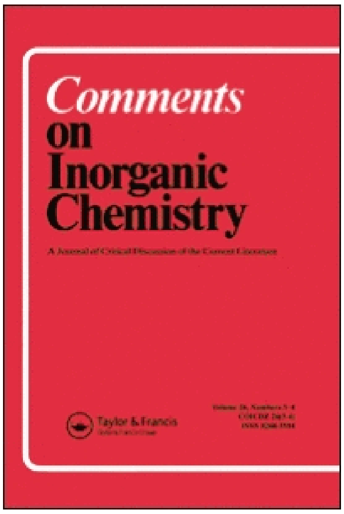

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The Design of Reagents for Photochemical and Thermal Multiple Electron Transfer Reactions

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The Design of Reagents for Photochemical and Thermal Multiple Electron Transfer Reactions

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Most, if not all, electron transfer reactions involving more than one electron can be considered as a series of sequential one electron transfer steps when evaluated on an appropriate timescale. Once the critical activation barrier for the first electron transfer to occur has been surmounted, the ensuing electrons are generally transferred in rapid succession. A number of multiple electron, inorganic systems, particularly those containing platinum, are evaluated; and the underlying principles for the design of these systems are discussed. Both thermally and photochemically activated systems are considered. Additionally, new thermodynamic criteria are proposed for certain inner sphere electron transfer reactions.

Key Words: *multiple electron charge transfer chemistry, photochemistry, inner sphere charge transfer, cyanometalates, platinum*

1. INTRODUCTION

One electron transfer processes have been extensively investigated over the past thirty years due to their extreme importance in energy conversion processes, bioinorganic chemistry, and molecular de-

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vices.[1] Systems capable of transferring several electrons are of particular interest since most fuel-forming reactions are inherently multiple electron in nature.[2] Such systems have received attention only recently. Of the thousands of reported electron transfer reactions involving inorganic compounds, only about thirty fall into this category. Most of these involve apparent outer sphere reactions between aquated metal ions, at least one of which possesses two stable oxidation states separated by greater than one electron. Notable examples include Tl(I/III), Cr(III/VI), V(III/V), Sn(II/IV), and Pt(II/IV). An excellent, though dated, review of these reactions has been reported by Sykes.[3]

Electron transfer reactions which differ by more than one electron have been claimed to occur by one of two possible mechanisms: sequential or simultaneous electron transfer. The reduction of thallium (III) by two equivalents of iron (II) in aqueous solution, for example, is proposed to go by a sequential mechanism with the formation of a thallium (II) intermediate. The two step mechanism is based on the fact that the rate constant is first order in both Tl(III) and Fe(II) and the observation that added Fe(III) but not Tl(I) decreases the rate constant for the reaction. On the other hand, the two electron reduction of thallium (III) by chromium (II) is reported to occur simultaneously,[4] according to Eqs. (1a) and 1(b).

$$\mathrm{Tl(III)} + \mathrm{Cr(II)} \rightarrow \mathrm{Tl(I)} + \mathrm{Cr(IV)}, \tag{1a}$$

$$\mathrm{Cr(II)} + \mathrm{Cr(IV)} \rightarrow [\mathrm{Cr(III)}_2]\ \text{dimer} \tag{1b}$$

Although a sequential one electron scheme could also be postulated for this reaction, the authors argue that the amount of chromium (III) formed as an intermediate would appear in much larger quantities than was observed, favoring the direct two electron transfer mechanism. Several other examples of simultaneous multielectron transfer reactions have been reported, including a four electron Cr(V) → Cr(I) chelate conversion.[5]

It is often quite difficult in these systems to determine whether a multiple electron transfer occurs simultaneously or sequentially.[3,6] The distinction is generally made on the basis of kinetics and the presence (or lack) of an intermediate of $(n + 1)$ oxidation state. Since thermal electron transfer can theoretically occur on the timescale of a single vibration (~picosecond), we argue that the point is moot. It is very likely that all so-called simultaneous multielectron charge transfer processes actually occur stepwise.

Within the confines of the semiclassical charge transfer theory developed by Marcus and Hush, two different energetic schemes can be put forth to describe a two electron transfer reaction which occurs in a stepwise manner. These two schemes are shown in Fig. 1 for the oxidation of reactant A(II) by reagent B(III). Within this framework, multiple electron transfer reactions necessarily require a potential energy diagram with (n + 1) overlapping potential energy surfaces (where n is the total number of electrons transferred). For Case I, two electrons are moved to generate A(IV) from A(II) under conditions where A(III) is a low energy, thermodynamically unstable species. This situation arises because the redox potential of the A(II/III) couple (E_1°) is greater than or equal to the A(III)/A(IV) redox potential (E_2°). In this situation, once the activation barrier which leads to the A(III) intermediate is surmounted, the second one electron transfer will occur if enough oxidant is present in the system. Note that once A(III) forms, the thermodynamics of this system preclude the back reaction to regenerate A(II). The rate of formation of A(IV) is only a function

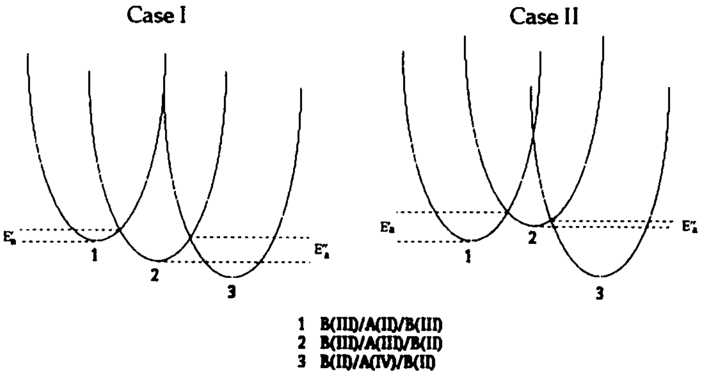


FIGURE 1 Potential energy diagrams for two different mechanisms of sequential, net two electron oxidations of A(II) to A(IV) by a one electron oxidant B(III). The differences between the two cases are discussed in the text. E_a' and E_a'' represent thermal activation energies corresponding to the processes 1 → 2 and 2 → 3, respectively.

of the second activation barrier height, E''_a, once A(III) has formed. The hydroquinone/benzoquinone couple provides a classic example of this chemistry occurring on a ground state potential energy surface. Case II provides a scenario in which two electrons are transferred through a high energy intermediate species. In this case, the formation of the charge transfer intermediate A(III) does not endow reaction control solely to E''_a. Once A(III) forms, whether A(II) is regenerated or A(IV) is formed depends on the relative values of E''_a and E'_a. These two quantities are controlled, in part, by the redox potentials of the reacting couples. Note that unlike Case I, the initial formation of A(III) requires a high energy process (the A(II) to A(III) transformation is positive in free energy).

Whether a Case I or Case II system is encountered, the second electron transfer step will be facilitated by the fact that the reactant ions are already at the reaction distance. Thus, the electron transfer rate for the second electron can exceed the diffusion limit. The determination of the presence of an intermediate state is therefore expected to be limited by the timescale of the observational technique. Likewise, the latter fast step of the mechanism would not appear in the kinetic rate expression for the overall reaction. Consequently, in a sequential electron transfer mechanism, since the secondary electron transfer steps are often rapid,[7] what is really a stepwise multiple electron transfer reaction will take on the character of a simultaneous multielectron transfer. The design of systems capable of transferring more than one electron therefore reduces to one in which several electrons can be transferred sequentially.

2. EXAMPLES OF MULTIPLE ELECTRON TRANSFER REACTIONS

Although the self-exchange redox chemistry of platinum complexes was recognized early on as an example of a multiple electron transfer system,[8] little work has been undertaken to explore the charge transfer dynamics and potential applications of these systems. Platinum is an ideally suited element for the study of multiple charge transfer processes since it forms stable oxidation states in its complexes of Pt(II) and Pt(IV), while Pt(III) species are typically transient in nature. In the mid-1980's, we reported[9] on the photoinitiated oxidation of primary and secondary alcohols to their corresponding aldehydes or ketones in a system which employed hexachloroplatinate (IV) salts. From a practical standpoint, the system is of interest in that primary alcohols are not overoxidized to the acid and up to four electrons can be transferred leading to the production of platinum metal. Further, the reaction can be made catalytic by the addition of $CuCl_2$ and O_2. The four electron photoinduced reduction of $[PtCl_6]^{2-}$ in alcohol/water mixtures does not require heating and occurs at all wavelengths for which the compound absorbs light.

The initial step in this particular system involves photosubstitution to form an alkoxy substituted platinum (IV) species. The nature of the primarily reactive species has been determined to be $[PtCl_3(OR)_3]^{2-}$ by UV-vis spectroscopy, ^1H NMR, and elemental analysis. This complex is then photoexcited to yield a Pt(III) intermediate and an oxygen based alkoxy radical. Although the latter free radical is less stable than its carbon analog, its presence has been implicated by two experimental results. First, the photooxidation of t-butanol leads primarily to the formation of acetone, while an isopropanol substrate yields acetaldehyde as the major product. Methyl radical loss has been previously associated with oxygen based, rather than carbon based, free radicals. Secondly, the photooxidation of methanol does not lead to ethylene glycol, as would be expected for the formation of a carbon based radical. Evidence for a Pt(III) intermediate was supplied by monitoring the reaction using ^{195}Pt NMR. Irradiation initially leads to loss of the Pt(IV) associated signal, followed by an induction period of NMR silence before Pt(II) species are observed in the reaction mixture. This conclusion is in agreement with low-temperature ESR results on the photochemical reaction of $[PtCl_6]^{2-}$ in a frozen methanol matrix (77 K) which show the growth of a Pt(III) signal upon photolysis.[10] The results are also in agreement with the aqueous photochemistry of $[PtCl_6]^{2-}$, which leads initially to the formation of Pt(III) and $Cl^{\bullet}$ radicals[11] with quantum yields in excess of unity upon irradiation into the lowest energy $PtCl_6^{2-}$ LMCT absorption.

A complete reaction mechanism for the two and four electron reduction of $[PtCl_6]^{2-}$ is depicted in Fig. 2.[9(c)] The reaction becomes catalytic when the one electron oxidant, $CuCl_2$ is added to

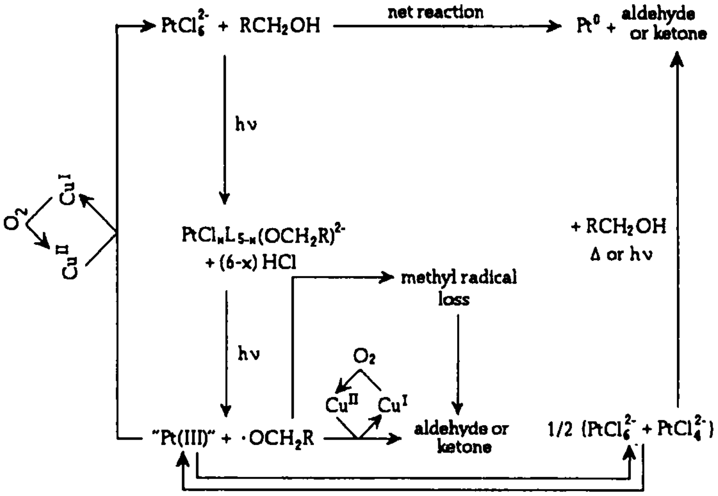


FIGURE 2 Reaction mechanism for the photochemically driven, four electron reduction of $PtCl_6^{2-}$ to platinum metal in alcoholic solutions.

the system in the presence of O_2, as shown, through both the oxidation of the alkoxy radicals to product and the oxidation of Pt(III) intermediates back to the Pt(IV) form. It is also speculated that two Pt(III) intermediates might disproportionate into Pt(II) and Pt(IV) according to the equilibrium proposed by Taube.[12]

A second example of photoinduced multiple electron transfer is given by Eqs. (2a)–(2c) reported by Gray *et al.*[13] where M represents Mo or W and L is phenylisocyanide.

$$ML_6 + h\nu \rightarrow {}^*ML_6, \tag{2a}$$

$$^*ML_6 + HCCl_3 \rightarrow ML_6^+ + HCCl_3^{-\cdot}, \tag{2b}$$

$$ML_6^+ + HCCl_3^{-\cdot} \rightarrow ML_6Cl^+ + HCCl_2^{\cdot} \tag{2c}$$

Irradiation leads to an excited MLCT state, which then undergoes electron transfer quenching by chloroform to form a M(I) intermediate species. In the cases where L = CNIPh (IPh = 2,6-diisopropylphenyl), due to the steric hindrance of the ligand, the reaction stops with Eq. (2b) and only one electron photoproducts are produced. However, if the less bulky CNPh ligand is employed, the reaction proceeds to the seven-coordinate, two electron oxidation product via Eq. (2c). The resulting seven-coordinate, net two electron oxidation products have been isolated and compared to previously reported Mo(II) complexes of similar composition.[14] Maverick has recently demonstrated the sequential two electron oxidation of $Mo(NCS)_6^{3-}$ in CCl_4, in which the first electron is transferred photochemically.[14(e)] Both these examples again provide evidence of the sequential nature associated with multiple charge transfer reactions.

Multiple electron transfer reactions are not limited to two electrons. Recently, Meyer[15] has synthesized both pure and mixed styrene/chloromethylstyrene copolymers loaded with the $Ru(bpy)_3^{2+}$ and/or $Os(bpy)_3^{2+}$ chromophores by nucleophilic displacement of the chloride (Fig. 3). Photoexcitation of these soluble polymers leads to the formation of a long-lived MLCT excited state. This excited state undergoes bimolecular electron transfer with an irreversible oxidative quencher such as $4\text{-}CH_3OC_6H_4N_2^+$ (ArN_2^+), leading to the formation of Ru(III) and/or Os(III) sites on the polymeric chain. When the polymer is fully loaded, it was found that intrapolymer quenching by neighboring oxidized chromophores was slow compared to intermolecular quenching by ArN_2^+; the former process is retarded since it lies in the Marcus inverted region. In this manner, the production of multiple redox equiva-

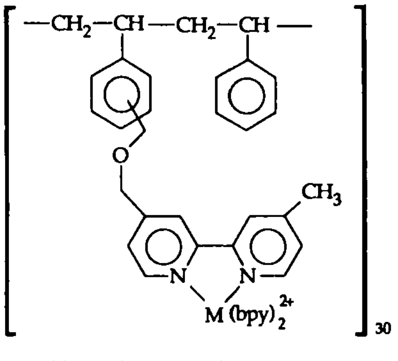


FIGURE 3 Polymer backbone for a substituted styrene/chloromethylstyrene copolymer which can undergo photoinduced multiple electron transfer reactions.

lents can be efficiently generated. Unlike the prior examples given, in this case the thermodynamic requirements for consecutive electron transfer are not met. Sequential multiple charge transfer is achieved by sequential photon absorption with each absorption event leading to at most a one electron transfer.

3. THEORETICAL BASIS OF MULTIPLE ELECTRON TRANSFER: A CASE STUDY

We have previously shown[16] that the sequential two electron oxidation of $[Pt(NH_3)_4](NO_3)_2$ by two moles of $K_3Fe(CN)_6$ leads to a trinuclear, cyanide-bridged "Fe–Pt–Fe" species. The reaction proceeds by two consecutive, inner sphere electron transfer steps according to Case II in Fig. 1 forming a stable trinuclear complex, as illustrated by Eqs. (3a) and (3b).

$$Pt^{II}(NH_3)_4^{2+} + Fe^{III}(CN)_6^{3-} \rightarrow [(H_3N)_4Pt^{III}NCFe^{II}(CN)_5]^{-}, \tag{3a}$$

$$[(H_3N)_4Pt^{III}NCFe^{II}(CN)_5]^{-} + Fe^{III}(CN)_6^{3-} \rightarrow [(NC)_5Fe^{II}CNPt^{IV}NCFe^{II}(CN)_6]^{4-} \tag{3b}$$

The kinetics of formation of the trinuclear species[16] have been reported to show a first order dependence on both the concentration of ferricyanide and tetraammineplatinum(II), consistent with the above sequential mechanism, with (3a) as the rate-determining step (under steady state conditions for Pt(III)).

The resulting complex is mixed valent and possesses an intervalent (IT) charge transfer transition in the visible corresponding to optical excitation from Fe(II) → Pt(IV). Photoexcitation of this absorption band leads to a net two electron transfer reaction according to the reverse sequence of Eqs. (3a) and (3b). Initial optical excitation leads to a transient Fe(III)/Pt(III)/Fe(II) intermediate (a one electron charge transfer), which either undergoes reverse electron transfer to reform the starting material or reacts thermally with the second equivalent of Fe(II) to form the reactants in (3a).

A series of cyanobridged complexes of this type have been synthesized and characterized electrochemically and by UV-vis spectroscopy.[17] A linear relationship was found between the IT band maxima and the differential redox free energy of the ground states. With a knowledge of the rate constant of the trinuclear complex, IT absorption band energy, and appropriate redox potentials, the vertical free energy parameters in Fig. 1 can be generated for each complex.

The relative heights of the thermal activation barriers for parabola 2 (the Pt(III) intermediate) in Fig. 1 have been used to explain the observed lack of photochemistry for the homologous Os complex.[17] As a result of the differing thermodynamic driving force for this species, the differentiation in activation barriers for the formation of the Os(III)/Pt(II)/Os(III) versus Os(II)/Pt(IV)/Os(II) complex from the Pt(III) photogenerated intermediate is a factor of ~6 times higher than that for the iron complex, preventing efficient photochemical conversion.

We have shown[17] that the relative heights of these activation barriers (which depend principally on the ground state free energy difference since the reorganization energy for these structurally similar compounds is essentially a constant) can be modulated by employing aprotic solvents such as DMSO which cannot hydrogen bond to the cyanide nitrogen. Addition of incremental amounts of DMSO to an aqueous solution of the complex therefore readjusts the relative energies of the parabolas in Fig. 1 with respect to the others. Parabola 2 is lowered twice as much as parabola 3, as a result of the number of electrons transferred, relative to parabola 1. Figure 4 shows the effect of the relative ground state free energies of these parabolas on the thermal activation barriers for electron transfer. By appropriate addition of aprotic solvent to the Os complex, it has been demonstrated that the relative energies of the parabolas with respect to one another can be modulated such that it matches that of the purely aqueous Fe species. At this point, irradiation of the Os complex *does* lead to productive photochemistry, identical to that observed for the iron species.[18]

4. SUBSTITUTIONALLY MEDIATED, INNER SPHERE ELECTRON TRANSFER

The energetics of the trinuclear "Fe–Pt–Fe" system points to a seldom discussed aspect of the inner sphere electron transfer mech-

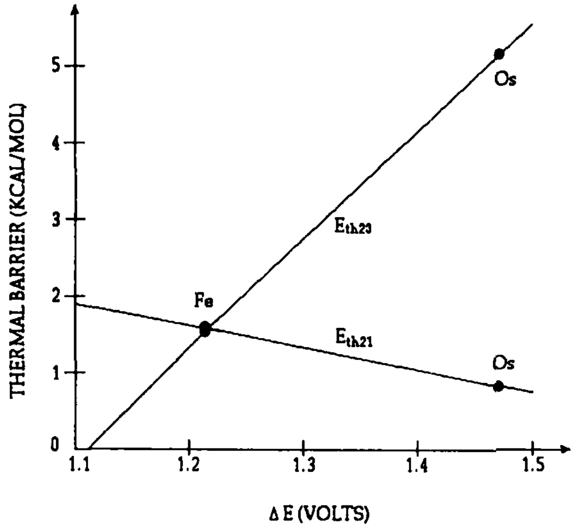
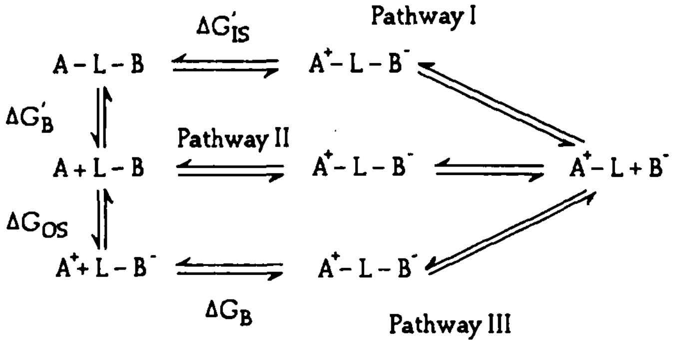


FIGURE 4 Correlation diagram showing the change in the thermal activation barriers E_{th23} and E_{th21} as a function of the ground state free energy difference. The first numerical subscript represents the number of the parabola in Fig. 1 from which the electron transfer takes place, while the second numerical subscript represents the parabola to which the electron transfer takes place. The points indicated refer to the general complex $[(NC)_5M^{II}CNPt^{IV}(NH_3)_4NCM^{II}(CN)_5]^{4-}$ where M = Fe or Os. The relative free energy differences between the three overlapping parabolas can be adjusted by the incremental addition of DMSO to the aqueous solution, according to the correlations shown.

anism, namely that selection of an inner sphere reaction channel over an outer sphere channel may include thermodynamic considerations in addition to kinetic limitations. In the classical inner sphere mechanism, an ambidentate ligand (usually donated by the more inert metal center) substitutionally displaces a leaving group on the other metal center, forming a bridged precursor complex. Electron transfer is then generally followed by dissociation of the precursor complex with the more inert metal center retaining the formerly bridged ligand. The above system provides an exception to this rule, since the ligand bridge remains intact in the product. As shown in Scheme 1, a series of thermochemical cycles can be written for the generic inner sphere reaction in which the generation of chemical bonds associated with the formation of the ligand bridge is separated from the actual passage of the electron.



SCHEME 1

Pathway II in this scheme represents a reaction channel in which the electron transfer occurs simultaneously with the formation of the ligand bridge, while Pathway I represents the reaction in terms of bridge formation followed by charge transfer. Either of these two pathways corresponds to an inner sphere reaction. Pathway III, on the other hand, views the reaction as being a consecutive outer sphere charge transfer followed by bridge formation. This latter view obviously does not fit the inner sphere mechanistic requirements. Nonetheless, from a purely thermochemical point of view, it describes the requisite reactant and product states.

The normal thermodynamic analysis of a redox reaction, independent of whether it is inner sphere or outer sphere, is typically based on the free energy associated with the first step shown for Pathway III. Thus, for example, if one wishes to ascertain if $\mathrm{Pt(NH)_4^{2+}}$ might react with $\mathrm{Fe(CN)_6^{3-}}$ in an aqueous solution, then the standard redox potentials of these two species are combined to obtain ΔG_{OS}. For an outer sphere charge transfer reaction, this is of course correct since $\Delta G_{\mathrm{B}} = 0$. In the case of an inner sphere charge transfer mechanism, the assumption is made that ΔG_{OS} is a reasonable approximation for $\Delta G'_{\mathrm{IS}}$. In reality, however, as shown by Scheme 1, the only thermodynamic restraint on this type of reaction is given by Eq. (4).

$$\Delta G_{\mathrm{OS}} + \Delta G_{\mathrm{B}} = \Delta G'_{\mathrm{IS}} + \Delta G'_{\mathrm{B}} = \Delta G_{\mathrm{Pathway\ II}} \tag{4}$$

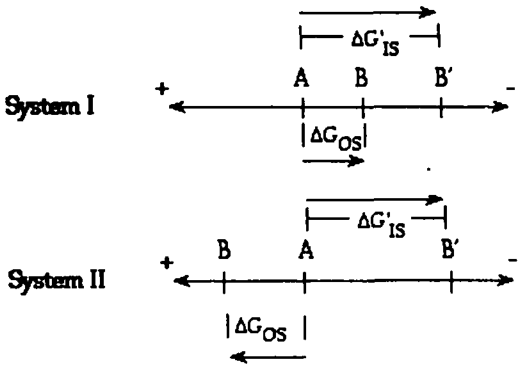
Based on this type of analysis, it might be assumed that any error introduced by the assumption that $\Delta G'_{\mathrm{IS}} = \Delta G_{\mathrm{OS}}$ could be associated with the increased thermodynamic stability of the charge transfer intermediate due to the generation of a bonding interaction ($\Delta G'_{\mathrm{B}}$). In this case, according to Eq. (4), $\Delta G'_{\mathrm{IS}}$ could conceivably be positive, yet the reaction could have an overall negative $\Delta G_{\mathrm{Pathway\ I}}$. Note, however, that based on these types of arguments and the nature of Eq. (4), it would *appear* that a reaction could not proceed (independent of the mechanism) if ΔG_{OS} were to take on a positive value. In other words,

$$\Delta G_{\mathrm{OS}} \leq \Delta G'_{\mathrm{IS}} \tag{5}$$

should hold based on the assumptions mentioned above.

The redox properties of cyanometalate complexes are particularly sensitive to the environment of the cyanide nitrogen lone pair. For example, in the trinuclear complex described by Eq. (3a), the formation of cyanide bridges shifts the redox potential of the ferrous units 360 mV more positive than found in free ferrocyanide.[6(a)] Therefore, in this situation, ΔG_{OS} is experimentally found to be significantly less negative than $\Delta G'_{\mathrm{IS}}$. That is, the inequality stated above in Eq. (5) is incorrect in this case. Applying this information to Eq. (4) yields $\Delta G'_{\mathrm{B}} > \Delta G_{\mathrm{B}}$. The hypothetical bond energy ($-\Delta G_{\mathrm{B}}$) for Pathway III is greater than the actual bond energy ($-\Delta G'_{\mathrm{B}}$) found using Pathway I. Therefore, this shift in energetics is *not* due to increased product stability associated with inner sphere bond formation. The change in energetics is directly related to the mechanism required for charge transfer.

This unusual situation arises because the standard redox potentials for transition metal complexes paint an incomplete picture of the actual charge transfer energetics. Since it is usually assumed that all redox reactions can occur via an outer sphere type mechanism, inner sphere reactions are postulated to only exist due to a kinetic advantage associated with this reaction channel. While in many cases this is true, there also exist free energy relationships (related solely to the charge transfer free energy) which can be selective for an inner sphere charge transfer. In the example given above, and for the general case depicted by System I of Scheme 2, this shift in free energy of the oxidizing agent, B, with respect to the reducing agent, A, has few implications with respect to the expected behavior of the reaction (B′ represents the redox poten-



SCHEME 2

tial of the shifted oxidant). At most, if the charge transfer step is rate limiting (and typically it is bond formation which is limiting), then the reaction will occur faster than expected as predicted by the Marcus cross relationship, Eq. (6), where k_{11} and k_{22} are the self-exchange rates for the two redox couples, A and B, and f is related to the collision frequency.

$$k_{12} = \left[k_{11} k_{22} f \exp\left(\frac{-\Delta G'_{\mathrm{IS}}}{RT} \right) \right]^{1/2} \tag{6}$$

On the other hand, if the redox potentials for hypothetical redox couples (A + B) are as shown by System II of Scheme 2, then the shift in the redox potential of oxidant B accompanying the formation of the ligand bridge (as described by Pathway I of Scheme I) can shift the value of $\Delta G'_{\mathrm{IS}}$ from positive to negative. Thus, it should be possible to carry out certain redox reactions via an inner sphere pathway which one would predict to be thermodynamically unfavorable based on known standard redox potentials. Within the confines of cyanometalate redox chemistry, such reactions require the redox potentials of the unbridged species to be similar to one another (since the effect only covers the range of several hundred millivolts). During the reaction, a bridged precursor complex must be formed through nucleophilic substitution between two complexes which are thermodynamically incapable of undergoing an electron transfer in the unbridged form. The formation of this intermediate complex must shift the redox potential of the metal center(s) in a manner similar to that observed for the ferrricyanide/ platinum case discussed above.

We have preliminary evidence that just such a substitutionally mediated, inner sphere electron transfer reaction occurs between cis-$Pt^{II}(NH_3)_2Cl_2$ ("cisplatin") and $Na_2Fe^{III}(CN)_5$(4-CN-py) (where 4-CN-py = 4-cyano-pyridine). The reported redox potential for the $[Fe(CN)_5(4\text{-CN-py})]^{3-/2-}$ couple is +0.32 V vs. SCE,[19] which is insufficient to oxidize cisplatin (+0.43 V vs. SCE[20]) by an outer sphere electron transfer. The susceptibility of the chloride ligands in cisplatin to substitution reactions with amino ligands, however, is well-documented.[21] Therefore the substitution of a chloride on cisplatin by the nitrogen end of a $Na_2Fe(CN)_5$(4-CN-py) ligated cyanide ligand is expected. Infrared spectroscopic analysis of the product of this reaction provides evidence for the presence of both bridging (2108 cm^{-1}) and terminal (2066 cm^{-1}) Fe(II) cyanide ligands indicating that the reaction proceeds as discussed. Stoichiometrically, two ferric species are required to oxidize one molecule of Pt(II) to Pt(IV). Thus, we assume that a trinuclear, cyanide-bridge "Fe–Pt–Fe" complex such as those discussed in the previous section has been formed. Consistent with this result is the appearance of an intervalent charge transfer absorption band in the visible spectrum which is centered at 406 nm with a tail to the red. The tail is presumably due to the Fe(II) → 4-CN-py MLCT transition, formerly at 476 nm in the isolated iron complex. A more detailed characterization of this complex is necessary; however, these preliminary results provide strong support for the notion that bridge formation can mitigate an unfavorable charge transfer free energy.

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References

1. (a) C. Creutz. Prog. Inorg. Chem. **30**, 1 (1989). (b) T. J. Meyer, Acc. Chem. Res. **11**, 94 (1978). (c) N. Sutin, Acc. Chem. Res. **15**, 275 (1982). (d) V.

Balzani and F. Scandola, in *Photoinduced Electron Transfer*, eds. M. A. Fox and M. Chanon (Elsevier, Amsterdam, 1988). (e) V. Balzani, F. Barigelletti and L. De Cola, Topics Curr. Chem. **158**, 31 (1990). (f) F. Scandola, M. T. Indelli, C. Chiorboli, and C. A. Bignozzi, Topics Curr. Chem. **158**, 73 (1990). (g) V. Balzani, Pure Appl. Chem. **62**, 1099 (1990). (h) V. Balzani and F. Scandola, *Supramolecular Photochemistry* (Ellis Horwood Ltd., West Sussex, 1991).

2. (a) A. Heller, Acc. Chem. Res. **14**, 154 (1981). (b) J. P. Collin and J. P. Sauvage, Coord. Chem. Rev. **93**, 245 (1989).
3. A. Sykes, *Kinetics of Inorganic Reactions* (Pergamon Press, Oxford, 1966).
4. M. Arden and R. A. Plane, J. Am. Chem. Soc. **81**, 3197 (1959).
5. N. Rajasekar, R. Subramanian, and E. S. Gould, Inorg. Chem. **21**, 4110 (1982).
6. J. D. Atwood, *Inorganic and Organometallic Reaction Mechanisms* (Wadsworth, Inc., Belmont, 1985).
7. Under special circumstances, the second electron transfer might be slow enough for the intermediate to be detected. For example, if the second reaction occurred at a sufficiently large free energy, it could fall in the Marcus inverted region (Ref. 1(c)), where the thermodynamic driving force for the reaction exceeds the reorganization energy necessary to achieve the precursor complex.
8. (a) R. L. Rich and H. Taube, J. Am. Chem. Soc. **76**, 2608 (1954). (b) D. L. Swihart and W. R. Mason, Inorg. Chem. **9**, 1749 (1970). (c) L. E. Cox, D. G. Peters, and E. L. Wehry, J. Inorg. Nucl. Chem. **34**, 297 (1972).
9. (a) R. E. Cameron and A. B. Bocarsly, J. Am. Chem. Soc. **107**, 6116 (1985). (b) R. E. Cameron and A. B. Bocarsly, Inorg. Chem. **25**, 2910 (1986). (c) A. B. Bocarsly, R. E. Cameron and M. Zhou, in *Photochemistry and Photophysics of Coordination Compounds*, eds. H. Yershin and A. Vogler (Springer-Verlag, Berlin, Heidelberg, 1987). (d) M. Zhou, Ph.D. Thesis, Princeton University (1990).
10. I. I. Blinov and G. A. Shagisultanova, Koord. Khim. **8**, 191 (1982).
11. L. E. Cox, D. G. Peters and E. L. Wehry, J. Inorg. Nucl. Chem. **34**, 297 (1972).
12. R. L. Rich and H. Taube, J. Am. Chem. Soc. **76**, 2608 (1954).
13. K. R. Mann, H. B. Gray and G. S. Hammond, J. Am. Chem. Soc. **99**, 306 (1977).
14. (a) D. L. Lewis and S. J. Lippard, J. Am. Chem. Soc. **97**, 2697 (1975). (b) M. Novotny and S. J. Lippard, J. Chem. Soc., Chem. Comm. 202 (1973). (c) D. R. Lewis and S. J. Lippard, Inorg. Chem. **11**, 621 (1972). (d) F. Bonati and G. Minghetti, Inorg. Chem. **9**, 2642 (1970). (e) Q. Yao and A. W. Maverick, J. Am. Chem. Soc. **108**, 5364 (1986).
15. L. A. Worl, G. F. Strouse, J. N. Younathan, S. M. Baxter and T. J. Meyer, J. Am. Chem. Soc. **112**, 7571 (1990); and references therein.
16. (a) M. Zhou, B. W. Pfennig, J. Steiger, D. Van Engen and A. B. Bocarsly, Inorg. Chem. **29**, 2456 (1990). (b) B. W. Pfennig and A. B. Bocarsly, Coord. Chem. Rev. **111**, 91 (1991).
17. B. W. Pfennig and A. B. Bocarsly, J. Phys. Chem. **96**, 226 (1992).
18. C. J. Warren, B. W. Pfennig and A. B. Bocarsly, unpublished results.
19. J.-L. Brisset and M. Biquard, Inorg. Chim. Acta **53**, L125 (1981).
20. Y. N. Kukushkin and S. Ch. Dkhara, Zh. Neorg. Khim. **14**, 2816 (1961).
21. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed. (John Wiley & Sons, New York, 1988).