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

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Abstract

In order to understand how the separation between the electron and proton-accepting sites affects proton-coupled electron transfer (PCET) reactivity, we have prepared ruthenium complexes with 4'-(4-carboxyphenyl)terpyridine ligands, and studied reactivity with hydrogen atom donors (H-X). $\text{Ru}^{\text{II}}(\text{pydic})(\text{tpy-PhCOOH})$ (**Ru^{II}PhCOOH**), was synthesized in one pot from [(*p*-cymene) RuCl_2]₂, sodium 4'-(4-carboxyphenyl)-2,2':6',2''-terpyridine ($[\text{Na}^+]\text{tpy-PhCOO}^-$), and disodium pyridine-2,6-dicarboxylate (Na_2pydic). **Ru^{II}PhCOOH** plus $n\text{Bu}_4\text{NOH}$ in DMF yields the deprotonated Ru(II) complex, $n\text{Bu}_4\text{N}[\text{Ru}^{\text{II}}(\text{pydic})(\text{tpy-PhCOO})]$ (**Ru^{II}PhCOO⁻**). The Ru(III) complex (**Ru^{III}PhCOO**) has been isolated by one-electron oxidation of **Ru^{II}PhCOO⁻** with triarylaminium radical cations ($\text{NAr}_3^{+\bullet}$). The bond dissociation free energy (BDFE) of the O–H bond in **Ru^{II}PhCOOH** is calculated from $\text{p}K_{\text{a}}$ and $E_{1/2}$ measurements as 87 kcal mol⁻¹, making **Ru^{III}PhCOO** a strong hydrogen atom acceptor. There are 10 bonds and ca. 11.2 Å separating the metal from the carboxylate basic site in **Ru^{III}PhCOO**. Even with this separation, **Ru^{III}PhCOO** oxidizes the hydrogen atom donor TEMPOH (BDFE = 66.5 kcal mol⁻¹, $\Delta G^\circ_{\text{rxn}} = -21$ kcal mol⁻¹) by removal of an electron and a proton to form **Ru^{II}PhCOOH** and TEMPO radical in a *concerted* proton-electron transfer (CPET) process. The second order rate constant for this reaction is $(1.1 \pm 0.1) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ with $k_{\text{H}}/k_{\text{D}} = 2.1 \pm 0.2$, similar to the observed kinetics in an analogous system without the phenyl spacer, $\text{Ru}^{\text{III}}(\text{pydic})(\text{tpy-COO})$ (**Ru^{III}COO⁻**). In contrast, hydrogen transfer from 2,6-di-*tert*-butyl-*p*-methoxyphenol [$n\text{Bu}_2(\text{OMe})\text{ArOH}$] to **Ru^{III}PhCOO** is several orders of magnitude slower than the analogous reaction with **Ru^{III}COO**.

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

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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>.

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, $\text{Ru}^{\text{II}}(\text{pydic})(\text{tpy-PhCOOH})$ (**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 ($[\text{Na}^+]\text{tpy-PhCOO}^-$) and pyridine-2,6-dicarboxylate (Na_2pydic).^{3,9} Deprotonation of this complex with $n\text{Bu}_4\text{NOH}$ in DMF yields $n\text{Bu}_4\text{N}[\text{Ru}^{\text{II}}(\text{pydic})(\text{tpy-PhCOO})]$ (**Ru^{II}PhCOO⁻**). Both compounds have been characterized by ^1H NMR and UV-Visible spectroscopies, electrochemistry, ESI-MS, and elemental analyses. Based on the structure of the related homoleptic complex $\text{Ru}^{\text{II}}(\text{tpy-PhCOO}^-)_2$, the distance between the Ru and the carboxylate oxygens is $11.2 \pm 0.1 \text{ \AA}$.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 additions of acid and base.⁹ Titration of **Ru^{II}PhCOO⁻** with benzoic acid ($\text{p}K_{\text{a}} = 20.7 \pm 0.1^{11}$) in MeCN gives a $\text{p}K_{\text{a}}$ 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 $E_{1/2} = 0.081 \pm 0.006 \text{ V}$ and $0.083 \pm 0.019 \text{ V}$ vs $\text{FeCp}_2^{+/0}$, respectively.

Oxidation of **Ru^{II}PhCOO⁻** by $[(p\text{-tol})_3\text{N}^{+}]\text{PF}_6^-$ in MeCN gives the neutral, deprotonated Ru(III) carboxylate complex, $\text{Ru}^{\text{III}}(\text{pydic})(\text{tpy-PhCOO})$ (**Ru^{III}PhCOO**, Scheme 1). This zwitterionic complex can be precipitated as a brown solid with CH_2Cl_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 $[(p\text{-BrC}_6\text{H}_4)_3\text{N}^{+}][\text{B}(\text{C}_6\text{F}_5)_4^-]$ in MeCN. The ^1H NMR spectrum of **Ru^{III}PhCOO** shows all nine paramagnetic peaks, and the optical spectrum has a shoulder at 435 nm ($\epsilon \sim 9,000 \text{ M}^{-1} \text{ cm}^{-1}$). Reduction of *in situ*-generated **Ru^{III}PhCOO** with $(\text{C}_5\text{Me}_5)_2\text{Fe}$ rapidly regenerates Ru(II), with a yield of $\sim 95\%$ 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

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. ΔG° for **Ru^{II}PhCOOH** $\rightarrow$ **Ru^{III}PhCOO** + $\text{H}^\bullet$ in MeCN = $23.1E_{1/2} + 1.37\text{p}K_{\text{a}} + C_{\text{G}}^{13} = 87 \pm 1 \text{ kcal mol}^{-1}$, using the $\text{p}K_{\text{a}}$ given above and $E_{1/2} = 0.17 \pm 0.03 \text{ V}$ vs $\text{FeCp}_2^{+/0}$ 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** ($81 \pm 1 \text{ kcal mol}^{-1}$). 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 ^1H 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, $\Delta G^\circ_1 = -21 \text{ kcal mol}^{-1}$, based on the 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% 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 S10⁹) indicating a simple second-order rate law, with $k_{1H} = (1.1 \pm 0.1) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and $\Delta G_1^\ddagger = 10.6 \pm 0.1 \text{ kcal mol}^{-1}$.⁹ Using rate data from 17 – 52 °C, the activation parameters are $\Delta H_1^\ddagger = 6.8 \pm 1.1 \text{ kcal mol}^{-1}$ and $\Delta S_1^\ddagger = -13 \pm 4 \text{ cal mol}^{-1} \text{ K}^{-1}$. The reaction with TEMPOD gives $k_{1D} = (5.6 \pm 0.3) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. 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_as of **Ru^{III}PhCOOH⁺** and TEMPOH are 20.5 and 39, respectively, so the initial step in path (i) has $\Delta G^\circ_{PT} = 25.3 \text{ kcal mol}^{-1}$.⁹ Similarly, using the reduction potentials of the reactants, $\Delta G^\circ_{ET} = 12.5 \text{ kcal mol}^{-1}$. Since these are the minimum barriers for initial PT and ET ($\Delta G^\ddagger > \Delta G^\circ$), and they are larger than the observed $\Delta G_1^\ddagger$ ($10.6 \pm 0.1 \text{ kcal mol}^{-1}$), neither of the stepwise pathways can be occurring. 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 ($\Delta E_{1/2} = 2 \pm 20 \text{ mV}$), indicating that there is essentially no communication between the redox and basic sites. This is also indicated by the close similarity of pK_as 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 values³). 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-*t*-butyl-4-methoxy-phenol, (ArOH), to give the aryloxy radical ArO[•] 18 and **Ru^{II}Ph-COOH**.⁹ Pseudo-first order kinetic studies give $k_{ArOH} = (1.0 \pm 0.1) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ 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 ΔG°_{PT} and ΔG°_{ET} (10.8 ± 0.5 and $11.8 \pm 0.8 \text{ kcal mol}^{-1}$)⁹ are both lower than the observed $\Delta G^\ddagger = 13.4 \pm 0.1 \text{ kcal mol}^{-1}$. Therefore k_{ArOH} is an upper limit for the CPET rate constant. The mechanism is still likely to be CPET because ΔG°_{PT} and ΔG°_{ET} are much larger than ΔG°_{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 ΔG° 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 ten 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 force²⁰ and on the position and interaction of redox and acid/base sites.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References

- (a) Huynh MHV, Meyer TJ. *Chem Rev* 2007;107:5004–5064. [PubMed: 17999556] Hynes, JT.; Klinman, JP.; Limbach, HH.; Schowen, RL., editors. *Hydrogen-Transfer Reactions*. Wiley-VCH; Weinheim: 2007. (c) Hammes-Schiffer S, Soudackov AV. *J Phys Chem B* 2008;112:14108–14123. [PubMed: 18842015] (d) Mayer JM. *Annu Rev Phys Chem* 2004;55:363–390. [PubMed: 15117257]
- Edwards PP, Gray HB, Lodge MTJ, Williams RJP. *Angew Chem Int Ed* 2008;47:6758–6765. and references therein
- Manner VW, DiPasquale AG, Mayer JM. *J Am Chem Soc* 2008;130:7210–7211. [PubMed: 18479096]
- (a) Meyer TJ, Huynh MHV, Thorp H. *Angew Chem, Int Ed* 2007;46:5284–5304. (b) Stubbe J, Nocera DG, Yee CS, Chang MCY. *Chem Rev* 2003;103:2167–2202. [PubMed: 12797828]
- (a) Angelis FD, Fantacci S, Selloni A, Nazeeruddin MK, Grätzel M. *J Am Chem Soc* 2007;129:14156–14157. [PubMed: 17960934] (b) Wang D, Mendelsohn R, Galoppini E, Hoertz PG, Carlisle RA, Meyer GJ. *J Phys Chem B* 2004;108:16642–16653.
- The term CPET was coined by: Costentin C, Evans DH, Robert M, Savéant JM, Singh PS. *J Am Chem Soc* 2005;127:12490–12491. [PubMed: 16144387]
- Reactions of the form $XH + Y \rightarrow X + YH$ are also sometimes called hydrogen atom transfer (HAT); see Ref. 3 and references therein.
- Another type of PCET is ET modulated by a hydrogen-bonded interface, *e.g.* with 4-carboxybipyridine-Ru complexes: Kirby JP, Roberts JA, Nocera DG. *J Am Chem Soc* 1997;119:9230–9236. (b) Ref. 5a.
- Full details are given in the Supporting Information.
- Constable EC, Dunphy EL, Housecroft CE, Neuburger M, Schaffner S, Schaper F, Batten SR. *Dalton Trans* 2007:4323–32. [PubMed: 17893822] (b) Ru^{II}COO⁻³ and Ru^{II}(tpy-COO⁻)₂^{10a} are 6.9 Å.
- Izutsu, K., editor. *Acid-Base Dissociation Constants in Dipolar Aprotic Solvents*. Blackwell Scientific; London: 1990. Chemical Data Series, No. 35
- In our experience, it is very difficult to avoid the formation of trace acid when working with strong oxidants in organic solvents.
- $C_G = 54.9 \text{ kcal mol}^{-1}$: Tilset, M. *Electron Transfer in Chemistry 2*. Balzani, V., editor. Wiley-VCH; Weinheim: 2001. p. 677–713. (b) Mader EA, Davidson ER, Mayer JM. *J Am Chem Soc* 2007;129:5153–66. [PubMed: 17402735]
- Quantitative determination of the protonation state of the product is difficult (Fig. 1) particularly since Ru(II) is formed in only 80% yield. The remaining 20% is likely to be Ru^{III}PhCOOH⁺ which may be present in the reactant (see above). Independent experiments show that *in situ*-generated Ru^{III}PhCOOH⁺ reacts with TEMPOH more slowly, to form a product other than Ru^{II}PhCOOH.⁹
- Mader EA, Manner VW, Markle TF, Wu A, Franz JA, Mayer JM. *J Am Chem Soc* 2009;131:4335–4345. [PubMed: 19275235] (b) Ref. 13b.

16. Carpenter, BK. Determination of Organic Reaction Mechanisms. John Wiley & Sons, Inc.; New York: 1984.
17. Lebeau EL, Binstead RA, Meyer TJ. J Am Chem Soc 2001;123:10535–10544. [PubMed: 11673985]
18. (a) Altwicker ER. Chem Rev 1967;67:475–531. (b) Waidmann CR, Zhou X, Tsai EA, Kaminsky W, Hrovat DA, Borden WT, Mayer JM. J Am Chem Soc 2009;131:4729–4743. [PubMed: 19292442]
19. (a) $\text{BDFE}(\text{ArOH}) = 73.7 \text{ kcal mol}^{-1} \cong \text{BDE}^{18\text{b}} - T\Delta S^\circ(\text{H}^\bullet)$.^{13b} Lucarini M, Pedrielli P, Pedulli GF. J Org Chem 1996;61:9259–9263.
20. See, for instance, references 1a, 1b, 1d, ⁶ and Fecenko CJ, Thorp HH, Meyer TJ. J Am Chem Soc 2007;129:15098–15099. [PubMed: 17999500]

Figure 1.

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

Scheme 1.

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

X-H	ΔG°	$\text{Ru}^{\text{III}}\text{PhCOO} + \text{X-H}$ k	ΔG°	$\text{Ru}^{\text{III}}\text{COO} + \text{X-H}$ 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 $\ln \text{M}^{-1} \text{s}^{-1}$.

^b $\ln \text{kcal mol}^{-1}$.

^c Ref. 3.

^d 2,6-*t*Bu₂(4-MeO)ArOH.

^e Ref. 19.