Photo-induced charge separation by ruthenium(II) photosensitizers

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Abstract. The values of the cage escape yields of redox products (η_{ce}) were determined for the reductive quenching of the excited states of homo- and heteroleptic complexes of Ru(II) and 2,2'-bipyridine (bpy), 2,2'-bipyrimidine (bpm), and 2,2'-bipyrazine (bpz) by triethanolamine (TEOA) as a sacrificial reductive quencher in aqueous, acetonitrile, and propylene carbonate solutions. In aqueous solution, η_{ce} varies with the standard reduction potential (E^0) of the complex, describing a weak dependence. The values of η_{ce} are independent of E^0 in propylene carbonate, but exhibit an inverted dependence in acetonitrile; the values of η_{ce} in acetonitrile are generally higher than those in aqueous and propylene carbonate solutions, due to the higher diffusional rate constant for cage escape of the redox geminate pair in acetonitrile. The variable dependencies of η_{ce} in the different solvents on the driving force of back electron transfer require that the conventional model be modified to account for the reorientation of the geminate pair within the solvent cage.

Keywords. Charge separation; photochemistry; ruthenium(II) complexes; photosensitizers; electron transfer.

1. Introduction

The yield of redox products (η_{ce}) released into bulk solution upon electron-transfer quenching is the critical parameter governing the efficacy of a redox photosensitizer; Ru(II) complexes are among the most popular and effective photosensitizers. In the simplest model (1)–(3) below, the quenching reaction can be visualized as occurring via the formation of a geminate redox pair within a solvent cage as a result of the transfer of one electron, with η_{ce} a measure of the competition between back electron transfer (k_{bt}) and diffusional escape of the redox products (k_{ce}) (Balzani and Scandola 1983). According to this model, the experimental determination of η_{ce} , the calculation of k_{ce} from (4) and (5) below, and the application of the equations that describe the diffusion of species in fluid solution permit the dependence of energetics and solution medium on k_{bt} to be evaluated. If, in a series of photosensitizer-quencher pairs, k_{ce} and the parameters that affect k_{bt} , except ΔG_{bt}^0 , can be kept constant, the variation of η_{ce} would be dependent only on the variation of the exoergicity of the back electron transfer reaction.

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$$\eta_{ce} = \frac{k_{ce}}{k_{ce} + k_{bt}}, \quad (4)$$

$$\frac{k_{bt}}{k_{ce}} = \frac{1}{\eta_{ce}} - 1. \quad (5)$$

The back electron-transfer reaction of the geminate redox pair within the solvent cage is a subset of the general phenomenon of intramolecular electron transfer, for which many examples of well-defined dependencies of k_{et} on the reaction driving force in accord with Marcus' theory are now in the literature. Recently, Yonemoto *et al* (1992) reported on the values of k_{et} for the forward electron transfer between the MLCT excited state of Ru(II) and covalently bound viologen acceptors, and the back electron transfer between the Ru(III) center and the reduced viologen radical; the dependence on ΔG^0 of the reactions traversed the "normal" and "inverted" Marcus regions. However, when the viologens are uncoupled from the complex and act as bimolecular quenchers, the plot of $\ln(\eta_{ce}^{-1} - 1)$ vs ΔG^0 is very scattered and does not show any evident correlation. A very weak (or no) correlation of $\ln(\eta_{ce}^{-1} - 1)$ vs ΔG_{bt}^0 was also obtained for the oxidative quenching of the excited states of nine Ru(II) complexes by methylviologen (4,4'-dimethylpyridinium dication; MV^{2+}) (Ohno *et al* 1991) as well as no evident dependency for the reductive quenching of a derivative of $*Ru(bpy)_3^{2+}$ ($bpy = 2,2'$ -bipyridine) by aromatic amines (Ohno *et al* 1993). On the other hand, Ohno *et al* (1986, 1987, 1989, 1990) obtained very dramatic "bell-shaped" curves for the quenching of the excited states of Ru(II) complexes by aromatic amines and methoxybenzenes. These conflicting results suggest the need to investigate further the validity of the simple model.

In this work, values of η_{ce} for the reductive quenching of the excited states of a series of Ru(II) complexes that contain bpy, bpm (2,2'-bipyrimidine) and bpz (2,2'-bipyrazine) ligands by TEOA (triethanolamine) were determined in aqueous, acetonitrile and propylene carbonate solution. In this way, a common quencher is used and the complexes all have the same size, shape, and charge: the use of the different solvents permits a variation in viscosity and dielectric constant, which will affect the value of k_{ce} in a systematic way.

2. Experimental

The Ru(II) complexes (RuL^{2+}) were from our laboratory supply; their structures and abbreviations are shown in figure 1, and their photophysical and electrochemical properties are given in table 1. Methylviologen dichloride (Aldrich) was converted to the PF_6^- salt and was recrystallized three times from water. TEOA (Fluka) and propylene carbonate (Fluka) were fractionally distilled thrice. Acetonitrile (Aldrich Optima) was used without further purification. Distilled water was further purified by passage through a Millipore purification train. All quencher solutions were freshly prepared prior to use. The pH values of the solutions were set at 10.0 with the use of 1–3 mM borax buffer.

Solutions contained 50 μM Ru(II), 2–7 mM MV^{2+} , and up to 0.6 M TEOA. The excitation wavelength for the continuous photolysis was chosen as the absorption maximum of the 400-nm charge transfer band for each complex under examination.

Figure 1. Structures of and notations for the Ru(II) photosensitizers used in this study.

The concentration of the reduced methylviologen radical cation ($\text{MV}^{+\cdot}$) was evaluated from its absorbance at 605 nm by taking $\epsilon_{605} = 1.37 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (Watanabe and Honda 1982).

The continuous photolysis experiments were performed using a Bausch & Lomb high-intensity monochromator in conjunction with a 100 W quartz-halogen lamp; the light intensity was monitored by an associated photon counter that was calibrated by potassium ferrioxalate actinometry. In a typical experiment, 4 ml of Ar-purged

Table 1. Photophysical and electrochemical properties of Ru(II) photosensitizers in aqueous solution.

Complex	λ_{em} (nm)	τ_0 (μs)	$E^0(2+/+)$ (V) ^a	$E^0(*2+/+)$ (V) ^a
zzz	602	0.94	−0.50	1.68
zzm	613	0.71	−0.55	1.63
mmz	634	0.52	−0.61	1.43
zzy	640	0.40	−0.63	1.44
mzy	666	0.22	−0.67	1.33
zyy	695	0.092	−0.77	1.16
mmm	622	0.077	−0.73	1.34
mmy	660	0.044	−0.77	1.28
myy	680	0.014	−0.83	1.15
yyy	610	0.060	−1.22	0.93

^aD'Angelantonio *et al* (1991)

Figure 2. Reaction scheme for the $\text{RuL}^{2+}/\text{TEOA}/\text{MV}^{2+}$ system.

and magnetically stirred solution was contained in a sealed 1×1 cm spectrofluorimeter cuvette.

3. Results and discussion

3.1 Cage escape yields

The mechanism for the quenching of $^*\text{RuL}^{2+}$ by TEOA in the presence of MV^{2+} can be expressed by (6)–(11) below, where $\text{TEOA}_{\text{ox}}^{+\cdot}$ is the cation radical produced as a result of the one-electron oxidation of TEOA, and $\text{TEOA}_{\text{red}}^{\cdot}$ is the reducing radical derived from the irreversible transformation of $\text{TEOA}_{\text{ox}}^{+\cdot}$.

The generation of the lowest energy luminescent excited state with an efficiency of ~ 1 via (6) is followed by quenching (8), in competition with the natural decay of $^*\text{RuL}^{2+}$ (7), forming $\text{RuL}^{+\cdot}$ and $\text{TEOA}_{\text{ox}}^{+\cdot}$ in bulk solution. $\text{TEOA}_{\text{ox}}^{+\cdot}$ undergoes transformation (9) ($k_{tr} = 3.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) (Chan *et al* 1981), converting the oxidative species to a reductive one ($\text{TEOA}_{\text{red}}^{\cdot}$). Both $\text{RuL}^{+\cdot}$ and $\text{TEOA}_{\text{red}}^{\cdot}$ reduce MV^{2+} to $\text{MV}^{+\cdot}$ (10) and (11) with rate constants in the order of 10^8 – $10^9 \text{ M}^{-1} \text{ s}^{-1}$ (D'Angelantonio *et al* 1991). The reaction scheme is given in figure 2.

The efficiency of the quenching reaction, η_q , is the result of the competition between the natural decay (7) and the electron transfer quenching (8) of the excited states, and can be expressed as (12) below. The efficiency of (8) with regard to the escape of the redox pair from the solvent cage, in which they were generated by the quenching interaction, into the bulk solution is given by (4). The quantum yield of $\text{MV}^{+\cdot}$ formation for the system upon continuous photolysis is given in (13) below.

$$\eta_q = \frac{k_q[D]}{k_0 + k_q[D]}, \quad (12)$$

$$\Phi(\text{MV}^{+\cdot}) = 2\eta_{ce}\eta_q. \quad (13)$$

The excited states of six complexes (zzz, mmz, zzy, zzm, mzy, mmm) in aqueous solution and all but $\text{Ru}(\text{bpy})_3^{2+}$ in acetonitrile and propylene carbonate were quenched by TEOA; the values of $\Phi(\text{MV}^{+\cdot})$ were determined in all three solvents. As predicted by (13), plots of $\Phi(\text{MV}^{+\cdot})$ vs η_q were, indeed, all linear, and the values of η_{ce} were obtained from such plots; examples of the plots are given in figure 3. Taking $E^0(\text{TEOA}_{\text{ox}}^{+\cdot}/\text{TEOA}) = 0.84 \text{ V}$ (Sun and Hoffman 1993), the standard free energy change for the back electron-transfer between $\text{RuL}^{+\cdot}$ and $\text{TEOA}_{\text{ox}}^{+\cdot}(\Delta G_{\text{bt}}^0)$ can be

Figure 3. Plots of $\Phi(\text{MV}^{+\cdot})$ vs η_q for $\text{RuL}^{2+}/\text{TEOA}/\text{MV}^{2+}$ systems in acetonitrile.

Figure 4. Plots of η_{ce} vs ΔG_{bt}^0 for aqueous, acetonitrile, and propylene carbonate solutions.

estimated from the excited state reduction potentials (table 1) (D'Angelantonio *et al* 1991). Plots of η_{ce} vs ΔG_{bt}^0 are given in figure 4. The data in propylene carbonate show no dependence of η_{ce} on ΔG_{bt}^0 . In aqueous solution, η_{ce} increases as ΔG_{bt}^0 becomes more negative, suggesting that k_{bt} decreases as the reaction driving force is increased, which is "inverted" Marcus behavior. However, the data in acetonitrile show the opposite dependence of η_{ce} on ΔG_{bt}^0 to that obtained in aqueous solution, although the variation of η_{ce} is smaller. Overall, the dependencies of η_{ce} on ΔG_{bt}^0 are rather weak, especially for propylene carbonate and acetonitrile solutions; the values of η_{ce} in the different solvents reflect the variation of solution medium parameters, especially the viscosity.

The weak dependencies of η_{ce} on ΔG_{bt}^0 observed in this work (and in other studies) are in sharp contrast to the predicted bell-shaped curves, and those reported earlier, suggesting that the kinetic events within the solvent cage may be very different from that of the simple model for those systems.

3.2 Solvent cage models

The observation of unpredicted dependencies of η_{ce} on ΔG_{bt}^0 indicates that the cage events may be more complicated than those described by (1)–(3). Before modifications are made to the model, it should be noted that in the reductive quenching of the MLCT excited state of Ru(II) complexes, which can be described as possessing a one-electron reduced ligand coordinated to a Ru(III) center ($[\text{Ru}^{\text{III}}\text{L}^{\cdot-}]^{2+}$), different orbitals in the complex are involved in the quenching reaction and back electron-transfer reaction within the cage. The electron-rich quencher might approach the excited complex at a side opposite to the reduced ligand, and transfer its electron into the t_{2g} orbital of the metal center. However, back electron-transfer occurs between the reduced ligand and the oxidized quencher, they are well separated, and are in a sterically unfavorable position for rapid transfer unless the geminate pair undergoes reorientation to permit the establishment of overlap (or coupling) between the donating and accepting orbitals (figure 5). Similarly, for the oxidative quenching of the MLCT

Figure 5. Schematic diagram of the reductive quenching of $^*\text{Ru}(\text{II})$ complexes by an electron donor and the subsequent reorientation and back electron-transfer reactions.

Figure 6. Schematic diagram of the oxidative quenching of ^{*}Ru(II) complexes by an electron acceptor and the subsequent reorientation and back electron-transfer reactions.

excited state of Ru(II) complexes, the quencher might approach the electron-rich reduced ligand of the excited state and accept the electron from its π^* orbital in the quenching act, and then donate the electron to the metal center d orbital in the back transfer process. A reorientation process may be needed to reposition the redox pair and allow the establishment of the orbital overlapping (or coupling) between the two donating and accepting orbitals (figure 6).

We wish to propose a modification to the cage model in order to account for the increasing body of evidence that values of η_{ce} in bimolecular quenching reactions involving Ru(II) sensitizers are weakly dependent, if at all, on ΔG_{bt}^0 . In this new model, $[M^{-/+} \dots Q^{+/-}]_1$ and $[M^{-/+} \dots Q^{+/-}]_2$ represent the solvent cage before and after the reorientation processes, respectively, k_{reo} is the rate constant for reorientation, and k'_{bt} is the back electron-transfer rate constant after the reorientation has occurred. By applying the steady-state approximation to $[M^{-/+} \dots Q^{+/-}]_2$, (14) and (15) are obtained.

$$\frac{1}{\eta_{ce}} - 1 = \frac{k_{bt}k'_{bt} + k_{bt}k_{ce} + k'_{bt}k_{reo}}{k_{ce}(k'_{bt} + k_{ce} + k_{reo})} \quad (15)$$

There are two limiting cases for which (14) and (15) can be simplified. If $k_{reo} \ll k_{bt}$ and $k_{reo} \ll k_{ce}$, (15) reduces to (5); the previous model can be viewed as a limiting case in which the reorientation process is very slow compared to back electron-transfer

and cage escape. If, on the other hand, the back transfer in $[M^{-/+} \dots Q^{+/-}]_1$ is very slow due to an unfavorable orientation of the reacting species ($k_{bt} \ll k_{reo}$ and $k_{bt} \ll k_{ce}$), and the back transfer in $[M^{-/+} \dots Q^{+/-}]_2$ is faster than cage escape ($k'_{bt} \gg k_{ce}$), (15) is reduced to (16) below; η_{ce} becomes a measure of the competition between the cage escape and reorientation processes. Thus, the observed weak or negligible dependencies of η_{ce} on ΔG_{bt}^0 can be viewed as representing this limiting case, since k_{reo} is not expected to be dependent on the driving force of the back electron-transfer reaction.

$$(1/\eta_{ce}) - 1 = k_{reo}/k_{ce}. \quad (16)$$

For intermediate cases, (14) and (15) would be operative, resulting in a range of observed dependencies of η_{ce} on ΔG_{bt}^0 that are functions of the magnitudes of the rate constants of the mechanistic steps. Of course, the reorientation process, like cage escape and back electron-transfer, will be dependent on the solvent and the counter ions within the cage. The various rate constants are likely to have different activation parameters, resulting in further changes in the functional relationships between η_{ce} and ΔG_{bt}^0 with changes in temperature. The challenge for the future is to discover the molecular features that control the values of the rate constants in order to be capable of fine-tuning the efficiency of photoinduced charge separation in excited state quenching reactions.

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