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Energy Transfer in the "Inverted Region"

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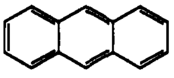
In 1960 Marcus predicted the existence of the "inverted region" for electron transfer.[1] In this region $-\Delta G^\circ > \lambda$ and rate constants for electron transfer are predicted to decrease as the driving force, ΔG°, becomes more favorable. The quantity λ is the sum of the solvent and intramolecular reorganizational energies (λ_o, λ_i). Experimental confirmation of the existence of the inverted region has been found for electron transfer[2-6] and for intermolecular, vibrational-translational energy transfer in the gas phase.[7] We report here an example of solution-phase energy transfer in the inverted region and, further, that the dependence of the quenching rate constants on ΔG° can be analyzed quantitatively by using parameters derived from a Franck-Condon analysis of emission spectral profiles.

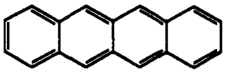
In the reactions studied, the quenching of the metal to ligand charge transfer (MLCT) excited states of a series of 2,2′-bipyridyl complexes of Os^{II} by anthracene (An, a) or the anthracene derivative 2,3-benzanthracene (b) was investigated by emission and/or lifetime quenching, e.g., reaction 1. The complexes used in the study were $[Os(bpy)_3]^{2+}$ (**1**), $[Os(bpy)_2(das)]^{2+}$ (**2**), $[Os(bpy)(dppene)_2]^{2+}$ (**3**), $[Os(bpy)_2(dppm)]^{2+}$ (**4**), $[Os(bpy)_2(dppe)]^{2+}$ (**5**), $[Os(bpy)_2(pz)_2]^{2+}$ (**6**), $[Os(bpy)_2(CO)(py)]^{2+}$ (**7**), $[Os(bpy)_2(CO)(CH_3CN)]^{2+}$ (**8**), and $[Os(bpy)_2(das)]^{2+}$ (**9**).[8] The ligand abbreviations are bpy for 2,2′-bipyridine, dppene for *cis*-$Ph_2PCH{=}CHPPh_2$, dppm for $Ph_2PCH_2PPh_2$, dppe for $Ph_2PCH_2CH_2PPh_2$, das for 1,2-bis(dimethylarsino)benzene, and py for pyrazine.

$$[Os(bpy)_3]^{2+*} + An \rightarrow [Os(bpy)_3]^{2+} + {}^3An \tag{1}$$



anthracene

(a)



2,3-benzanthracene

(b)

The kinetics data were acquired at 298 ± 1 K in 3:1 (v/v) benzene-acetonitrile solutions that had been deoxygenated by flushing with solvent-saturated nitrogen or argon for at least 10 min. The use of the solvent mixture was required for solubility reasons. The kinetics data were analyzed satisfactorily by the usual Stern-Volmer intensity (I) or lifetime (τ) equations, $I_0/I = 1 + k_q\tau[Q]$ or $\tau_0/\tau = 1 + k_q[Q]$, where [Q] is the quencher concentration, with I_0 and I or τ_0 and τ being the emission intensities or lifetimes in the absence and presence of the quenchers.[9]

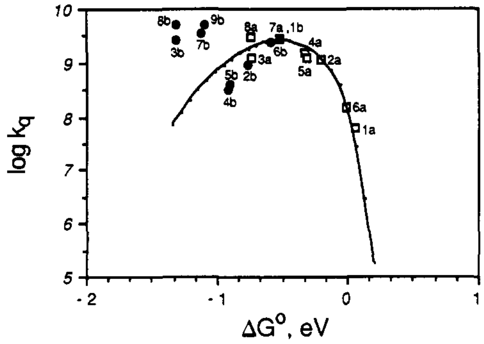


Figure 1. Plot of log k_q vs ΔG° for energy-transfer quenching of $Os^{II}*$ in 1:3 (v/v) CH_3CN-benzene at 298 ± 1 K for anthracene (□) or 2,3-benzanthracene (●). The numbering scheme is explained in the text. The line drawn through the data *for anthracene as the quencher* was calculated by using eq 4a. In this calculation the values $k_d = 9.1 \times 10^9$ M^{-1} s^{-1} and $K_A = 2.3$ were used and k_{et} was calculated from eq 7 by using the emission spectral fitting parameters and assuming that $V = 4$ cm^{-1}.

The experimental data are shown in Figure 1 as a plot of log k_q vs ΔG°. The labeling scheme is based on the numbers assigned to the complexes and the letters used for the quenchers. For the examples labeled 1a, 1b, 4a, or 4b the appearance of the organic triplet (λ = 430 nm for anthracene, 460 nm for 2,3-benzanthracene)[10] was verified by transient absorbance measurements following laser flash photolysis. From the data in Figure 1, k_q increases with $-\Delta G^\circ$ up to ΔG° ~-0.5 eV and reaches a maximum value of 3.1×10^9 M^{-1} s^{-1}. This is below the diffusion-controlled limit of ~9.1×10^9 M^{-1} s^{-1} in 3:1 benzene-CH_3CN at 298 K.[11] For 2,3-benzanthracene as quencher, k_q decreases as $-\Delta G^\circ$ is increased further, reaching 2.0×10^8 M^{-1} s^{-1} at $\Delta G^\circ = -0.91$ eV. This is a factor of ~50 below the diffusion-controlled limit. A further increase in $-\Delta G^\circ$ leads to an *increase* in k_q, ultimately to near the diffusion-controlled limit. We attribute the increase to the intervention of an additional energy-transfer pathway in which the second triplet excited state of 2,3-benzanthracene is formed. The energy of this state is ~2.56 eV, which is ~1.29 eV higher than the lowest triplet.[13]

We have analyzed the anthracene data by utilizing the results of emission spectral fitting to calculate relative rate constants for energy transfer, k_{et}. The spectral fitting procedure has been applied to emission from the $Os^{II}*$ excited states by including contributions from an averaged, medium-frequency, ν(bpy) mode, an averaged low-frequency mode, and the solvent.[8,14] Application of the same procedure to the emission spectrum of ^3An at 77 K in 4:1 (v/v) ethanol-methanol gave the parameters $E_0 = 14\,700$ cm^{-1}, $\hbar\omega = 1390$ cm^{-1}, $S = 1.47$, and $\Delta\bar{\nu}_{0,1/2} = 860$ cm^{-1} for ^3An. The quantities $\hbar\omega$ and S are the vibrational spacing and electron-vibrational coupling constant for an averaged ring-stretching

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mode. The quantity $\Delta\bar{\nu}_{0,1/2}$ is the full width at half maximum for the individual vibronic components, and E_0 is the energy of the 0 → 0 vibronic transition for the mode $\hbar\omega$.

We have utilized the results of emission spectral fitting to calculate $\Delta G°$ from $\Delta G° = (E_0 + (\Delta\bar{\nu}_{0,1/2})^2/16k_BT \ln 2)_{\text{acceptor}} - (E_0 + (\Delta\bar{\nu}_{0,1/2})^2/16k_BT \ln 2)_{\text{donor}}$. In this equation the band width at half maximum is related to λ', as shown in eq 2. The quantity λ' is the sum of reorganizational energies for the solvent and the averaged, low-frequency vibrational mode treated classically.

$$\lambda' = (\Delta\bar{\nu}_{0,1/2})^2/16k_BT \ln 2 \qquad (2)$$

The quenching scheme involves the series of reactions in eq 3.[12,15,16b] A kinetic analysis based on this scheme gives the

$$\mathrm{Os^{II}}{*} + \mathrm{Q} \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} \mathrm{Os^{II}}{*}, \mathrm{Q} \underset{k_{-et}}{\overset{k_{et}}{\rightleftharpoons}} \mathrm{Os^{II}}, {}^3\mathrm{Q} \xrightarrow{k'_{-d}} \mathrm{Os^{II}} + {}^3\mathrm{Q} \qquad (3)$$

relationships shown in eqs 4a and 4b. In applying these equations,

$$k_q = k_d/(1 + k_{-d}/k_{et} + 1/K_{et}) \qquad (4a)$$

$$k_{et} = (K_A\{1/k_q - (1 + K_{et})/k_dK_{et}\}]^{-1} \qquad (4b)$$

it was assumed that $k_{-d} = k'_{-d}$ and the relationships in eqs 5 and 6 were utilized.[17]

$$K_A = k_d/k_{-d} \qquad (5)$$

$$k_{et}/k_{-et} = K_{et} = \exp -(\Delta G°/RT) \qquad (6)$$

A quantum mechanically derived expression for k_{et} is shown in eq 7. It is based on the coupling to the energy-transfer process of averaged, medium-frequency, ring-stretching modes in the donor (m) and acceptor (n) and low-frequency and solvent modes treated classically.[8,16] In eq 7b, S_m and S_{n*} are the electron-vibrational

$$k_{et}(\text{calcd}) = (2\pi V^2/\hbar)F(\text{calcd}) \qquad (7a)$$

$$F(\text{calcd}) = [1/(4\pi\lambda' k_BT)^{1/2}] \sum_{n^*=0}^{\infty} \sum_{m=0}^{\infty} [\exp(-S_{n*})] \times [\exp(-S_m)](S_{n*}^{n*}/n^*!)(S_m^m/m!) \times [\exp\{-(\Delta G° + \lambda'_{12} + n^*\hbar\omega + m\hbar\omega)^2/4\lambda'_{12}k_BT\}] \qquad (7b)$$

coupling constants. The sums are over the ground-state vibrational levels of the donor (m) and the excited-state vibrational levels of the acceptor (n^*). The terms in the sums past $n^* = 4$ and $m = 4$ were negligible.

In Figure 1 is shown a calculated plot of log k_q vs $\Delta G°$ for the data *with anthracene as quencher*. The line was calculated by using eq 4a with $k_d = 9.1 \times 10^9$ M^{-1} s^{-1} and $k_d/k_{-d} = 2.3$,[17] eq 6 to calculate K_{et}, and eq 7 to calculate k_{et}. In the calculation of k_{et}, average values of S (1.2) and λ' (1860 cm^{-1}) were utilized for the complexes with $\hbar\omega$ = 1300 cm^{-1}.[8] The parameters for anthracene were taken from the emission spectral fitting results. The quantity λ'_{12} is the average value for the complexes (λ'_{11}) and λ' for anthracene (λ'_{22}), $\lambda'_{12} = (\lambda'_{11} + \lambda'_{22})/2 = 1090$ cm^{-1}. The magnitude of the energy exchange matrix element, V, used in eq 7 to calculate the line was $V = 4$ cm^{-1}. This is consistent with literature values found for energy transfer involving organic triplets.[18]

Several important conclusions emerge from our results. The first is that the inverted region can be reached for energy transfer as well as for electron transfer. It is more easily observed for energy transfer because, in forming the lowest triplets of anthracene and 2,3-benzanthracene, the maximum rate constant is below the diffusion-controlled limit. The second is that, as for electron transfer, higher lying, accessible excited states can interfere with the observation of inverted behavior in energy transfer. Finally, it is possible to utilize structural and energetic parameters derived from emission spectral profiles to calculate relative rate constants for energy transfer. This approach has been utilized to calculate relative rate constants for nonradiative decay for MLCT excited states including polypyridyl complexes of Os^{II} and Ru^{II}.[8,19] It may have additional applications elsewhere.

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Reaction of a Distorted Amide with Nucleophilic Thiolate-Containing Zwitterions Produced from Thiolamines. A Model for the Acylation Step in Cysteine Proteases and Transglutaminases

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Distorted amide **1** (2,3,4,5-tetrahydro-2-oxo-1,5-ethanobenzazepine)[1] has been shown to be susceptible toward bifunctional nucleophiles such as β-amino alcohols[2] and certain dicarboxylic acids[3] as simple model systems for the serine and aspartate proteases, respectively. Herein, we report the reactions of **1** with β-amino thiols which can be taken as a simple model for the third of the four classes of proteases, namely, the cysteine proteases[4] (and phenomenologically similar transglutaminases[5]).

The maximum rate of disappearance of **1** in the presence of thiolamines **2a–c** occurs at pH levels above the value of pK_{thiol} and lower than the value of pK_{NH^+} so that the zwitterionic ammonium thiolate is the active attacking species.[6] Alkyl thiols

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