Intramolecular Electron Transfer in the Inverted Region

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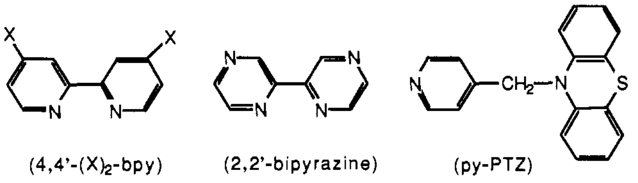
Received June 12, 1989

In 1960 Marcus predicted that rate constants for electron transfer should decrease with $-\Delta G$ in the inverted region.[1] In the inverted region, $-\Delta G > \lambda$, where λ is the reorganization energy and ΔG the free energy loss associated with the electron transfer. Experimental verification of this prediction has been difficult to obtain but has been found by pulse radiolysis in rigid organic glasses, by Closs, Miller, and co-workers in unsymmetrical, linked organics,[2] in accounting for separation yields in photoinduced electron transfer,[3] and by light-induced electron transfer in linked porphyrin-quinone systems.[4] We report here the first examples based on transition-metal complexes and, as predicted theoretically, that there is a clear relationship between electron transfer in the inverted region and nonradiative decay in a closely related family of excited states.

Our experiments were based on the complexes $[(4,4'\text{-}(X)_2\text{-bpy})Re(CO)_3(py\text{-}PTZ)]^+$ (X = CO_2Et, $C(O)NEt_2$, H, CH_3, OCH_3) and $[(bpz)Re(CO)_3(py\text{-}PTZ)]^+$ (bpz = 2,2'-bipyrazine).



Earlier studies based on $[(bpy)Re(CO)_3(py\text{-}PTZ)]^+$ (bpy = 2,2'-bipyridine) have shown that following Re → bpy metal to ligand charge transfer (MLCT) excitation, rapid intramolecular electron transfer occurs to give a redox separated state, reaction 1.[5] Subsequent decay of the redox separated state occurs by back

$$[(bpy)Re^{I}(CO)_3(py\text{-}PTZ)]^+ \xrightarrow{h\nu} [(bpy^{\bullet -})Re^{II}(CO)_3(py\text{-}PTZ)]^{+*} \quad (1a)$$

$$[(bpy^{\bullet -})Re^{II}(CO)_3(py\text{-}PTZ)]^{+*} \xrightarrow[(295\ K,\ CH_3CN)]{k = 4.8 \times 10^9\ s^{-1}} [(bpy^{\bullet -})Re^{I}(CO)_3(py\text{-}PTZ^{\bullet +})]^{+*} \quad (1b)$$

electron transfer. This reaction, which is a ligand to ligand electron transfer,[5,6] occurs with $\Delta G \sim -2.0$ eV in 0.1 M $[N(n\text{-}C_4H_9)_4](PF_6)$ in CH_3CN and is well within the inverted region.[5]

$$[(bpy^{\bullet -})Re^{I}(CO)_3(py\text{-}PTZ^{\bullet +})]^{+*} \xrightarrow[(295\ K,\ CH_3CN)]{k_{elt} = 4.0 \times 10^7\ s^{-1}} [(bpy)Re^{I}(CO)_3(py\text{-}PTZ)]^+ \quad (2)$$

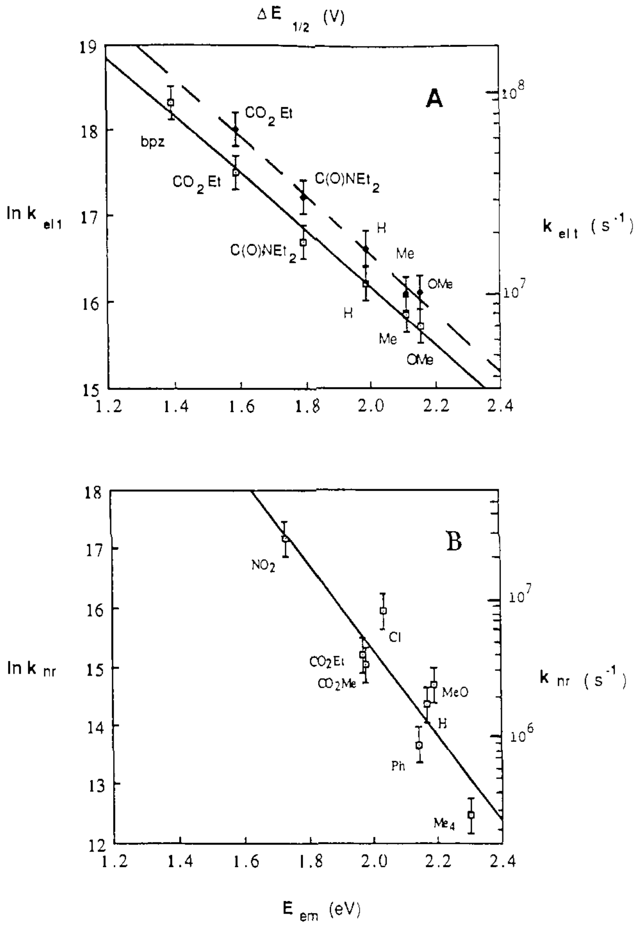


Figure 1. (A) Plot of ln k_{elt} vs $\Delta E_{1/2}$ ($=E_{1/2}(PTZ^{+/0}) - E_{1/2}(4,4'\text{-}(X)_2\text{-bpy}^{-/0})$) for the complexes $[(4,4'\text{-}(X)_2\text{-bpy})Re(CO)_3(py\text{-}PTZ)]^+$ and $[(bpz)Re(CO)_3(py\text{-}PTZ)]^+$ in DCE (—) and in 0.1 M $[N(n\text{-}C_4H_9)_4](PF_6)$ DCE (---). The substituents are indicated on the plot. The lines drawn through the data points are the least-squares fits to the equations $\ln k_{elt} = 22.9\ (\pm 1) - 3.34\ (\pm 0.3)\Delta E_{1/2}$ in DCE and $\ln k_{elt} = 23.4\ (\pm 1) - 3.42\ (\pm 0.3)\Delta E_{1/2}$ in 0.1 M $[N(n\text{-}C_4H_9)_4](PF_6)$ DCE. (B) Plot of ln k_{nr} vs the emission energy maximum, E_{em}, in DCE for the complexes $[(4,4'\text{-}(X)_2\text{-bpy})Re(CO)_3(4\text{-}Etpy)]^+$. The substituents are indicated on the graph. The least-squares line drawn through the data points is of the equation $\ln k_{nr} = 29.8\ (\pm 3) - 7.3\ (\pm 1.4)E_{em}$. The point labeled Me_4 refers to the ligand $4,4',5,5'\text{-}(CH_3)_4\text{-}2,2'$-bipyridine.

In the series $[(4,4'\text{-}(X)_2\text{-bpy})Re(CO)_3(py\text{-}PTZ)]^+$ and $[(bpz)Re(CO)_3(py\text{-}PTZ)]^+$, the ability of the π^* orbitals at the polypyridyl ligands to accept electrons changes by 0.7 eV as X is varied. This has provided the basis for a quantitative study of the dependence of the rate constant for back electron transfer on ΔG in the inverted region.

The procedures used for the preparation and characterization of the complexes have been described previously.[5] Electrochemical, emission, and transient absorbance measurements were made in CH_2ClCH_2Cl (DCE) by using instrumentation and procedures that have been described elsewhere.[7] Values of $E_{1/2}$ for the $(4,4'\text{-}(X)_2\text{-bpy})^{0/-}$ and $PTZ^{+/0}$ couples for each complex were obtained by cyclic voltammetry.

In Figure 1A is shown a plot of ln k_{elt} for reaction 2 vs $\Delta E_{1/2} = E_{1/2}(PTZ^{+/0}) - E_{1/2}(4,4'\text{-}(X)_2\text{-bpy}^{0/-})$ in DCE that was 0.1 M in $[N(n\text{-}C_4H_9)_4](PF_6)$. The rate constants were determined by analyzing transient absorbance decay curves which were obtained following excitation at 355 nm by using a Quanta Ray DCR-2A Nd:YAG laser.[7b] Analysis of the absorbance decay profiles at λ_{max} = 510-520 nm for $PTZ^{\bullet +}$ or at 370-390 nm, which is a region of maximum absorbance for $(4,4'\text{-}(X)_2\text{-bpy}^{\bullet -})$, gave the same

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0002-7863/89/1511-8305$01.50/0

values for k within experimental error. The decay profiles followed single exponential kinetics. Given the decay times and the concentrations used, 1-2 × 10^{-4} M, the first-order kinetics show that the reactions are intramolecular in nature.

The quantity $\Delta E_{1/2}$ is related to the free energy change for intramolecular electron transfer by including the electrostatic term in eq 3. The expression in eq 3 assumes spherical ions of the same size separated by a distance d in a solvent of static dielectric constant D_s.[8] In eq 3, e is the unit electron charge and κ is the

$$-\Delta G = \Delta E_{1/2} - \frac{e^2}{D_s d}\left(\frac{1}{1 + \kappa d}\right) \tag{3}$$

Debye–Hückel inverse length, which is proportional to the square root of the ionic strength. From standard bond lengths and angles, it can be estimated that d can vary from ca. 4 to 12 Å, depending upon the relative orientation of the PTZ group around the $-CH_2-$ link.[5] The comparison in Figure 1A between the data in DCE and the data in DCE that is 0.1 M in $[N(n\text{-}C_4H_9)_4](PF_6)$ shows that ionic strength effects do play a role in the intramolecular electron transfer.

In Figure 1B is shown a plot of ln k_{nr} vs emission energy, E_{em}, for nonradiative decay in the related series of excited states $[(4,4'\text{-}(X)_2\text{-bpy}^{\bullet-})\text{Re}^{II}(\text{CO})_3(4\text{-Etpy})]^+$ (4-Etpy = 4-ethylpyridine).

$$[(4,4'\text{-}(X)_2\text{-bpy}^{\bullet-})\text{Re}^{II}(\text{CO})_3(4\text{-Etpy})]^{+*} \rightarrow [(4,4'\text{-}(X)_2\text{-bpy})\text{Re}^{I}(\text{CO})_3(4\text{-Etpy})]^+ \tag{4}$$

The preparation and characterization of the complexes are described elsewhere.[9] The nonradiative decay rate constants, k_{nr}, were calculated from emission lifetimes (τ) and quantum yields for emission, which varied from 0.002 to 0.4, by using the equation $k_{nr} = 1/\tau(1 - \phi_{em})$.

The linear *decreases* in ln k_{elt} or ln k_{nr} with energy gap are predicted qualitatively by the "energy gap law", eq 5.[10,11] In eq

$$\ln k_{nr} \propto -\frac{\gamma E}{\hbar\omega} \tag{5}$$

$$\gamma = \left(\ln \frac{E}{S\hbar\omega}\right) - 1 \tag{5a}$$

5, E is the energy gap between the excited and ground states and $\hbar\omega = h\nu$ is the average vibrational spacing of the acceptor modes. The quantity S is the electron-vibrational coupling constant. It is proportional to the square of the difference in equilibrium displacements in the acceptor modes between the excited and ground states. For bpy-based MLCT excited states, the energy acceptor role is played by seven ν(bpy) modes which can be approximated by an average mode having $\hbar\omega \sim$ 1300–1400 cm^{-1}.[11,12] For intramolecular electron transfer, the energy acceptor role is expected to be played by a combination of $\nu(4,4'\text{-}(X)_2\text{-bpy})$ and ν(PTZ) ring stretching modes.[13]

The decrease in slope for electron transfer compared to nonradiative decay is predicted qualitatively by eq 5. For MLCT excited states, S increases with the energy gap since the extent of charge transfer increases with the energy gap.[11,12] For intramolecular electron transfer between $\text{PTZ}^{\bullet+}$ and $4,4'\text{-}(X)_2\text{-bpy}^{\bullet-}$, a complete electron transfer occurs, leading to an increase in S, a decrease in γ, eq 5a, and the decrease in slope.

The quality of the fit to the electron transfer data is impressive. It must be a consequence of the relatively minor perturbations caused by the changes in substituents and points to a common electron transfer distance. The linear correlation verifies the applicability of the energy gap law to electron transfer in the inverted region and points to a close, fundamental relationship between electron transfer in this region and nonradiative decay.

Acknowledgement is made to the National Science Foundation for financial support under Grant No. CHE-8906794. We also thank Drs. L. D. Ciana and W. J. Dressick for providing samples of some of the 4-Etpy complexes. Acknowledgement is also made to the Department of Energy under Grant No. DE-FG05-85ER75216 for much of the equipment used in the transient absorbance experiments.

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The Timing of Aromatic Deoxygenation in Aflatoxin Biosynthesis

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Received May 8, 1989

Deoxygenation of phenols is a difficult reaction to execute synthetically. Yet among polyketide-derived natural products many instances can be found where such reactions appear to occur in the course of their biosynthesis. Of these the majority may be characterized by the absence of an "expected" hydroxyl group at a position (e.g., C-4 in **2**) where hypothetical polyketide intermediates are proposed to turn back on themselves leading to self-condensation reactions and aromatization. In the classic study of this behavior experiments with 6-methylsalicylic acid synthase[1] demonstrated that, in fact, preparatory to formation of **2** a *pre*aromatic reduction/dehydration sequence takes place to give a cis double bond, e.g., **1**. However, exceptions involving *post*-aromatic deoxygenation have emerged that cannot be rationalized according to this model. Among these, two may be cited. The first is the apparent reduction of emodin (**3**) to chrysophanol (**4**) at an early stage of ergochrome biosynthesis reported by Franck.[2] In an important advance at the cell-free level this transformation was unambiguously shown by Anderson and Scott to be mediated by NADPH.[3] Reasoning by analogy to a second system, they suggested (quite persuasively) that deoxygenation of versicolorin A (**5**, R = OH) could occur at C-6 to provide a necessary reduction in the course of its conversion to sterigmatocystin (**6**), a late intermediate in aflatoxin B_1 (**7**) biosynthesis.[4] We record in this communication three lines of evidence that indicate 6-deoxy-

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