Table I

reaction	$-\Delta G_{est}$, eV	k_{obsd}, s^{-1}	$^*k_{pred}$,[a] s^{-1}	ref
$(porph(cytc))^{\bullet -}/Fe^{III}cop \rightarrow porph(cytc)/Fe^{II}ccp$	0.9	150 ± 2.0	200	4
$^3(Zn(cytc))^*/Fe^{III}ccp \rightarrow (Zn(cytc))^{\bullet +}/Fe^{II}ccp$	0.6	30 ± 2	18	*b*
$Fe^{III}cytc/Fe^{II}ccp \rightarrow Fe^{II}cytc/Fe^{III}ccp$	0.5	0.23 ± 0.2	3	4
$^3(porph(cytc))^*/Fe^{III}ccp \rightarrow (porph(cytc)^{\bullet +}/Fe^{II}ccp$	0.25	~0	0.003	*b*

[a] k_{pred} calculated by assuming $\lambda = 1.5$ eV and $A = 2 \times 10^3$ s^{-1}. [b] This work.

emission maximum) the acceptor extinction coefficient $\epsilon_A \leq 30$ M^{-1} cm^{-1}.[8]

Interestingly in our photoexcited systems ($^3(Zn(cytc))^*/ccp$ and $^3(porph(cytc))^*/ccp$) as well as those of others,[1c,16] transient redox products generally were not directly observed, for the following reason. It has been well established that in such systems formation of ground-state products

$$(Mcytc)^{\bullet +} + Fe^{II}ccp \xrightarrow{k_b} Mcytc + Fe^{III}ccp$$

$k_b >> k_t$. Consequently, no significant concentration build up of product transients occurs. This commonly observed phenomenon that $k_b >> k_t$ is not well understood, but could be rationalized if "hole" transfer via a superexchange mechanism[15] is particularly common in proteins. However, redox products *can* be demonstrated by trapping of the $Fe^{II}ccp$ product by CO, following the approach of Hoffman.[1c,g] Thus, when $Zn(cytc)/Fe^{III}ccp$ is irradiated under CO, a difference spectrum assignable to $Fe^{II}CO(ccp)$ grows in. Details of these experiments will be presented elsewhere.

These new photochemical results can be combined with the thermal (radiolysis) data on the cytc/ccp system to provide a more complete picture of how electron transfer varies with ΔG. The combined data suggest a relatively simple relationship between the intramolecular electron-transfer rate, k_t, and free energy, ΔG. As shown in Table I, the data for all four reactions are consistent with predictions using the classical Marcus theory for electron-transfer rates:[4]

$$k_t = A \exp(-(\Delta G + \lambda)^2/4\lambda kT)$$

where A = frequency factor related to donor-acceptor distance, $A \propto \exp(-\alpha R)$, and λ is the reorganization energy arising from all nuclear displacements between reactant and product states that accompany electron transfer.

Recently, Hoffman et al.[5] studied a related photochemical electron transfer reaction. They observed the electron-transfer rate within the $^3(Zn(ccp))^*/cytc$ complex.

$$^3(Zn(ccp))^* + Fe^{III}cytc \xrightarrow{k_t} (Zn(ccp))^{\bullet +} + Fe^{II}cytc$$
$$\Delta E \sim 0.9 \text{ eV}$$

The measured electron-transfer rate within this complex $k_t = 17 \pm 3$ s^{-1} at 20 °C. This rate cannot directly be compared to ours, since one involves reduction of $Fe^{III}cytc$ while the other involves reduction of $Fe^{III}ccp$. Significantly different reorganization energies are expected for these two couples. However, it is interesting to note that electron transfer is facile in *both* directions, in contrast to recent observations for Ru-substituted cytochrome *c*.[1e]

These results demonstrate that the rate of electron transfer in the cytc/ccp complex is quite sensitive to ΔG for the electron-transfer step. They also support the suggestion that a large reorganization energy, λ, is associated with protein repolarization around the developing charge in the cytc/ccp complex. Similar trends seem to be emerging in other studies of electron-transfer reactions with protein/protein complexes.[1] For example, in the cytc/cyt b_5 complex the available data suggest $\lambda = 0.8$ eV,[1f] and for the Zn/Fe hybrid of hemoglobin, temperature-dependence studies suggest $\lambda = 2.3$ eV.[1g]

Acknowledgment. This work was supported by the NIH (Grant GM 33881). We also gratefully acknowledge helpful discussions with Brian Hoffman and Harry Gray.

Department of Chemistry
University of Rochester
Rochester, New York 14627

Karen Taylor Conklin
George McLendon*

Received July 17, 1986

---

(16) Liang, N.; Kang, C. H.; Ho, P. S.; Margoliash, E.; Hoffman, B. M. *J. Am. Chem. Soc.* **1986**, *108*, 4665–4666.

Nineteen-Electron Adducts: Measurement of $\Delta G°$ for the Reactions of $CpMo(CO)_3$ with Halide Ligands (Cp = $CH_3C_5H_4$)

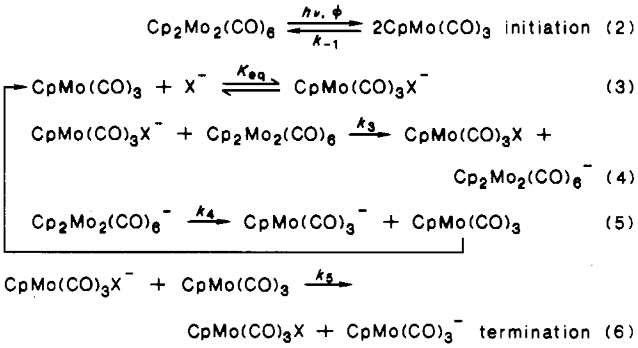
Sir:

In a series of recent papers, we demonstrated that 17-electron organometallic radicals react with Lewis bases to form 19-electron adducts.[1-3] In this communication, we present evidence showing that 19-electron adducts are, in some cases, thermodynamically downhill with respect to the 17-electron precursor and the Lewis base.

Halides and pseudohalides react photochemically with $Cp_2Mo_2(CO)_6$ according to the disproportionation reaction in eq 1.[5] In our previous study of this reaction,[2] we showed that the

$$Cp_2Mo_2(CO)_6 + X^- \xrightarrow{h\nu} CpMo(CO)_3X + CpMo(CO)_3^- \quad (1)$$

reaction followed the pathway in eq 2–6. Note that a key step



$$Cp_2Mo_2(CO)_6 \underset{k_{-1}}{\overset{h\nu,\ \phi}{\rightleftharpoons}} 2CpMo(CO)_3 \quad \text{initiation} \quad (2)$$

$$CpMo(CO)_3 + X^- \overset{K_{eq}}{\rightleftharpoons} CpMo(CO)_3X^- \quad (3)$$

$$CpMo(CO)_3X^- + Cp_2Mo_2(CO)_6 \xrightarrow{k_3} CpMo(CO)_3X + Cp_2Mo_2(CO)_6^- \quad (4)$$

$$Cp_2Mo_2(CO)_6^- \xrightarrow{k_4} CpMo(CO)_3^- + CpMo(CO)_3 \quad (5)$$

$$CpMo(CO)_3X^- + CpMo(CO)_3 \xrightarrow{k_5} CpMo(CO)_3X + CpMo(CO)_3^- \quad \text{termination} \quad (6)$$

in the reaction pathway is eq 3, in which the 17-electron $CpMo(CO)_3$ species reacts with X^- to form the 19-electron adduct $CpMo(CO)_3X^-$. In our previous study we also showed that the quantum yield for disappearance of $Cp_2Mo_2(CO)_6$ in eq 1 is given by eq 7, where $K' = K_{eq}k_3[Cp_2Mo_2(CO)_6]$, $K = k_5K_{eq}$, and I =

$$\Phi = \phi\left(1 - \frac{k_{-1}}{k_{-1} + K[X^-]}\right) + \left(\frac{K'[X^-]}{(k_{-1} + K[X^-])^{1/2}}\right)(\phi/I)^{1/2} \quad (7)$$

the absorbed light intensity. This equation is useful in that it allows us to find K_{eq} from the dependence of Φ on $[X^-]$.

---

(1) (a) Stiegman, A. E.; Stieglitz, M.; Tyler, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 6032–6037. (b) Goldman, A. S.; Tyler, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 4066–4067. (c) Stiegman, A. E.; Tyler, D. R. *Coord. Chem. Rev.* **1985**, *63*, 217–240.

(2) Stiegman, A. E.; Tyler, D. R. *J. Am. Chem. Soc.* **1985**, *107*, 967–971.

(3) The phrase 19-electron complex is used to describe the adducts that form when 17-electron metal radicals react with 2-electron ligands. A thorough discussion of the electronic structures of these complexes is found in ref 4.

(4) Stiegman, A. E.; Tyler, D. R. *Comments Inorg. Chem.*, in press.

(5) Burkett, A. R.; Meyer, T. J.; Whitten, D. G. *J. Organomet. Chem.* **1974**, *67*, 67–73.

0020-1669/86/1325-4806$01.50/0 © 1986 American Chemical Society

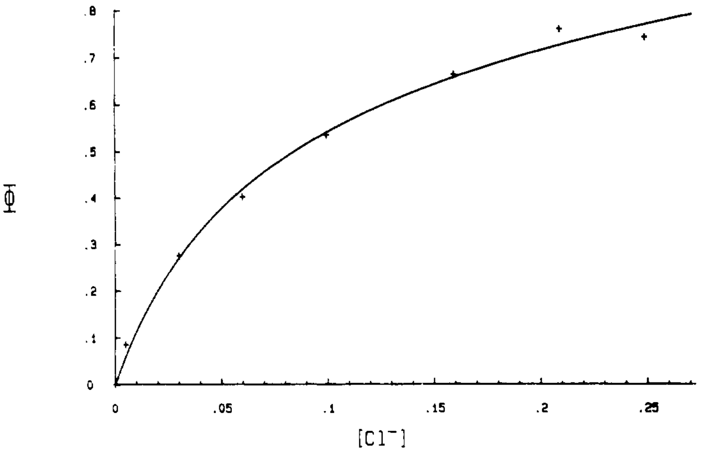


Figure 1. Plot of the disappearance quantum yield for reaction 1 at 505 nm in THF vs. [Cl⁻]. $I = 4.8 \times 10^{-8}$ einstein/min. The curve is a nonlinear least-squares fit of the data points to eq 7.

A plot of Φ vs. [Cl⁻] is shown in Figure 1.[6,8] The curve in the figure is a nonlinear least-squares fit[9] of the data points to the expression in eq 7. The best fit was obtained for the following values: $K' = 3.7$; $K = 3.4 \times 10^{10}$; $\phi = 0.63$. Because $K = k_5K_{eq}$, we can determine K_{eq} if we have a value for k_5. Although the value for k_5 is unknown (it is the rate constant for a termination step in which a 17-electron species reacts with a 19-electron species, eq 6), we can estimate its maximum value as the diffusion-controlled rate constant ($\approx 10^9$ M^{-1} s^{-1}). Using this value, we find $K_{eq} \geq 3.4 \times 10^1$, which, in turn, yields a maximum value for $\Delta G°$ (eq 3, $X^- = Cl^-$) ≤ -2.1 kcal/mol. A similar analysis using Br⁻ yields $K = 6.5 \times 10^{10}$ and $\Delta G°$ (eq 3, $X^- = Br^-$) ≤ -2.5 kcal/mol. For I⁻, we find $K = 2.0 \times 10^{11}$ and thus $\Delta G° \leq -3.1$ kcal/mol.[10] Obviously, if reaction 6 proceeds at less than the diffusion-controlled rate, then $\Delta G°$ will be even more negative. The driving force for the formation of the 19-electron adduct is presumably the formation of the Mo–X bond.[4]

These results demonstrate two important points. First, for the specific case of the disproportionation reaction in eq 1, the 19-electron adducts are reasonable intermediates. Second, in a general sense, these results demonstrate that 19-electron species are not necessarily high-energy species with respect to 17-electron metal radical complexes and a halide ligand. The implication of this last statement is that if reaction pathways involve 17-electron metal radicals (and if Lewis bases are present), then 19-electron species must also be considered as possible reaction intermediates.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for the support of this research. We thank Luanne Rolly for assistance with the least-squares program and Prof. H. B. Gray for helpful discussions.

---

(6) Quantum yields were measured in THF as described previously.[2] Samples for quantum yield measurements were prepared in a dry box by adding an appropriate amount of $P(n\text{-}Bu)_4{}^+Br^-$ or $P(n\text{-}Bu)_4{}^+Cl^-$ to a 10-mL volumetric flask containing 22 mg of $Cp_2Mo_2(CO)_6$. $N(n\text{-}Bu)_4{}^+PF_6{}^-$ was then added to bring the total ionic strength of the sample up to 0.25 M. Lamp intensities were determined by using Aberchrome 540.[7] All reactions were run at room temperature (298 K).

(7) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 1* **1981**, 341–343.

(8) $(\eta^5\text{-}CH_3C_5H_4)_2Mo_2(CO)_6$ was used instead of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ because the former complex is more soluble in THF.

(9) Nonlinear Regression, a program written by Brian W. Clare, was used for the least-squares analysis.

(10) The best fits for Br⁻ and I⁻ were obtained with the following values (errors are expressed with a 90% confidence interval): Br⁻, $K = 6.5 \times 10^{10} \pm 1.4 \times 10^{10}$, $K' = 1.6 \times 10 \pm 6 \times 10^{-1}$, $\phi = 0.24 \pm 0.02$; I⁻, $K = 2.0 \times 10^{11} \pm 0.7 \times 10^{11}$, $K' = 5.3 \times 10 \pm 1.0 \times 10$, $\phi = 0.52 \pm 0.02$.

Department of Chemistry
University of Oregon
Eugene, Oregon 97403

Cecelia E. Philbin
Cynthia A. Granatir
David R. Tyler*

Received August 11, 1986

---

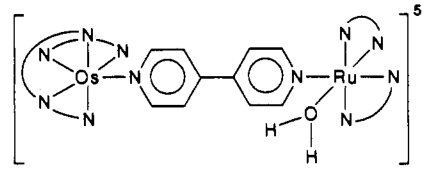
pH-Induced Intramolecular Electron Transfer

Sir:

Oxidation of transition-metal complexes containing aqua ligands characteristically leads to an enhanced acidity and to redox couples whose potentials are pH-dependent, e.g.[1]

$$[(bpy)_2(py)Ru^{II}(OH_2)]^{2+} \xrightarrow{-e^-} [(bpy)_2(py)Ru^{III}(OH)]^{2+} + H^+$$

where py is pyridine and bpy is 2,2′-bipyridine. We demonstrate here that in the ligand-bridged, mixed-valence dimer $[(trpy)(bpy)Os^{III}(4,4'\text{-}bpy)Ru^{II}(H_2O)(bpy)_2]^{5+}$ (trpy is 2,2′:6′,2″-terpyridine and 4,4′-bpy is 4,4′-bipyridine), which contains both an aqua-based, pH-dependent couple and a pH-independent couple, changes in pH can be utilized to induce intramolecular electron transfer across the ligand bridge. The structure of the dimer is



where N atoms connected by arcs are used to illustrate the polypyridyl ligands, and the cis geometry at the Ru site is also shown. Further, in the twice-oxidized Os(III)–Ru(III) dimer, pH-induced intramolecular electron transfer can be used to concentrate the stored redox equivalents at a single site, thus gaining a significantly enhanced oxidative reactivity toward an organic substrate.

The dimer $[(trpy)(bpy)Os^{II}(4,4'\text{-}bpy)Ru^{II}(H_2O)(bpy)_2](BF_4)_4$ was prepared by the reaction between $[(trpy)(bpy)Os^{II}(4,4'\text{-}bpy)]^{2+}$ and $[(bpy)_2Ru^{II}(OH_2)_2]^{2+}$ in refluxing 1:1 EtOH/0.1 M CF_3SO_3H(aq) for 4 h.[2] The dimer was precipitated as the PF_6^- salt, purified by passing through a Sephadex C-25-120 cation-exchange column by eluting with aqueous $NaBF_4$, and isolated as the BF_4^- or PF_6^- salt.[3]

In the related monomer $[(bpy)_2(py)Ru^{II}(OH_2)]^{2+}$, the pH dependences of both the Ru(III/II) and Ru(IV/III) couples have been described.[1] The results of pH-dependent cyclic voltammetric and differential pulse polarographic studies on the dimer are summarized in the $E_{1/2}$ vs. pH or Pourbaix diagram in Figure 1, where $E_{1/2}$ is measured vs. the saturated calomel electrode, SCE. The electrochemical studies provide clear evidence for a pH-independent Os(III/II) couple at $E_{1/2} = +0.63$ V and the expected pH-dependent Ru(III/II) and Ru(IV/III) couples. In the diagram the oxidation state distributions and proton contents of the various forms of the dimer are shown in the potential–pH regions where they are dominant. Slow electrode kinetics for the $Ru^{IV}(O)/Ru^{III}(OH)$ couple (as observed for related monomers)[1] makes direct observation of this couple in the dimer difficult below pH 8. The potential for the $Os^{III}\text{–}Ru^{IV}(O)/Os^{III}\text{–}Ru^{III}(OH)$ couple shown by the dashed line was estimated by adding the potential difference between the $Os^{II}\text{–}Ru^{III}(OH)/Os^{II}\text{–}Ru^{II}(OH_2)$ and

---

(1) (a) Moyer, B. A.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 436. (b) Takeuchi, K. J.; Thompson, M. S.; Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 1845.

(2) The monomer $[(trpy)(bpy)Os^{II}(4,4'\text{-}bpy)]^{2+}$ was prepared by the reaction between $[(trpy)(bpy)Os^{III}(TFMS)](TFMS)_2$ (TFMS is trifluoromethanesulfonate anion) and a 20-fold excess of 4,4′-bpy, which were heated in refluxing ethylene glycol for 30 min. The PF_6^- salt was isolated by the addition of aqueous NH_4PF_6 and then purified by column chromatography on alumina using 1:1 acetonitrile/toluene as eluant. $[(trpy)(bpy)Os^{III}(TFMS)](TFMS)_2$ was isolated from the reaction between $[(trpy)(bpy)Os^{II}Cl](PF_6)$ and neat trifluoromethanesulfonic acid (ref 1b) by dropping the reaction mixture into 500 mL of anhydrous diethyl ether, collecting the precipitate, and storing the water-sensitive solid under vacuum. The complex $[(bpy)_2Ru(OH_2)_2]^{2+}$ was prepared in situ by dissolving $[(bpy)_2Ru(CO_3)]$ (Johnson, E. C.; Sullivan, B. P.; Salmon, D. J.; Adeyemi, S. A.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 2211) in the acidic solvent. Rapid loss of carbonate as CO_2 occurs upon the addition of acid. (Durham, B.; Wilson, S. R.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 600.)

(3) Anal. Calcd for $[(trpy)(bpy)Os(4,4'\text{-}bpy)Ru(H_2O)(bpy)_2](PF_6)_4 \cdot 3H_2O$: C, 36.67; H, 2.86; N, 8.56. Found: C, 36.63; H, 2.88; N, 8.44.

0020-1669/86/1325-4807$01.50/0 © 1986 American Chemical Society