Table III. Emission Lifetimes at λ_{max} for Pd_2 and Pt_2 Complexes

	τ_e, μs (λ_{max}, nm)	
	295 K	77 K
$Pd_2(dba)_3$[a]	0.22 ± 0.01 (740)	8.0 ± 0.2 (740)
$Pt_2(dba)_3$[a]	0.23 ± 0.01 (800)	0.95 ± 0.2 (800)
$Pd_2(dppm)_3$[b]	5.93 ± 0.01 (710)	107 ± 1 (685)
$Pt_2(dppm)_3$[b]	<0.02 (790)	10.6 ± 0.2 (790)
$Pt_2(pop)_4^{4-}$	9.8 (517[c])	10.3 (515[d])
$Pt_2(pcp)_4^{4-}$[e]	0.055 (510)	10.0 (510)

[a] This work. [b] From ref 9. [c] From ref 3g. [d] From ref 3 h. [e] King, C.; Auerbach, R. A.; Fronczek, F. R.; Roundhill, D. M. *J. Am. Chem. Soc.* **1986**, *108*, 5626.

same. Exactly the opposite is observed. The energy gap between the singlet $p\sigma \leftarrow d\sigma^*$ and emission transitions is much too large in the $M_2(dba)_3$ cases ($\Delta \sim 12800$ cm^{-1}, which is ~4600 cm^{-1} greater than Δ in the $M_2(dppm)_3$ complexes).[9] On the basis of transition energies, an M-M-localized emissive state is ruled out. Similarly, due to the M dependence of λ_{em}, the absence of a dba band in the excitation spectra (see Figures 2 and 5), and complete absence of dba luminescence in the 700-900-nm region, the possibility of emission arising from a ligand-localized state also is eliminated. The energy gap between the MLCT absorption and emission bands is ~5000 cm^{-1} (for both complexes), which is identical with the energy gap measured for $Ru(bpy)_3^{2+}$ (which also possesses a low-energy MLCT absorption system[27]). Considering the transition energies, it is likely that an MLCT triplet excited state is responsible for the emission in $M_2(dba)_3$.[28]

The emissions at 295 and 77 K are relatively long-lived and are comparable to τ_e of other Pd_2 and Pt_2 complexes (Table III). Interestingly, for the $M_2(dba)_3$ complexes, $\tau_e(Pd) = \tau_e(Pt)$ at 295 K.[29] The significant decrease in τ_e from $Pd_2(dppm)_3$ to $Pd_2(dba)_3$ (5.93 to 0.22 μs at 295 and 107 to 8.0 μs at 77 K) indicates that the dba ligand possesses a high degree of flexibility.

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Free Energy Dependence of the Electronic Factor in Biological Long-Range Electron Transfer

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Abstract: The donor and acceptor orbitals in long-range electron transfer are strongly exposed to environmental inertial polarization fluctuations. The most likely polarization at the moment of electron transfer is determined by the intersection region of two potential surfaces spanned by collective polarization coordinates and depends strongly on the temperature and reaction free energy. These effects must therefore be reflected in corresponding variation of the electronic transmission coefficient with these quantities and not solely in the nuclear Franck-Condon factors. We have estimated these effects for system parameters appropriate to intramolecular electron transfer in $(NH_3)_5Ru^{3+}$- and Zn^{2+}-modified myoglobin. The estimates rest on variational calculation of a set of exponential trial wave functions in the instantaneous inertial polarization field and on a Hartree-Fock estimate of the distance decay of the Ru^{3+} and excited Zn orbitals involved. The effects are significant and dominated by a horizontal shift of the overall free energy relation by up to 0.5 eV toward numerically smaller values of the reaction free energy. This observation has important implications for electron tunnel distances in long-range electron transfer.

1. Introduction

Electron transfer between molecular centers separated by distances that notably exceed the geometric extension of the molecular reactant groups is of great importance in several contexts. "Long-range" electron transfer of this kind is, for example, a key element in multisite redox proteins,[1] in the electron-transfer sequences of photosynthesis and respiration,[2,3] and in intramolecular chemical[4-6] or biological[7-9] electron-transfer systems, where the donor and acceptor groups are separated by molecular bridge groups. Physically, rather similar features characterize crucial events in electrochemical electron transfer at surface-modified electrodes where the electron tunnels through a thin-surface oxide or polymer film and in inelastic tunneling assisted by local impurity or dislocation sites inside the surface film.[10-13]

Theoretical approaches specifically to long-range electron transfer have focused on the electronic factor in diabatic electron

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transfer and on its dependence on the nature of the environmental matter between the electron-transfer centers. These effects have been handled by higher order perturbation and superexchange theory,[14-16] by quantum chemical approaches involving multielectron basis sets,[17-22] by tunnel theory,[10,11,23] and by environmental continuum theory including vibrational and spatial dielectric dispersion.[24-26] Common to nearly all approaches to the electronic factor except the latter group (cf., however, ref 21 and 22) is, however, that bulk environmental polarization effects on the electronic factor are omitted. This factor is thus regarded as independent of the instantaneous nuclear inertial polarization configuration and therefore also independent of both temperature and reaction free energy.

On the other hand, in long-range electron transfer the "tails" of the electronic wave functions, which induce the reaction, are directly exposed to environmental polarization fluctuations. The crucial polarization configuration, with which the donor and acceptor wave functions interact at the moment of electron transfer and which determine the value of the electronic transmission coefficient, is furthermore not the equilibrium configuration but the particular nonequilibrium configuration at the intersection of two suitably constructed potential surfaces, spanned by the collective inertial polarization coordinates[27-29] (and the set of intramolecular coordinates). This configuration most commonly differs strongly from the equilibrium values in both the initial and final states, coinciding with these values only for activationless (strongly exothermic) and barrierless (strongly endothermic) processes, respectively.[27-29] The configuration also depends strongly on both the reaction free energy and the temperature. For these reasons also the tail features of the donor and acceptor wave functions and the value of the electronic transmission coefficient depend on the temperature and reaction free energy. For long-range electron transfer these effects are comparable to effects aroused by variation of the nuclear factor and cannot be disregarded in detailed electron-transfer data analysis.[24-26]

We provide here an estimate of these effects. Although we do not undertake a specific data analysis, our numerical estimates are appropriate, for example, to recent investigations of intramolecular electron transfer in myoglobin modified by ruthenium complex fragments at specific histidine surface groups of the protein structure.[30,31] This system is structurally, thermodynamically, and kinetically well characterized. Modification at different surface sites, furthermore, constitutes a basis for investigations of the distance dependence of the electron-transfer rate, while modification by different ruthenium residues or by metal substitution in the heme group is a basis for construction of free energy relations. This class of systems would therefore be well suited for illumination of subtler electron-transfer effects, such as the reaction free energy or temperature dependence of the electronic factor.

2. Environmental Modulation Effects on the Electronic Factor in the High-Temperature Limit

We shall use the following single-parameter exponential form of the donor (i) and acceptor (f) wave functions[24-26]

$$\psi_i = (\lambda_i^3/\pi)^{1/2} \exp(-\lambda_i|\vec{\rho}|); \quad \psi_f = (\lambda_f^3/\pi)^{1/2} \exp(-\lambda_f|\vec{\rho} - \vec{R}|) \qquad (1)$$

where $\vec{\rho}$ is the distance from the electron-transfer center, $\vec{R}$ the interreactant distance, and the only parameters are the orbital exponents λ_i and λ_f.

The choice of this simple form is prompted by the analytical transparency of the resulting electronic transmission coefficient expressions and the insight it provides as to the variation of this quantity with the instantaneous environmental nuclear configuration, the reaction free energy, and the temperature. These results, furthermore, extend to low temperatures and to vibrationally and spatially dispersive dielectric media.[24-26] Similar handling of environmental effects on many-electron functions is not feasible and restricted to motion of a single solvent molecule or small protein fragment.

Equation 1 is, however, more generally representative at "long" distances than immediately implied by its single-parameter and single-electron basis nature. Exponential distance decay of the form given by eq 1 thus emerges from quantum chemical calculations on the ab initio level,[17-22] from tunnel theory,[23] and from rather broad ranges of experimental electron-transfer data in chemical,[32-34] electrochemical,[35] and biological systems.[30,31,36] Exponential electronic wave functions therefore reflect the inherence of many-electron effects in the value of the orbital exponents, this form being suitable specifically in long-range electron transfer. For the same reasons the exponential form can be expected to be a suitable basis also for photoinduced two-center

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electron-transfer band shapes.[37,38]

The orbital exponents are estimated by the total free energy functional of the wave functions in eq 1 in the "preset" field determined by "effective" donor (z_De) and acceptor (z_Ae) core charges and the particular overall inertial polarization $\vec{P}^*(\vec{r})$ at the moment of electron transfer, $\vec{r}$ being a space coordinate and e the (numerical) electronic charge. The free energy functional in the initial state is[24-26]

$$F_i[\psi_i; \vec{P}^*(\vec{r})] = \frac{\hbar^2}{2m_e}\int |\vec{\nabla}\psi_i|^2 \, d\vec{\rho} - \int \vec{P}^*(\vec{r})\vec{D}_i^e(\psi_i; \vec{r}) \, d\vec{r} - \frac{z_De}{\epsilon_o}\int d\vec{\rho} \, \frac{1}{\rho}|\psi_i|^2 - \frac{z_Ae}{\epsilon_o}\int d\vec{\rho} \, \frac{1}{|\vec{\rho} - \vec{R}|}|\psi_i|^2 \quad (2)$$

with a similar equation for the product state. m_e is the electronic mass, $\hbar$ Planck's constant divided by 2π, ϵ_o the inertialess (optical) dielectric constant, and $\vec{D}_i^e(\psi_i; \vec{r})$ the electric vacuum field aroused by the electron to be transferred. $\vec{D}_i^e(\psi_i; \vec{r})$ is specifically

$$\vec{D}_i^e(\psi_i; \vec{r}) = -e\int d\vec{\rho} \, |\psi_i|^2 \frac{\vec{r} - \vec{\rho}}{|\vec{r} - \vec{\rho}|^3} \quad (3)$$

The first term in eq 2 is the kinetic energy of the electron; the second one is its potential energy in the nonequilibrium polarization field created by the donor and acceptor ionic centers and by the "excess" electron itself. The last two terms represent the potential energies of interaction of the electron with the donor and acceptor ionic centers. These interactions have the correct form at long distances and are screened only by the inertialess polarization, as the inertial part is included in $\vec{P}^*(\vec{r})$.

$\vec{P}^*(\vec{r})$ is finally available from the initial- and final-state equilibrium polarizations, $\vec{P}_{io}(\vec{r})$ and $\vec{P}_{fo}(\vec{r})$, respectively, by prescriptions in electron-transfer theory.[27-29] In the high-temperature limit

$$\vec{P}^*(\vec{r}) = (1 - \theta^*)\vec{P}_{io}(\vec{r}) + \theta^*\vec{P}_{fo}(\vec{r}) \quad (4)$$

where θ^* is the transfer coefficient (the Brønsted coefficient) of electron-transfer theory and is a measure of the variation of the transition probability, W_{fi}, with the reaction free energy, ΔG_o, i.e.

$$\theta^* = -k_BT \, d \ln W_{fi}/d\Delta G_o \quad (5)$$

k_B being Boltzmann's constant and T the temperature. In the high-temperature limit $\vec{P}_{io}(\vec{r})$ and $\vec{P}_{fo}(\vec{r})$ are simply related to the vacuum fields of the excess electron in the initial and final states, $\vec{D}_{io}^e(\vec{r})$ and $\vec{D}_{fo}^e(\vec{r} - \vec{R})$, respectively, and of the donor $\vec{D}_o^D(\vec{r})$ and acceptor cores, $\vec{D}_o^A(\vec{r} - \vec{R})$, i.e.[24-29]

$$\vec{P}_{io}(\vec{r}) = \frac{c}{4\pi}[\vec{D}_{io}^e(\vec{r}) + \vec{D}_o^D(\vec{r}) + \vec{D}_o^A(\vec{r} - \vec{R})]$$

$$\vec{P}_{fo}(\vec{r}) = \frac{c}{4\pi}[\vec{D}_{fo}^e(\vec{r} - \vec{R}) + \vec{D}_o^D(\vec{r}) + \vec{D}_o^A(\vec{r} - \vec{R})] \quad (6)$$

where $c = \epsilon_o^{-1} - \epsilon_s^{-1}$ and ϵ_s the static dielectric constant. At lower temperatures the environmental vibrational dispersion must be included, such as treated in detail elsewhere.[24-26]

λ_i and λ_f are obtained from eq 4–6 by a variational scheme that consists of the following steps:[24-26]

(A) The free energy functionals are first calculated at given θ^*; i.e., $F_i = F_i(\theta^*)$ and $F_f = F_f(\theta^*)$ by inserting eq 1, 3, 4, and 6 into eq 2.

(B) The functionals are next minimized with respect to the variational parameters λ_i and λ_f. From this step the dependence of λ_i and λ_f on θ^* emerges; i.e., $\lambda_i = \lambda_i(\theta^*)$ and $\lambda_f = \lambda_f(\theta^*)$.

(C) The latter relations can be converted to the corresponding dependence of λ_i and λ_f on ΔG_o and T by means of electron-transfer theory.[27-29] In particular, $\theta^* = 0$ for activationless processes where $\Delta G_o = -E_s$ and E_s is the total environmental reorganization free energy, while $\theta^* = 0.5$ when $\Delta G_o = 0$.

(D) In the high-temperature limit and when the donor–acceptor distance is sufficiently large that the interaction of the donor electron with the acceptor region can be disregarded, the estimate of $\lambda_i(\theta^*)$ can be brought to rest on the following simple form

$$\frac{\hbar^2}{2m_e}\lambda_i - (1 - \theta^*)\frac{ce^2}{2\pi}\left(\frac{\lambda_{io}}{\lambda_i}\right)^4 \int_0^\infty \frac{du}{[(\lambda_{io}/\lambda_i)^2 + u^2]^2(1 + u^2)^3} = 0; \quad \lambda_i = \lambda_i(\theta^*) \quad (7)$$

where λ_{io} is the value of λ_i at equilibrium, i.e. for $\theta^* = 0$. $\lambda_f(\theta^*)$ can be similarly determined.

(E) The following simple result valid for $\theta^* \lesssim 0.3$ emerges when eq 7 is expanded around $\theta^* = 0$.

$$\lambda_i(\theta^*) \approx \lambda_{io}(1 - \xi_i\theta^*); \quad \xi_i = \frac{5/11}{1 + (16/11)(z_D/5c\epsilon_s)} \quad (8)$$

The corresponding equation for $\lambda_f(\theta^*)$ is

$$\lambda_f(\theta^*) \approx \lambda_{fo}[1 - \xi_f(1 - \theta^*)]; \quad \xi_f = \frac{5/11}{1 + (16/11)(z_A/5c\epsilon_s)} \quad (9)$$

These equations show in a more transparent form that the environmental field variation along the solvent potential has caused both the donor and acceptor electron clouds to "swell" in the normal free energy region ($\theta^* > 0$), as the nonequilibrium inertial polarization becomes increasingly unfavorable. Opposite effects, i.e. electron cloud contraction, emerge in the inverted free energy range where $\theta^* < 0$.

(F) Both $\lambda_i(\theta^*)$ and $\lambda_f(\theta^*)$ are smaller than their equilibrium values when $0 < \theta^* < 1$ or $-E_s < \Delta G_o < E_s$, giving larger overlap integrals, S_{fi}, and exchange matrix elements, V_{fi}. However, when ΔG_o increases from $-E_s$ to 0, i.e. θ^* increases from 0 to 0.5, then $\lambda_i(\theta^*)$ and $\lambda_f(\theta^*)$ vary in opposite directions. This means that S_{fi} and V_{fi} do not vary significantly when $\lambda_i \approx \lambda_f$. On the other hand, they do vary when one exponent significantly exceeds the other one, in which case S_{fi} and V_{fi} are determined primarily by the smaller orbital exponent.

(G) The variation of $\lambda_i(\theta^*)$ and $\lambda_f(\theta^*)$ is weaker for positive effective core charges and stronger for negative charges compared with localization solely by the environmental polarization field. On the other hand, positive core charges may also give larger values of the equilibrium orbital exponents, thus maintaining a strong free energy variation of the electronic transmission coefficient (cf. eq 14 below).

3. Electronic Factor Modulation in Intramolecular Electron Transfer in Modified Myoglobins

We have previously discussed the effects of electronic modulation on the temperature-dependent blue shift of optical charge-transfer bands.[37,38] In this section we shall illustrate the effects that might be expected for long-range intramolecular electron transfer in modified metalloprotein systems. We refer specifically to $Ru(NH_3)_5^{2+}$-modified sperm whale myoglobin as a suitable representative of this rapidly expanding area of electron transfer, as data for distance and reaction free energy variation have recently become available for these particular systems.[30,31] The reactions are

$$Ru^{3+}\text{-Mb} \xrightarrow{h\nu} Ru^{3+}\text{-Mb}^* \xrightarrow{k_r} Ru^{2+}\text{-Mb}^+ \rightarrow Ru^{3+}\text{-Mb} \quad (10)$$

where Mb* represents excited states of the Mb heme or modified (Zn, Pd) heme group and k_r the electron-transfer rate constant to be investigated. The distance variation is represented by Ru-modification at the His-12, -48, -81, and -116 positions and the reaction free energy variation by modification with different Ru fragments or different metal substitution in the central mesoporphyrin IX group. In these ways the center-to-center electron-transfer distance can be changed from 12 to 22 Å and the reaction free energy from zero to −1 eV.

In relation to the electronic modulation formalism the modified myoglobin systems possess the following additional specific properties:

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(A) The reactions belong to the "normal" free energy range, i.e. $\theta^* > 0$, with a total reorganization free energy of about 2 eV. θ^* varies from 0.5 for $\Delta G_o \approx 0$ eV ($(NH_3)_5Ru(48)MbFe$) to 0.25 for $\Delta G_o \approx -1$ eV ($(NH_3)_4pyRu(48)MbPd$).

(B) The electron donor is an excited electronic state of the heme or modified heme group, giving a donor wave function significantly less localized than the acceptor wave function at the ruthenium site. The coupling features are therefore dominated by the donor wave function. Also, the maximum of the overlap is close to the acceptor site, rather than in between the donor and acceptor sites for similar orbital exponent values.

(C) The excited-state delocalization can be illustrated by quantum chemical estimates of the decay properties of the electronic wave functions for two crude models of the donor and acceptor centers. We have carried out Hartree–Fock calculations[39,40] for a Ru^{3+} ion, simulating the acceptor center, by means of the electronic structure program SIRIUS (a direct second-order MCSCF program) developed by H. J. Ågaard Jensen and H. Ågren.[41] The split-valence basis set was generated by splitting the outer valence shells in two parts with N-1 and a single primitive Gaussian-type orbital, respectively. The basis set was (15s, 9p, 6d) – ⟨6s, 4p, 3d⟩, giving for the optimized highest filled Ru^{3+} orbital (R in au)[42]

$$\psi_{Ru^{3+}} = -0.32 d_{yz}^{(1)} + 0.82 d_{yz}^{(2)} + 0.34 d_{yz}^{(3)} \tag{11}$$

where

$$d_{yz}^{(1)} = yz[0.128e^{-7.377\times10^{1}R^2} + 0.496e^{-2.023\times10^{-1}R^2} + 0.580e^{-6.184R^2}]$$

$$d_{yz}^{(2)} = yz[0.234e^{-2.823R^2} + 0.559e^{-9.3494\times10^{-1}R^2}] \tag{12}$$

$$d_{yz}^{(3)} = yz1.0e^{-2.912\times10^{-1}R^2}$$

With reference to eq 1 the dominating $d_{yz}^{(3)}$ amplitude would correspond to unscreened orbital exponents of $\lambda_{fo} \approx 5.5$ Å^{-1} for $R = 2.65$ Å and 11 Å^{-1} for $R = 5.3$ Å. In reality they are, of course, much smaller due to screening of the electron density decay by the ligands and the environments.

A similar calculation is less feasible for the donor center. The first excited state of a Zn atom for which we have carried out such a calculation gives an orbital exponent of 0.83 Å^{-1} for $R = 2.65$ Å and 1.7 Å^{-1} for $R = 5.3$ Å, i.e. indeed substantially smaller than for Ru^{3+}. However, the excited Zn–porphyrin state corresponds to excitation in the porphyrin part rather than at the Zn atom. An indication of the orbital decay properties of the aromatic frame can be obtained from reported distance decay for a Hartree–Fock calculation of the electronic transition matrix element for the symmetric electron-exchange reaction between benzene and its anion radical.[21] When the two rings are both located in a position perpendicular to a common D_{6h} axis to ensure maximum overlap, the distance decay corresponds to an orbital exponent of 2.5 Å^{-1} for $R \approx 5$ Å, i.e. again much smaller than for the Ru^{3+} ion. The distance decay is slower when a water molecule is located between the benzene rings but may be faster in other directions more representative of the electron-transfer path of the donor and acceptor groups in the modified myoglobins.

These calculations support the expectation that the excited-state donor orbital decays significantly more slowly than the acceptor orbital. In view of the very crude representation of the electron-transfer center, they cannot, of course, be viewed as a proper substantiation of this expectation.

(D) When $\lambda_i \ll \lambda_f$, a simple form of the overlap integral emerges.[26]

$$S_{fi} \approx 8(\lambda_i/\lambda_f)^{3/2} \exp[-\lambda_i R^*]; \quad \lambda_i = \lambda_i(\theta^*); \quad \lambda_f = \lambda_f(\theta^*) \tag{13}$$

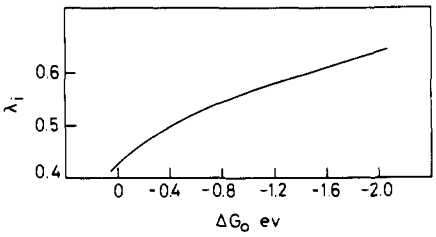

Figure 1. Dependence of the donor orbital exponent on the reaction free energy. $E_s = 2$ eV, $T = 298$ K, and $\lambda_{io} = 0.64$ Å^{-1}. The latter value is based on the estimated distance decay of the rate constant in ref 30.

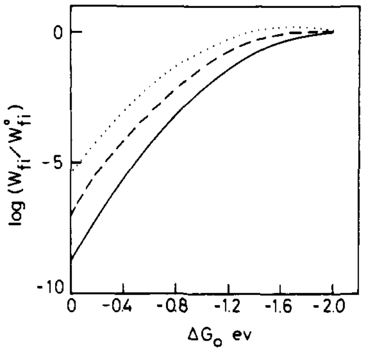

Figure 2. Calculated reaction free energy plots including modulation of the electronic factor and orbital decay parameters from Figure 1. W_{fi} is the transition probability per unit time obtained from eq 15 and W_{fi}^{o} the transition probability per unit time in the absence of modulation, i.e. when the first term in the exponent on the right-hand side of eq 15 vanishes. The preexponential factors in W_{fi} and W_{fi}^{o} are cancelled in the ratio W_{fi}/W_{fi}^{o}: (—) no electronic modulation; (---) electronic modulation included and 10-Å electron-transfer distance; (···) electronic modulation included and 20-Å electron-transfer distance.

In the following we assume that the variation of S_{fi} with θ^* or ΔG_o and T essentially reflects the variation of the transition matrix element V_{fi}.[22] The electronic transmission coefficient, $\varkappa_{fi}$, then takes the approximate form

$$\varkappa_{fi} \approx \varkappa_{fi}^{oo} \exp[-2\lambda_{io}(1 - \xi\theta^*)R^*] \equiv \varkappa_{fi}^{o} \exp(2\lambda_{io}\xi\theta^* R^*) \tag{14}$$

where $\varkappa_{fi}^{oo}$ is the value of $\varkappa_{fi}$ at the minimum donor–acceptor distance, R_{min}, while $\varkappa_{fi}^{o}$ is the transmission coefficient at the initial-state equilibrium environmental nuclear configuration for given R^*. R^* coincides approximately with the intersite separation when $\lambda_i \ll \lambda_f$.

(E) The experimental distance dependence data for electron transfer in modified myoglobins can be represented approximately by the exponential relation $\exp[-0.9(R - R_{min})]$[30] (R in angstroms). By eq 7 and 13 this gives $\lambda_{io} \approx 0.6$ Å^{-1} for the donor orbital exponent equilibrated with the environmental polarization. This value is in line with estimates for several strongly exothermic, activationless processes[33,34] where the electron-transfer configuration is that of initial-state equilibrium.

The variation of the nuclear factor with θ^* in the transition probability, $W_{fi}(\theta^*)$ is, from electron-transfer theory,[28,29] $W_{fi} \propto \exp(-\beta E_s \theta^{*2})$; $\beta = (k_B T)^{-1}$. By including the electronic modulation in eq 14, the overall variation of $W_{fi}(\theta^*)$ with θ^* becomes, in the high-temperature limit

$$W_{fi}(\theta^*) \propto \exp[2\lambda_{io}\xi\theta^* R^* - \beta E_s \theta^{*2}] \tag{15}$$

This equation has two implications in particular:

(1) $W_{fi}(\theta^*)$ assumes its maximum value for $\theta^* = \theta_m^* = (\xi/\beta E_s)\lambda_{io}R^*$, i.e. for positive θ^* or $|\Delta G_o| < E_s$. If modulation is disregarded, $W_{fi}(\theta^*)$ has maximum for $\theta^* = 0$, or $\Delta G_o = -E_s$. For $\xi = {}^5/_{11}$, $T = 298$ K and $E_s = 2$ eV; θ_m^* is 0.034 and 0.068 when $\lambda_{io}R^* = 6$ ($R = 10$ Å) and 12 ($R = 20$ Å), respectively. This corresponds to shifts in the $W_{fi}(\theta^*)$ maximum of 0.14 and 0.28 eV, respectively. The shift is smaller at lower temperatures when nuclear tunneling in the solvent vibrational spectrum is important.[26]

Free energy plots based on eq 25 are shown in Figures 2 and 3. The parameters in Figure 2 are appropriate to the modified

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(42) For the sake of transparency only three significant figures in the coefficients of the Gaussians are shown.

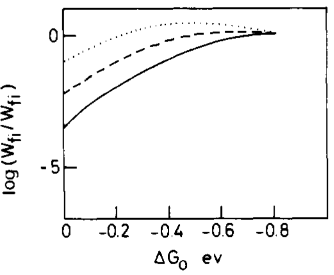

Figure 3. Same plot as in Figure 2, but for E_s = 0.8 eV. Other parameters as in Figures 1 and 2.

myoglobins,[30,31] while Figure 3 corresponds to a somewhat smaller reorganization free energy.

(2) Inclusion of the modulation effects also shifts the whole free energy plot horizontally toward lower values without significant changes of its shape (Figures 2 and 3). For the data in ref 31 (R = 12 Å), the shift would amount to 0.15–0.20 eV but would be expected to be larger for free energy relations based on substitution at more remote sites from the heme group.

Free energy relations based on Ru modification at different histidines might offer a new perspective also for illumination of environmental modulation of the electronic factor in electron-transfer theory. At the same time the continuum formalism used,[24-26] which can be extended to solvent structural effects in the form of vibrational and spatial dielectric dispersion, is a useful frame for incorporation of large numbers of solvent molecules and nonequilibrium solvation effects for which quantum chemical approaches are not feasible. On the basis of this formalism, a family of almost parallel free energy plots would be expected when the Ru fragments are attached to different His sites. These plots are shifted to lower reaction free energies with increasing electron-transfer distance, and the equilibrium values of the electronic parameters can, in principle, be extracted from the shifts.

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Structure and Reactivity of Titanium/Platinum and Palladium Heterobinuclear Complexes with μ-Methylene Ligands

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Abstract: A series of titanium/platinum and palladium heterobinuclear μ-methylene complexes $Cp_2\overline{TiCH_2MX}(Me)L$ has been prepared: M = Pt, X = Cl, L = PMe_3 (**2b**), PMe_2Ph (**2c**), $PMePh_2$ (**2d**); M = Pt, X = Me, L = PMe_2Ph (**2e, 2f**); M = Pd, X = Cl, L = PMe_3 (**2g**). The μ-CH_2/μ-Cl complex **2c** crystallizes in the monoclinic system in space group $P2_1/n$ (No. 14), with a = 13.249 (3) Å, b = 11.646 (3) Å, c = 14.542 (5) Å, β = 114.45 (2)°, V = 2042.6 (10) Å^3, Z = 4, and density = 1.87 g cm^{-3}. The μ-CH_2/μ-CH_3 analogue **2e** is isostructural to **2c** and also crystallizes in space group $P2_1/n$ (No. 14) with a = 13.333 (4) Å, b = 11.686 (2) Å, c = 14.351 (2) Å, β = 115.03 (2)°, V = 2026.0 (8) Å^3, Z = 4, and density = 1.82 g cm^{-3}. Structural studies indicate the following: (1) the Ti–CH_2 bond possesses residual double-bond character, (2) there is a dative Pt → Ti interaction, which may be regarded as π back-donation from the platinum atom to the "Ti=CH_2" group, and (3) the μ-CH_3 group in **2e** is bound to the titanium atom through a three-center, two-electron agostic bond. Complexes **2c** and **2d** react with tertiary phosphines to give $Cp_2(Cl)TiCH_2Pt(Me)L_2$ species, which form μ-(C,O)-ketene complexes $Cp_2(Cl)TiOC(=CH_2)Pt(Me)L_2$ upon carbonylation. The palladium complex **2g** undergoes a reductive elimination reaction to give $Cp_2Ti(Et)Cl$ and Pd^0PMe_3 complexes.

Recently much attention has been focused upon early-transition-metal/late-transition-metal heterobinuclear complexes[1] because of their potential applications in catalytic organic reactions. Also, these complexes have been studied in order to gain an understanding of the phenomenon of so-called "strong metal-support interactions (SMSI)" in heterogeneous catalysis.[2] It is well documented that late transition metals, which are finely dispersed on early-transition-metal oxide supports such as TiO_2 and ZrO_2, serve as highly active catalysts in the catalytic hydrogenation of carbon monoxide. SMSI have been observed in such systems. While the exact nature of the interaction is still unclear, SMSI are regarded as the prime reason for the enhanced catalytic activity.[3]

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