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Effect of solution medium on the rate constants of excited-state electron-transfer quenching reactions of ruthenium(II)-diimine photosensitizers

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Contents

Abstract

In this paper, we review the effects of solution medium (pH, solvent, temperature, ionic strength, specific electrolytes) on the oxidative and reductive quenching rate constants k_q of the excited states of Ru(II)-diimine photosensitizers. Diffusion of the donor and acceptor

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species together to form the precursor complex (k_d) and electron transfer within the complex (k_{et}) contribute to the value of k_q. Values of k_d vary with bulk solution properties; variations of k_{et} can be described within the context of Marcus theory, wherein dynamic solvent effects influence the nuclear frequency factor and electronic coupling, and static properties cause changes in the driving force of electron transfer ΔG°_{et} and the reorganization energy λ. The pH can affect the state of protonation of the excited photosensitizer and/or the quencher, thereby altering k_{et} through changes in ΔG°_{et} and k_d through changes in the charges of the reactants. Ionic species are ion-paired by the dominant counterion; the Olson–Simonson treatment allows the electron transfer components of quenching for ion-paired (k_{ip}) and non-ion-paired (k_{nip}) species to be extracted. The quenching of $^*Ru(bpy)_3^{2+}$ by methylviologen is used to demonstrate specific salt effects, which result in variations in λ; λ is lowest, and k_q highest, for the anions with the most weakly-held hydration spheres and the strongest structure-breaking abilities (e.g. ClO_4^-, I^-). Quenching rate constants can be fine-tuned through the variation of solvent, pH, electrolyte, ionic strength, and temperature. © 1997 Elsevier Science S.A.

Keywords: Excited-state electron-transfer quenching reactions; Ruthenium(II)-diimine photosensitizers

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1. Introduction

1.1. Ruthenium(II)-diimine photosensitizers

Light-induced electron-transfer reactions have been extensively studied in recent years with a view toward the understanding of the primary mechanisms of natural photosynthetic processes, and the designing of artificial systems for the conversion and storage of solar energy [1]. Although any practical system for solar energy conversion and storage will involve heterogeneous reactions at some stage of the process, there is a continued need for the elucidation of the factors that govern electron transfer in homogeneous solution. One goal in the design of systems for the chemical conversion and storage of light energy is to achieve efficient separation of highly energetic charge-separated species.

An effective sensitizer for photoinduced redox reactions must have a strong optical absorption over a broad wavelength range and an excited state with a sufficiently long lifetime to experience bimolecular quenching; the ground- and excited-state redox potentials must be such that forward electron transfer occurs rapidly but back electron transfer within the quenching solvent cage occurs slowly in competition with the release of the redox pair into bulk solution [2]. Transition metal coordination complexes possess a wide range of absorption and luminescence characteristics, excited-state lifetimes, and electron-transfer properties that make them attractive candidates as photosensitizers, and useful in systems designed to test the theories of photoinduced electron transfer [3]. Ruthenium(II) complexes, especially those possessing diimine ligands, are readily synthesized with a range of charges, structures, redox potentials, and photochemical/photophysical properties; they exhibit the attractive combination of ground-state stability, excited-state reactivity, and luminescence detectability [4]. The first reports appeared almost 25 years ago on the characterization of the luminescent excited state of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) [5] and its use in the sensitization of electron-transfer reactions [6]. Since that time, thousands of papers have been published on the photochemistry and photophysics of Ru(II)-diimine complexes in homogeneous solution, mixed media, organized assemblies, and on surfaces [3,4,7]. Yet, because of the magnitude of the work done with $Ru(bpy)_3^{2+}$, particularly on the oxidative quenching of its excited state by methylviologen (*N*,*N*-dimethyl-4,4′-bipyridinium dication; MV^{2+}), this complex still serves as the standard against which other complexes with different metal centers and/or ligands are compared.

1.2. Photoinduced electron-transfer reactions

Photoinduced electron-transfer chemistry occurs from the redox quenching of the lowest excited state of the Ru(II) photosensitizer, which possesses metal-to-ligand charge-transfer (MLCT) character [8]. Excitation results in the transfer of an electron from the filled t_{2g} orbital of the metal into an empty π^* orbital of the diimine ligand that possesses the lowest unoccupied molecular orbital. The dipolar excited state is both a stronger oxidizing agent and a stronger reducing agent than the ground state; an approximate value of the redox potentials of the excited state can be obtained from the standard potentials of the ground state E° and the 0–0 excitation energy E_{00}, as given in Eq. (1) and 2 [3].

$$E^\circ(M^*/M^-) = E^\circ(M/M^-) + E_{00} \tag{1}$$

$$E^\circ(M^+/M^*) = E^\circ(M^+/M) - E_{00} \tag{2}$$

Cyclic voltammetric studies of solutions of $Ru(bpy)_3^{2+}$ show reversible waves, corresponding to one-electron oxidations and reductions. Inasmuch as $E_{00} = 2.12$ eV, $E^\circ(2+/+) = -1.28$ V and $E^\circ(3+/2+) = 1.26$ V *vs.* the normal hydrogen electrode (NHE) in H_2O [9], the excited-state potentials can be easily calculated: $E^\circ(^*2+/+) = 0.84$ V and $E^\circ(3+/^*2+) = -0.86$ V; recent work on the direct measurement of the potentials of the excited states has roughly confirmed these values [10].

Upon the excitation of $Ru(bpy)_3^{2+}$ (reaction 3), $^*Ru(bpy)_3^{2+}$, in competition with its natural radiative and non-radiative decays (reaction 4), is oxidatively or reductively quenched by Q (reaction 5), generating $Ru(bpy)_3^{3+}$ or $Ru(bpy)_3^{+}$ and Q^- or Q^+ in bulk solution, respectively.

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu^*} Ru(bpy)_3^{2+} \tag{3}$$

$$^*Ru(bpy)_3^{2+} \xrightarrow{k_0} Ru(bpy)_3^{2+} + h\nu' \tag{4}$$

$$^*Ru(bpy)_3^{2+} + Q \xrightarrow{k_q} Ru(bpy)_3^{3+/+} + Q^{-/+} \tag{5}$$

The efficiency of cage escape η_{ce} of the redox products released into bulk solution can be viewed, according to the conventional cage escape model [11], as arising from the formation of the geminate redox pair within the solvent cage (Eq. (6)) followed by competitive intramolecular back electron transfer (Eq. (7)) and diffusional cage escape (Eq. (8)): $\eta_{ce} = k_{ce}/(k_{ce} + k)$.

$$^{*}\mathrm{Ru(bpy)}_3^{2+} + \mathrm{Q} \rightarrow [\mathrm{Ru(bpy)}_3^{3+/+} \cdots \mathrm{Q}^{-/+}] \tag{6}$$

$$[\mathrm{Ru(bpy)}_3^{3+/+} \cdots \mathrm{Q}^{-/+}] \xrightarrow{k_{bt}} [\mathrm{Ru(bpy)}_3^{2+} \cdots \mathrm{Q}] \tag{7}$$

$$[\mathrm{Ru(bpy)}_3^{3+/+} \cdots \mathrm{Q}^{-/+}] \xrightarrow{k_{ce}} \mathrm{Ru(bpy)}_3^{3+/-} + \mathrm{Q}^{-/+} \tag{8}$$

The redox pair in bulk solution can subsequently engage in electron transfer charge recombination, regenerating the starting species in their ground states (Eq. (9)).

$$\mathrm{Ru(bpy)}_3^{3+/+} + \mathrm{Q}^{-/+} \xrightarrow{k_{rec}} \mathrm{Ru(bpy)}_3^{2+} + \mathrm{Q} \tag{9}$$

Over the past decade we have investigated the nature of the intermediates, in particular excited states, unusual oxidation states, and free and coordinated radicals, that are involved in electron-transfer reactions of Ru(II)-diimine complexes. The goal of the work has been to understand the kinetics and mechanisms of the reactions cascades, and to define the parameters that control the yields of redox products toward the design of systems that optimize the photochemical production of potential fuels. Recently, we reviewed our work on the solution medium and temperature effects on the photophysics of an homologous structural series of ten complexes [12]; we have also determined η_{ce} as a function of driving force, molecular structure, temperature, and solution medium [13]. In this paper, we review the role of solution medium on the control of k_q of excited Ru(II)-diimine photosensitizers, with a special focus on our recent work on the effect of specific electrolytes.

2. Electron transfer

2.1. Marcus theory

In the semi-classical formulation of Marcus theory, the rate constant of an electron-transfer reaction k_{et} is given by Eq. (10), where V is the electronic coupling coefficient, λ is the reorganization energy, and ΔG^* is the activation energy of the reaction [14]. ΔG^* contains contributions from both the solvent (outer sphere) and reactant (inner sphere) vibrations. When V is large, there is strong coupling between the donor and acceptor orbitals, and the reaction is adiabatic; conversely, when the coupling is weak and V is small, the reaction is non-adiabatic.

$$k_{et} = \frac{4\pi^2 V^2}{h(4\pi\lambda RT)^{1/2}} \exp(-\Delta G^*/RT) \tag{10}$$

The theory connects the activation energy for the electron transfer reaction to the driving force of the reaction and the reorganization energy through Eq. (11).

$$\Delta G^{*}=\frac{(\Delta G^{\circ}+\lambda)^{2}}{4\lambda} \tag{11}$$

Values of ΔG° for a photoinduced electron-transfer reaction can be estimated with Eq. (12), where $E^{\circ}(\mathrm{D}^{+}/\mathrm{D})$ and $E^{\circ}(\mathrm{A}/\mathrm{A}^{-})$ are the standard reduction potentials of the ground-state donor and acceptor couples respectively, and w_{p} and w_{r} are the coulombic work terms for the products and the reactants respectively, which correct for the work involved in bringing ionic species together. The coulombic terms are usually small (ca. 10^{-2} eV), and vanish for neutral species [14].

$$\Delta G^{\circ}=E^{\circ}(\mathrm{D}^{+}/\mathrm{D})-E^{\circ}(\mathrm{A}/\mathrm{A}^{-})-E_{00}+w_{\mathrm{p}}-w_{\mathrm{r}} \tag{12}$$

In order to obtain a good estimate for ΔG°, the ground-state potentials must be well established. However, in many cases, the one-electron reduced or oxidized forms of organic quenchers are unstable, making it difficult to obtain reversible cyclic voltammograms [15]. It is customary to use half-wave potentials, particularly for aromatic amine quenchers; unfortunately, these may be poor estimates of their one-electron potentials. This problem can be resolved by use of fast-scan potentiostats; if the scan rate is fast enough to compete with secondary reactions of the radicals, the electrochemical system becomes reversible [16].

The value of λ is a measure of the free energy required to move all the atoms in the precursor complex, including those of the solvent shell, from their initial equilibrium positions to their equilibrium positions in the successor complex without any electron transfer. The reorganization energy is the sum of two contributions, $\lambda=\lambda_{\mathrm{out}}+\lambda_{\mathrm{in}}$, where λ_{in} represents the activation of the vibrational modes of the reactants, which is generally near zero for electron transfer into and out of orbitals that do not result in significant changes in the molecular structure, and λ_{out} represents changes in the solvent structure around the reactants, which is strongly dependent on the solution medium. Recent laser-induced optoacoustic spectroscopy measurements of changes in volumes of activation confirm that medium reorganization around reacting ion pairs is an important contribution to λ_{out} in excited-state electron-transfer reactions of $\mathrm{Ru(bpy)}_{3}^{2+}$ [17].

Marcus theory predicts that k_{et} will follow a bell-shaped energy gap dependence as a function of ΔG°, initially increasing in value with more negative ΔG° in the normal region, but decreasing with increasing driving force in the inverted region [18]. For Ru(II)-diimine complexes, the inverted region has been observed for intramolecular electron transfer in covalently linked Ru(bpy)–MV^{2+} systems [19], and for back electron transfer between geminate radical pairs formed by intermolecular reductive quenching of a series of Ru(II) excited states by aromatic amines [20]. There have been many studies of the driving force dependence of k_{q}, where ΔG° is altered through the use of an homologous series of Ru(II) complexes or quenchers; in all cases, Rehm–Weller behavior is observed in which k_{q} increases with more negative ΔG°, but reaches a plateau at the diffusion limit with no evidence of the inverted region (for example, see Ref. [21]). The criterion of an homologous series is especially critical in studies of this type; steric effects can result in different values of V and/or λ, and values of k_q that lie on different Marcus curves [22].

2.2. k_q: *diffusional and electron transfer components*

In its simplest model, electron-transfer quenching can be represented by the diffusion of the donor and acceptor species, generating a precursor complex (Eq. (13)), followed by the diffusional breakup of the complex (reverse of the reaction in Eq. (13)) in competition with the electron-transfer step (Eq. (14)). When D and/or A are high energy species (e.g. excited states, radicals, or unusual oxidation states), the reverse of the reaction in Eq. (13) is highly endoergic, making that reaction very slow compared with subsequent steps.

$$\mathrm{D}+\mathrm{A} \underset{k_{-\mathrm{d}}}{\overset{k_{\mathrm{d}}}{\rightleftharpoons}} [\mathrm{D}\cdots\mathrm{A}] \tag{13}$$

$$[\mathrm{D}\cdots\mathrm{A}] \xrightarrow{k_{\mathrm{et}}} [\mathrm{D}^{+}\cdots\mathrm{A}^{-}] \tag{14}$$

A steady-state treatment of the reactions in Eqs. (13) and (14) yields Eq. (15), where $K_\mathrm{d} = k_\mathrm{d}/k_{-\mathrm{d}}$.

$$\frac{1}{k_\mathrm{q}} - \frac{1}{k_\mathrm{d}} = \frac{1}{K_\mathrm{d} k_\mathrm{et}} \tag{15}$$

Values of k_d can be calculated from the Debye–Smoluchowski equation (Eq. (16)) [23,24]; $k_{-\mathrm{d}}$ is calculated from the Eigen equation (Eq. (17)) [25]. Here, k is Boltzmann's constant, N is Avogadro's number, η is the solution viscosity, and r_A and r_B are the radii of the reactants; $a = r_\mathrm{A} + r_\mathrm{B}$. The terms $w(r,\mu)$ and β are given by Eqs. (18) and (19) [26]; $w(a,\mu)$ equals $w(r,\mu)$ when $r = a$. In addition, z_A and z_B are the ionic charges of the reactants, ε is the solution static dielectric constant, e is the electron charge, μ is the ionic strength of the solution, and σ_A and σ_B are the radii of the reactants plus that of the dominant counterion; inasmuch as water is a strongly solvating medium for ions, ionic hydrated radii should be used in the calculations for aqueous solutions.

$$k_\mathrm{d} = \frac{2kTN}{3000\eta}\left(2 + \frac{r_\mathrm{A}}{r_\mathrm{B}} + \frac{r_\mathrm{B}}{r_\mathrm{A}}\right)\frac{1}{a\displaystyle\int_a^\infty r^{-2}\exp[w(r,\mu)/kT]\,\mathrm{d}r} \tag{16}$$

$$k_{-\mathrm{d}} = \frac{kT}{2\pi\eta a^2}\left(\frac{1}{r_\mathrm{B}} + \frac{1}{r_\mathrm{A}}\right)\frac{\exp[w(a,\mu)/kT]}{a\displaystyle\int_a^\infty r^{-2}\exp[w(r,\mu)/kT]\,\mathrm{d}r} \tag{17}$$

$$w(r,\mu) = \frac{z_\mathrm{A} z_\mathrm{B} e^2}{2\varepsilon r}\left(\frac{\exp(\beta\sigma_\mathrm{A}\sqrt{\mu})}{1+\beta\sigma_\mathrm{A}\sqrt{\mu}} + \frac{\exp(\beta\sigma_B\sqrt{\mu})}{1+\beta\sigma_B\sqrt{\mu}}\right)\exp(-\beta r\sqrt{\mu}) \tag{18}$$

$$\beta=\left(\frac{8\pi Ne^2}{1000\epsilon kT}\right)^{1/2} \tag{19}$$

Thus, values of k_d and k_{-d} vary with bulk solution properties: viscosity, dielectric constant, ionic strength, temperature. The addition of salts to the solution increases the viscosity and the static dielectric constant; the latter term can be calculated from $\epsilon=\epsilon_w+2\delta^*c$ [27], where ϵ_w is the value for pure water, δ^* is the average of the molar dielectric constant depression coefficients of the cations and anions of the electrolyte [28], and c is its molar concentration. The viscosities of salt solutions have been compiled [29].

3. Temperature

The temperature dependence of k_q can be treated in a number of ways [30]; of course, the usual plot of ln k_q vs. $1/T$ yields the activation energy E_a. The enthalpy $\Delta H^‡$ and entropy $\Delta S^‡$ of activation of quenching can be obtained from the Eyring equation (Eq. (20)).

$$\ln\frac{k_q}{T}=\ln\frac{k}{h}-\frac{\Delta H^‡}{RT}+\frac{\Delta S^‡}{R} \tag{20}$$

The Eyring treatment has been used extensively by Tazuke and coworkers [31] to probe the mechanism of the quenching reactions of Ru(II)-diimine complexes: (1) negative temperature dependencies in reductive quenching by aromatic amines and oxidative quenching by nitroaromatics were attributed to back electron-transfer, reforming the excited state rather than the ground state; (2) positive values of $\Delta H^‡$ for reductive quenching and negative values for oxidative quenching were attributed to differences in the degree of rigidity of the intermediates; (3) for a series of complexes undergoing reductive quenching by aromatic amines, the values of $\Delta H^‡$ and $\Delta S^‡$ were taken to indicate non-adiabatic behavior, with bulky ligands preventing good overlap of the donor and acceptor orbitals; (4) for the reaction of $^*\mathrm{Ru(bpy)_3^{2+}}$ with an extensive series of amines, k_q varied according to the nature of the amines; tertiary≫primary, secondary, suggesting the variation of λ_{out} with the nature of the quencher. For a series of tris complexes with increasingly hindered alkylated bpy ligands, both $\Delta H^‡$ and $\Delta S^‡$ increase with increasing steric hindrance in the same solvent for the same amine. For $\mathrm{Ru(bpy)_3^{2+}}$ in different solvents, k_q, $\Delta H^‡$, and $\Delta S^‡$ vary with differences in solvent polarity and viscosity.

From the Marcus equations (Eqs. (10) and (11)), values of λ can be determined from the slopes of plots of $\ln(kT^{1/2})$ vs. $1/T$ [19,32]. The mechanism of electron transfer can also be investigated through the variation of temperature, by comparing the experimental results with the predictions of the Marcus theory. For example, in the reductive quenching of $^*\mathrm{Ru(bpy)_3^{2+}}$ by aromatic amines in a series of solvents, $\Delta H^‡$ and $\Delta S^‡$ demonstrate Marcus behavior in aprotic solvents; however, in protic solvents, k_q depends on the structure of the aromatic moiety rather than the driving force [22]. In the oxidative quenching of $^*Ru(bpy)_3^{2+}$ by MV^{2+} in mixed acetonitrile–water solutions, the evaluation of the activation energy for back electron transfer within the solvent cage has led to the introduction of the concept of a kinetically important reorientation within the cage [33].

4. Solvent

The nature of the solvent affects k_q by controlling the rates of diffusion and by establishing the microscopic environment of the solvent cage, which impacts on the value of k_{et} [34]; a number of researchers have recently evaluated the effect of solvent on k_{et} [35]. In any study of medium effects on k_{et}, it is necessary to take into account the influence of the solvent on each term of Eq. (10). In general, dynamic solvent effects influence the pre-exponential term, whereas static medium effects influence k_{et} mainly through the exponential term (λ_{out} and ΔG°), but the effects on these two parameters may show opposite trends. For some electron-transfer reactions between ions of the same sign, k_{et} increases when ϵ decreases, but opposite trends have also been observed [34]. There are times when the observed electron-transfer rate constant is independent of the solvent due to compensating effects of changes in ϵ on the ion-pairing association constant and λ_{out} [36]. The effect of solvent on electronic coupling is difficult to quantify due to the generally dominating effects on the exponential term.

4.1. Ion-pairing association constant

The equilibrium constant for the formation of 1:1 ion pairs K_{ip} between ionic species and counterions can be calculated through the use of the Fuoss equation (Eq. (21)) [37], where $w(\sigma)$ is given by Eq. (22), σ is the distance of closest approach of the anion and cation within the ion pair, and the remaining symbols have been previously defined.

$$K_{ip} = \frac{4\pi N\sigma^3}{3000}\exp[-w(\sigma)/kT] \tag{21}$$

$$w(\sigma) = \frac{z_c z_a e^2}{\epsilon\sigma(1+\beta\sigma\mu^{1/2})} \tag{22}$$

Thus, K_{ip} varies with both the static dielectric constant of the solvent and the solution ionic strength. Although it is common practice to calculate K_{ip} from these equations, it may be difficult to estimate it accurately with this simplified model; a more detailed approach is often required [34]. Early studies on the variation of k_q as a function of different solvents probed the quenching mechanism (static vs. dynamic) by altering the importance of ion-pairing through changes in solvent polarity [38].

4.2. Dynamic solvent effect

On the basis of Kramers' theory [39], dynamic solvent effects result from the collisions with the solvent, which serve to impede the progress of the system along the reaction coordinate. These are most easily observed in fast electron-transfer reactions, but have also been observed in slower reactions [34]. The work of Zusman [40] predicts a dependence of this factor on $1/\tau_L$, where τ_L is the longitudinal relaxation time of the solvent, corresponding to a situation where λ_{in} is small. When this energy increases, k_{et} becomes dependent on $\tau_L^{-\alpha}$, where $0 \leq \alpha \leq 1$. The value of α also depends on the adiabaticity of the reaction; for a non-adiabatic reaction, the dependence of the pre-exponential term in Eq. (10) on τ_L disappears, since k_{et} is now controlled by V rather than by the nuclear frequency factor. However, when reactions are strongly coupled to the solution medium (i.e. adiabatic), k_q does show the expected inverse dependence on τ_L [41].

Many quenching experiments have been performed on mixed solvents, particularly $CH_3CN–H_2O$, due to solubility reasons or as a probe of selective solvation [42], making a detailed interpretation of the values of k_q very difficult. Still, the dynamic solvent effect can be seen from the work of Rau and coworkers [43] on the oxidative quenching of sterically hindered Ru(II) complexes with alkylated bpy ligands by MV^{2+}; k_q passes through a minimum as the mole fraction of CH_3CN is increased from 0 to 1, correlating with the changes in τ_L.

4.3. Reorganization energy

The overall outer reorganization energy has contributions from both the solvent molecules and the counterion atmosphere that surrounds the reactants in the solvent cage: $\lambda_{out} = \lambda_{sol} + \lambda_{ion}$. The value of λ_{sol} can be estimated from Eq. (23) [44], where r_a and r_d are the radii of the donor and acceptor respectively, r_{da} is the distance between the donor and acceptor, and n is the refractive index of the medium. The value of λ_{sol} at 25 °C in water is ca. 1 eV.

$$\lambda_{sol} = e^2\left(\frac{1}{2r_a} + \frac{1}{2r_d} - \frac{1}{r_{da}}\right)\left(\frac{1}{n^2} - \frac{1}{\epsilon}\right) \tag{23}$$

The influence of the solvent is explicitly taken into account through the second term of Eq. (23). However, the model that leads to the equation is an oversimplification, inasmuch as it assumes that the medium is a continuous dielectric and that the reactants are spherical. When the transition state of the reaction is modified by the solvent, as in the case of dipolar excited states, the equation is less than adequate. In some cases, negative values of λ_{sol} have been obtained experimentally [45]. Hydrogen bonding of the reactants to the solvent may also be important, which is equivalent to increasing the values of ϵ and n [46]. In mixed solvent, where preferential solvation may be important, Eq. (23) also breaks down [47]. Estimates of λ_{out} from simulations that use the 'mean spherical approximation' and Monte Carlo methods indicate that Eq. (23) overestimates the value of λ_{out} [48].

When the medium contains electrolytes, λ_{out} includes the reorganization of the ionic atmosphere, which usually results in an increase in that quantity. Values of λ_{ion} can be estimated from Eq. (24) [49], where Γ is a measure of the screening of the ionic atmosphere that surrounds each charged reactant.

$$\lambda_{ion} = \frac{e^2}{\epsilon r_{da}} \left[\frac{\Gamma r_{da} - 1 + \exp(-\Gamma r_{da})}{1 + \Gamma r_{da}} \right] \tag{24}$$

Thus, λ_{out} has a contribution from the counterions present in solution, which, although small (ca. 0.005 eV in water at 25 °C [50]), could result in differences in k_q. In addition, Eq. (24) assumes that the solvent can be described as a bulk dielectric. The value of λ_{ion} could be significantly different within the microscopic environment of the solvent cage.

4.4. Reaction driving force

Although it is preferable to measure redox potentials in different solvents and calculate ΔG° directly from Eq. (12), the change in free energy ΔG° relative to that in a particular solvent ΔG°_s can often be estimated through the use of theoretical continuum models, which incorporate the solvent dielectric constant. If the reference solvent has a dielectric constant ϵ_s, the Born solvation model could be used to estimate changes in the potentials of the donor and acceptor in any other salt solution or solvent. This method was used recently by Thompson and Simon [51] to quantify electrolyte effects on the energetics and the rate constant of charge transfer within a contact ion pair. The free energy change is given by Eq. (25) [52].

$$\Delta G^\circ = \Delta G^\circ_s + \frac{e^2}{2}\left(\frac{1}{r_a} + \frac{1}{r_d}\right)\left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon}\right) - \frac{e^2}{\epsilon_s r_{da}} \tag{25}$$

Unfortunately, this model is too simplistic, inasmuch as ΔG° may also be influenced by hydrogen bonding, pH, and changes in the nature of the redox couple due to the presence of different electrolytes.

5. pH effects

The variation of the pH of the solution can alter the state of protonation of the Ru(II)-diimine sensitizer if it possesses protonatable sites on the ligands. Owing to the MLCT character of the excited state, which results in an increased electron density on the peripheral ligands and an increased basicity of the protonatable site, the protonated form of the excited state is a weaker acid (more positive pK_a) than is the corresponding form of the ground state [53]. Similarly, the quencher can exhibit acid–base behavior. Inasmuch as the protonated forms of excited states and quenchers are generally stronger oxidizing, but weaker reducing, agents than are their deprotonated analogs, the driving forces of the electron-transfer quenching reactions, and hence their rate constants, can be dramatically altered through the variation of pH. In addition, acid–base behavior changes the charges on the species, thereby altering the diffusion characteristics of the system. Studies have shown the effect of pH on k_q [54], excited-state photophysics [55], and the chemistry of the one-electron reduced forms [56] that result from reductive quenching.

In addition, variation of pH can alter the conformation of polymers, including biopolymers such as DNA, thereby affecting the binding of the photosensitizer in the organized medium and access of the quencher to the excited state [57]. An example of this effect is the quenching of $^*Ru(bpy)_3^{2+}$ by MV^{2+} in the presence of polymethacrylic acid [58]; k_q is a function of pH, being lowest at pH 5 where the polymer is coiled, resulting in the binding of the photosensitizer in its swollen interior and reducing access of the quencher.

6. Ionic strength

The rate constants of reactions between ions have long been known to be influenced by the ionic strength of the solution; the behavior is conveniently described by the extended Debye–Hückel equation (Eq. (26)) [59], where k_o is the rate constant at $\mu=0$, A and β are constants, z_a and z_b are the effective charges on the two reactants, and α is the effective size parameter.

$$\log k = \log k_o + \frac{2Az_a z_b \mu^{1/2}}{1+\alpha\beta\mu^{1/2}} \tag{26}$$

Thus, an increase in μ causes an increase in the rate constant for reactants of the same charge type, and a decrease for oppositely-charged species. There have been many experimental reports on the effect of μ on k_q for Ru(II)-diimine photosensitizers [60], although the use of Eq. (26) is limited because it is only approximated at ionic strengths much lower than are usually employed, and is strictly valid only in the limit as $\mu \rightarrow 0$.

6.1. *Olson–Simonson effect*

Olson and Simonson [61] noted in their study of the effect of the presence of 'inert' salts on the reaction between ions of the same charge that variations in the rate constants were almost exclusively due to the concentration and nature of the counterions rather than μ. With regard to the effect of anions on k_q for the reaction of cations, the Olson–Simonson approach is to consider the overall rate constant of the reaction as being made up of contributions from the fraction of the species that is ion-paired (k_{ip}) and the fraction that is not ion-paired (k_{nip}). Eq. (27) relates these quantities, where [X] is the concentration of the dominant anion and K_{ip} is the ion-pairing equilibrium constant from Eq. (21).

$$k_q = \frac{k_{nip}}{1+K_{ip}[X]} + \frac{k_{ip}K_{ip}[X]}{1+K_{ip}[X]} \tag{27}$$

Chiorboli et al. [62] showed that the dependence of the values of k_q for the reaction of $^*Ru(bpy)_3^{2+}$ and MV^{2+} in the presence of Cl^- salts of various cations correlated better with $[Cl^-]$ than with μ, in accordance with this effect.

6.2. *Specific electrolyte effects*

There have been a number of reports on the effect of specific anions on the value of k_q in the $Ru(bpy)_3^{2+}$–MV^{2+} system. In one of the first systematic studies, Gaines [63] noted the accelerating effect of $NaClO_4$ compared with NaCl. Ochiai et al. [64] studied the effect of LiI, LiCl, and KI on k_q at the same concentration; no difference was observed for LiI compared with KI, but k_q was higher in the presence of LiI compared with LiCl. More recently, Chiorboli et al. [62] examined k_q as a function of μ for NaCl, $CaCl_2$, and $NaClO_4$; again the accelerating effect of $NaClO_4$ was noted.

As part of our continuing investigation of the molecular factors that affect the yields of energetic species upon the electron-transfer quenching of the excited states of photosensitizers, we have examined the dependence of k_q on the temperature and concentrations of added salts to the $Ru(bpy)_3^{2+}$–MV^{2+} system in aqueous solution [65]. At 25 °C, the value of k_q at a particular μ is independent of the cation but is a function of the anion; values vary in the order $CH_3CO_2^- \sim H_2PO_4^- < HPO_4^{2-} \sim SO_4^{2-} < ClO_4^-$ and $F^- < Cl^- < Br^- < I^-$ for Na^+ salts. Activation energies for solutions containing ClO_4^- (10 kJ mol^{-1}) are lower than for the other oxyanions (16 kJ mol^{-1}). The ion-pair component of k_q (k_{ip}), when evaluated with Eq. (27) as a function of temperature, leads to values of λ of

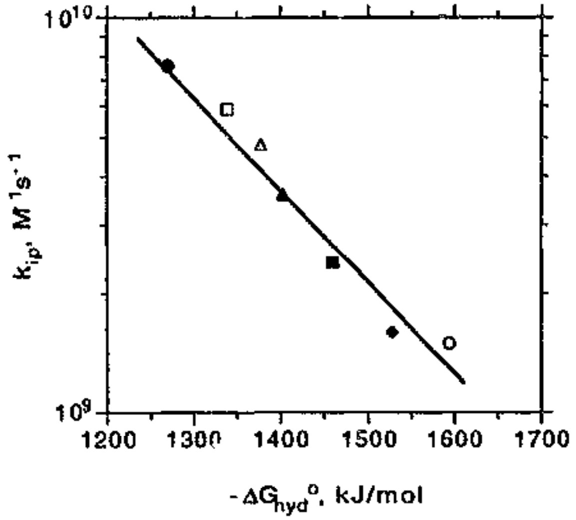

Fig. 1. The ion-pair component of k_q (k_{ip}) for the quenching of $^*Ru(bpy)_3^{2+}$ by MV^{2+} as a function of ΔG^o_{hyd} for different anions at 25 °C: ClO_4^- (●); I^- (□); Br^- (△); Cl^- (▲); $CH_3CO_2^-$ (■); F^- (◆); $H_2PO_4^-$ (○). Adapted from Ref. [67].

1.2 eV for ClO_4^- and 1.4 eV for the other oxyanions; λ is 1.3 eV for I^- and 1.5 eV for F^-. Inasmuch as the reorganization of the anions and their hydration spheres contributes to the value of λ, it is clear that the different species offer different barriers to that reorganization. The linear correlation between k_{ip} and ΔG°_{hyd}, the standard free energy of hydration, for the monovalent anions (Fig. 1) shows that k_{ip} is highest when the dominant anion possesses the most weakly-held hydration sphere and the strongest structure-breaking ability in water (ClO_4^-, I^-) [66].

The interesting conclusion is that seemingly 'innocent' anions in a polar medium can significantly affect the rate of intermolecular electron-transfer quenching between cationic species. The variation of λ due to the anions could result in a family of Marcus curves, rather than one unique curve, for homologous reactants unless the nature of the solution medium was carefully controlled. The rate constants of electron transfer, including those of excited-state quenching and charge recombination between the redox products, both in bulk solution and within the solvent cage, can be fine-tuned through the variation of electrolyte, ionic strength, and temperature [67].

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