in 30 cm^3) was added $(NH_4)_2Ce(NO_3)_6$ (0.15 g) with stirring. The yellow solution became green immediately. The green solution was filtered through paper to remove any excess Ce^{4+} salt, and then the solution volume was reduced to 15 cm^3. Diethyl ether was added to the green solution to cause a reddish green oily material to appear. This was separated by decantation (the filtrate was kept for the isolation of *trans*-$[RuCl(O)(py)_4]^+$). The oily material was dissolved in water and a minimum amount of NH_4PF_6 was added to afford a brown precipitate (*trans*-$[RuCl(NO)(py)_4](PF_6)_2$). The solution volume of filtrate (obtained by decantation) was reduced, and then NH_4PF_6 was added to cause *trans*-$[RuCl(O)(py)_4]PF_6$ to appear.

$$[\mathrm{RuCl(OH)(py)_4}]^+ \rightarrow [\mathrm{RuCl(O)(py)_4}]^+ + e^- \tag{10}$$

oxidation of $\mathrm{Ru^{II}{-}OH_2}$ species to the corresponding $\mathrm{Ru^{IV}{=}O}$ species has been known to be a common preparative route for high-valent ruthenium complexes with an oxygen ligand,[5-13] and in fact, eq 10 has been demonstrated.[27]

In contrast, the analogous *trans*-$[\mathrm{Ru(NO_2)(H_2O)(py)_4}]^+$ changed to *trans*-$[\mathrm{Ru(ONO)(O)(py)_4}]^+$ with retention of the nitro nitrogen, as was indicated by a ^{15}N labeling experiment (Table I). Although both *trans*-$[\mathrm{RuCl(O)(py)_4}]^+$ and *trans*-$[\mathrm{Ru(ONO)(O)(py)_4}]^+$ have identical oxo ligands, the origin of the ligand in each product is clearly different. The oxygen-transfer process expressed by Scheme III is not necessary for the explanation. One possible oxidation process of *trans*-$[\mathrm{Ru(NO_2)(H_2O)(py)_4}]^+$ is expressed by Scheme IV (eqs 11-13). Equation 13 will proceed rapidly before $[\mathrm{HO{-}Ru^{III}{-}ONO}]^+$ dimerizes with $[\mathrm{HO{-}Ru^{III}{-}NO_2}]^+$ to give a transient intermediate because $[\mathrm{HO{-}Ru^{III}{-}ONO}]^+$ is less reactive toward the dimerization reaction, as is suggested by electrochemical observations.

Scheme IV

$$[\mathrm{H_2O{-}Ru^{II}{-}NO_2}]^+ \rightarrow [\mathrm{HO{-}Ru^{III}{-}NO_2}]^+ + e^- + \mathrm{H^+} \tag{11}$$

$$[\mathrm{HO{-}Ru^{III}{-}NO_2}]^+ \rightarrow [\mathrm{HO{-}Ru^{III}{-}ONO}]^+ \tag{12}$$

$$[\mathrm{HO{-}Ru^{III}{-}ONO}]^+ \rightarrow [\mathrm{O{=}Ru^{IV}{-}ONO}]^+ + e^- + \mathrm{H^+} \tag{13}$$

The source of the oxygen atom in *trans*-$[\mathrm{RuCl(O)(py)_4}]^+$ can be the one oxygen atom of the nitro ligand in *trans*-$[\mathrm{RuCl(NO_2)(py)_4}]$, while that in *trans*-$[\mathrm{Ru(ONO)(O)(py)_4}]^+$ can be ascribed to the aqua ligand, which existed originally in *trans*-$[\mathrm{Ru(NO_2)(H_2O)(py)_4}]^+$. The selectivity observed in the formation reaction of the high-valent ruthenium complexes with a monooxygen ligand can reasonably be explained by a consideration of the reactivity of *trans*-$[\mathrm{RuX(NO_2)(py)_4}]^n$ where a strong dependence of the X ligand trans to $\mathrm{NO_2^-}$ is seen. One reason that gives rise to the selectivity appears to be that while the nitro-nitrito isomerization occurs rapidly at 25 °C in both nitro complexes, a concomitant oxygen transfer to give a monooxygen moiety (Scheme I, compound e to A or B), via the formation of transient intermediate (Scheme I, compound c to compound e), is relatively slow in *trans*-$[\mathrm{Ru(NO_2)(H_2O)(py)_4}]^+$. How $\mathrm{OH_2}$ (or OH) ligand deaccelerates the oxygen transfer reaction is a problem for future study.

Conclusion

A chemical oxidation reaction of *trans*-$[\mathrm{RuX(NO_2)(py)_4}]^n$ depends on the X ligand, which exists trans to $\mathrm{NO_2^-}$. For X = Cl, *trans*-$[\mathrm{RuCl(O)(py)_4}]^+$ is formed as the sole product (95% yield is usual), while *trans*-$[\mathrm{Ru(ONO)(O)(py)_4}]^+$ is produced when X = $\mathrm{H_2O}$, with retention of the original nitro nitrogen. The conversion processes were revealed through electrochemical investigations at various temperatures (−25 to −40 °C). Both chemical and electrochemical oxidation of *trans*-$[\mathrm{RuCl(NO_2)(py)_4}]$ proceed by an oxygen transfer from one nitro group to another, via an intermediate consisting of *trans*-$[\mathrm{RuCl(NO_2)(py)_4}]^+$ and its isomer, *trans*-$[\mathrm{RuCl(ONO)(py)_4}]^+$. The key to the occurrence of the rare reaction is a decomposition mode of the intermediate existing transiently.

Such an intermediate process is not required for the oxidation of *trans*-$[\mathrm{Ru(NO_2)(H_2O)(py)_4}]^+$ to give *trans*-$[\mathrm{Ru(ONO)(O)(py)_4}]^+$. It can reasonably be assumed that a one-electron oxidation of *trans*-$[\mathrm{Ru(NO_2)(H_2O)(py)_4}]^+$ gives first predominantly *trans*-$[\mathrm{Ru(ONO)(OH)(py)_4}]^+$, which then changes directly to *trans*-$[\mathrm{Ru(ONO)(O)(py)_4}]^+$ by a further one-electron oxidation.

Acknowledgment. We wish to express our thanks to Associate Professor Kunio Shimizu of Sophia University for his helpful discussions on the electrochemical experiment. We also thank K. Hisamatsu and J. Morita for their technical assistance. We appreciate the support of this work in part by Grants-in-Aid for Scientific Research No. 61540454 and No. 01790284 from the Ministry of Education, Science and Culture (to M.M. and H.N.).

Contribution from the Institute for Inorganic Chemistry, University of Witten/Herdecke,
Stockumer Strasse 10, 5810 Witten, Federal Republic of Germany

Temperature and Pressure Effects on the Outer-Sphere Electron-Transfer Reaction between Hexacyanoferrate(II) and Pentaamminecobalt(III) Complexes in Aqueous Solution. Comparison of Experimental and Theoretical Volumes of Activation

I. Krack and R. van Eldik*

Received June 16, 1989

The kinetics of a series of outer-sphere electron-transfer reactions of the type $\mathrm{Co(NH_3)_4(NH_2R)X^{(3-n)+}} + \mathrm{Fe(CN)_6^{4-}} \rightarrow \mathrm{Co^{2+}} + 4\mathrm{NH_3} + \mathrm{NH_2R} + \mathrm{X^{n-}} + \mathrm{Fe(CN)_6^{3-}}$ ($\mathrm{X = N_3^-}$, R = H; $\mathrm{X = Cl^-}$, R = H, $\mathrm{CH_3}$, *i*-$\mathrm{C_4H_9}$) were studied as a function of temperature and pressure. It was possible to separate the ion-pair formation constant and the electron-transfer rate constant in a kinetic way, and the corresponding thermodynamic and activation parameters were determined. For the electron-transfer process, the rate and activation parameters lie in the ranges $0.06 \le k \times 10^2 \le 20\ \mathrm{s^{-1}}$, $84 \le \Delta H^* \le 118\ \mathrm{kJ\ mol^{-1}}$, $+11 \le \Delta S^* \le 113\ \mathrm{J\ K^{-1}\ mol^{-1}}$, and $+19 \le \Delta V^* \le +34\ \mathrm{cm^3\ mol^{-1}}$. The experimentally observed activation volumes are in good agreement with those predicted theoretically on the basis of an average λ^* value of 0.48 ± 0.07. The results are discussed in reference to related studies reported in the literature.

Introduction

In recent years significant advances have been achieved in the application of pressure as a kinetic parameter in mechanistic studies of transition-metal complexes.[1-3] This has in many cases added a further dimension to our mechanistic insight, since such studies enable us to visualize the chemical process in terms of volume changes along the reaction coordinate. We have in the past systematically studied the pressure dependence of a wide range of typical reactions of inorganic and organometallic systems[1-3] and are convinced of the mechanistic discrimination ability of pressure when employed as a kinetic parameter. In this respect, we and others have studied the effect of pressure on some typical outer-sphere electron-transfer reactions.[4-12] Theoretical calcu-

---

(1) van Eldik, R., Ed. *Inorganic High Pressure Chemistry: Kinetics and Mechanisms*; Elsevier: Amsterdam, 1986.

(2) Kotowski, M.; van Eldik, R. *Coord. Chem. Rev.* **1989**, *93*, 19.

(3) van Eldik, R.; Asano, T.; le Noble, W. J. *Chem. Rev.* **1989**, *89*, 549.

(4) van Eldik, R.; Kelm, H. *Inorg. Chim. Acta* **1983**, *73*, 91.

(5) Krack, I.; van Eldik, R. *Inorg. Chem.* **1986**, *25*, 1743.

(6) Krack, I.; van Eldik, R. *Inorg. Chem.* **1989**, *28*, 851.

0020-1669/90/1329-1700$02.50/0 © 1990 American Chemical Society