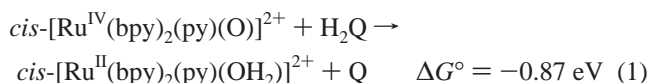# Proton-Coupled Electron Transfer from Nitrogen. A N−H/N−D Kinetic Isotope Effect of 41.4

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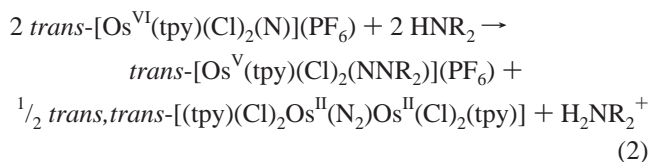Chapel Hill, North Carolina 27599-3290*

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An extensive redox chemistry associated with high oxidation state Ru(IV) oxo complexes has been uncovered by kinetic and mechanistic studies.[1−4] This includes pathways involving well-defined, multiple electron transfer such as O-atom[5] or hydride ion[3,6] transfer. Large H_2O/D_2O solvent kinetic isotope effects have been identified in a series of reactions and interpreted as involving synchronous transfer of an electron and a proton (proton-coupled electron transfer).[2,7] For example, $k(H_2O)/k(D_2O) = 30 \pm 1$ for the oxidation of hydroquinone (H_2Q) to benzoquinone (Q) by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ at 20.0 ± 0.2 °C.

$$cis\text{-}[Ru^{IV}(bpy)_2(py)(O)]^{2+} + H_2Q \rightarrow$$
$$cis\text{-}[Ru^{II}(bpy)_2(py)(OH_2)]^{2+} + Q \qquad \Delta G° = -0.87 \text{ eV} \quad (1)$$

This reaction occurs by sequential Ru(IV) → Ru(III), Ru(III) → Ru(II) steps with rate-limiting proton-coupled electron transfer.[2] We report here the existence of a parallel chemistry based on proton-coupled electron transfer from nitrogen. In this case, the reaction is between quinone and the morpholine-based protonated Os(IV) hydrazido complex, *trans*-$[Os^{IV}(tpy)(Cl)_2(N(H)N(CH_2)_4O)]$-$(PF_6)$ (tpy = 2,2′:6′,2″-terpyridine)[8] and occurs with $k(H_2O)/k(D_2O) = 41.4 \pm 1.3$ at 25.0 ± 0.1 °C.
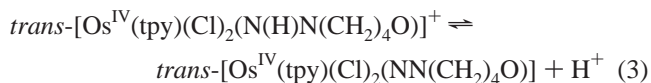
The preparations of a series of Os(V) hydrazido complexes by reaction between the corresponding Os(VI) nitrido complex and a secondary amine have been described elsewhere.[9] For example, *trans*-$[Os^{VI}(tpy)(Cl)_2(N)](PF_6)$ undergoes a rapid reaction with morpholine, $HN(CH_2)_4O$, in CH_3CN under argon to give *trans*-

$[Os^{IV}(tpy)(Cl)_2(NN(CH_2)_4O)]$ followed by oxidation to the Os-(V) form (**1**) by the Os(VI) nitrido complex.[9] The net reaction is,

$$2 \text{ } trans\text{-}[Os^{VI}(tpy)(Cl)_2(N)](PF_6) + 2 \text{ } HNR_2 \rightarrow$$
$$trans\text{-}[Os^V(tpy)(Cl)_2(NNR_2)](PF_6) +$$
$$^1/_2 \text{ } trans,trans\text{-}[(tpy)(Cl)_2Os^{II}(N_2)Os^{II}(Cl)_2(tpy)] + H_2NR_2^+$$
$$(2)$$

trans-$[Os^V(tpy)(Cl)_2(NN(CH_2)_4O)]^+$ has been isolated as its PF_6 salt and characterized by X-ray crystallography.[10] In the structure, the distorted octahedral arrangement of ligands around the Os atom in the parent nitrido complex is retained. The Os−N(tpy) bond lengths range from 2.007(8) to 2.116(10) Å with the shortest Os−N bond trans to the hydrazido ligand. The Os−N(hydrazido) bond length is rather short at 1.865(8) Å, the N(1)−N(2) bond length is 1.235(14) Å, and ∠Os−N(1)−N(2) is 158.9(12) °. These features point to Os−N(hydrazido) multiple bonding. There are structural similarities with $[Os^{IV}(tpy)(bpy)(NN(CH_2)_4O)]^{2+}$ (bpy = 2,2′-bipyridine).[11]

Cyclic voltammetric measurements in 1:1 (v/v) $CH_3CN:H_2O$ mixtures 0.1 M in $[N(n\text{-}C_4H_9)_4](PF_6)$ (TBAH) containing **1** from pH 1.0 to 8.0 reveal the existence of a pH-independent Os(VI/V) couple at 0.81 V versus SSCE and a pH-dependent Os(V/IV) couple. Based on the pH dependence of the $E_{1/2}$ value for this couple, $pK_a = 3.20 \pm 0.04$ for the equilibrium in eq 3.[12]

$$trans\text{-}[Os^{IV}(tpy)(Cl)_2(N(H)N(CH_2)_4O)]^+ \rightleftharpoons$$
$$trans\text{-}[Os^{IV}(tpy)(Cl)_2(NN(CH_2)_4O)] + H^+ \quad (3)$$

trans-$[Os^{IV}(tpy)(Cl)_2(N(H)N(CH_2)_4O)]^+$ (**2**) undergoes rapid oxidation by benzoquinone, Q, to give *trans*-$[Os^V(tpy)(Cl)_2(NN-(CH_2)_4O)]^+$ and hydroquinone,

$$2 \text{ } trans\text{-}[Os^{IV}(tpy)(Cl)_2(N(H)N(CH_2)_4O)]^+ + Q \rightarrow$$
$$2 \text{ } trans\text{-}[Os^V(tpy)(Cl)_2(NN(CH_2)_4O)]^+ + H_2Q$$
$$\Delta G° = -0.045 \text{ eV} \quad (4)$$
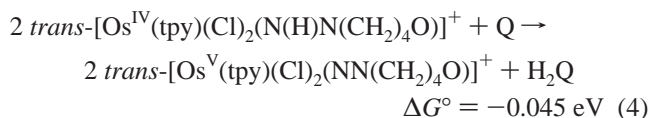
The kinetics and stoichiometry of this reaction at 25.0 ± 0.1 °C were studied in 1:1 (v/v) $CH_3CN:H_2O$ at pH 1.0 ($\mu = 0.1$ M KNO_3) by following characteristic changes in the absorption spectra of Os(V) and Os(IV)[13] under pseudo-first-order conditions

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(8) There is no evidence for paramagnetic broadening in ^{1}H NMR spectra of the related complexes, $[Os^{IV}(tpy)(Cl)(NCCH_3)(NN(CH_2)_4O)](PF_6)$; $[Os^{IV}$-$(tpy)(NCCH_3)_2(NN(CH_2)_4O)](PF_6)_2$; $[Os^{IV}(tpm)(Cl)_2(N(H)N(CH_2)_4O)](PF_6)$; and $[Os^{IV}(tpm)(Cl)_2(NN(CH_2)_4O)]$ (tpm = tris(1-pyrazolyl)methane), showing that they are d^4 diamagnetic complexes.

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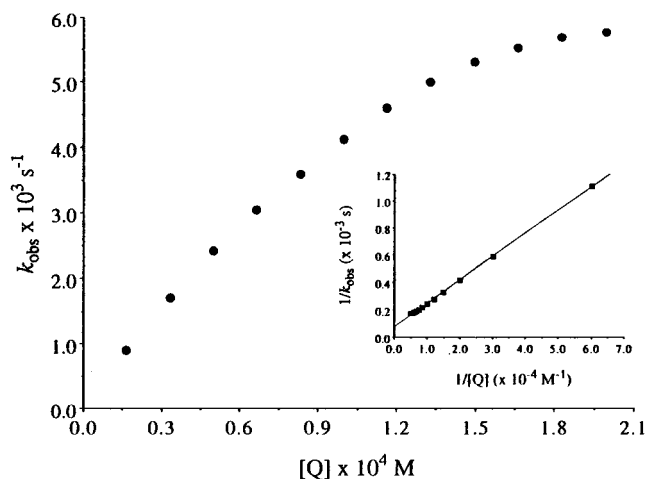
(10) Crystals of *trans*-$[Os^V(tpy)(Cl)_2(NN(CH_2)_4O)](PF_6)$ were grown by vapor diffusion of Et_2O into an CH_3CN solution of the salt. They are orthorhombic, space group *P2nn*, with $a = 8.5914(4)$ Å, $b = 23.2244(11)$ Å, $c = 11.8603(6)$ Å, $V = 2366.49(20)$ Å^3, $Z = 4$, fw = 739.45, $d_{calc} = 2.076$ g/cm^3, and $\mu = 5.75$ mm^{-1}. Intensity data were collected at -100 °C on a Siemens CCD SMART Diffractometer with Mo Kα radiation and a graphite monochromator by using the ω scan mode. A total of 11966 reflections were collected, and 4170 of them are unique. 2961 reflections with $I > 3.0\sigma(I)$ were used in the structure refinement by full-matrix least-squares techniques (316 parameters). Absorption corrections were made by using SADABS. Final $R_f = 4.1\%$, $R_w = 4.4\%$, GoF = 1.56 ($R = 5.9\%$, $R_w = 4.6\%$, for all reflections). NRCVAX was used as the software package. Full details can be found in the Supporting Information.

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(12) In the pK_a measurements, buffer solutions from pH 1.0 to 8.0 ($\mu = 0.1$ M) were prepared from HNO_3 (pH 1−2), KHP (pH 3−6), KH_2PO_4, and Na_2HPO_4 (pH = 7−8) before each measurement. Since *trans*-$[Os^V(tpy)(Cl)_2$-$(NN(CH_2)_4O)]^+$ is not soluble in H_2O, a mixture of 1:1 (v/v) $CH_3CN:H_2O$ was used as the solvent in the electrochemical experiments. The pH values reported are those measured in the mixed solvents. The difference in measured pH values between the aqueous and mixed solvent was 0.1 pH unit or less.

(13) UV−visible spectra of *trans*-$[Os^V(tpy)(Cl)_2(NN(CH_2)_4O)](PF_6)$ (**1**) and *trans*-$[Os^{IV}(tpy)(Cl)_2(N(H)N(CH_2)_4O)](PF_6)$ (**2**) in 1:1 (v/v) $CH_3CN:H_2O$ (pH 1, $\mu = 0.1$ M KNO_3) (λ_{max}, nm (ϵ, M^{-1} cm^{-1}): For **1**, 658 (9.75×10^2); 424 (3.92×10^3); 402 (4.02×10^3); 314 (2.02×10^4); 258 (2.65×10^4); 234 (2.93×10^4); 212 (2.63×10^4). For **2**, 572 (1.44×10^3); 454 (7.06×10^3); 318 (2.41×10^4); 280 (1.90×10^4); 272 (1.89×10^4); 250 (1.69×10^4)).

Figure 1. Plot of k_{obs} versus [Q] for the reaction between *trans*-[Os^{IV}-(tpy)(Cl)$_2$(N(H)N(CH$_2$)$_4$O)](PF$_6$) and benzoquinone in 1:1 (v/v) CH$_3$CN−H$_2$O (25.0 ± 0.1 °C, pH 1, and μ = 0.1 M KNO$_3$). A plot of $1/k_{obs}$ versus $1/[Q]$ is shown in the inset.

in benzoquinone. A plot of k_{obs} versus [Q] is shown in Figure 1. As shown by the inset, the data are linearized by a plot of $1/k_{obs}$ versus $1/[Q]$ consistent with saturation kinetics ($k_{obs} = \{(2k_1K_a[H^+] + 2k_2K_a)/([H^+] + K_a)\}$) and the mechanism,

$$[Os^{IV}(N(H)N(CH_2)_4O)]^+ + H\dot{Q} \longrightarrow [Os^V(NN(CH_2)_4O)]^+ + H_2Q \quad (rapid) \quad (5b)$$
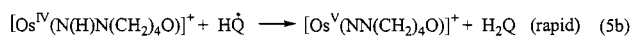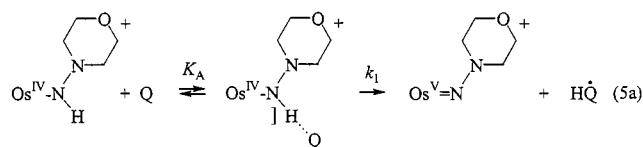
This mechanism is similar in detail to that proposed for the oxidation of H$_2$Q by *cis*-[Ru(bpy)$_2$(py)(O)]$^{2+}$.

As calculated from the slope and intercept-to-slope ratio of the plot in Figure 1, $K_A(H_2O) = (4.43 \pm 0.18) \times 10^3$ M^{-1} and $k_1(H_2O) = (6.61 \pm 0.09) \times 10^{-3}$ s^{-1} at 25.0 ± 0.1 °C. Direct evidence has been obtained for the proposed H-bonded adduct at high added concentrations of Q, for example, a band at 454 nm in the UV−visible spectrum shifts to 424 nm (Figure 1, Supporting Information).

The kinetics were also measured in 1:1 (v/v) CH$_3$CN:H$_2$O/D$_2$O mixtures. The plot of k_X/k_D versus χ_D in Figure 2 (k_X is the rate constant in H$_2$O/D$_2$O mixtures of mole fraction D, χ_D.) reveals a k_X/k_D isotope effect of 41.4 ± 1.3 at 25.0 ± 0.1 °C, and the linearity of the plot implies that a single proton is involved.[14] Kinetic studies as a function of benzoquinone were also investigated in 1:1 (v/v) CH$_3$CN:D$_2$O (25.0 ± 0.1 °C, pH 1, μ = 0.1 M KNO$_3$). Based on the analysis in eqs 5a,b and the data treatment illustrated for CH$_3$CN:H$_2$O in Figure 2, $K_A(D_2O)$ and $k_1(D_2O)$ are (4.28 ± 0.04) × 10^3 M^{-1} and (1.65 ± 0.03) × 10^{-4} s^{-1},

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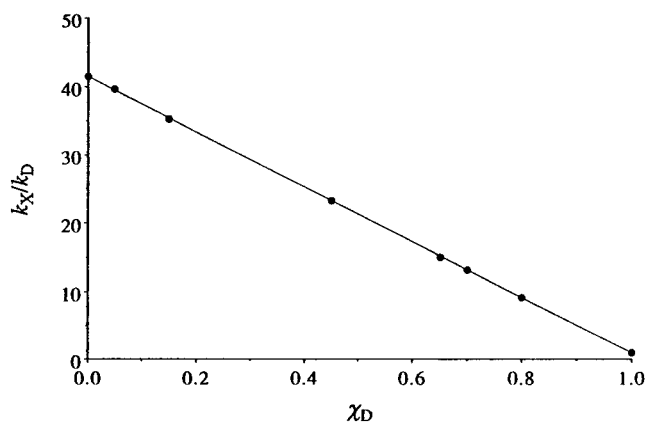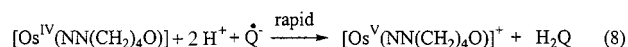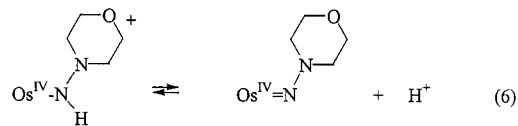
Figure 2. Plot of k_X/k_D versus χ_D for the reaction between *trans*-[Os^{IV}-(tpy)(Cl)$_2$(N(H)N(CH$_2$)$_4$O)](PF$_6$) and benzoquinone in 1:1 (v/v) CH$_3$CN−H$_2$O/D$_2$O mixtures (25.0 ± 0.1 °C, pH 1, μ = 0.1 M KNO$_3$).

respectively. From these data, $k(H_2O)/k(D_2O) = 40.0 \pm 1.6$ for the redox step (k_1) and $K_A(H_2O)/K_A(D_2O) = 1.04 \pm 0.03$.

The kinetic analysis reveals a mechanism for net electron transfer involving preassociation to form an intermediate with the large value of K_A attributable to H-bonding as suggested in eq 5a. The large magnitude of the kinetic isotope effect points to synchronous electron−proton transfer in the redox step by proton-coupled electron transfer. This result is notable for the demonstration of this pathway at a nitrogen atom and for the magnitude of the kinetic isotope effect.

The importance of proton composition on mechanism is illustrated by the appearance of a second pathway as the pH is increased. Under pseudo-first-order conditions and with UV−visible absorption monitoring, the variations in k_{obs} with [Q] and [H$^+$] fit well to the expression $k_{obs} = \{(2k_1K_a[H^+] + 2k_2K_a)/([H^+] + K_a)\}$ (Figure 2, Supporting Information). These data are consistent with prior deprotonation at Os(IV) and the intervention of a second pathway as illustrated in eqs 6−8,

$$[Os^{IV}(NN(CH_2)_4O)] + Q \xrightarrow{k_2} [Os^V(NN(CH_2)_4O)]^+ + \dot{Q}^- \quad (7)$$

$$[Os^{IV}(NN(CH_2)_4O)] + 2 H^+ + \dot{Q}^- \xrightarrow{rapid} [Os^V(NN(CH_2)_4O)]^+ + H_2Q \quad (8)$$

with $k_2 = (4.1 \pm 0.1) \times 10^2$ s^{-1}. From electrochemical measurements, $\Delta G° = -0.045$ eV for the net reaction.

Supporting Information Available: Tables containing crystal data, supplementary Figure 1, atomic coordinates, isotropic thermal parameters, bond distances and angles, and packing diagrams (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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