Table II. MIKE Spectra of m/e 356 and (O-Deuterated) m/e 357 Ions[a]

m/e	compd							
	1	3	5	6	2	4	7	4-OD
341 (342[b])	23.9	24.7	24.5	23.4	(100.0)	(100.0)	(100.0)	(100.0)
338	16.8	22.0	22.0	25.0				
265 (266[b])	(100.0)	(100.0)	(100.0)	(100.0)	1.7	0.8	0.7	9.8
251 (252[b])					7.2	7.3	6.1	6.8
236 (237[b])	44.0	37.0	37.2	35.1	3.6	3.1	2.7	6.0
147	13.4	10.5	10.1	9.4				
105					0.4	0.5	0.3	0.5

[a] Low abundance ions have not been included. [b] These m/e values relate to O-deuterated 4 only.

rearrangement of ionized 5–7.[6] The overall 356⁺ MIKE spectra of 1, 3, 5, and 6 or 2, 4, and 7 are very similar (Table II). The four compounds 1, 3, 5, and 6 showed the metastable transition 356⁺ → 147⁺. The ion at m/e 147 is $C_{10}H_{11}O^+$ according to high-resolution mass spectrometry and is presumably the mesitoyl ion 2,4,6-Me₃C₆H₂C≡O⁺. Compounds 2, 4, and 7 showed the two metastable transitions 356⁺ → 105⁺ (PhCO⁺), 356⁺ → 251⁺ (Mes₂CH⁺, by high resolution). A study of O-deuterated 4, (Mes₂C=C(OD)Ph, m/e 357) showed a major m/e 252 peak, corresponding to the Mes₂CD⁺ ion (Table II). Kinetic-energy release values ($T_{1/2}$) were calculated from the metastable peak widths at half-height. The peak shapes for the 356⁺ → 147⁺ reaction of 3, 5, and 6 were identical within the experimental error: the exponent for a Gaussian-type peak[7] (n) equals 1.8. In contrast, the $T_{1/2}$ value for 1 is definitely lower, and the peak shape is different, n ≃ 1.4. Likewise, the $T_{1/2}$ values for 4 and 7 for both the 356⁺ → 105⁺ and the 356⁺ → 251⁺ reactions are identical[8] but those for 2 are lower (Table I).

Appearance energies (AE) were determined in order to evaluate the activation energy difference (ΔE_a) between the enol and ketone dissociations. The values have been measured for the metastable ion transition 356⁺ → 147⁺ in 1 and 3, using the metastable transition 398⁺ → 147⁺ for Mes₂C=C(OH)Mes as the reference reaction in both cases. The value for 3 is 2.1 eV higher than for 1, indicating a ΔE_a value of 2.7 eV.

Two important conclusions emerge from the data: (a) The same enol ions are formed from the enol and the enol acetates, i.e., 3⁺ from 3 and 6, and 4⁺ from 4 and 7. This is additional direct evidence that the loss of the CH₂CO fragment from an enol acetate gives the enol in a four-center transition state. Previous evidence[6] was based on the difference between the relative abundances of several peaks which are presumably derived from the peak at m/e of the ionized ketone in the mass spectra of the ketone and the enol acetate. Here we show that the $T_{1/2}$ values are similar, starting from the stable enols and their acetates. Since 5 should give the unknown E isomer of the enol 3 by a four-center fragmentation, the identy of $T_{1/2}$ values suggests either that $E \rightleftharpoons Z$ interconversion of the enols is rapid or that the geometry of the enol has little influence on its cleavage to the mesitoyl ion. (b) The enol ions are not freely interconverting to the keto forms below their respective dissociation limits, since in this case the kinetics-energy releases and metastable peak shapes should have been the same. The data suggest that the ionized enol 3⁺ undergoes a rate-determining isomerization in which the intermediate ionized ketone 1⁺ is formed with ≥2 eV energy above the dissociation limit. Consequently, the $T_{1/2}$ value for the enol dissociation is higher than for the keto dissociation.

Further studies on this and related systems which should throw light on the mechanistic question as to whether the enols dissociate to form the aroyl cation via a rate-determining isomerization to the keto form are in progress.

Proton-Coupled Electron Transfer between [Ru(bpy)₂(py)OH₂]²⁺ and [Ru(bpy)₂(py)O]²⁺. A Solvent Isotope Effect (k_{H_2O}/k_{D_2O}) of 16.1

Robert A. Binstead, Bruce A. Moyer, George J. Samuels, and Thomas J. Meyer*

Department of Chemistry, The University of North Carolina Chapel Hill, North Carolina 27514

We reported recently that oxidation of the complex [Ru(bpy)₂(py)OH₂]²⁺ occurs in two reversible, one-electron steps (Scheme I).[1] The redox chemistry of the system is remarkable in that the Ru(IV)/Ru(II) couple appears to undergo mechanistically well-defined multiple electron-transfer pathways via net O-atom or hydride ion transfers.[2,3] In addition, the Ru(IV)/Ru(II) couple of the related complex [Ru(trpy)(bpy)OH₂]²⁺ has been shown to provide the basis for the electrocatalytic oxidation of a series of oragnic substrates including aromatic hydrocarbons, olefins, and primary and secondary alcohols.[4]

The one-electron-transfer redox chemistry of these systems is also of potential interest, arising from the proton demands imposed by simple electron transfer. Oxidation of [Ru(bpy)₂(py)OH₂]²⁺ above pH ~2 results in [Ru(bpy)₂(py)OH]²⁺. Further oxidation by one electron gives the oxo complex, [Ru(bpy)₂(py)O]²⁺, for which there is no evidence for protonation of the oxo ligand, even in strongly acidic media.

The importance of a proton demand upon electron transfer is readily apparent in the comproportionation reaction between the Ru(IV) and Ru(II) complexes in eq 1, which is favored in the

$$[Ru(bpy)_2(py)H_2O]^{2+} + [Ru(bpy)_2(py)O]^{2+} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2[Ru(bpy)_2(py)OH]^{2+} \quad (1)$$
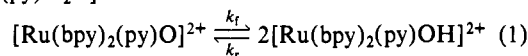
forward direction by a driving force $\Delta G°$ of –2.5 kcal mol⁻¹ (K_{com} = k_f/k_r = 72, $\Delta E°$ = 0.110 V) at 25 °C for 2 < pH < 9. Stopped-flow kinetics studies show that this reaction is first order in both Ru(II) and Ru(IV). The reaction is remarkable both for the absence of a pH dependence over a broad pH range (2.4–9.2) and slowness of the electron-transfer rate constant ($k_f = k_{H_2O} = (2.10 \pm 0.02)10^5$ M⁻¹ s⁻¹ at 25.3 °C, I = 0.10 M, Na₂SO₄) when

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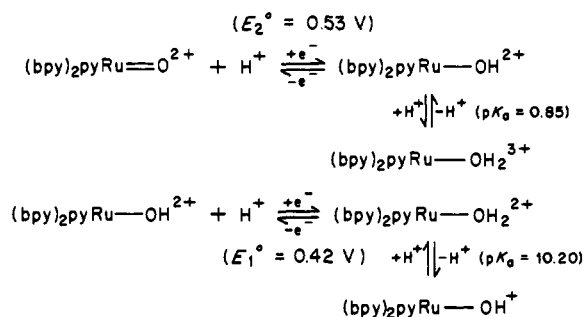(8) Due to the lower intensity of the metastable peak for the 356 → 105 reaction, the $T_{1/2}$ values are less accurate than for the 356 → 251 reaction.

(1) Moyer, B. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3601. *Inorg. Chem.* **1981**, *20*, 436.
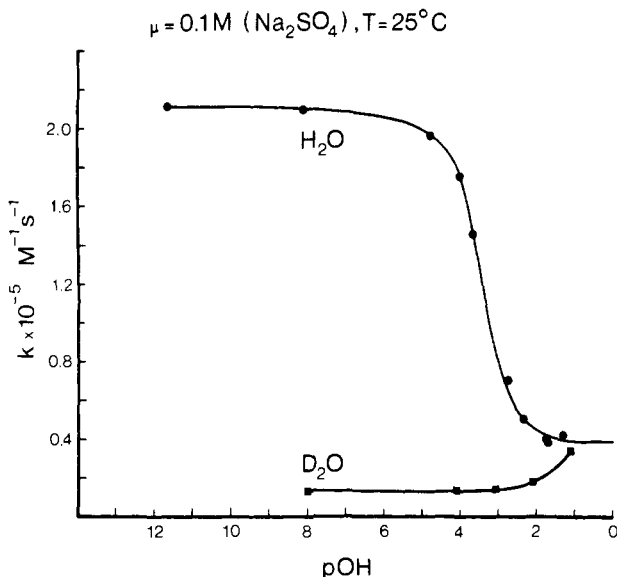(2) Moyer, B. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 1326. *Inorg. Chem.*, in press.
(3) Thompson, M. S.; Meyer, T. J., manuscript in preparation.
(4) Moyer, B. A.; Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 2310.

Scheme I[a]

$$(E_2^\circ = 0.53 \text{ V})$$

$$(\text{bpy})_2\text{pyRu}{=}\text{O}^{2+} + \text{H}^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} (\text{bpy})_2\text{pyRu}{-}\text{OH}^{2+}$$

$$+\text{H}^+ \| -\text{H}^+ \quad (\text{p}K_a = 0.85)$$

$$(\text{bpy})_2\text{pyRu}{-}\text{OH}_2^{3+}$$

$$(\text{bpy})_2\text{pyRu}{-}\text{OH}^{2+} + \text{H}^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} (\text{bpy})_2\text{pyRu}{-}\text{OH}_2^{2+}$$

$$(E_1^\circ = 0.42 \text{ V}) \quad +\text{H}^+ \| -\text{H}^+ \quad (\text{p}K_a = 10.20)$$

$$(\text{bpy})_2\text{pyRu}{-}\text{OH}^+$$

[a] $(T = 25 \,^\circ\text{C}, I = 0.10 \text{ M}, \text{pH } 7$; potential values are vs. SCE).

Figure 1. pOH or pOD dependence of the rate constant for the comproportionation reaction in H_2O and D_2O, respectively. $I = 0.10$ M (Na_2SO_4), $T = 25 \,^\circ$C.

compared to the outer-sphere electron-transfer rate constants for related reactions.[5,6] At higher pH values the dominant form of Ru(II) becomes $[\text{Ru(bpy)}_2(\text{py})\text{OH}]^+$. Under these conditions there is a switch to a second, pH-independent pathway for which the observed rate constant becomes even slower (Figure 1), approaching a limiting value of $k_{OH} = (0.39 \pm 0.03)10^5$ M^{-1} s^{-1}. The curve drawn through the data points in Figure 1 was calculated from the expression

$$k_{obsd} = \frac{k_{H_2O} + k_{OH}K_a/[\text{H}^+]}{1 + K_a/[\text{H}^+]}$$

This expression is derived for the case where both $[\text{Ru(bpy)}_2(\text{py})\text{H}_2\text{O}]^{2+}$ (k_{H_2O}) and $[\text{Ru(bpy)}_2(\text{py})\text{OH}]^+$ (k_{OH}) undergo reactions with $[\text{Ru(bpy)}_2(\text{py})\text{O}]^{2+}$ to give $[\text{Ru(bpy)}_2(\text{py})\text{OH}]^{2+}$. Values for k_{H_2O} and k_{OH} are cited above and K_a was taken from Scheme I and $pK_w = 13.68$ under our conditions.
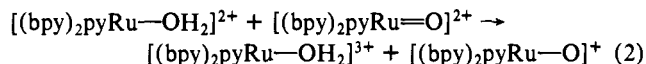
The substitution of D_2O for H_2O as the solvent results in a profound solvent isotope effect on the rate constant for the pathway involving $[\text{Ru(bpy)}_2(\text{py})\text{H}_2\text{O}]^{2+}$ (Figure 1); for $I = 0.10$ M, $k_{H_2O}/k_{D_2O} = 16.4 \pm 0.3$ over a broad pH range. Variations of pH in both D_2O and H_2O were made by using standard buffers, e.g., $H_2PO_4^-/HPO_4^{2-}$. In the absence of supporting electrolyte, where k_{H_2O} is $(4.45 \pm 0.03)10^4$ M^{-1} s^{-1} at 25.3 $^\circ$C, the solvent rate constant ratio is nearly the same ($k_{H_2O}/k_{D_2O} = 16.1 \pm 0.2$). Electrochemical measurements at 25 $^\circ$C show that ΔG° for the

comproportionation reaction is the same in H_2O and D_2O within experimental error. It follows that the large isotope effect, which appears to be well outside the range normally observed for simple outer-sphere or inner-sphere electron transfers,[7,8] is kinetic in origin.
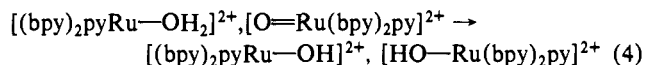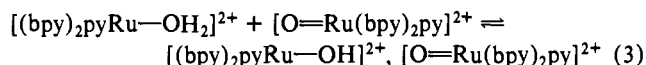
The electron-transfer rate constant k_{H_2O} shows a linear dependence on mole fraction of D_2O. The mole fraction data are consistent with the explicit involvement of a single proton in the electron-transfer act, assuming that a thermodynamic OH/OD fractionation factor of 1 exists for the active proton site.[9,10] From the absence of a pH dependence for the pathway, we conclude that the single proton site is not in the solvent where H-bonding interactions should lead to the coupling of several proton sites but rather on the aquo ligand (note eq 4).

The temperature dependences of the rate constants for the k_{H_2O} pathway are surprisingly small. Plots of $(\ln k)/T$ vs. $1/T$ or $\ln k$ vs. $1/T$ are reasonably linear over the temperature range investigated (278–328 K for H_2O, 279–318 K for D_2O) giving the associated activation parameters: H_2O, $\Delta H^\ddagger = 2.33 \pm 0.13$ kcal mol^{-1} ($E_a = 2.93 \pm 0.13$ kcal mol^{-1}) and $\Delta S^\ddagger = -29.5 \pm 0.4$ cal deg^{-1} mol^{-1} [$A = (6.1 \pm 1.3)10^6$s^{-1}]; D_2O, $\Delta H^\ddagger = 3.86 \pm 0.23$ kcal mol^{-1} ($E_a = 4.45 \pm 0.24$ kcal mol^{-1}) and $\Delta S^\ddagger = -29.8 \pm 0.8$ deg^{-1} mol^{-1} [$A = (5.2 \pm 2.3)10^6$ s^{-1}].
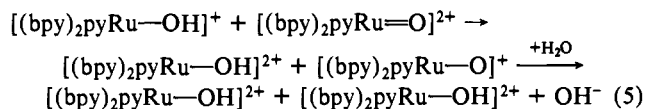
The pH-independent pathway cannot be interpreted as simple outer-sphere electron transfer. The initial products following outer-sphere electron transfer, $[\text{Ru(bpy)}_2(\text{py})\text{O}]^+$ and $[\text{Ru(bpy)}_2(\text{py})\text{H}_2\text{O}]^{3+}$, are energetically highly unfavorable in neutral solution compared to the final product, $[\text{Ru(bpy)}_2(\text{py})\text{OH}]^{2+}$. Given the pK_a values of 0.85 for $[\text{Ru(bpy)}(\text{py})\text{H}_2\text{O}]^{3+}$ and >12 for $[\text{Ru(bpy)}_2(\text{py})\text{OH}]^{2+}$ [11] and the reduction potentials in Scheme I, simple electron transfer (eq 2) is thermodynamically disfavored

$$[(\text{bpy})_2\text{pyRu}{-}\text{OH}_2]^{2+} + [(\text{bpy})_2\text{pyRu}{=}\text{O}]^{2+} \rightarrow$$
$$[(\text{bpy})_2\text{pyRu}{-}\text{OH}_2]^{3+} + [(\text{bpy})_2\text{pyRu}{-}\text{O}]^+ \quad (2)$$

by $\Delta G \geq 12.7$ kcal mol^{-1} at pH 7. This minimum barrier, for which $k \; [=(k_B T)/h \exp(-\Delta G^\ddagger/RT)] = 2.7 \times 10^3$ M^{-1} s^{-1}, would exist in addition to the usual activational inner-sphere and preequilibrium requirements for the reaction. Rather, the system appears to adopt a new, more facile pathway in which, after prior association of the reactants (eq 3), proton transfer is coupled with electron transfer (eq. 4). In strongly basic solution (note Figure

$$[(\text{bpy})_2\text{pyRu}{-}\text{OH}_2]^{2+} + [\text{O}{=}\text{Ru(bpy)}_2\text{py}]^{2+} \rightleftharpoons$$
$$[(\text{bpy})_2\text{pyRu}{-}\text{OH}]^{2+}, [\text{O}{=}\text{Ru(bpy)}_2\text{py}]^{2+} \quad (3)$$

$$[(\text{bpy})_2\text{pyRu}{-}\text{OH}_2]^{2+}, [\text{O}{=}\text{Ru(bpy)}_2\text{py}]^{2+} \rightarrow$$
$$[(\text{bpy})_2\text{pyRu}{-}\text{OH}]^{2+}, [\text{HO}{-}\text{Ru(bpy)}_2\text{py}]^{2+} \quad (4)$$

1), $[\text{Ru(bpy)}_2(\text{py})\text{OH}]^+$ becomes the dominant form of Ru(II) and a new, even slower pathway [$k_{OH} = (0.39 \pm 0.03)10^5$ M^{-1} s^{-1}, 25 $^\circ$C, $I = 0.10$ M] begins to dominate electron transfer. This pathway may well be a true outer-sphere reaction, slowed considerably because of the thermodynamic cost of forming the deprotonated Ru(III) product $[\text{Ru(bpy)}_2(\text{py})\text{O}]^+$ in the first step (eq 5). This conclusion is supported by the considerably smaller

$$[(\text{bpy})_2\text{pyRu}{-}\text{OH}]^+ + [(\text{bpy})_2\text{pyRu}{=}\text{O}]^{2+} \rightarrow$$
$$[(\text{bpy})_2\text{pyRu}{-}\text{OH}]^{2+} + [(\text{bpy})_2\text{pyRu}{-}\text{O}]^+ \xrightarrow{+\text{H}_2\text{O}}$$
$$[(\text{bpy})_2\text{pyRu}{-}\text{OH}]^{2+} + [(\text{bpy})_2\text{pyRu}{-}\text{OH}]^{2+} + \text{OH}^- \quad (5)$$

solvent isotope effect (Figure 1; $k_{H_2O}/k_{D_2O} < 3$) for the k_{OH} pathway.

The microscopic details of the proton coupled pathway are clearly of interest, and the following comments appear to be

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relevant: (1) Given the substitutional and valence electronic characteristics of the reactants, electronic coupling by orbital overlap between donor and acceptor sites is presumably weak, as in a typical outer-sphere electron-transfer.[12] (2) Since electron and proton transfer are inherently coupled, there is no real charge-transfer component to the reaction, and so no significant contribution from outer-sphere reorganization (medium vibrations) is expected. (3) Because of the high frequency vibrations involved $\nu_{OH} \sim 3600$ cm^{-1}, $\nu_{Ru=O} \sim 795$ cm^{-1}, and the low thermal activation energy, the reaction must proceed largely from the $v = 0$ level of the ν_{OH} mode and hence involve vibrational tunneling. In this sense, with regard to what are most probably the critical vibrational modes, the reaction occurs in the low-temperature (quantum mechanical) limit.[13-21] (4) The case reported here may be a limiting example of H-atom (proton-coupled, 1-electron) transfer where the distinguishing feature is weak electronic coupling between the electron donor and acceptor sites.

Our results may have important implications for a number of redox related observations including the electron-transfer chemistry of metal–oxo compounds, the interpretation of kinetic isotope effects, and the general role of proton-coupled electron transfer in both chemical and biological systems.

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An Iron(III)–Porphyrin Complex with a Vinylidene Group Inserted into an Iron–Nitrogen Bond: Relevance to the Structure of the Active Oxygen Complex of Catalase

Bernard Chevrier and Raymond Weiss*

*Institut Le Bel, Laboratoire de Cristallochimie (ERA 08)
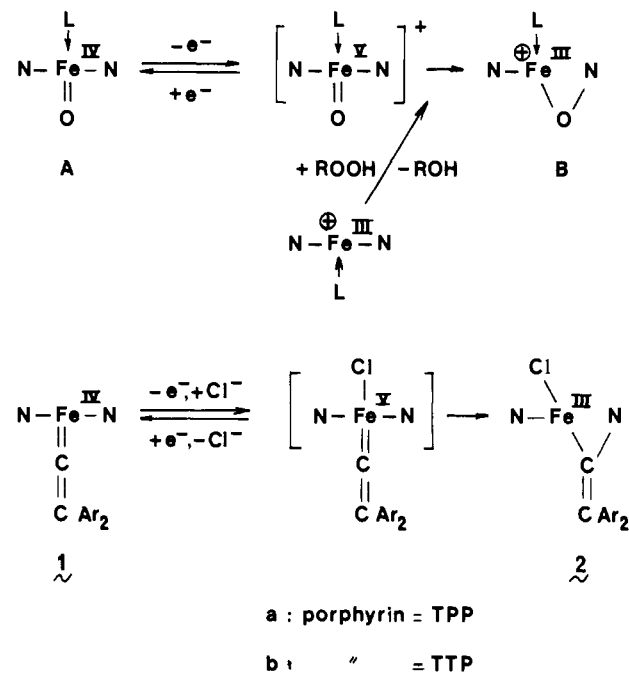Université Louis Pasteur, 4 rue Blaise Pascal
67070 Strasbourg Cedex, France*

Marc Lange, Jean-Claude Chottard, and Daniel Mansuy*

*Laboratoire de Chimie de l'Ecole Normale
Supérieure (LA 32), 24 rue Lhomond
75231 Paris Cedex 05, France*

Various hemoproteins including cytochrome P450, catalases, and peroxidases catalyze the oxidation of organic compounds by two-electron oxidants such as hydroperoxides. The reactions of catalases and peroxidases with these oxidants lead to intermediate complexes called compounds I and II which retain, respectively, two and one oxidizing equivalents above the native ferrihemoproteins.[1] Though the structures of these intermediates are not

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Scheme I

a : porphyrin = TPP

b : " = TTP

definitely established, compound II is generally believed to be an iron(IV) complex with an oxo (A in Scheme I) or OH exogenous ligand.[2] The structure of compound I which retains one oxidizing equivalent above compound II is even less known. The relative stability of horseradish peroxidase (HRP) compound I has allowed its study by various spectroscopic methods[3] which support an iron(IV) [porphyrin π-cation radical] structure.[4] There are less spectroscopic data[5] available for catalase compound I (CAT I) probably because of its instability. However, a similar iron(IV) [porphyrin π cation radical] structure has been proposed for CAT I taking into account the analogy of its electronic spectrum with those of cobalt porphyrin π cation radicals.[4]

The porphyrin–iron–carbene complexes PFe^{IV}=CRR' ↔ PFe^{II} ← CRR', which we have recently synthesized,[6] are carbon analogues of the porphyrin–iron–oxo species A possibly present in compounds II. Upon one-electron oxidation of the vinylidene–iron complex[7] Fe(TPP)[C=C(p-ClC$_6$H$_4$)$_2$] (**1a**) by CuCl$_2$, the stable complex Fe(TPP)[C=C(p-ClC$_6$H$_4$)$_2$]Cl (**2a**) was isolated as a crystalline solid.[8] This complex, which exhibits a visible spectrum strikingly similar to that of CAT I, can be considered formally as a carbon analogue of CAT I (Scheme I).[8]

We present in this paper an X-ray structure analysis of the complex Fe(TTP)[C=C(p-ClC$_6$H$_4$)$_2$]Cl (**2b**) which shows that

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