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Calculation of Electron Transfer Rate Constants from Spectra in Re(I) Chromophore−Quencher Complexes

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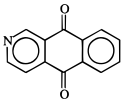
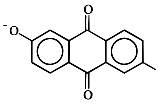
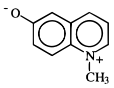
We report here the use of emission measurements to calculate rate constants for electron transfer in polypyridyl complexes of Re^I. The complexes $[(4,4'-(Me)_2bpy)Re(CO)_3(BIQD)](OTf)$ (BIQD is benz[*g*]isoquinoline-5,10-dione; OTf is $CF_3SO_3^-$), $[(4,4'-(Me)_2bpy)Re(CO)_3]_2(AFA)$ (AFA^{2-} is 2,6-dioxyanthraquinone dianion), and $[(4,4'-(^tBu)_2bpy)Re(CO)_3(OQD)]$-(OTf) (OQD is 1-methyl-6-oxyquinoline)[1,2] were chosen for study as examples where electron transfer acceptor ligands and a metal-to-ligand charge transfer (MLCT) chromophore are linked with moderate to weak electronic coupling.



BIQD



AFA^{2-}



OQD

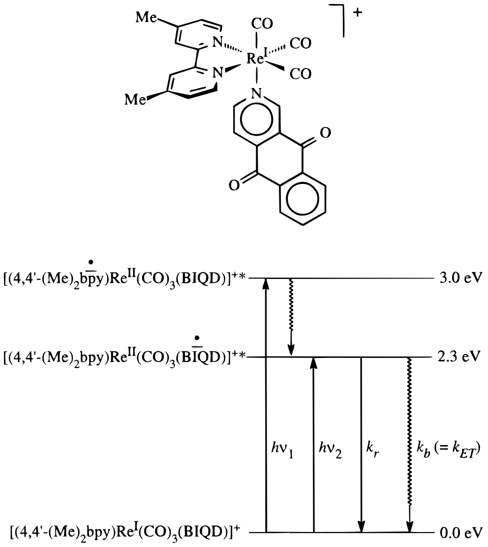
Absorption spectra for these complexes are typical of related Re^I complexes. For $[(4,4'-(Me)_2bpy)Re(CO)_3(BIQD)](OTf)$ in 1,2-dichloroethane (DCE) a band at 339 nm arises from a $Re^I \rightarrow 4,4'-(Me)_2bpy$ transition and lower energy bands from $Re^I \rightarrow$ BIQD transitions.

Transient absorption changes following 355−460 nm laser flash photolysis in DCE are consistent with formation of MLCT redox-separated states based on BIQD, AFA^{2-}, or OQD as acceptor ligands. For example, for the BIQD complex a double maximum appears at 600 and 650 nm similar to the absorption spectrum of $[(4,4'-(Me)_2bpy)Re^I(CO)_3(BIQD^\bullet)]$ generated by electrochemical reduction at −0.34 V vs SSCE in 0.1 M $[N(n\text{-}C_4H_9)_4](PF_6)$ (TBAH) in DCE ($n = 1.0$). The complex undergoes reducti at $E_{1/2} = -0.39$ V ($BIQD^{0/-}$) and −1.31 ($4,4'-(Me)_2bpy^{0/-}$) by cyclic voltammetry. For the BIQD complex, the redox-separated state is formed by a combination of direct $Re^I \rightarrow$ LA excitation and $Re^I \rightarrow 4,4'-(Me)_2bpy$ excitation followed by $4,4'-(Me)_2bpy \rightarrow$ LA electron transfer, as in Scheme 1.[3]

The redox-separated states return to the ground state by a combination of radiative (k_r in Scheme 1) and nonradiative processes (k_b in Scheme 1) with the latter occurring by electron transfer, $k_{ET} = k_b$. Values are given in Table 1.

The appearance of emission allows an important test to be made of electron transfer theory. These reactions occur deeply in the inverted region[4] with $-\Delta G° > \lambda$ as shown by the analysis below. $\Delta G°$ is the free energy change and λ the reorganizational energy. The electron transfer rate constant is given by[5]

Scheme 1



$$\ln k_{ET} = \ln \nu_{ET} + \ln[F(\text{calc})] \tag{1}$$

ν_{ET} is the frequency factor and $\ln[F(\text{calc})]$ is the electron transfer barrier. In the nonadiabatic limit, ν_{ET} is related to H_{DA}, the delocalization energy arising from electronic coupling between donor and acceptor, by[8]

$$\nu_{ET} = \frac{2\pi H_{DA}^{\;2}}{\hbar} \tag{2}$$

With a single high or medium frequency coupled vibration or average mode with $E_0 \gg \hbar\omega_M$, and $\hbar\omega_M \gg k_BT$, $\ln[F(\text{calc})]$ is given by the energy gap law result in eq 3. In this equation, S_M and $\hbar\omega_M$ are the electron-vibrational coupling constant and quantum spacing for the coupled mode. λ_0' is the sum of the solvent reorganizational energy (λ_0) and the reorganizational energy contributed by coupled low-frequency vibrations treated classically ($\lambda_{i,L}$). E_0 $(=|\Delta G°| - \lambda_0')$ is the $v^* = 0$ to $v = 0$ energy gap.[6,7] Multiple vibrations are coupled to the transition between states. The mode-averaging procedure used here has been used successfully for nonradiative decay of MLCT excited states, for example.[6,8]

$$\ln[F(\text{calc})] = -\frac{1}{2}\ln(2\pi\hbar\omega_M E_0) - S_M - \frac{\gamma E_0}{\hbar\omega_M} + \left(\frac{\gamma + 1}{\hbar\omega_M}\right)^2 (k_BT\lambda_0') \tag{3}$$

$$\gamma = \ln\left(\frac{E_0}{S_M\hbar\omega_M}\right) - 1 \tag{4}$$

All of the quantities in eq 3 can be evaluated by Franck−Condon analysis of the emission spectra. The results are given in Table 1, $\Delta\bar{\nu}_{0,1/2} = (k_BT\lambda_0'16\ln(2))^2$. H_{DA} can be calculated

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(2) Syntheses for the complexes, elemental analysis, and ^{1}H-NMR and FT-IR data are available as supporting information.

(3) The energies of the MLCT excited state and the redox-separated state of the BIQD complex relative to the ground state were calculated from $E_0 = |\Delta G°| - \lambda_0'$, $E_{abs} = |\Delta G°| + S_M\hbar\omega_M + \lambda_0'$, and the data in Table 1. The absorption maximum for the $Re^I \rightarrow 4,4'-(Me)_2bpy$ transition occurs at 339 nm.

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Table 1. Calculated and Experimental Quantities for Electron Transfer in Scheme 1 in 1,2-Dichloroethane at Room Temperature

	complex		
	BIQD	AFA^{2-}	OQD
E_{em} (cm^{-1})[a]	14530	15060	13370
τ (ns)[b]	25	5.6×10^3	1.5×10^4
$\phi_{em}c$	1.8×10^{-3}	1×10^{-3}	5×10^{-4}
$\langle\bar{\nu}^{-3}\rangle^{-1}$ (cm^{-3})	2.48×10^{12}	2.86×10^{12}	1.80×10^{12}
E_0 (cm^{-1})[d]	14920	15490	13610
S_M[d]	0.81	0.95	1.11
$\Delta\bar{\nu}_{0,1/2}$ (cm^{-1})[d]	2900	2830	1770
$\hbar\omega_M$ (cm^{-1})[d]	1625	1500	1376
λ_0' (cm^{-1})[d]	3660	3500	1360
E_{abs} (cm^{-1})[e]	23560	23910	17870
ϵ_{max} (M^{-1} cm^{-1})[e]	2.2×10^1	7.9×10^{-2}	1.6×10^{-2}
$\Delta\bar{\nu}_{0,1/2}$(abs) (cm^{-1})[e]	3834	4052	3170
d (Å)[f]	6	6	5
H_{DA} (cm^{-1})	153	9.5	3.9
ln[F(calc)]	−21.65	−22.84	−21.43
$k_{ET,obs}$ (s^{-1})[b]	4.0×10^7	1.8×10^5	6.6×10^4
$k_{ET,calc}$ (s^{-1})[g]	1.1×10^7	1.3×10^4	8.9×10^3

[a] Energy of the emission maximum. [b] From time-resolved absorption measurements. [c] Based on [(bpy)Re^I(CO)$_3$(4-ethylpyridine)](PF$_6$) in 1,2-dichloroethane or [Os(bpy)$_3$](PF$_6$)$_2$ in acetonitrile at 296 K as standards.[6,16] [d] By emission spectral fitting.[8] [e] Molar extinction coefficient, maximum, and bandwidth for absorption $h\nu_2$ in Scheme 1. ϵ_{max} from eq 5; $E_{abs} \approx E_0 + S_M\hbar\omega_M + 2\lambda_0'$;[3] $\Delta\bar{\nu}_{0,1/2}$(abs) taken as the experimental band width at half height for the emission band. [f] Distance between the Re^I ion and the center of the LA acceptor, estimated from crystal structure data of related complexes. [g] Calculated from eq 1.

from the emission quantum yield (ϕ_{em}) and lifetime ($k_r = \phi_{em}/\tau$) from the Strickler−Berg equation (eq 5),[9] and an equation originally applied to mixed-valence compounds by Hush, eq 7.[10,11]

$$k_r = (3.05 \times 10^{-9})n^2\langle\bar{\nu}^{-3}\rangle^{-1}\frac{\epsilon_{max}\Delta\bar{\nu}_{0,1/2}(\mathrm{abs})}{E_{abs}} \quad (5)$$

$$\langle\bar{\nu}^{-3}\rangle^{-1} = \frac{\int I(\bar{\nu})\,\mathrm{d}\bar{\nu}}{\int \bar{\nu}^{-3}I(\bar{\nu})\,\mathrm{d}\bar{\nu}} \quad (6)$$

$$H_{DA} = \frac{2.06 \times 10^{-2}}{r}(\epsilon_{max}E_{abs}\Delta\bar{\nu}_{0,1/2}(\mathrm{abs}))^{1/2} \quad (7)$$

These give

$$H_{DA}{}^2 = (1.39 \times 10^5)\left(\frac{E_{abs}}{nd}\right)^2\langle\bar{\nu}^{-3}\rangle k_r \quad (8)$$

In eq 8, n is the index of refraction of the solvent and d the electron transfer distance. The quantities ϵ_{max}, $\Delta\bar{\nu}_{0,1/2}$(abs), and E_{abs} are the molar extinction coefficient, bandwidth, and band maximum for absorption $h\nu_2$ in Scheme 1. These bands are not resolved in the UV−visible spectra, but E_{abs} can be estimated from $E_{abs} \approx E_0 + S_M\hbar\omega_M + 2\lambda_0'$ [3] and $\Delta\bar{\nu}_{0,1/2}$(abs) from the bandwidth of the emission spectrum (Table 1).

Quantities of relevance to electron transfer in these complexes are listed in Table 1. There are some notable entries. One is k_{ET}, where there is agreement to within 4−14 between calculated and observed values. The calculated values are systematically lower than the observed values. In other studies eq 7 has been found to underestimate H_{DA}.[12] This case is one of a small but increasing number of examples where spectroscopic results have been used successfully to calculate rate constants or relative rate constants for radiative or nonradiative decay,[6,9] electron transfer in the normal region,[16] and electron or energy transfer in the inverted region.[14]

Given the energy gaps for $AFA^{\bullet 3-} \rightarrow Re^{II}$ and $OQD^{\bullet -} \rightarrow Re^{II}$ electron transfer, k_{ET} is remarkably slow ($k_{ET}{}^{-1} = \tau = 5.6$ and 15 μs). The photochemically produced redox equivalents are stored for extended periods in these structurally simple chromophore−quencher complexes. The long lifetimes are a direct consequence of weak electronic coupling through the aryloxy bridge with H_{DA} = 9.5 ($AFA^{\bullet 3-}$) and 3.9 ($OQD^{\bullet -}$) cm^{-1}.[15]

From emission spectral analysis, the magnitude of $\hbar\omega_M$ for $OQD^{\bullet -} \rightarrow Re^{II}$ emission is typical of values found for other polypyridyl and pyridinium acceptors.[6,16] $\hbar\omega_M$ is higher for the quinone acceptor because of contributions from quinoid stretching modes[18a] which appear at 1612 cm^{-1} (C=C) and 1683 cm^{-1} (C=O) in [(4,4′-(Me)$_2$bpy)Re(CO)$_3$(BIQD)]$^+$ by resonance Raman measurements.[18b] λ_0' is also higher for the quinone acceptors, presumably due to strong specific interactions between solvent molecules and the quinoid O-atoms in the semiquinone radical anion part of the redox-separated states (Scheme 1).

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Supporting Information Available: Syntheses for the complexes and elemental analysis, and ^{1}H-NMR and FT-IR data (3 pages). See any current masthead page for ordering and Internet access instructions.

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