Communications to the Editor

Nitro Complexes of Ruthenium(III) as Oxidation Catalysts. Chemically Catalyzed, Net Electrochemical Oxidation of Triphenylphosphine

Sir:

cis-$[Ru^{II}(bpy)_2(NO_2)Cl]$ (bpy = 2,2′-bipyridine) and related complexes can be oxidized to Ru(III), but as Ru(III) are only kinetic transients. Their stability is limited by a facile intermolecular disproportionation reaction (reactions 1 and 2), which gives both nitrosyl and nitrato complexes as products.[1] In the disproportionation reaction, a two-electron oxidation occurs at a nitro group on one ruthenium and the corresponding reduction at both metal ($Ru^{III} \rightarrow Ru^{II}$) and nitrosyl ($Ru\text{-}^{+}NO \rightarrow Ru\text{-}\dot{N}O$) sites. Nitrosyl complexes like $[Ru(bpy)_2(^{+}NO)Cl]^{2+}$ are known to undergo reversible electron transfer localized largely at the NO group (reaction 2).[2] In reaction 1, $[Ru^{III}(bpy)_2(NO_2)Cl]^{+}$ acts as an oxide donor, two-electron acceptor oxidant. Its formal reduction potential (eq 3) has been determined to be 0.31 V (0.72 V at pH 7) in 1.0 M aqueous NaCl at 25.0 °C vs. NHE and that for the related pyridine complex, $[Ru^{III}(bpy)_2(NO_2)py]^{2+}$, has been estimated to be ≥0.26 V (≥0.67 V at pH 7).[1]

$$[Ru^{III}(bpy)_2(NO_2)Cl]^{+} + H_2O + 2e \rightarrow [Ru^{II}(bpy)_2(\dot{N}O)Cl]^{+} + 2OH^{-} \quad (3)$$

Even though disproportionation (reaction 1) is a competing pathway, in the presence of a sufficiently reactive substrate, it should be possible to capture the nitroruthenium(III) intermediates and so to exploit their properties as oxidants. Electrochemical oxidation of an acetonitrile solution (0.1 M $[N(C_4H_9)_4](PF_6)$) containing $[Ru(bpy)_2(NO_2)py]^{+}$ (1×10^{-3} M) and triphenylphosphine (3×10^{-3} M) at 1.15 V vs. the saturated sodium chloride calomel electrode (n = 2.0/Ru by coulometry)[3] gave as products $[Ru(bpy)_2(NO)py]^{3+}$ (by cyclic voltammetry; Figure 1) and triphenylphosphine oxide (by IR, ν(P=O) 1194 cm^{-1}). Oxidation of the Ru(II) complex occurs at $E_{p,a}$ = 1.06 V. The results of the experiment show that although oxidation of PPh_3 and disproportionation may be competing processes, disproportionation is unimportant under the conditions of the experiment,[4] and the net reaction is

$$[Ru^{II}(bpy)_2(NO_2)py]^{+} + PPh_3 \xrightarrow{-2e^-} [Ru^{II}(bpy)_2(^{+}NO)py]^{3+} + OPPh_3 \quad (4)$$

Electrochemical oxidation of $[Ru(bpy)_2(NO_2)Cl]$ in the presence of PPh_3 also gave $OPPh_3$ and it was possible to study the reaction in detail. The $[Ru^{III}(bpy)_2(NO_2)Cl]^{+}$–

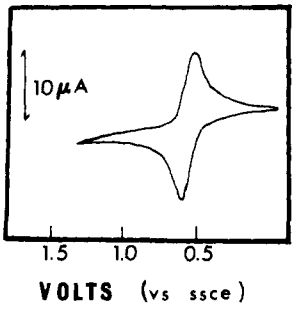


Figure 1. Cyclic voltammogram following electrolysis at 1.15 V (n = 2.0/Ru by coulometry) of a solution containing initially $[Ru(bpy)_2(NO_2)py]^{+}$ (1×10^{-3} M) and PPh_3 (3×10^{-3} M) in 0.1 M $[N(C_4H_9)_4]PF_6$–CH_3CN vs. the SSCE.

$[Ru^{II}(bpy)_2(NO_2)Cl]$ couple is reversible on the cyclic voltammetry time scale (200 mV/s; $E_{1/2}$ = 0.58 V in acetonitrile).[3] Electrochemical oxidation (at 0.80 V) of ^{18}O-enriched $[Ru(bpy)_2(NO_2)Cl]$[5] (5×10^{-4} M) in dichloromethane in the presence of a threefold excess of PPh_3 gave n = 2.0 and as products $[Ru(bpy)_2(NO)Cl]^{2+}$ and $Ph_3P{=}O$. The extent of ^{18}O labeling in the $OPPh_3$ product was identical with that in the initial nitro complex as shown by $\nu(N^{18}O)/\nu(N^{16}O)$ and $\nu(P^{18}O)/\nu(P^{16}O)$ ratios in the IR.[7] The initial step in the electrochemical experiment is oxidation of Ru(II) to Ru(III) which is followed by oxidation of PPh_3 to $OPPh_3$. The rate of the reaction between $[Ru^{III}(bpy)_2(NO_2)Cl]^{+}$ and PPh_3 was studied by chronoamperometry. The reaction is first order in both $[Ru^{III}(bpy)_2(NO_2)Cl]^{+}$ and PPh_3, and in propylene carbonate as solvent, k(25.0 °C, I = 0.2) = 200 ± 10 $M^{-1}\,s^{-1}$. The reaction is considerably more rapid than the rate of disproportionation of $[Ru(bpy)_2(NO_2)Cl]^{+}$ (reaction 1) under the same conditions (k = 3.0 $M^{-1}\,s^{-1}$),[1] which explains why Ru(III)–NO_2 once formed is captured by PPh_3 rather than by disproportionation. The rate of oxidation of PPh_3 by $[Ru^{III}(bpy)_2(NO_2)py]^{2+}$ must be even more rapid. At a PPh_3/Ru ratio of 3:1, electrochemically generated $[Ru^{III}(bpy)_2(NO_2)py]^{2+}$ is completely captured by PPh_3 (Figure 1) and yet the rate of disproportionation of the Ru(III)–nitro complex exceeds 10^7 $M^{-1}\,s^{-1}$.[1]

The electrochemical results, the ^{18}O labeling experiment, and the second-order rate law for oxidation all suggest that oxidation of PPh_3 occurs as in reactions 5–7.

$$[Ru^{II}(bpy)_2(NO_2)Cl] \xrightarrow{-e^-} [Ru^{III}(bpy)_2(NO_2)Cl]^{+} \quad (5)$$

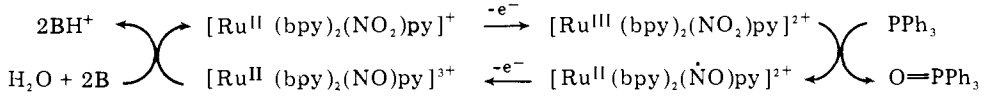
$$[Ru^{III}(bpy)_2(NO_2)Cl]^{+} + PPh_3 \rightarrow [(bpy)_2ClRu^{III}\text{-}\overset{O}{\overset{\|}{\underset{+}{N}}}\cdots O\cdots PPh_3]^{+} \rightarrow [Ru^{II}(bpy)_2(\dot{N}O)Cl]^{+} + OPPh_3 \quad (6)$$

$$[Ru^{II}(bpy)_2(\dot{N}O)Cl]^{+} \xrightarrow{-e^-} [Ru^{II}(bpy)_2(^{+}NO)Cl]^{2+} \quad (7)$$

At the potentials used in the electrolyses, the reduced nitrosyl complexes are known to be oxidized to $[Ru(bpy)_2(^{+}NO)L]^{n+}$.[2]

The Ru(III)–nitro intermediates are weak to moderately strong oxidants as shown by their reduction potential values.

Scheme I (note Figure 2)



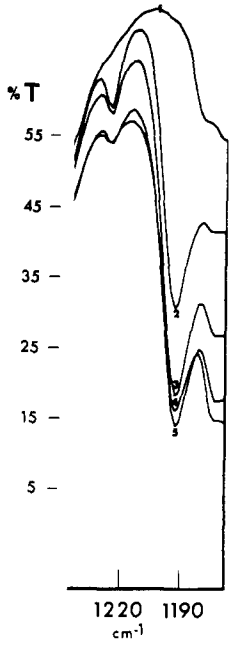


Figure 2. Infrared spectra following electrolysis of an acetonitrile solution containing initially $[Ru(bpy)_2(NO_2)py]^+$ (1.2×10^{-3} M), PPh_3 (7×10^{-3} M), 1% 2,6-lutidine, and 1% water in 0.1 M $[N(C_4H_9)_4]PF_6$. ν(PO) in $O{=}PPh_3$ occurs at 1194 cm^{-1}. The lower energy band arises from $[Ru(bpy)_2(NO_2)py]^+$: (1) before electrolysis; (2) electrolysis to 25% completion based on the initial amount of PPh_3; (3) electrolysis to 50% completion; (4) electrolysis to 60% completion; (5) electrolysis to 75% completion.

Rather than thermodynamic driving force, the origin of the relatively rapid rates of disproportionation and of PPh_3 oxidation may lie in the existence of two one-electron acceptor sites (Ru(III) and Ru-$^+$NO) in the oxidant rather than a single two-electron site and in the ability of the oxidant to donate an oxide ion. Kinetic barriers to electron transfer at both Ru(III)[8] and Ru($^+$NO)[2] sites are known to be low and there are no profound changes in coordination environment on reduction except for the loss of O^{2-}.

$[Ru(bpy)_2(NO_2)py]^+$ and $[Ru(bpy)_2(NO)py]^{3+}$ are interrelated by the acid-base equilibrium in eq 8 and in water, the two ions are present in equimolar amounts at pH 3.8.[1,9]

$$[Ru(bpy)_2(NO)py]^{3+} + 2OH^- \rightleftharpoons [Ru(bpy)_2(NO_2)py]^+ + H_2O \quad (8)^1$$

$$K(25.0\ °C;\ 1.0\ M\ NaCl) = 1 \times 10^{20}\ M^{-2}$$

In slightly basic solution the nitrosyl complex once formed (eq 6 and 7) is converted into the nitro complex. The nitro complex reenters the oxidation sequence in reactions 5-7, which means that the oxidation of PPh_3 can be made catalytic. Exhaustive electrolysis (at 1.15 V) of an acetonitrile solution containing $[Ru(bpy)_2(NO_2)py]^+$ (1×10^{-3} M), PPh_3 (1×10^{-2} M), H_2O (1%), and 2,6-lutidine (1%) gave $n = 21.1$ by coulometry. The final ruthenium product was $[Ru(bpy)_2(NO_3)py]^{2+}$ (by cyclic voltammetry). The results are consistent with the catalytic cycle in Scheme I ($n = 20$) followed by reaction 9 ($n = 3$) when the $PPh_3 \rightarrow O{=}PPh_3$ conversion (Figure 2) is complete.

$$[Ru^{II}(bpy)_2(NO_2)py]^+ + 2B + H_2O \xrightarrow{-3e^-} [Ru^{III}(bpy)_2(NO_3)py]^{2+} + 2BH^+ \quad (9)^1$$

The electrolytic chemistry observed here is the chemically catalyzed, net electrochemical oxidation of PPh_3 to $O{=}PPh_3$.

$$PPh_3 + H_2O + 2B \rightarrow O{=}PPh_3 + 2BH^+ + 2e^- \quad (10)$$

In an acetonitrile solution containing $[Ru(bpy)_2(NO_2)Cl]$, water, and triethylamine, the oxidation of PPh_3 is also catalytic. Under these conditions cyclic voltammetry shows only a distorted wave for the $[Ru^{II}(bpy)_2(NO_2)Cl] \rightarrow [Ru^{III}(bpy)_2(NO_2)Cl]^+$ oxidation and no rereduction wave, nor does a wave for $[Ru(bpy)_2(NO)Cl]^{2+}$ appear. The experiment shows that the chemical steps in Scheme I are rapid and that the *rate determining step in the catalyzed oxidation of PPh_3 is diffusion of $[Ru(bpy)_2(NO_2)Cl]$ to the electrode.*

The Ru(III)-nitro intermediates appear to have an extensive oxidase-like redox chemistry and their reactions with various reagents are currently under investigation. They are promising as oxidants, since in contrast to commonly used inorganic oxidants like Cr(VI) or MnO_4^-, their reactivity properties can be varied systematically by controlled chemical synthesis, and their reactions can be made catalytic.

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References and Notes

(1) F. R. Keene, D. J. Salmon, and T. J. Meyer, *J. Am. Chem. Soc.*, **99**, 2384 (1977).
(2) T. J. Meyer, R. W. Callahan, and G. M. Brown, *J. Am. Chem. Soc.*, **97**, 894 (1975); R. W. Callahan and T. J. Meyer, *Inorg. Chem.*, **16**, 574 (1977).
(3) Unless otherwise noted electrochemical results were obtained in solutions 0.1 M in $[N(n\text{-}C_4H_9)_4]PF_6$ at 22 ± 2 °C vs. the saturated sodium chloride calomel eletrode (SSCE). Platinum bead electrodes were used in cyclic voltammetry and platinum gauze electrodes for electrolyses. *n* values were obtained by coulometry, where *n* is the number of electrons passed per Ru in a constant potential electrolysis.
(4) Disproportionation gives nitrosyl *and* nitrato complexes as products and $n = 3.0$ (eq 1 and 2).[1]
(5) Ca. 7% ^{18}O-enriched $[Ru(bpy)_2(NO_2)Cl]$ was prepared by treating a suspension of $[Ru(bpy)_2(NO)Cl](PF_6)_2$ with base in ^{18}O-enriched water.[6]
(6) T. J. Meyer and J. B. Godwin, *Inorg. Chem.*, **10**, 2150 (1971).
(7) Quantitative IR experiments were carried out using a Digilab FTS-14 spectrometer.
(8) R. W. Callahan, F. R. Keene, T. J. Meyer, and D. J. Salmon, *J. Am. Chem. Soc.*, **99**, 1064 (1977); R. C. Young, F. R. Keene, and T. J. Meyer, *J. Am. Chem. Soc.*, **99**, 2468 (1977).
(9) For the $[Ru(bpy)_2(NO)Cl]^{2+}$-$[Ru(bpy)_2(NO_2)Cl]$ equilibrium, *K* is 1.4×10^9 under the same conditions.[6]

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An Anionic Equivalent of the Friedel-Crafts Cycloacylation

Sir:

Our interest in the potent anticancer agent daunomycin[1] (**1**) has led us to consider possible synthetic routes[2] to this and other anthracycline antibiotics.[3] The problem, as we see it, is to develop methods for ring building as in eq 1 wherein the alicyclic ring possesses the desired functionality. In this manner one may reduce the regiospecificity problems[2] associated with