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Concerted Proton−Electron Transfer in a Ruthenium Terpyridyl-Benzoate System with a Large Separation between the Redox and Basic Sites

Virginia W. Manner and James M. Mayer*

Department of Chemistry, University of Washington, Seattle, Washington 98195-1700

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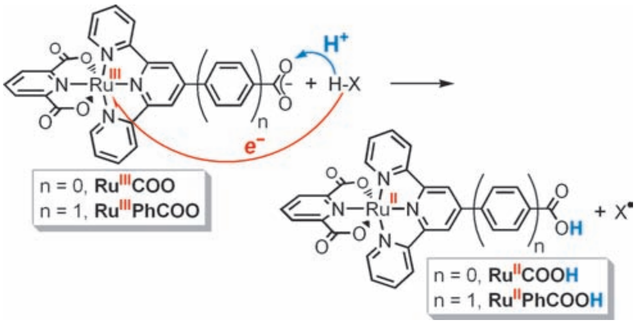
Coupling electron transfer to proton transfer is key to a wide range of chemical and biochemical processes, such as converting solar energy to chemical fuels.[1] While many of the fundamentals of electron transfer (ET) are well understood, the principles of proton-coupled electron transfer (PCET) are still being developed. The effects of increasing the distance between reaction centers has been much studied for ET,[2] and we have started to explore PCET systems in which the electron- and proton-accepting sites are increasingly separated.[3] PCET processes with large separations appear to be important in a number of biological systems, such as ribonucleotide reductases and photosystem II.[4] They may also be involved in charge injection into oxide semiconductors from ruthenium polypyridyl-carboxylate complexes.[5] In our previously reported ruthenium terpyridine-4′-carboxylate complex **Ru^{III}COO** (Scheme 1), the Ru is six bonds and 6.9 Å removed from the basic carboxylate oxygen atoms.[3] Despite this separation, the reported reactions occur with H^+ and e^- transferring in the same kinetic step, by concerted proton−electron transfer (CPET).[1,3,6−8] In this report, the distance between the metal and basic sites is extended further, by inserting a phenyl spacer between the terpyridine and the carboxylate. Reactivity is contrasted between the two systems, which are the first studies of long, well-defined separations.

The new protonated Ru(II) complex, Ru^{II}(pydic)(tpy-PhCOOH) (**Ru^{II}PhCOOH**), was prepared from $[(\eta^6\text{-cymene})\text{RuCl}(\mu\text{-Cl})]_2$ and the known ligands, 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine ([Na$^+$]tpy-PhCOO$^-$) and pyridine-2,6-dicarboxylate (Na$_2$pydic).[3,9] Deprotonation of this complex with ^{n}Bu$_4$NOH in DMF yields ^{n}Bu$_4$N[Ru^{II}(pydic)(tpy-PhCOO)] (**Ru^{II}PhCOO$^-$**). Both compounds have been characterized by ^{1}H NMR and UV−visible spectroscopies, electrochemistry, ESI-MS, and elemental analyses. Based on the structure of the related homoleptic complex Ru^{II}(tpy-PhCOO$^-$)$_2$, the distance between the Ru and the carboxylate oxygens is 11.2 ± 0.1 Å.[10] The optical spectra of **Ru^{II}PhCOOH** and **Ru^{II}PhCOO$^-$** in the visible region are very similar, as shown in Figure 1a.[9] The differences in the spectra are small, but they are consistent and reversible upon addition of acid and base.[9] Titration of **Ru^{II}PhCOO$^-$** with benzoic acid (pK_a = 20.7 ± 0.1[11]) in MeCN gives a pK_a for **Ru^{II}PhCOOH** of 20.5 ± 0.2. Cyclic voltammograms of **Ru^{II}PhCOOH** and **Ru^{II}PhCOO$^-$** in DMF show almost identical chemically reversible oxidations, with $E_{1/2} = 0.081 \pm 0.006$ V and 0.083 ± 0.019 V vs FeCp$_2^{+/0}$, respectively.

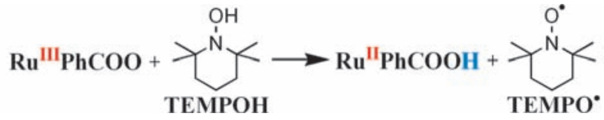
Oxidation of **Ru^{II}PhCOO$^-$** by $[(p\text{-tol})_3\text{N}^{\bullet+}]\text{PF}_6^-$ in MeCN gives the neutral, deprotonated Ru(III) carboxylate complex, Ru^{III}(pydic)(tpy-PhCOO) (**Ru^{III}PhCOO**, Scheme 1). This zwitterionic complex can be precipitated as a brown solid with CH$_2$Cl$_2$ but it is difficult to handle without some decomposition in solution,[9] so it is more conveniently generated *in situ* from **Ru^{II}PhCOO$^-$** plus $[(p\text{-BrC}_6\text{H}_4)_3\text{N}^{\bullet+}][\text{B}(\text{C}_6\text{F}_5)_4^-]$ in MeCN. The ^{1}H NMR spectrum of **Ru^{III}PhCOO** shows all nine paramagnetic peaks, and the optical spectrum has a shoulder at 435 nm ($\varepsilon \approx 9000$ M^{-1} cm^{-1}). Reduction of *in situ* generated **Ru^{III}PhCOO** with (C$_5$Me$_5$)$_2$Fe rapidly regenerates Ru(II), with a yield of ~95% based on the absorption at 531 nm, along with other product(s). Addition of base to this solution causes a shifting of the 400 nm peak, suggesting that the product mixture is ca. 70/30 **Ru^{II}PhCOO$^-$/Ru^{II}PhCOOH**.[9] The data indicate that **Ru^{III}PhCOO** is predominantly deprotonated in solution but may contain some **Ru^{III}PhCOOH$^+$**.[12]

Scheme 1



A formal O−H bond dissociation free energy (BDFE) can be defined for **Ru^{II}PhCOOH**, despite the 11.2 Å distance between Ru and O. Δ$G°$ for **Ru^{II}PhCOOH** → **Ru^{III}PhCOO** + H$^\bullet$ in MeCN $= 23.1E_{1/2} + 1.37\text{p}K_a + C_G$[13] $= 87 \pm 1$ kcal mol^{-1}, using the pK_a given above and $E_{1/2} = 0.17 \pm 0.03$ V vs FeCp$_2^{+/0}$ for **Ru^{II}PhCOO$^-$** in 90/10 MeCN/DMF.[9] The BDFE is 6 kcal mol^{-1} higher than that found for the complex without the phenyl spacer, **Ru^{II}COOH** (81 ± 1 kcal mol^{-1}). Thus, **Ru^{III}PhCOO** is a strong hydrogen atom acceptor,[3] which may partly explain its instability.

Ru^{III}PhCOO reacts with the hydroxylamine TEMPOH within seconds to form the nitroxyl radical TEMPO and predominantly **Ru^{II}PhCOOH**, (eq 1), as indicated by ^{1}H NMR and UV−visible spectra.[9] The protonated **Ru^{II}PhCOOH** product is implicated by the peak at 400 nm in the optical spectrum, which shifts to 394 nm upon addition of base (Figure 1a).[9,14] The reaction is quite downhill, $\Delta G°_1 = -21$ kcal mol^{-1}, based on BDFE(TEMPOH) = 66.5 kcal mol^{-1}.[15] Stopped flow rapid-scanning spectrophotometry under pseudo first-order conditions of excess TEMPOH shows a ca. 80%



(1)

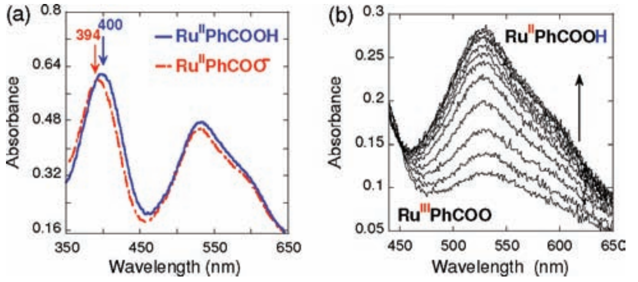


Figure 1. (a) UV−vis spectra [λ/nm (ε/M^{-1} cm^{-1})] for **Ru^{II}PhCOOH** [400 (20 000), 533 (15 000)] and **Ru^{II}PhCOO$^-$** [394 (20 000), 531 (15 000)], each 0.030 mM in MeCN; ε's all ±1000.[9] (b) Spectra for **Ru^{III}PhCOO** (0.026 mM) + TEMPOH (0.20 mM) in MeCN over 0.5 s, showing the growth of **Ru^{II}PhCOOH**.

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Table 1. Rate Constant k^a and $\Delta G^{\circ b}$ for **Ru^{III}(Ph)COO** + X−H

	Ru^{III}PhCOO + X−H		**Ru^{III}COO** + X−H	
X−H	$\Delta G°$	k	$\Delta G°$	k
TEMPOH	−21	$(1.1 \pm 0.1) \times 10^5$	−15	$(2.0 \pm 0.6) \times 10^{5c}$
ArOH [d]	-13^e	$(1.0 \pm 0.1) \times 10^3$	-7^e	$(1.5 \pm 0.6) \times 10^6$

[a] In M^{-1} s^{-1}. [b] In kcal mol^{-1}. [c] Reference 3. [d] 2,6-^{t}Bu$_2$(4-MeO)ArOH. [e] Reference 19.

yield of **Ru^{II}PhCOOH** (Figure 1b). It is possible that the low yield is due to the presence of protonated Ru(III) in solution, which reacts more slowly with TEMPOH.[14] The pseudo-first-order rate constants vary linearly with [TEMPOH] (Figure S10[9]) indicating a simple second-order rate law, with $k_{1H} = (1.1 \pm 0.1) \times 10^5$ M^{-1} s^{-1} and $\Delta G_1^{\ddagger} = 10.6 \pm 0.1$ kcal mol^{-1}.[9] Using rate data from 17−52 °C, the activation parameters are $\Delta H_1^{\ddagger} = 6.8 \pm 1.1$ kcal mol^{-1} and $\Delta S_1^{\ddagger} = -13 \pm 4$ cal mol^{-1} K^{-1}. The reaction with TEMPOD gives $k_{1D} = (5.6 \pm 0.3) \times 10^4$ M^{-1} s^{-1}. The small primary isotope effect, $k_{1H}/k_{1D} = 2.1 \pm 0.2$, indicates that the proton is transferred in the rate limiting step.[16]

Reaction 1 could occur by (*i*) initial proton transfer (PT) to form **Ru^{III}PhCOOH$^+$** and TEMPO$^-$ followed by electron transfer (ET), (*ii*) ET followed by PT, or (*iii*) CPET with no intermediates. The pK_a's of **Ru^{III}PhCOOH$^+$** and TEMPOH are 20.5 and 39, respectively, so the initial step in path (*i*) has $\Delta G°_{PT} = 25.3$ kcal mol^{-1}.[9] Similarly, using the reduction potentials of the reactants, $\Delta G°_{ET} = 12.5$ kcal mol^{-1}. Since these are the minimum barriers for initial PT and ET ($\Delta G^{\ddagger} > \Delta G°$), and they are larger than the observed $\Delta G_1^{\ddagger}$ (10.6 ± 0.1 kcal mol^{-1}), neither of the stepwise pathways can be occurring. Thus even with the large separation between Ru and COO$^-$, the reaction still occurs by CPET. This is also indicated by the primary kinetic isotope effect (KIE) of 2.1.

An important issue in a PCET reagent is the amount of interaction or communication between the redox and basic sites.[3] One measure of this is the thermodynamic coupling, in this system how much the pK_a shifts depending on the Ru oxidation state (ΔpK_a), and equivalently[1d] how much the $E°$ shifts with the protonation state ($\Delta E_{1/2}$). Cyclic voltammograms of **Ru^{II}PhCOO$^-$** and **Ru^{II}PhCOOH** in DMF are the same within error ($\Delta E_{1/2} = 2 \pm 20$ mV), indicating that there is essentially no communication between the redox and basic sites. This is also indicated by the close similarity of pK_a's of **Ru^{II}PhCOOH** and benzoic acid. For comparison, $\Delta E_{1/2}$ for **Ru^{II}COO(H)** (with no Ph spacer) is 0.13 V (other systems have larger values[3]). CPET may be the favored mechanism for reaction 1 because of the large $\Delta E_{1/2}$ for TEMPO(H), ca. 2.6 V.[9] In a related intermetal PCET system without this large $\Delta E_{1/2}$, concerted transfer was not observed.[17]

Ru^{III}PhCOO also rapidly oxidizes 2,6-di-*tert*-butyl-4-methoxyphenol (ArOH) to give the aryloxyl radical ArO$^•$[18] and **Ru^{II}PhCOOH**.[9] Pseudo first-order kinetic studies give $k_{ArOH} = (1.0 \pm 0.1) \times 10^3$ M^{-1} s^{-1} and $k_H/k_D = 2.6 \pm 0.4$.[9,16] In this case, thermochemical analyses do not rule out initial PT or ET mechanisms since $\Delta G°_{PT}$ and $\Delta G°_{ET}$ (10.8 ± 0.5 and 11.8 ± 0.8 kcal mol^{-1})[9] are both lower than the observed $\Delta G^{\ddagger} = 13.4 \pm 0.1$ kcal mol^{-1}. Therefore k_{ArOH} is an upper limit for the CPET rate constant. The mechanism is still likely to be CPET because $\Delta G°_{PT}$ and $\Delta G°_{ET}$ are much larger than $\Delta G°_{CPET}$ and because the KIE of 2.6 is larger than would be expected for ET or for PT between oxygen atoms.

Table 1 compares the rate constants and $\Delta G°$ values for the reactions of **Ru^{III}PhCOO** vs **Ru^{III}COO**. For the reactions with TEMPOH, the rate constants are within a factor of 2, even though CPET to **Ru^{III}PhCOO** is 6 kcal mol^{-1} more exoergic.[3] For oxidation of ArOH, the **Ru^{III}PhCOO** rate constant is a thousand times slower despite the 6 kcal mol^{-1} larger driving force. Thus the larger driving force for the reactions of **Ru^{III}PhCOO** is offset by the decreased communication and longer distance.

In conclusion, we have designed and prepared a system with a well-defined separation of 10 bonds and 11.2 Å between the metal (Ru) and basic (carboxylate) sites. At this distance, there is almost no interaction between the redox and basic sites, as indicated by thermodynamic and spectroscopic measurements. Despite this lack of communication, the reaction of **Ru^{III}PhCOO** with TEMPOH (eq 1) occurs by concerted transfer of H$^+$ and e^- (CPET). However, the more exoergic reactions of **Ru^{III}PhCOO** proceed more slowly than those of **Ru^{III}COO**. Thus the increased distance and decreased communication do appear to affect the reaction rates, as will be discussed in a future report focused on the dependence of CPET rate constants on driving force[20] and on the position and interaction of redox and acid/base sites.

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Supporting Information Available: Details for the synthesis, kinetic measurements, and additional analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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