Temperature Dependence of an Oxygen Transfer Reaction induced by the Oxidation of a Nitro Complex of Ruthenium(II), *trans*-[RuCl(NO$_2$)(py)$_4$] (py = pyridine)

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A single electron oxidation of a nitro complex of Ru^{II} at 25 °C gives three complexes containing (Ru^{IV}=O^{2-}), (Ru^{III}–OH$^-$), and (Ru^{II}–NO$^+$) moieties as final products, while two products involving (Ru^{III}–ONO$_2^-$) and (Ru^{II}–NO$^+$) are formed at *ca.* −40 °C; at 25 °C the reaction appears to proceed from an intermediate species involving an (Ru^{III}–$\dot{O}$) moiety, generated during the oxidation process.

Chemical and electrochemical oxidations of nitro complexes of Ru^{II} generate a reactive nitro complex of Ru^{III} which rapidly undergoes an intermolecular disproportionation at the nitro ligand to give both nitrosyl and nitrato complexes.[1,2] The overall reaction (n = 1.5 mole of electrons per mole of nitro complex) has been described by equation (1).[1] A detailed mechanism which proceeds by the transfer of oxygen from one nitro group to another *via* a nitro–nitrito isomerization has been reported.[1] We found, unexpectedly, that during electrochemical oxidation at 25 °C, the (Ru^{II}–NO$_2^-$) moiety in *trans*-[RuCl(NO$_2$)(py)$_4$] (py = pyridine) rapidly changes to three species involving (Ru^{IV}=O^{2-}), (Ru^{III}–OH$^-$), and (Ru^{II}–NO$^+$), while oxidation at *ca.* −40 °C gave (Ru^{III}–ONO$_2^-$) and (Ru^{II}–NO$^+$) moieties as in the reaction sequence shown in

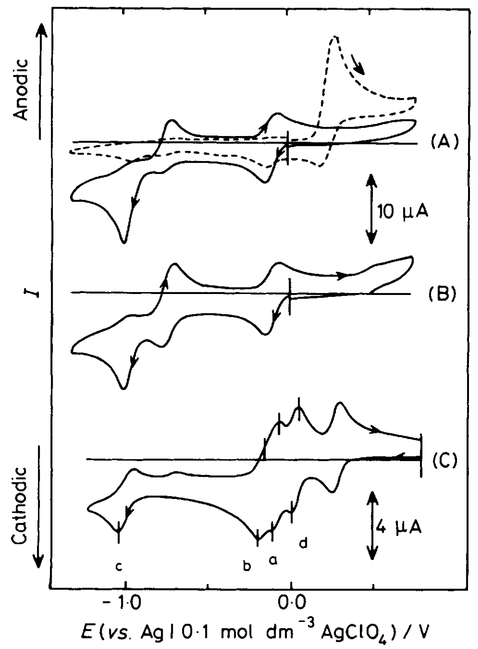

Figure 1. A: Cyclic voltammograms of *trans*-$[RuCl(NO_2)(py)_4]$ (**1**) (1.05×10^{-3} mol dm^{-3}) in MeCN, after controlled potential electrolysis at 0.4 V (25 °C). (Dotted line indicates a first scan before the electrolysis). B: As for A, with *trans*-$[RuCl(H_2O)(py)_4]ClO_4$ (1.75×10^{-4} mol dm^{-3}) added to the solution. C: Cyclic voltammograms observed during the course of the controlled potential electrolysis of (**1**) at *ca.* −40 °C (0.4 V), a, $[RuCl(ONO)(py)_4]^{+/0}$ (**6**); b and c, $[RuCl(NO)(py)_4]^{2+/+,+/0}$ (**3**); d, $[RuCl(ONO_2)(py)_4]^{+/0}$ (**7**); scan rate, 200 mV s^{-1}. Et_4NClO_4, 1×10^{-1} mol dm^{-3}.

equation (1).[1] This paper describes an unusual reaction of the ligand co-ordinated to the Ru atom, for which a marked temperature dependence is observed.

$$2[RuCl(NO_2)(bpy)_2] \longrightarrow [RuCl(NO)(bpy)_2]^{2+} + [RuCl(ONO_2)(bpy)_2]^{+} + 3e^{-} \quad (1)$$

bpy = 2,2′-bipyridine

Cyclic voltammetry of *trans*-$[RuCl(NO_2)(py)_4]\cdot H_2O$ (**1**) under argon at 25 °C in MeCN, showed an irreversible oxidation wave at $E_{pa} = 0.28$ V [*vs.* Ag|AgClO$_4$ (0.1 mol dm^{-3} in MeCN)],† within the potential range expected for $Ru^{2+/3+}$ oxidation. On scan reversal from 2.0 to −1.8 V, small reduction waves appeared around −0.1, −0.7, and −1.0 V. When the controlled potential electrolysis was performed (at 0.4 V) on the identical solution these three waves developed (Figure 1A); the experiment consumed nearly 1.3 moles of electrons per mole of (**1**) (n = 1.26—1.34 for 9 runs). The lack of the cathodic response, corresponding to the pair of oxidation waves observed at 0.28 V, and the appearance of new waves are evidently due to a rapid decomposition of the oxidized species $[RuCl(NO_2)(py)_4]^{+}$ (**2**).

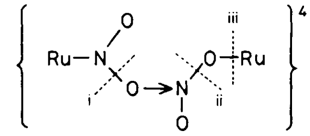

Figure 2. Possible decomposition scheme for the intermediate species.

The products generated by the oxidation were identified as *trans*-$[RuCl(NO)(py)_4]^{2+}$ (**3**) ($E_{1/2} = -0.11$ V, $E_{pc} = -0.98$ V), *trans*-$[RuCl(OH)(py)_4]^{+}$ (**4**) ($E_{1/2} = -0.72$ V), and *trans*-$[RuCl(O)(py)_4]^{+}$ (**5**) ($E_{pc} = -0.99$ V), by comparison to the potential data for authentic samples.[3,4] The generation of a half equivalent of nitrosyl (**3**), based on the original nitro complex (**1**), was confirmed. The other half equivalent of (**1**) was converted into hydroxo (**4**) and oxo (**5**) complexes in nearly equal amounts. Since E_{pc} of the oxo complex (**5**) appeared in almost the same potential region as that of the irreversible cathodic wave of the nitrosyl complex (**3**), the existence of (**5**) could not be confirmed solely by comparison of the potential data with those of the authentic samples. However, its existence was evident from the following results: when the aqua complex of Ru^{II} was added to the previously described electrolysed solution, the small reduction wave of (**4**), observed at $E_{1/2} = -0.72$ V, increased to almost the same height as the reversible wave at −0.11 V due to the nitrosyl complex (**3**) (Figure 1B), while the height of the irreversible wave at −0.98 V was reduced. The results can be explained by the reaction sequence: $[RuCl(O)(py)_4]^{+}$ (**5**) + $[RuCl(H_2O)(py)_4]^{+} \longrightarrow 2[RuCl(OH)(py)_4]^{+}$ (**4**). Direct evidence for the existence of (**5**) in the oxidized solution of (**1**) was obtained by chemical oxidation of (**1**) in MeCN by Ce^{4+} (molar ratio = 1 : 1.2—1.3). This produced a small amount of (**5**) as its PF_6 salt, identified by elemental analysis and by a characteristic i.r. absorption band due to ν(Ru=O).[4]

The controlled potential electrolysis described above was also carried out at *ca.* −40 °C (Figure 1C). Cyclic voltammograms of the solution exhibited four waves which were assigned to *trans*-$[RuCl(ONO)(py)_4]^{+}$ (**6**) [Figure 1C(a)], *trans*-$[RuCl(NO)(py)_4]^{2+}$ (**3**) [Figure 1C(b) and (c)] and *trans*-$[RuCl(ONO_2)(py)_4]^{+}$ (**7**) [Figure 1C(d)], in accord with the oxidation sequence described by equation (1). Equation (2) accounts for the stoicheiometry of the present oxidation at 25 °C, [except for the hydroxy hydrogen atom in (**4**)]. A mechanistic study of equation (2) is now in progress; we provisionally assume the following sequence: the nitro complex (**1**) undergoes a one-electron oxidation to give a dimeric intermediate $\{-Ru-N(O)O-N(O)O-Ru-\}^{4+}$ which is essential for the oxygen transfer within the nitro ligand.[1] An N–O bond breaks [Figure 2(i)], allowing the intermediate to transfer the oxygen atom from one nitro group to the other, producing equal amounts of nitrosyl (**3**) and nitrato (**7**) complexes, as described by equation (1).[1] When the intermediate undergoes bond cleavage at (i), a nitrato complex of Ru^{II} is also formed with (**3**), *via* a transient (Ru^{III}–ONO_2^{2-}) species, prior to the formation of (**7**).[1] The transient (Ru^{III}–ONO_2^{2-}) moiety probably decomposes further to NO_2^{-} and (Ru^{III}–O) [Figure 2(ii)] which can then convert into (Ru^{IV}=O^{2-}) (**5**) by intramolecular electron transfer. Under more moderate conditions a process that yields nitrite from co-ordinated nitrate has been found to occur.[5]

$$2[RuCl(NO_2)(py)_4] \longrightarrow [RuCl(NO)(py)_4]^{2+} + 1/2[RuCl(OH)(py)_4]^{+} + 1/2[RuCl(O)(py)_4]^{+} + NO_2^{-} + 2.5e^{-} \quad (2)$$

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† Acetonitrile was purified by three distillations with calcium hydride, followed by distillation with sodium hydride, then with phosphorus pentoxide, using a long Widmer type distillation column (*ca.* 100 cm) under argon. The purified acetonitrile was used within seven days of the last distillation. The water content of the solvent, as determined by the Karl Fisher titration, was less than 1 mmol dm^{-3}.[6]

Our explanation for the origin of the hydroxo ligand in (**4**) is rather speculative. One possibility is that hydride transfer may occur between MeCN and the transient $(\mathrm{Ru^{III}{-}\dot{O}})$ moiety to produce $(\mathrm{Ru^{II}{-}OH^-})$. The $(\mathrm{Ru^{II}{-}OH^-})$ species [0.5 equiv. based on 2 equiv. of (**1**) in equation (2)] undergoes oxidation to give (**4**) as one of the final products. Cleavage of the Ru–O bond [Figure 2(iii)] may also occur in the $(\mathrm{Ru^{III}{-}ONO_2{}^{2-}})$ moiety, where *trans*-$[\mathrm{Ru^{II}Cl(H_2O)(py)_4}]^+$ is expected to be formed because of unavoidable moisture in dry MeCN.‡ The water of crystallization of (**1**) also participates in this equation (2). It should be emphasised that the presence of the solvated complex of Ru(II), *trans*-$[\mathrm{RuCl(MeCN)(py)_4}]^+$, could not be observed using cyclic voltammetry at any stage of the reaction.

In conclusion, we have presented a new single electron oxidation of *trans*-$[\mathrm{RuCl(NO_2)(py)_4}]$ which rapidly gives *trans*-$[\mathrm{RuCl(O)(py)_4}]^+$, which can be regarded as a two-electron oxidation product, along with *trans*-$[\mathrm{RuCl(OH)(py)_4}]^+$ and *trans*-$[\mathrm{RuCl(NO)(py)_4}]^{2+}$. We speculate that the formation of an intermediate species containing an $(\mathrm{Ru^{III}{-}\dot{O}})$ moiety is a key step of this unusual reaction.

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‡ In this case, $\mathrm{ONO_2{}^-}$ is generated in place of the $\mathrm{NO_2{}^-}$ in equation (2).